Macromolecules **2000,** *33,* 4125−4131

Structural, Conformational, and Polarization Changes of Poly(vinylidene fluoride−trifluoroethylene) Copolymer Induced by High-Energy Electron Irradiation

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Received November 22, 1999

ABSTRACT: Structural and molecular conformation changes of high-energy electron-irradiated poly(vinylidene fluoride−trifluoroethylene) 50/50 copolymer have been investigated by means of FT-IR spectroscopy, X-ray diffraction, and cross-linking density measurement and are compared with the change of polarization hysteresis loops with dose. Although in general the irradiation reduces the macroscopic polar ordering, which leads to the eventual disappearance of the remanent polarization in the copolymer at room temperature, the change in the mesoscopic structure and molecular conformation with dose is not monotonic. In the intermediate dose range, there is a reversal of the change of local ordering with dose, as revealed by the decrease of the fraction of the TG conformation in the copolymer and contraction of the lattice in directions perpendicular to the polymer chain with dose, which could be caused by the high cross-linking density due to irradiation. In addition, for irradiated polymers at doses above 30 Mrad, no transition behavior with temperature is observed in the FT-IR spectra, consistent with the early experimental results that the ferroelectric−paraelectric transition has been eliminated by irradiation.

I. Introduction

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (P(VDF−TrFE)) have attracted a great deal of attention because of their relatively high dielectric constant and piezoelectric response compared with those of other known polymers.[1] In the past several decades, the structures of PVDF homopolymer and P(VDF−TrFE) copolymers have been studied widely using analytical tools such as X-ray diffraction, infrared and Raman spectroscopy, and the nuclear magnetic resonance method.[2−12] From these studies, it has been established that depending on the crystallization conditions, such as crystallization temperature, casting solvent, mechanical stress, external electric field, etc., these polymers can crystallize into at least four types of crystal forms: named forms I(β), II(α), III(γ), and IV (polar form II, IIp, or δ). It has also been established that there exist three basic chain conformations: all-trans planar zigzag (TTTT), trans−gauche−trans−gauche′ (TGTG′), and TTTGTTTG′ in these crystalline phases. Among these crystalline forms, the β-phase (or form I), which has all-trans chains packed with their dipoles pointing in the same direction, is the most interesting and important one because it exhibits a strong ferroelectric behavior. When cooled from the melt, PVDF homopolymer will crystallize into the antipolar α-phase, in which the molecules are in a distorted TGTG′ conformation. By mechanically drawing the polymer, the α-phase can be converted into the β-phase, which is accompanied by a large change of molecular conformation. On the other hand, for copolymers with VDF between 50 and 85 mol %, the β-phase will form directly from the melt. One interesting feature for the copolymers in this composition range is the ferroelectric−paraelectric (F−P) transition at a temperature below the melting temperature of the polymer.[10,13] Above the F−P transition temperature, the polymer loses its polarization before melting (forming a paraelectric phase). One of the most characteristic features of this transition is a large change of conformation of polymer chains between the trans and gauche forms. Such conformational changes also cause large changes of physical properties of the polymer.

Recently, we reported that high-energy electron-irradiated P(VDF−TrFE) copolymers exhibit exceptionally high electrostrictive response,[14] which will have a great impact on electromechanical transducer, sensor, and actuator applications.[15,16] Obviously, these large response behaviors in the irradiated copolymers should originate from a P(VDF−TrFE) copolymer structure, which is quite different from that before the irradiation. It is also interesting to examine what other changes are taking place during the irradiation. In the present paper, we investigate the structural and conformational changes of the irradiated P(VDF−TrFE) 50/50 copolymer at different doses utilizing FT-IR spectroscopy and X-ray diffraction. In addition, the cross-linking density was also measured as a function of the electron dose. For comparison, polarization hysteresis loops were also recorded for the copolymer in the corresponding dose range.

II. Experimental Section

The samples used in the present study are P(VDF−TrFE) copolymers with 50 mol % VDF content, supplied by Solvay and Cie, Belgium, and the weight-average molecular weight of the polymer is about 200 000. Samples of various thicknesses were prepared for different measurements using the solution cast method. For the polarization hysteresis loop and X-ray measurements, the typical sample thicknesses were in the range between 20 and 30 μm. For FT-IR spectroscopy

10.1021/ma9919561 CCC: $19.00

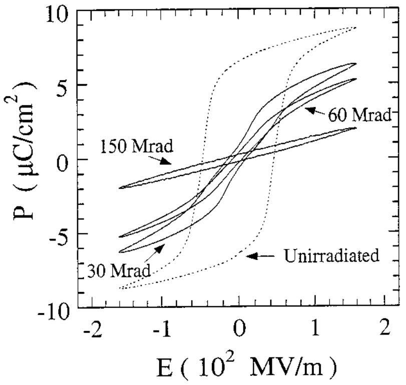

Figure 1. Polarization hysteresis loops of P(VDF–TrFE) 50/50 copolymer after different irradiation doses. The irradiation was carried out at 120 °C with 2.55 MeV electrons.

measurement, the sample thickness was 7 μm. The films were annealed at 140 °C for 4 h under vacuum and then cooled slowly to room temperature. The irradiation was carried out at 120 °C under a nitrogen atmosphere using electrons of 2.55 MeV energy with different doses.

The polarization hysteresis loops were measured using a Sawyer–Tower technique. The FT-IR spectra were obtained using a BIO-RAD WIN Fourier transform IR spectrophotometers in the wavenumber range 4000–400 cm^{-1}. The high-temperature FTIR spectra were measured using a high-temperature optical cell. The X-ray patterns were measured on a Scintag diffractometer (model PAD-V) with Ni-filtered Cu Kα radiation. The samples for polarization hysteresis measurement were sputtered with gold electrodes on both surfaces.

The measurement of the cross-linking factor was performed by measuring the gel content of each sample using the American standard test method (ASTM D2765-95) by placing the sample inside a Soxhlet extractor and extracting with methyl ethyl ketone at its boiling point for 12 h. After measuring the gel content, these films were kept in dimethylformamide solution for 10 days at room temperature to reach their equilibrium degree of swelling. The average molecular weight between cross-links (M_c) is calculated using the following equation

$$M_c = \frac{-\rho_2 V_1 \phi_2^{1/3}}{\ln(1-\phi_2) + \phi_2 + \chi_1 \phi_2^{2}} \tag{1}$$

where V_1 is the molar volume of the solvent, χ_1 is the polymer–solvent interaction parameter, and ϕ_2 is the volume fraction of the polymer in the swelling:

$$\phi_2 = \frac{W_2/\rho_2}{W_1/\rho_1 + W_2/\rho_2} \tag{2}$$

where W_1 and W_2 are the weight of the polymer and solvent and ρ_1 and ρ_2 are the density of polymer and solvent, respectively.

III. Results and Discussion

3.1. Structural and Conformational Changes with Irradiation. To illustrate the effect of the high-energy electron irradiation on the ferroelectric behavior of the copolymer, the polarization hysteresis loops of the polymer films under different irradiation doses were measured at room temperature, and the results are presented in Figure 1. The unirradiated film exhibits a well-defined near square polarization hysteresis loop with a large remanent polarization ($P_r \sim 7\ \mu$C/cm^2). The data in Figure 1 reveal two features due to irradiation: the reduction of the polarization hysteresis and also the reduction of the polarization level. At very high dosage (150 Mrad), the polymer exhibits a linear dielectric behavior, indicating nearly a total loss of coupling among the dipoles in the polymer chains.

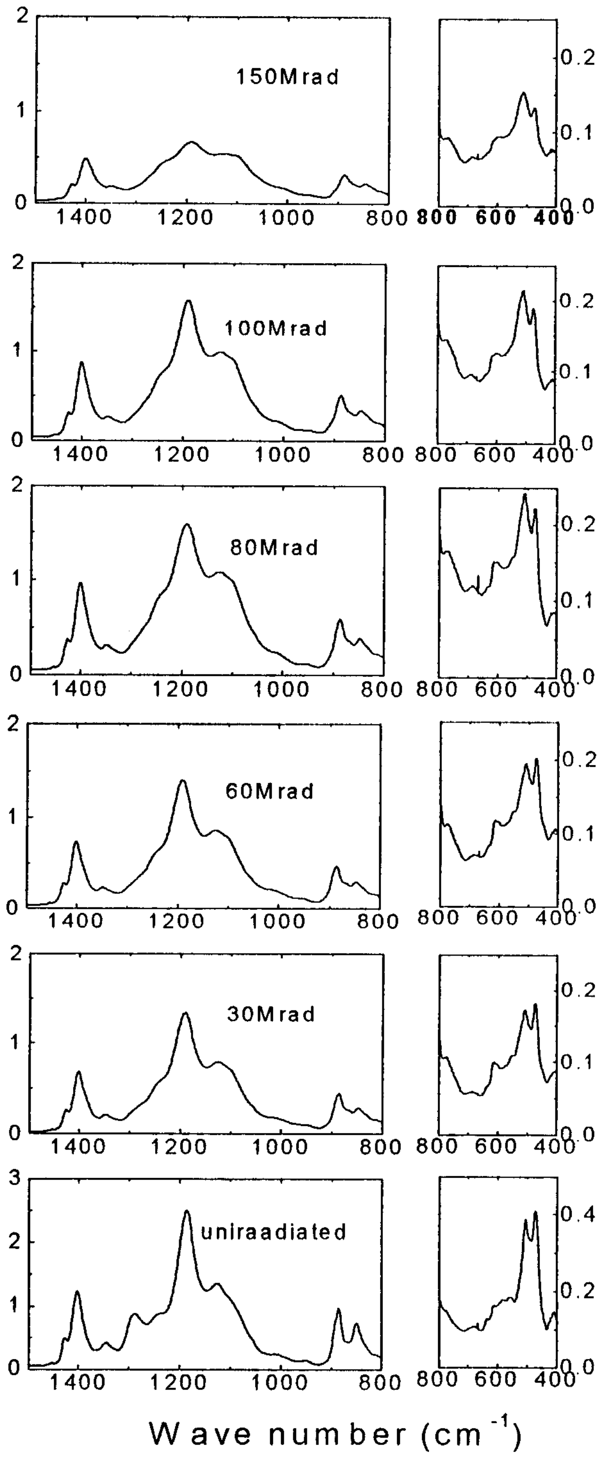

Figure 2. FTIR spectra of P(VDF–TrFE) copolymer films at different doses in wavenumber range 1500–400 cm^{-1}.

Figure 2 presents the FT-IR spectra in the wavenumber range between 1500 and 400 cm^{-1} for the P(VDF–TrFE) 50/50 copolymer in the dose range corresponding to the data in Figure 1. Before the irradiation, the spectrum is characterized by a strong absorbance peak at 1288 cm^{-1}, from the long trans sequence ($T_{m\geq 4}$) of the ferroelectric β-phase. Weak absorbance peaks corresponding to the TG (at 614 cm^{-1}) and T_3G (510 cm^{-1}) conformations are also present in the spectrum of

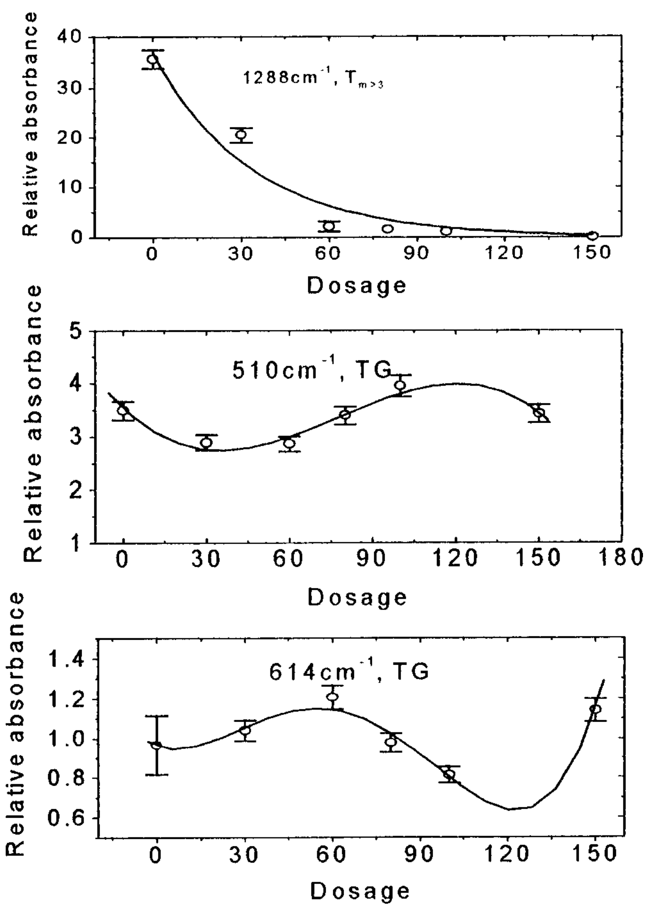

Figure 3. Dose dependence of infrared absorbances of the trans and gauche bands from P(VDF−TrFE) 50/50 copolymer films irradiated at 120 °C with 2.55 MeV electrons. The experimental data points are shown, and solid lines are drawn to guide the eye.

unirradiated copolymer, which are consistent with early experiment results and presumably due to the existence of the domain structure as has been suggested from the early X-ray diffraction and FT-IR data.[2,4] Although there are several peaks for each type of chain conformation, these three, i.e., 1288 cm^{-1} ($T_{m>4}$), 614 cm^{-1} (TG), and 510 cm^{-1} (T_3G), were chosen for the following analysis because these are all from the vibrations of the CF_2 group.[17]

Presented in Figure 3 is the dependence of the relative absorbance of these bands on the irradiation doses, deduced from the data in Figure 2. Each individual component of the bands has been fitted and separated from others by assuming a Lorentzian function peak shape. In the measurement, the samples for different doses have small variations in thickness. Moreover, the absorbance of even the same type of chain conformation may be different due to different cross-linking densities at different irradiation doses. To correct these factors, an internal standard should be used to compare the relative absorbance of different conformational sequences. The absorbance at 3022 cm^{-1} is the asymmetric stretching vibration of the C−H bond,[18] and as it is almost proportional to the thickness of the sample and does not depend on the state of the sample, it was used as an internal standard here. The data in Figure 3 are the relative absorbance after this correction.

The data in Figure 3 show that after irradiation the absorbance intensity of the all-trans peak decreases precipitously. At doses higher than 100 Mrad, this peak essentially disappears. Concomitantly, the absorbance peak corresponding to TG sequence increases with irradiation dose, and at doses beyond 60 Mrad, it shows irregular changes with dose. For the peak at 510 cm^{-1} for T_3G sequences, the absorbance does not show a monotonic change with dose, and irregular change is also observed at doses beyond 60 Mrad.

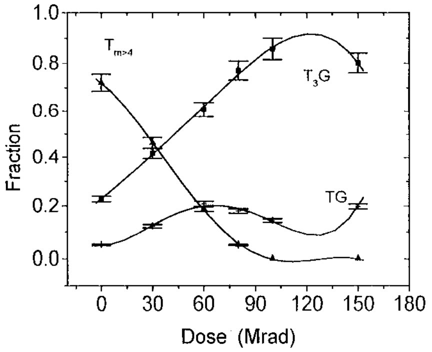

Figure 4. Fraction of trans and gauche conformations as a function of the dose for P(VDF−TrFE) 50/50 copolymer irradiated at 120 °C with 2.55 MeV electrons. The experimental data points are shown, and solid lines are drawn to guide the eye.

To quantify these changes with doses, we adopted the method used by Osaki et al.[18] to calculate the fraction of each chain sequence in the polymer from the infrared spectrum. Because three chain sequences are present, the fraction of each chain sequence is

$$F_i = \frac{A_i}{A_{\mathrm{I}} + A_{\mathrm{II}} + A_{\mathrm{III}}} \tag{3}$$

where i = I, II, and III, A_{I}, A_{II}, and A_{III} are the absorbances of crystal forms I, II, and III, i.e, with all-trans ($T_{m>4}$), T_3G, and TG sequences, respectively; and F_i is the fraction of chain sequence i. The result is presented in Figure 4.

The results in Figure 4 indicate that the change of the fraction of chain sequence with dose can be divided into three regions: below 60 Mrad, 60−100 Mrad, and above 100 Mrad. At doses below 60 Mrad, the fraction of all-trans sequences corresponding to macroscopic polarization drops rapidly with doses, while both TG and T_3G sequences increase. This is very similar to the observed macroscopic transformation of the ferroelectric to a nonpolar (paraelectric-like) phase of the copolymer with increased irradiation dose.[14,20,21] At 30 Mrad, the FT-IR data show that there are still relatively large regions of all-trans conformation in the polymer. Consistent with these observations, the polarization hysteresis data in Figure 1 show the presence of the polarization hysteresis and remanent polarization. At 60 Mrad, the fraction of the all-trans conformation drops to below 0.1, and correspondingly, the polarization loop has become very slim at this dose. At doses between 60 and 100 Mrad, the rate of decrease of the all-trans conformation with dose becomes lower, and more interestingly, the fraction of TG conformation exhibits a drop with dosage, suggesting a recovering of the local polar ordering in the copolymer with dose. At doses above 100 Mrad, the fraction of all-trans conformation becomes zero, and the fraction of the TG conformation increases again, due to the disappearance of the macroscopic crystal phase in the polymer at high doses, which will be discussed later.

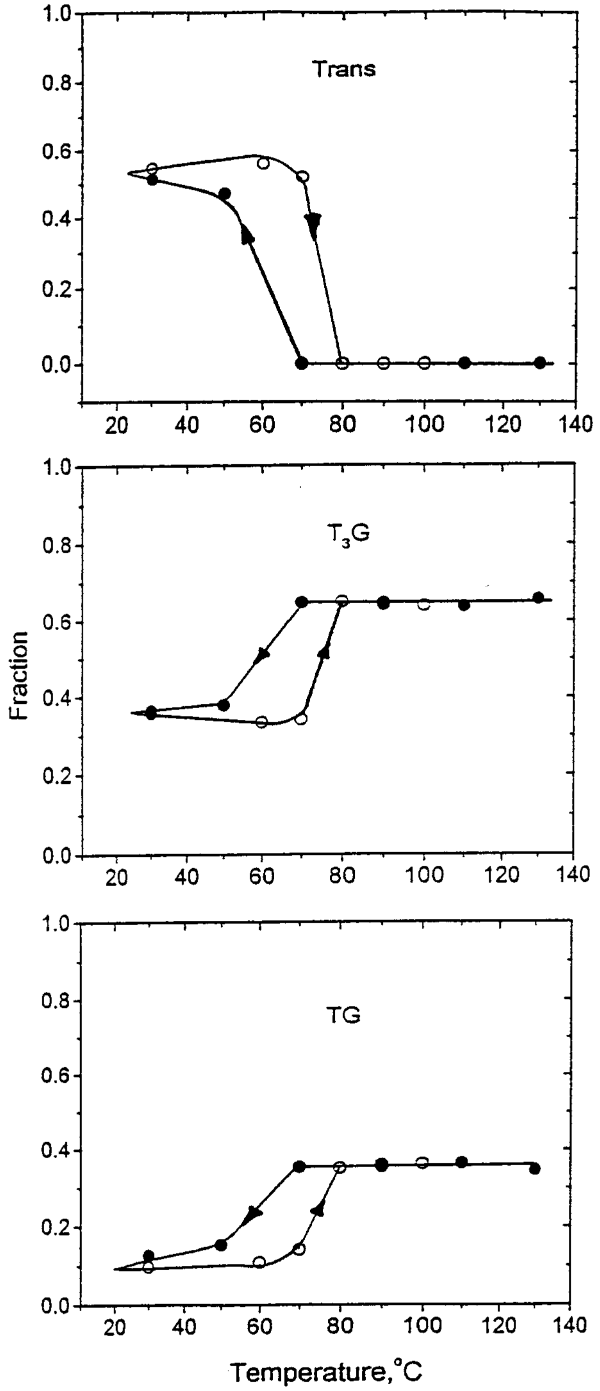

Figure 5. Fraction of trans and gauche conformations as a function of temperature for unirradiated P(VDF−TrFE) 50/50 copolymer. The data show a clear phase transition at temperatures near 70 °C. The experimental data points are shown. The solid lines are drawn to guide the eye, and arrows indicate the heating or cooling of the experiment.

Two more experiments were carried out in order to further elucidate the observed behavior. The FT-IR spectrum was measured for the unirradiated 50/50 copolymer as a function of temperature where a phase transformation from a macroscopically polar phase (ferroelectric β-phase) to a nonpolar phase the (paraelectric phase) occurs at the F−P transition temperature. X-ray diffraction data were also taken from irradiated copolymer samples as a function of dose. Presented in Figure 5 is the fraction of the three chain conformations in the unirradiated copolymer as a function of temperature (calculated using eq 3). The data reveal a clear transition between the ferroelectric and paraelectric phase as signified by a large increase of the TG fraction (from near zero in the ferroelectric phase), a moderate increase of the T_3G fraction, and a drop to zero in the all-trans conformation. This result indicates that the phenomenon observed in the irradiated copolymer in the doses from 60 to 100 Mrad is not related to the macroscopic change from a polar to a nonpolar phase.

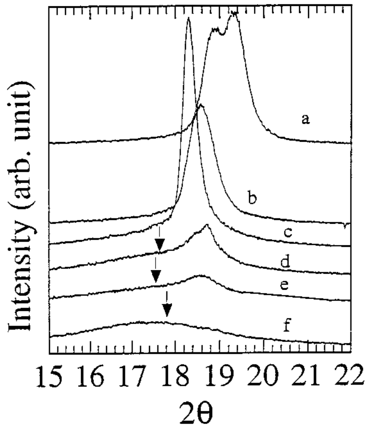

Figure 6. X-ray diffraction data at angles near the (200, 110) reflections of unirradiated film. The data were taken for films with different doses (in Mrad): a, 0; b, 30; c, 60; d, 80; e, 100; f, 150. The arrows indicate the center of a broad diffraction peak.

X-ray data taken at room temperature from the irradiated copolymer are presented in Figure 6. The data show the evolution of the (200, 110) reflection of the original ferroelectric phase with dose. For the unirradiated P(VDF−TrFE) 50/50 copolymer, a two-peak structure at θ angle near (200, 110) reflection has been observed by many early X-ray studies.[2,10] This two-peak structure is attributed to the presence of a mixture of disordered trans and $^{1}/_{3}$- helical conformations in the crystalline phase.[10] For irradiated samples, in analogy to the FT-IR data, the X-ray data also show three dose regions. Below 60 Mrad, the X-ray peak moves to a lower angle, indicating an expansion of the lattice perpendicular to the chain direction, and sharpens, due to the disappearance of the macroscopic polarization and hence the domain structure. Upon 60 Mrad irradiation, a peak appears at 4.84 Å, which is close to the lattice spacing of the paraelectric phase of unirradiated copolymer determined from X-ray data above the Curie temperature and consistent with early experimet results.[2,20,21] These results are consistent with the FT-IR data and the polarization data, showing the disappearance of the macroscopic polarization in the copolymer due to the irradiation. Interestingly, at doses higher than 60 Mrad, the X-ray peak moves back toward a higher angle, indicating a contraction of the lattice spacing in the directions perpendicular to the chain, and concomitantly the peak broadens, suggesting the reduction of the crystallite size due to the irradiation. The contraction of the lattice perpendicular to the polymer chain is consistent with the FT-IR observation, where in this dose range the fraction of TG sequence decreases with dose. TG sequences cause larger lattice spacing perpendicular to the chain compared with T_3G and all-trans sequences.[22] At 150 Mrad, the X-ray peak becomes very broad and moves to $2\theta = 17.6°$, indicating that no long-range crystalline ordering exists and the copolymer is nearly amorphous. This is consistent with the early experimental results.[20,23] The crystallinity can be esti-

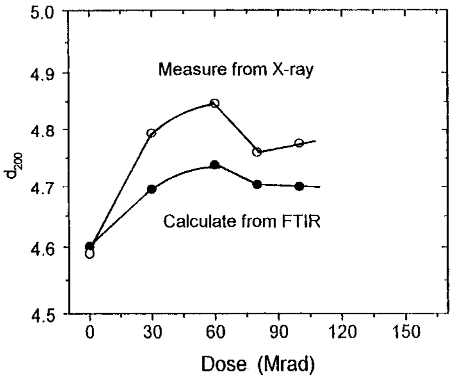

Figure 7. Lattice spacing d_{200} as a function of irradiation dose for 50/50 films irradiated at 120 °C. The open circles are taken from the fitting of X-ray data, and dots are calculated from the FT-IR data. Solid lines are drawn to guide the eye.

mated from the area of crystalline and amorphous diffraction peak. The results indicate that the crystallinity decreases with the dose. At doses of 60 Mrad or higher the crystallinity of the copolymer has been reduced to less than half as compared with the case of the unirradiated films.[23]

The change of d_{200} spacing with dose from the X-ray data is shown in Figure 7. In addition, the lattice spacing can also be estimated from the FT-IR results if the irradiated P(VDF−TrFE) copolymer is regarded as composed of TTTT, TGTG′, and T$_3$GT$_3$G′ conformations with each conformation having its own lattice spacing. Tashiro et al. calculated the d_{200} for these three different conformations: 4.425, 4.82, and 4.79 Å, respectively.[22] Combining this with the fraction of three different conformations obtained from the FT-IR results, the d_{200} value of the P(VDF−TrFE) film irradiated at different doses is calculated, and the results are also presented in Figure 7. As can be seen from the data, the two results are consistent with each other although the d_{200} value from the X-ray diffraction data is higher than those from the FT-IR data except for the unirradiated film. The reason for this might be that in the calculation we assumed that the d_{200} spacing for each conformation does not change with dose, while in reality lattice deformation should exist after irradiation.

Therefore, both FT-IR and X-ray data indicate that the reduction in the crystallite size (there is a large reduction in the crystallite size after 60 Mrad irradiation) and other changes (as will be discussed later in the paper) in the copolymer due to irradiation favor the T$_3$G conformation compared with TG (paraelectric phase).

Figure 8 shows the temperature dependence of T$_3$G and TG conformations derived from FT-IR spectra measured at different temperatures for the irradiated copolymer with a dose of 60 Mrad. As expected, no transition behavior is observed (in contrast to the data in Figure 5 for unirradiated samples where a transitional change in the molecular conformations was observed), indicating that indeed the macroscopic polarization in the normal ferroelectric β-phase has been destroyed.

3.2. Chemical Changes Due to Irradiation. In addition to the conformation changes, FT-IR data also reveal other changes in the copolymer due to irradiation. In Figure 9, the FT-IR spectra in the wavenumber range between 4000 and 1600 cm^{-1} are presented where the data from samples before and after irradiation are compared. In general, irradiation of polymers may lead to the formation of radical or ionic species due to heterolytic or homolytic bond scission reactions. These reactions will produce the following changes in the polymer:[24] (a) chain scission or cross-linking and the resulting changes in average molecular weight and (b) the formation of oxidative degradation products such as hydrofluoric acid, carboxylic acid, alcohol, and hyproperoxide groups if traces of oxygen are present during or after irradiation processing.

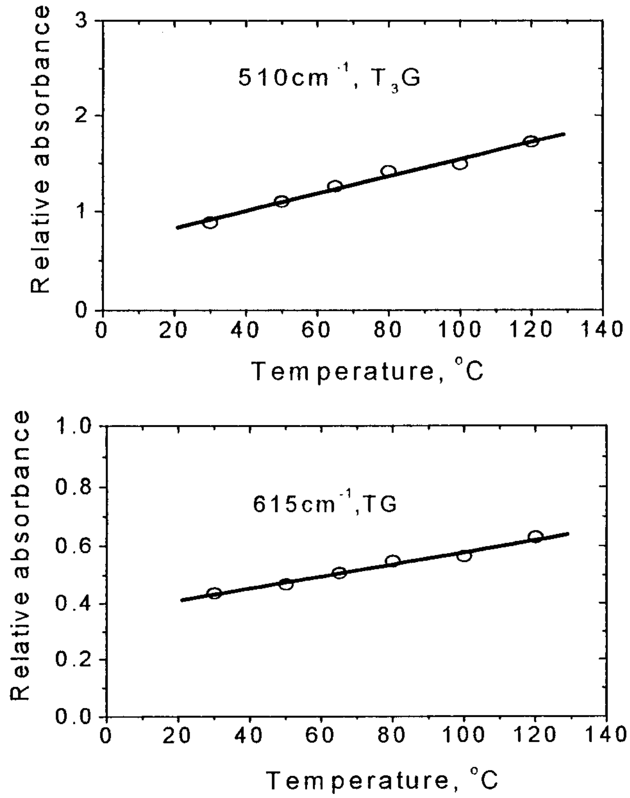

Figure 8. Relative absorbance of TG and T$_3$G conformations as a function of temperature for 50/50 copolymer irradiated at 120 °C with 60 Mrad dose. The open circles are the data, and solid lines are drawn to guide the eye.

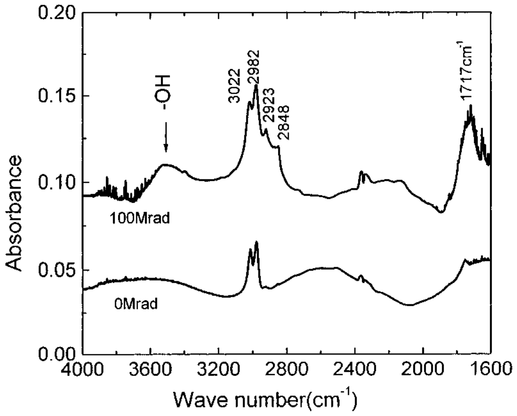

Figure 9. FT-IR spectra of irradiated P(VDF−TrFE) copolymer film (100 Mrad) compared with unirradiated film in wavenumber range 4000−1600 cm^{-1}.

For the copolymer studied here, it is observed that after irradiation an absorbance peak appears at 1717 cm^{-1}, which could be assigned to the double bond structure of −CH=CF−[24] as well as a carboxyl group (−C=O−). However, the appearance of a broad peak between 3200 and 3600 cm^{-1}, the typical absorbance frequency of hydroxyl (−OH) group, for samples after

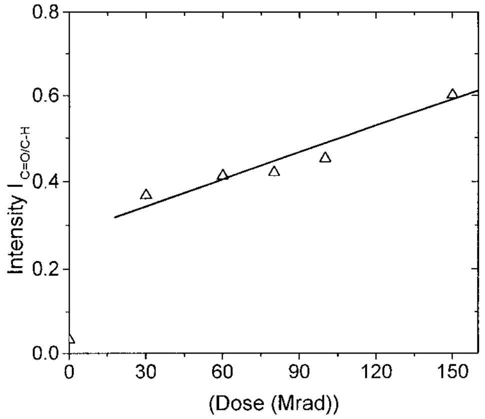

Figure 10. Intensity of FT-IR bands of carboxyl group of P(VDF−TrFE) 50/50 copolymer film irradiated under nitrogen atmosphere as a function of radiation dosage (C−H, 3022 cm^{-1}; C=O, 1717 cm^{-1}). The solid line is drawn to guide the eye.

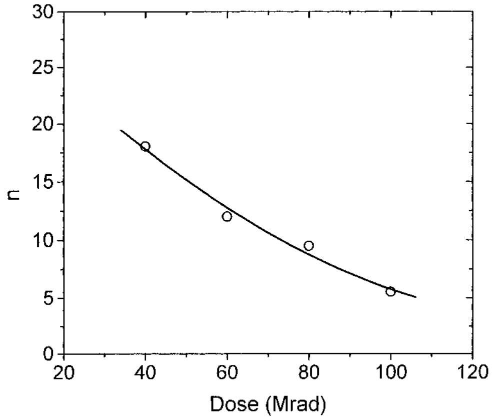

Figure 11. Number of repeating unit ($-CH_2CF_2CHFCF_2-$) *n* between two cross-links for P(VDF−TrFE) 50/50 copolymer film irradiated at different doses. The solid line is drawn to guide the eye.

irradiation seems to be more consistent with the interpretation that the peak at 1717 cm^{-1} is from a carboxyl group. The formation of a terminal carboxylic acid group in the irradiated samples could be caused by the presence of trace oxygen in the samples or in the irradiation chamber. Even though the irradiation chamber has a nitrogen circulation, a small amount of oxygen might still exist in the chamber. The change of the content of carboxylated groups with dose is summarized in Figure 10, which shows that the infrared absorption intensity of carboxylated groups (quotient of absorption peak of the C=O stretching vibration and nonspecific C−H) increases with doses linearly. However, in the dose range investigated, the content of carboxylated groups is still quite small in the polymer. As will be demonstrated in the following, irradiation-induced cross-linking seems to be the dominant chemical change in the copolymer investigated here.

Cross-linking density was measured for the irradiated copolymers, and the data are presented in Figure 11, where the change in the number of repeating units (*n*) between two cross-linking points along the chain in the unit of $-CH_2CF_2CHFCF_2-$ is plotted versus the irradiation dose. Although P(VDF−TrFE) is a random copolymer, $-CH_2CF_2CHFCF_2-$ is taken here as a repeating unit for the sake of convenience in the presentation. The cross-linking density is inversely proportional to *n* (or M_c). The result in Figure 11 demonstrates that the copolymer at doses higher than 60 Mrad is highly cross-linked. The result confirms that cross-linking is the dominant chemical change during high-energy electron irradiation.

IV. Summary

The changes in the crystalline structure, molecular conformation, and other possible chemical reactions in the P(VDF−TrFE) 50/50 copolymer due to high-energy electron irradiation were investigated in terms of FT-IR, X-ray diffraction, and cross-linking density measurements. The irradiation-induced structural and conformational changes are not monotonic. For the copolymer studied here (irradiated at 120 °C), the irradiation-induced changes can be divided into three regions. Below 60 Mrad, FT-IR and X-ray data indicate that the irradiation causes a continuous reduction of the macroscopic polarization in the polymer, and this can be compared directly with the evolution of the polarization hysteresis loop with dose (from the square polarization loop to slim loop). However, for doses between 60 and 100 Mrad, the rate of decrease of the all-trans conformation with dose becomes much slower, and the fraction of TG sequence, which is related to the randomization of the polarization in the copolymer, actually shows a decrease with dose. X-ray data in the same dose range also show a contraction of the lattice spacing perpendicular to the chain. This anomalous process could be caused by a high cross-linking density in the copolymer which would favor chain conformations that have smaller lattice spacings between chains, such as the T_3G sequences. At higher doses (~150 Mrad), the irradiation leads to a near amorphous phase in the copolymer, which exhibits a linear dielectric response in the polarization hysteresis data.

The experimental results also indicate that, in addition to the changes in the crystalline phase, there is a continuous reduction of the crystallinity in the copolymer with dose due to the increased cross-linking density, which leads to the eventual disappearance of the macroscopic crystalline ordering in the copolymer which is consistent with the early experimental observations.[20,21]

Acknowledgment. This work was supported by the Office of Naval Research under Grants N00014-98-1-0254 and N00014-97−1−0667 and the National Science Foundation under Grant ECS-9710459. The authors thank Dr. A. J. Lovinger for the careful reading of the manuscript and suggestions regarding the interpretation of the experiment data presented.

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