Macromolecules **2004,** *37,* 79−85

Recrystallization Study of High-Energy Electron-Irradiated P(VDF−TrFE) 65/35 Copolymer

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Received August 22, 2003; Revised Manuscript Received November 5, 2003

ABSTRACT: Electron-irradiated poly(vinylidene fluoride−trifluoroethylene) [P(VDF−TrFE)] copolymer exhibits a very high electromechanical performance that is attractive for many applications. A study of recrystallization of irradiated P(VDF−TrFE) 65/35 mol % copolymer is reported in this paper. The structure and morphology of the recrystallized samples were determined using DSC and X-ray diffraction, and the polarization behavior of the recrystallized samples was studied. The nonpolar phase content of the recrystallized samples was much lower than that of the irradiated samples. For irradiated samples that exhibited the best electromechanical performance, the corresponding recrystallized material had a high polar phase content, with a correspondingly high remanent polarization. For samples irradiated with higher doses, although the polarization level was low immediately after irradiation, after recrystallization the material exhibited a much higher polarization level with a very small remanent polarization, an attractive combination for many electromechanical applications.

Introduction

Electroactive polymers (EAP) convert energy between the electrical and mechanical forms.[1] This ability to change shape when an electric field is applied can be used in many areas, such as artificial muscles and organs, smart materials for vibration and noise control, electromechanical actuators and sensors for robots, acoustic transducers used for underwater navigation and medical imaging, and fluid pumps and valves.[2−4] In recent years, there has been a great deal of effort put into exploring different approaches in an attempt to improve the performance of existing polymers and/or to develop high-performance polymers, including studies of the effects of irradiation[5−7] and the behavior of elastomers,[8−10] terpolymers,[11−14] composites,[15−17] and polymer blends as well as thermal treatments.[18−20] Among these, high-energy electron-irradiated poly(vinylidene fluoride−trifluoroethylene) [P(VDF−TrFE)] copolymer exhibits high electrostrictive strain with high elastic modulus and high load capability,[7] a combination that is very attractive for a wide range of applications.

High-energy electron irradiation is known to induce many kinds of defects, including chain scission, isomerization, bond rearrangement, the formation of double bonds and bulky pendant groups, cross-linking, among others.[21−23] Irradiation also has a strong influence on the phase transitional behavior of P(VDF−TrFE) copolymers. It was first shown by Lovinger that the transition between the ferroelectric (polar) and paraelectric (nonpolar) phases in irradiated P(VDF−TrFE) copolymer occurs at a temperatures much lower than that in unirradiated copolymer.[24] Relaxor ferroelectric behavior was also recently observed in the irradiated copolymer.[5,25−27] The relaxor ferroelectrics represent a class of materials with high dielectric constants and superior electromechanical performance. For example, the electric-field-induced strain response in relaxor ferroelectric polymer can reach about 5%, much higher than the strain level (∼0.1%) observed in piezoelectric polymers.[7] The combination of a high strain response and a high dielectric constant is very attractive for a broad range of applications, as demonstrated by the high performance obtained in devices made of these polymers.[28−30]

On the basis of structure and property studies, it is believed that the high strain obtained in the irradiated P(VDF−TrFE) originates from electric-field-induced structure changes.[25,31,32] The structure of the crystalline regions in an irradiated copolymer is nonpolar, while an applied external electric field converts the structure from nonpolar to polar phase with an associated large strain response.[33] Thus, it is interesting from both application and physics points of view to understand what changes the irradiation induces in the polymer and the corresponding effect on the structure. A deeper understanding of what happens in irradiated copolymers will lead to the development of new materials with enhanced electromechanical performance.

Among irradiation defects, cross-linking and its influence on the structure have been extensively studied using different approaches, as new cross-linking sites are one of the principal effects of irradiating P(VDF−TrFE).[21−23] For example, a study of the effect of cross-linking on the properties of irradiated 50/50 mol % copolymer revealed that the cross-linking coefficient increases and the crystallinity decreases continuously with dose (for the sample irradiated with 60−80 Mrad, it was found that the repeating units between two cross-linking points along the chain are about 10 in unit of VDF−TrFE), but the effect of cross-linking density on field-induced polarization is not significant and direct.[34] However, an independent study of the influence of cross-linking on P(VDF−TrFE) copolymer[35,36] found that chemically induced cross-linking has a similar effect to irradiation on both the transition temperature between nonpolar and polar phases and the crystalline melting behavior. Therefore, the influence of cross-linking on the structure and properties is still an open question in the study of electroactive polymers.

To study the influence of irradiation-induced cross-linking and other defects on the structure of crystalline regions, the recrystallization of irradiated copolymer was studied using DSC, X-ray, and polarization loop techniques. On the basis of the DSC data, the melt

10.1021/ma035251h CCC: $27.50

temperature in recrystallized samples was lower than that in irradiated samples in the whole range of irradiation doses studies here, while the polar-to-nonpolar phase transition temperature in recrystallized polymers was higher than in corresponding irradiated samples when irradiation dose is not higher than 60 Mrad. It was also found that the percentage of polar phases in crystalline regions of recrystallized polymer was much higher than in irradiated samples. However, for samples irradiated with high dose, such as 85 Mrad, a high polarization level with a small remanent polarization, which is very attractive for electromechanical applications, was observed.

Experimental Method

The samples used in this study were P(VDF-TrFE) 65/35 mol % films with a thickness of 15−30 μm. Before irradiation, the solution cast films were uniaxially stretched at room temperature to 5 times their original length and then annealed to improve crystallinity, as described in a previous publication.[7] The irradiation was carried out in a nitrogen atmosphere at 100 °C with an electron energy of 1.2 MeV, and the irradiation doses used in this investigation were 0, 10, 20, 35, 50, 60, 65, 75, 85, and 100 Mrad. These irradiated films were used for the recrystallization study.

In the DSC study, which was conducted using a TA DSC system (model 2910), the sample was first heated at a rate of 10 °C/min to a temperature about 30−40 °C above its melt temperature (the highest temperature used here was 200 °C, which was for unirradiated film) and then cooled at a rate of 10 °C/min to −20 °C. A second heating was performed immediately from −20 °C at a rate of 10 °C/min to a temperature higher than its melting point.

The X-ray diffraction measurements were performed using a Rigaku system with a wavelength of 1.54 Å at room temperature. The (200, 110) diffraction peak, which is associated with the interchain spacing and ordering perpendicular to the polymer chain,[33] was determined using a reflection scan, while the (001) diffraction peak, which is associated with the intrachain spacing and ordering along the polymer chain direction,[33] was determined using a transmission scan. Two types of recrystallized films were used in this study. The first was produced by a fast recrystallization, as in the recrystallization process used in the DSC study in which the irradiated films were first heated to a temperature about 30−40 °C higher than the corresponding melt temperature to melt the crystalline regions and then cooled to room temperature at a rate of about 10 °C/min in oven. The second was the result of a slow recrystallization, in which the samples were first heated to a temperature a little higher than the corresponding melt temperature and kept for 30 min and then cooled and allowed to crystallize for 1 h. The crystallization temperature used here was about 5 °C below the onset temperature of the melt peak observed in the DSC data.

The samples used for the polarization hysteresis measurements were sputtered with gold electrodes on both surfaces. A ferroelectric test system (Precision LC Ferroelectric Test System, from Radiant) was employed in this work. An external electric field was applied in the form of a triangular waveform with a frequency of 10 Hz.

Results and Discussion

1. DSC Study. Data shown in Figure 1 are the DSC curves for samples irradiated with doses of 20, 60, 85, and 100 Mrad, where both the data from the first and second heating processes are presented. A very remarkable difference between the first and second heating processes for all samples is found. For example, for the sample irradiated with 60 Mrad, although the phase transition is too weak to be seen in the irradiated sample, the phase transition in recrystallized sample is very strong. Additionally, one can find that the melt peak observed in the second heating is broader than that in the first heating and that the melt peak broadens with increasing dose. For example, for the sample irradiated with 60 Mrad, the width at half-height of melt peaks for first heating and second heating are 2.87 and 7.77 °C, respectively, while for the sample irradiated with 100 Mrad, those are 9.73 and 21.07 °C, respectively. It is well-known that the melt temperature is related to the size of crystal regions. Therefore, the DSC data indicate that crystalline regions in recrystallized samples have a broader size distribution than the irradiated samples and that the crystalline size distribution broadens with irradiation dose in studied dose range. The DSC results for the irradiated films in all studied doses range are summarized in Figure 2, where T_C and ΔH_C are the temperature and enthalpy associated with the phase transition between polar and nonpolar phases, and T_m and ΔH_m are the temperature and enthalpy associated with the melting point of the crystalline regions. Here, T_C and T_m were defined as the peak temperatures obtained from the DSC data.

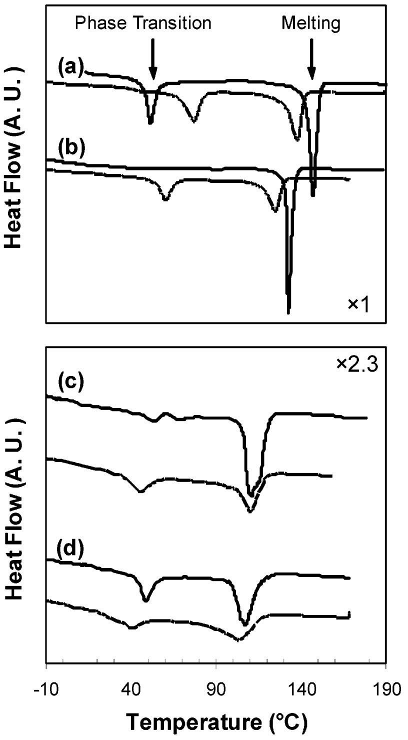

Figure 1. DSC data collected during heating. The heating rate was 10 °C/min (solid line, first heating; dashed line, second heating). (a) 20 Mrad,(b) 60 Mrad, (c) 85 Mrad, and (d) 100 Mrad. Note: (c) and (d) used a different scale for the *Y* axis from in (a) and (b) as indicated in the figure.

For the first heating process, the results illustrated in Figure 2 reflect the structure and behavior of the crystalline regions that were generated during irradiation. The data show that for the first heating process both T_m and ΔH_m decreased with increasing irradiation dose. This indicates the size of the crystalline regions is reduced along with the degree of crystallinity. However, although both T_C and ΔH_C also decreased as the irradiation dose increased when the irradiation dose is up to 60 Mrad, the ΔH_C increased only slightly with irradiation dose for samples irradiated with a higher dose, while the T_C for samples irradiated with a high dose was higher than that for samples irradiated with

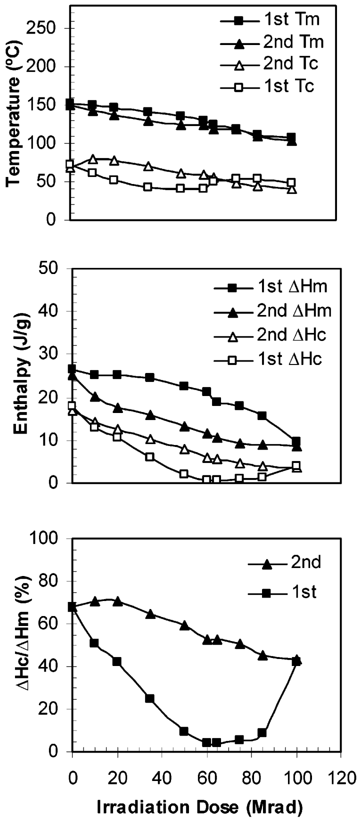

Figure 2. (a) Melt temperature (T_m) and transition temperature (T_C) between ferroelectric and paraelectric phases obtained during first and second heating processes. (b) Corresponding melting enthalpy (ΔH_m) and phase transition enthalpy (ΔH_C) obtained during first and second heating processes for 65/35 mol % copolymer irradiated with different doses. (c) The ratio of ΔH_C to ΔH_m vs irradiation dose for first and second heating processes.

60 Mrad. As a result, the ratio of ΔH_C to ΔH_m, which reflects the molar ratio of polar phase regions to nonpolar phase regions at room temperature, decreased with the dose for samples irradiated with doses of up to 60 Mrad and increased with the dose for samples irradiated with higher doses. This indicates the following at room temperature: (1) The fraction of nonpolar phase in the crystalline regions increases with irradiation dose if the dose is 60 Mrad or less. (2) For samples irradiated with a dose of 60 Mrad, which exhibit the best electromechanical performance, the nonpolar regions dominate the materials. (3) When the irradiation dose is higher than 60 Mrad, the fraction of polar phase slightly increases with dose. The increase of polar phase fraction for samples irradiated with high doses is likely to be a side effect of the high cross-linking density.[34] That is, the high cross-linking density results in a short distance between cross-linking points, which in turn induces high stress in the crystalline region and causes polar phase to be the more stable structure.

The results shown in Figure 2 for the first heating are consistent with the results obtained in high-energy electron-irradiated P(VDF−TrFE) 68/32 mol % copolymer. That is, the irradiated copolymers can be classified into three categories on the basis of the irradiation dose received.[6,31] According to the study of the 68/32 copolymer, it was found that these three categories are as follows: (1) When irradiated with a low dose, the sample exhibits a first-order phase transition and the crystalline morphology of the sample at room temperature displays two coexisting phases, polar and nonpolar, and the weight of the nonpolar phase increases with irradiation dose. (2) When irradiated with an optimum dose (~70 Mrad for 68/32 copolymer[6,7]), the sample exhibits the best electromechanical performance and the crystalline region displays a macroscopically uniform nonpolar phase. The data presented here indicate the optimum dose for 65/35 copolymer is 60 Mrad. (3) When irradiated with a high dose, the morphology is an amorphous matrix with pockets of very small crystallites. Both polar and nonpolar regions coexist in the material.

For the second heating process, the results reflect structural changes in the crystalline regions grown in a copolymer that contains cross-linking and other defects generated by irradiation. Thus, the phases obtained here present the stable structure that is possible in this type of copolymer, P(VDF−TrFE), with irradiation-induced defects. Both T_m and T_C, as well as both ΔH_m and ΔH_C, observed in the second heating process decrease with irradiation dose. In other words, the structure and morphology continuously change with irradiation defects. More importantly, the ratio of ΔH_C to ΔH_m monotonically decreases with irradiation dose, as shown in Figure 2c. Therefore, the percentage of crystalline regions that is polar at room temperature slightly decreases with irradiation dose, and the weight of the nonpolar portion increases with irradiation dose. It seems that the defects induced by the irradiation favor the nonpolar phase in the P(VDF−TrFE) copolymer studied here. However, compared to the data obtained in the first heating process, as shown Figure 2c, the weight of the nonpolar phase in the recrystallized samples is much smaller than that in the irradiated samples. Additionally, there are other possible explanations for this phenomenon. For example, the size of the crystalline regions may have an effect on the phase transition and melt behaviors observed here as both the phase transition temperature and melt temperature decrease with decreasing size of crystal.[37] As mentioned above, the size distribution of crystalline regions in recrystallized samples is broader than that in irradiated polymers. Thus, it seems likely that the increase of nonpolar phase with increased dose in the second heating is caused by this size distribution.

To clarify this issue, we compared the data and curves obtained from the two heating processes. This comparison revealed the following: (1) Although the T_m observed in the second heating was slightly lower than that in the first heating, the ΔH_m obtained in second heating was much smaller than that in the first heating. (2) For samples irradiated with doses up to 60 Mrad, the T_C obtained in the second heating was clearly higher than that in the first heating, while for samples irradiated with higher doses, the T_C obtained in the second heating was slightly lower than that in the first heating. (3) Although the ΔH_m obtained in the second heating was much smaller than that in the first heating, the ΔH_C obtained in the second heating was clearly higher than that in the first heating. Thus, it seems that the difference between the first and second heating processes increased with dose initially but past a certain point began to decrease as the irradiation dose increased. For samples irradiated with low doses, if the lower T_m observed in the second heating reflects a smaller size of crystalline regions due to rapid crystallization, the higher T_C observed in the second heating indicates a more stable polar phase. That is, for samples

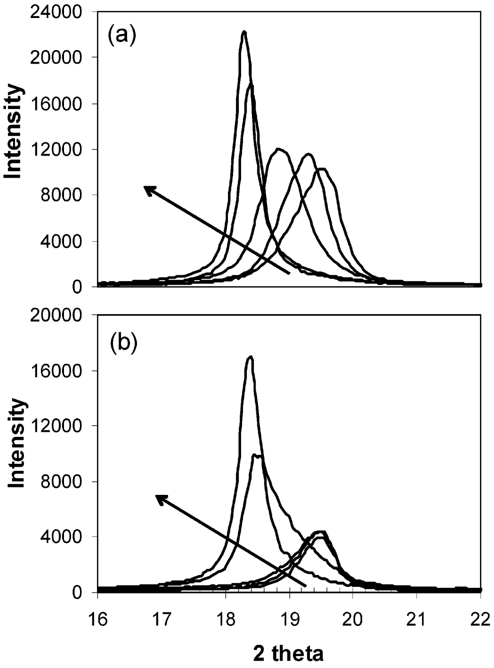

Figure 3. (200, 110) diffraction peak observed at room temperature using reflection scan for copolymer films irradiated with 0, 10, 35, 60, and 85 Mrad. The arrow shows doses from low to high. (a) Original irradiated films, (b) fast recrystallized films.

irradiated with a low dose, the polar phase obtained at room temperature in the second heating is more stable than that in the first heating.

2. X-ray Analysis. The crystalline structure of P(VDF−TrFE) copolymers has an orthorhombic unit cell in which the *c*-axis is parallel to the polymer chain.[33] Because the ratio of the lattice constants of the unit cell along the "*a*" and "*b*" axes is close to $\sqrt{3}$, the lattice has a quasi-hexagonal structure, resulting in the overlap of the (110) and (200) reflections. Let us first consider the X-ray data from the (200, 110) reflection. The (200, 110) peak changes continuously with the irradiation dose from 19.55° (polar phase) at 0 Mrad to 18.3° (nonpolar phase) at 85 Mrad for the irradiated copolymer prior to recrystallization, as shown in Figure 3a. This indicates there is a continuous expansion in the interchain dimension, and the crystalline structure gradually changes from polar phase to nonpolar phase with irradiation dose. This seems in contrast to the DSC results obtained in samples irradiated with higher doses, where an increase of polar regions in the samples was founded. This contrast could be due to the size effect. The samples irradiated with high doses have high defect densities that result in very small crystalline regions with the favorable polar phase.[34] Additionally, as mentioned above, the size distribution in recrystallized sample is broader than that in irradiated ones. Therefore, there are polar regions that are too small to be observed or result in a very broader peak in the X-rays diffraction. The fact that a relatively clear peak is observed in DSC due to the phase transition for samples irradiated with high doses (shown in Figure 1) indicates that the amount of these small crystalline regions containing the polar phase is relatively high.

For rapidly recrystallized samples, the (200, 110) diffraction peak is shown in Figure 3b. For samples irradiated with doses less than 60 Mrad, it is interesting to note that the (200, 110) peak moves back to a higher angle at the same location as that observed in unirradiated samples. This indicates that the structure of the crystalline regions in these recrystallized samples is the same as that in the unirradiated copolymer. That is, the influence that causes the appearance of the nonpolar phase during irradiation was eliminated during the recrystallization process. However, for samples irradiated with a higher dose, although the (200, 110) peak shifts a little to higher angle, the difference between irradiated and recrystallized samples is very small. From very first sight, this seems contrast to the DSC data shown in Figures 1 and 2, where a clear increase of polar phase in the recrystallized material was observed. This difference is caused by the size effect. As discussed above, the size of polar regions in this case may be too small to form a clearly X-ray diffraction peak.

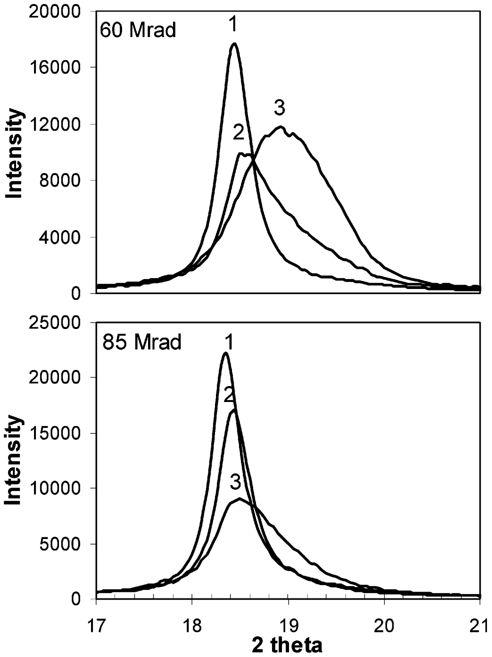

Figure 4. (200, 110) diffraction peak observed at room temperature using reflection scan for irradiated and recrystallized copolymer films: 1, original irradiated films; 2, fast recrystallized film; 3, slow recrystallized films.

It is well-known that polymer crystallization is a time-consuming process consisting of nucleation and growth processes, and there is a critical size which plays an important role in the final size of the crystalline regions and increases with crystallization temperature.[38] The small size of the crystalline regions obtained may be caused by the rapid cooling process, which limits the growth of crystalline regions. To study the crystallization process, slow recrystallization was also carried out. The X-ray diffraction data for samples irradiated with 60 and 85 Mrad are shown in Figure 4. For the sample irradiated with 60 Mrad, it is clear that the X-ray diffraction peak observed in the slowly recrystallized sample moved to a higher angle that is very close to the corresponding angle for the polar phase observed in unirradiated samples. For the sample irradiated with 85 Mrad, the X-ray diffraction peak obtained in slowly crystallized sample shifts to a higher angle than corresponding fast recrystallized sample. However, this shift is much smaller than that obtained in the sample irradiated with 60 Mrad. This indicates that the crystallization rate decreases with increasing irradiation doses, in other words, with increasing defects.

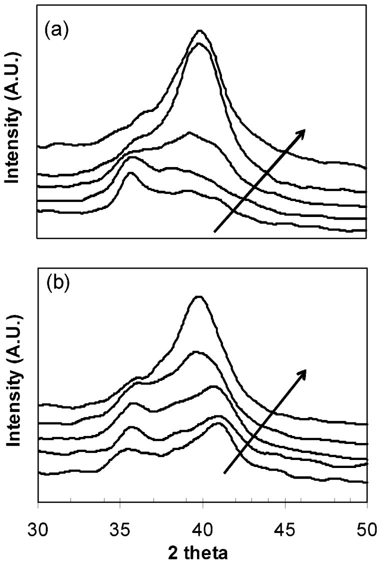

Figure 5. (001) diffraction peak observed at room temperature using the transmission scan for copolymer films irradiated with 0, 10, 35, 60, and 85 Mrad. The arrows show doses from low to high. (a) Original irradiated films, (b) after fast recrystallization at a cooling rate 10 °C/min.

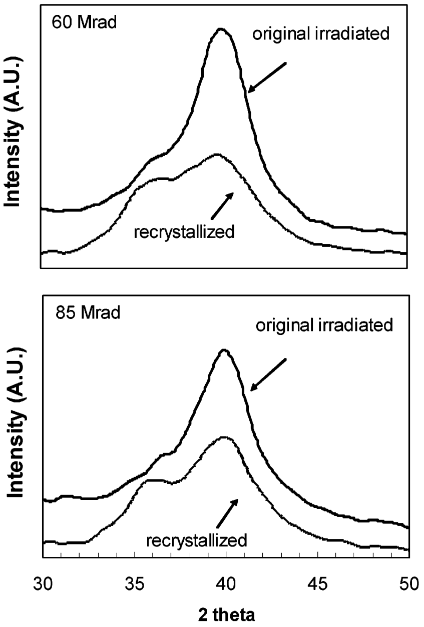

Figure 6. (001) diffraction peak observed at room temperature using the transmission scans for original irradiated and slow recrystallized copolymer films.

The X-ray diffraction for the (001) peaks is shown in Figure 5 for both irradiated samples and the rapidly recrystallized samples. For the P(VDF−TrFE) copolymer, the peak at about 40° is associated with the nonpolar phase, while the peak at about 36° is associated with the polar phase. For irradiated samples, the intensity of the peak at about 36° decreases while the intensity of the peak at about 40° increases with irradiation dose. This is consistent with the (200, 110) peak shown in Figure 3. However, in contrast to the (200, 110) peak where the peak position continuously shifts to lower angle with irradiation dose, the position of both (001) peaks almost does not change with irradiation. This confirms the conclusion that the broad (200, 110) peak shown in Figure 3 is the merged results of two peaks. Thus, in the irradiated copolymer, the polar and nonpolar phases coexist.

Compared to the irradiated samples, the rapidly recrystallized samples irradiated with high doses exhibit a clear intensity enhancement of the peak at about 36°, as shown in Figure 5. It should be mentioned that for samples irradiated with low doses the peak at about 41°, which is higher than the 40° seen for the (001) peak of the nonpolar phase, is clearly visible. This is probably due to the orientation induced by stretching being partially destroyed during the recrystallization process. Therefore, for a transmission scan, in addition to the (001) peak other peaks could be obtained. The peak at 41° shown in Figure 5 could originate from the (201, 111) reflection of the polar crystalline phase.

Figure 6 shows the (001) reflections for slowly recrystallized samples. The peak associated with the polar phase is much clearer in the slowly recrystallized samples than that in the rapidly recrystallized samples. This again indicates that the crystallization in copolymers with high defects densities induced by irradiation is much slower than in unirradiated copolymer samples and that the percentage of the polar phase in the recrystallized samples is much higher than that observed in the samples that were only irradiated. There are two possible reasons responsible for slower crystallization process: (1) smaller difference in energy state between amorphous and crystalline phase, which is the driving force for the transformation; (2) a higher energy barrier between amorphous and crystalline phase. Considering the polarization behavior presented below, where it is concluded that the energy barrier between amorphous and crystal is smaller than regular copolymer, we believe that the difference in energy state between amorphous and crystalline phase in polymers with high density of defects induced by irradiation is smaller than that in polymer without these defects.

3. Polarization Loop Measurement. For electromechanical materials, the polarization hysteresis loop is a very useful material property since the loop is related to the electromechanical performance of the materials due to the fact that the charge-related electrostrictive coefficients can be treated as a constant.[39] The polarization hysteresis loop for selected films is shown in Figure 7. For the unirradiated copolymer, a remanent polarization (P_r) of 10.9 μC/cm^2 was obtained. However, the recrystallized film exhibited a slightly lower polarization level (~9.2 μC/cm^2 at 125 MV/m) due to the deorientation effect discussed above. For film irradiated at 60 Mrad, the recrystallized sample exhibited a much larger P_r, 3.2 μC/cm^2, with a driving field of 125 MV/m. This indicates the appearance of the polar phase in the material, which is consistent with the DSC and X-ray data presented above.

Although film irradiated at 85 Mrad exhibited a very slim loop for a low polarization level (~3.96 μC/cm^2 at 125 MV/m), the slowly recrystallized sample exhibited a relatively high polarization level in a high electric field (~7.5 μC/cm^2 at 125 MV/m). More importantly, the loop for the recrystallized film shows a peanut shape with a much smaller remanent polarization, 0.953 μC/cm^2. A high polarization level in a high field with a small remanent polarization is very attractive for many applications. As the structure and morphology obtained in recrystallized samples correspond to a stable structure and morphology in copolymers with permanent defects induced by irradiation, the recrystallized copolymer appears to be a good candidate for electromechanical applications.

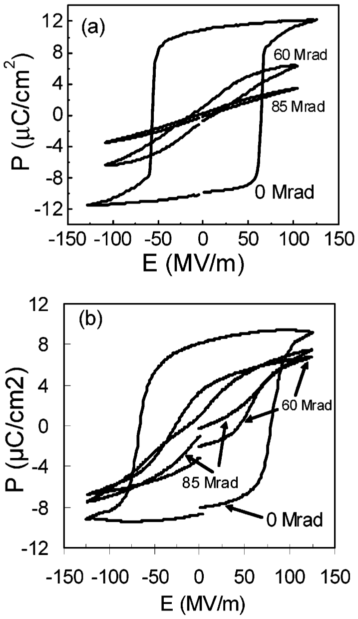

Figure 7. Polarization loops for (a) irradiated copolymer and (b) slowly recrystallized films that was irradiated with different doses (0, 60, and 85 Mrad).

Possible reasons responsible for high polarization level observed in the slow recrystallized sample with 85 Mrad are the following: (1) The slow recrystallized sample has high crystallinity. (2) The amorphous structure is not completely disordered due to the presence of irradiation defects, and the electric field converts some amorphous ranges to crystal-like regions due to the energy state difference between amorphous and crystal-like structure is small. To clarify the results, the DSC study was carried out for slow recrystallized samples. It is found that although the crystallinity in slow recrystallized samples is slightly higher than that in corresponding fast recrystallized samples, the crystallinity is still much smaller than that in only irradiated samples. For the sample irradiated with 85 Mrad, the melting enthalpy (ΔH_m) for only irradiated, fast recrystallized, and slow recrystallized samples is 15.6, 9.0, and 11.9 J/g, respectively. And for the sample irradiated with 60 Mrad, the melting enthalpy (ΔH_m) for only irradiated, fast recrystallized, and slow recrystallized samples is 22.5, 12.7, and 14.0 J/g, respectively. That is, the crystallinity in slow recrystallized 85 Mrad irradiated sample (11.9 J/g) is much smaller than that in only 60 Mrad irradiated sample (22.5 J/g). Considering the DSC results and polarization shown in Figure 7, one can conclude that contribution to the polarization from noncrystalline regions is relatively high for recrystallized samples comparing to regular P(VDF−TrFE) copolymers. That is, it is easy for external electric filed to convert the some regions from noncrystalline regions to crystal-like structure in recrystallized samples. This means that the difference in energy state and energy barrier between the crystalline region and amorphous in polymer with high density of defects induced by irradiation is smaller than that in regular P(VDF−TrFE) copolymer.

Conclusion

The structure and morphology of recrystallized P(VDF−TrFE) 65/35 mol % copolymer samples that had previously been irradiated were studied using DSC and X-ray techniques. Since the recrystallization occurred in polymer samples containing defects induced by irradiation, the structure and morphology obtained in the recrystallized polymers were found to contain thermally stable states of crystalline regions in a copolymer with defects, including cross-linking and bulkier groups. In recrystallized samples, a much high proportion of polar regions was obtained than in irradiated samples. For film irradiated at low doses, an almost completely polar phase was observed in recrystallized samples. For 60 Mrad irradiated film, which exhibits the best electromechanical performance, a very high fraction of the crystalline regions in the recrystallized sample was found to be in the polar phase, and this resulted in a much higher remanent polarization in the polarization loop. The X-ray study of slow and fast recrystallization processes combined with the results of polarization loop measurements on recrystallized sample show that the energy state difference between the crystalline and amorphous forms is small in irradiated samples, which results a slow recrystallization process. Of particular interest is the finding that although film irradiated with a higher dose (85 Mrad) exhibited a low polarization level, the recrystallized samples exhibited a much higher polarization with a very small remanent polarization, a combination which is very attractive for electromechanical applications.

Acknowledgment. The authors gratefully acknowledge financial support from an Auburn University Competitive Research grant and USDA 20013439410295. We are thankful to Dr. Q. M. Zhang of Penn State University and Drs. B. A. Chin and W. F. Gale of Auburn University for their helpful discussions and experimental support.

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MA035251H