Structure of P(VDF-TrFE) (80/20) Copolymers under Electron Irradiation and Recrystallization

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ABSTRACT: The structural changes of irradiated and recrystallized copolymers of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] (80/20) copolymers have been investigated through IR spectra, X-ray, and DSC. It is found that recrystallization has a reverse effect on irradiated P(VDF-TrFE) copolymers, by which the irradiated samples are turned back to original nonirradiated state partially. During recrystallization, trans-gauche sequences are replaced by all-trans conformation gradually and the irradiated P(VDF-TrFE) (80/20) copolymers change from nonpolar phase to polar one. The average crystallite size of polar phase is larger than that in irradiated samples, and the difference between recrystallized and irradiated samples reduces gradually with irradiation dosage. The C=C and conjugated C=C bonds are also found in the recrystallized-irradiated P(VDF-TrFE) (80/20) due to rearrangement of broken bonds. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4258–4263, 2006

Key words: irradiation; crystallization; FTIR; X-ray diffraction; DSC

INTRODUCTION

Polymeric ferroelectric materials have attracted much more attention these years because of their potential and various applications in many domains. Compared with ferroelectric ceramics, polymeric ferroelectric materials have lower density, are also easy to process, and more flexible, lower mechanical and acoustic impedance, which make them good candidates as sensors and transducers in ultrasonic medical imaging, blood pressure and pulse measurements, touch sensors in robotics, and so forth.[1–4] Among them, copolymers of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE), hereafter] are materials of great interest because of their outstanding piezoelectric and ferroelectric properties.[5,6]

Recently, it was found that under a proper electron irradiation treatment, a massive longitudinal electrostrictive strain could be induced in P(VDF-TrFE) copolymers, which is orders of magnitude larger than those of piezoelectric ceramics.[7] Hence, studies on irradiated P(VDF-TrFE) have been carried out to understand the irradiation effect and to indicate the microstructure.[8–10] But the nature of the transformation of ferroelectric P(VDF-TrFE) copolymer into the relaxor state and of the high performance induced by irradiation are still an open question. So it is important to do more studies on irradiation effect of P(VDF-TrFE) copolymers.

It is found that P(VDF-TrFE) copolymer crystallizes directly into polar ferroelectric phase with the VDF content of 50–80%. And it exhibits excellent electrostriction performances after irradiation, at the cost of lost of ferroelectric character. Thus, to do recrystallization treatment of irradiated copolymers may be helpful to deeply understand that what happens during irradiation. In fact, except for recrystallization study of irradiated P(VDF-TrFE) (65/35) copolymers from Cheng and coworkers,[11,12] few have been reported in this field. Further more, the VDF content, which controls the value of the spontaneous polarization, is responsible for determining the stability of ferroelectric structure, and the TrFE proportion is responsible for the crystalline structures.[13] And in these copolymers, composition with a VDF content of 70–80% are best suited to obtain high crystallinity, so it is valuable to do corresponding recrystallization studies on these molar ratio irradiated copolymers. Hence, following our previous work about reversible phase transition in electron-irradiated P(VDF-TrFE) (80/20) copolymers,[14] recrystallization effect of irradiated copolymers P(VDF-TrFE) with the VDF content of 80% is discussed here. And it will be helpful to make clear the microscopic mechanism understand the ferroelectric relaxor behavior and lead to the development of new materials with enhanced electromechanical performance.
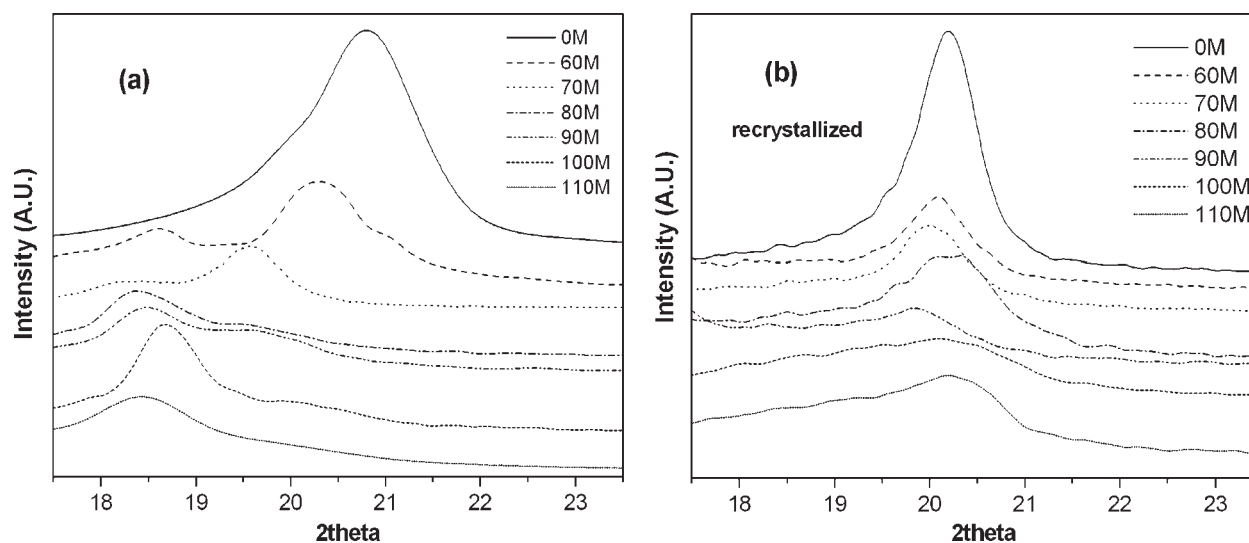
Figure 1 X-ray diffraction diagram of P(VDF-TrFE) (80/20) at room temperature: (a) irradiated samples and (b) irradiated samples after recrystallization.

EXPERIMENTAL

The P(VDF-TrFE) (80/20 mol %) was obtained from Piezotech, France in the form of white pellets. These pellets were dissolved in dimethylformamide (DMF) by stirring at room temperature. Thin films (about 20–30 μm) were then formed by solution casting on a glass substrate. The copolymer films were annealed at 120°C for 1 day to remove residual solvent. To further improve the crystallinity, the films were annealed at higher temperature (135°C) for 12 h. The electron irradiation was carried out at 70°C in vacuum with 3 MeV electrons. The dosage was in the range from 60 to 110 Mrad. And then the irradiated films were annealed at 150°C for 30 min for recrystallization and then cooled to room temperature at

2°C cooling rate. XRD was carried out using a Philips Dual X'Pert XRD system with Ni-filtered Cu Kα radiation at a scanning speed of 0.005° 2θ/s at room temperature. The IR spectra were obtained using a Shimadzu (FT-8201PC) Fourier transform infrared spectrophotometer. All spectra were obtained from KBr discs containing approximately 1 mg of sample and 100 mg of KBr. DSC was performed with a PerkinElmer DSC7 thermal analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

X-ray data taken at room temperature of irradiated and irradiated-recrystallized P(VDF-TrFE) copolymers are
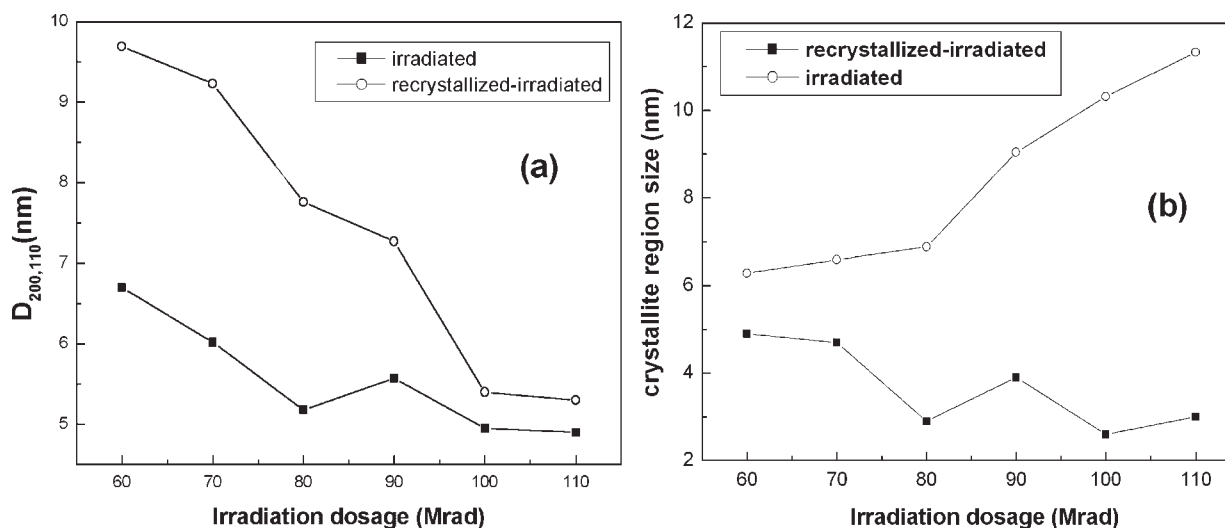

Figure 2 Crystallized region size before and after recrystallization as a function of the doses of the irradiation: (a) polar phase and (b) nonpolar phase.
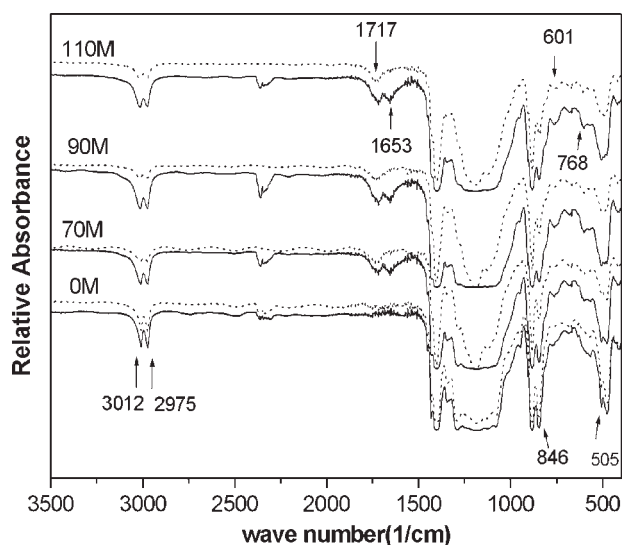
Figure 3 IR transmission spectra of irradiated (short dot line) and recrystallized (solid line) P(VDF-TrFE) at different irradiation doses.

presented in Figure 1. For unirradiated film, only one reflection at $2\theta = 20.5°$ is observed, which is the characteristic diffraction peak of ferroelectric β phase (polar phase) and represents the Bragg diffraction of (110) and (200).[15] For the 60 Mrad irradiated film, a new peak appears at 18.6°, corresponding to the nonpolar phase.[15] With increasing radiation dosage, the intensity of the peak corresponding to the ferroelectric phase decreases while the new peak from nonpolar phase gradually becomes more intense. When the radiation dose reaches 110 Mrad, the ferroelectric peak has nearly disappeared. At the same time, the position (2θ) of the two peak move to lower angle with irradiation dosage, which proves the expansion of lattice due to the introduction of defects in the crystalline phase during irradiation. It is believed that the large strain response observed in the irradiated copolymer is related to the electron field induced phase transition of the crystal regions between nonpolar and polar phase.[7,15]
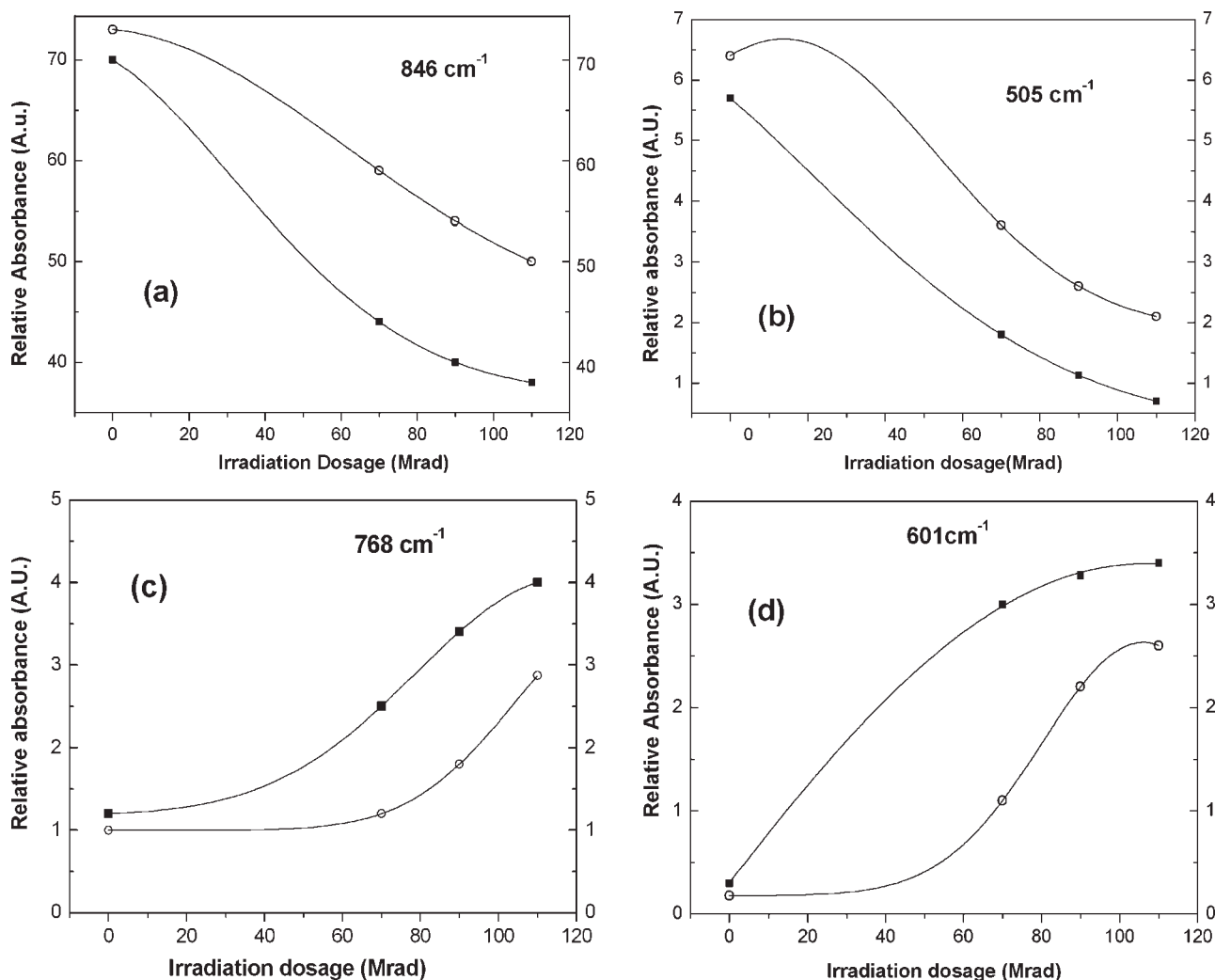

Figure 4 Relative absorbance of different bands of irradiated (solid square) and recrystallized-irradiated (hollow circle) P(VDF-TrFE) copolymers: (a) 846, (b) 505, (c) 768, and (d) 601 cm^{-1}.
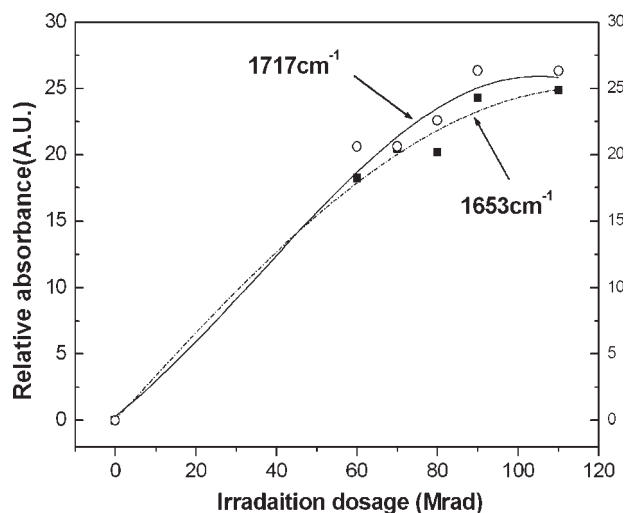
Figure 5 Relative absorbance of 1717 and 1653 cm^{-1} as a function of irradiation dose.

For the recrystallized samples, the intensity of peaks from (110) and (200) diffraction also decrease greatly with increasing irradiation dosage. But comparing with that of irradiated samples, these peaks became more intense. On the other hand, the peaks of nonpolar phase, which were induced by irradiation and located at the range from 18.2° to 18.6°, weaken greatly after crystallization. It should be point out that the peaks of polar phase in recrystallized samples move back to higher angle, which are close to that location observed in unirradiated samples. This indicates the structure of the crystalline regions in these recrystallized samples is the same as that in the unirradiated samples to some extent. That is, the influence causing the appearance of nonpolar phase by irradiation was recovered during recrystallization process.

The crystallite size of the domain D_{hkl} in the direction normal to the *hkl* plane can be evaluated on the basis of Scherrer's equation.[16]

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta}$$

where 2θ is the diffraction angle, K is a constant of value 0.9, β is the full width at half-maximum of the reflection peak (*hkl*), and λ is the X-ray wavelength. Using Gaussian function to fit the X-ray peaks, the average crystallite size is shown in Figure 2. It is found that average crystallite size of polar phase in recrystallized samples is larger than that in irradiated samples, and the difference between recrystallized and irradiated samples reduces gradually with increasing irradiation. On the contrary, the crystallite size of nonpolar phase reduces greatly after recrystallization, and the difference is large with the irradiation dosage. This indicates that recrystallization has great effect on irradiation-induced nonpolar phase and changes it into polar one.

Figure 3 shows the IR transmission spectra of irradiated and recrystallized P(VDF-TrFE) copolymers. The peaks at 3012 and 2975 cm^{-1} are the asymmetric stretching vibration of C—H bond. The absorbance of C—H bond is related with the thickness of sample and does not depend on the state of sample.[17] So it can be used as an internal standard here. The data in Figure 4 are the relative absorbance after correction. According to Hector's study, the peaks at 846 and 505 cm^{-1} are the vibration of all-trans sequences and the peaks at 601 and 768 cm^{-1} correspond to the trans-gauche sequence from paraelectric α and δ phase.[18] From Figure 4, it can be seen that after recrystallization the peaks at 846 and 505 cm^{-1} grow more intense than that corresponding
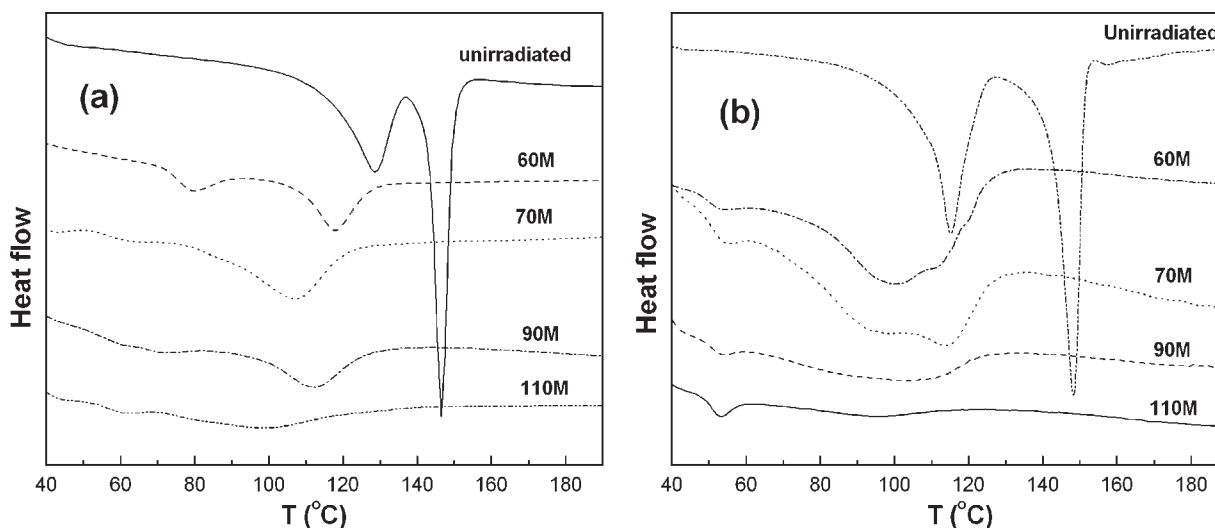

Figure 6 DSC curves of P(VDF-TrFE) (80/20) with different radiation doses: (a) irradiated samples and (b) irradiated and recrystallized samples.

irradiated samples, but decrease with the irradiation dosage. Conversely, the peaks at 601 and 768 cm^{-1} decrease in intensity due to recrystallization. So during recrystallization, trans-gauche sequence is replaced by all-trans conformation. Thus, it is suggested that there is a phase transformation from nonpolar to polar induced by recrystallization, in agreement with the results of XRD.

The band at 1717 cm^{-1} appearing after irradiation can be assigned to a C=C double bond. These microscopic defects (double bond) produced in P(VDF-TrFE) during the irradiation are basically related to the dehydrofluorination reaction.[18,19] It should be pointed out that a new band at 1653 cm^{-1} appears in the recrystallized-irradiated sample, but cannot be found in the nonirradiated one. It shows the new band must be relative to the further changes in the recrystallization process of the structure induced by electron irradiation. According to the principle that the less of double bonds energy in conjugate system, the lower is the wave number of absorbance band,[20] so the new band 1653 cm^{-1} might be the vibration of conjugate C=C, which produces and forms stable conjugated system during recrystallization process, accompanying with the rearrangement of broken bonds. As shown in Figure 5, the intensity of band corresponding to vibration of C=C and conjugate C=C increases with irradiation dosage. The more irradiation dosage on the P(VDF-TrFE), the more C=C produce, and the more conjugate C=C form after recrystallization.

DSC data of the irradiated and recrystallized copolymers are presented in Figure 6. The unirradiated sample exhibits two endothermic peaks located at 146 and 128°C. The peak at the lower temperature (T_c) is associated with (F-P) phase transition in the crystalline regions, while the one at the higher tem-
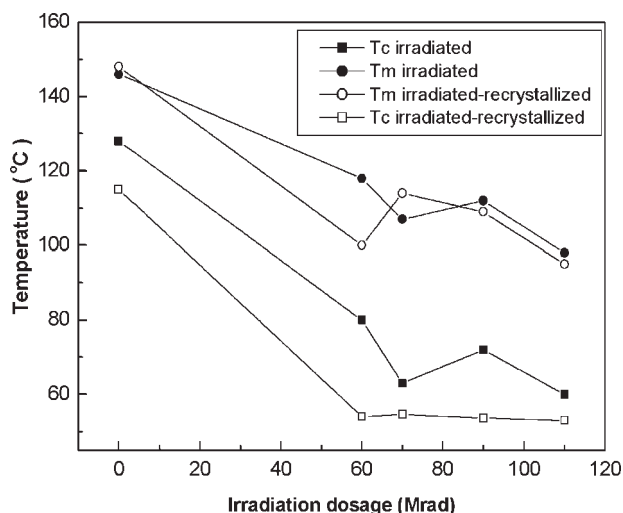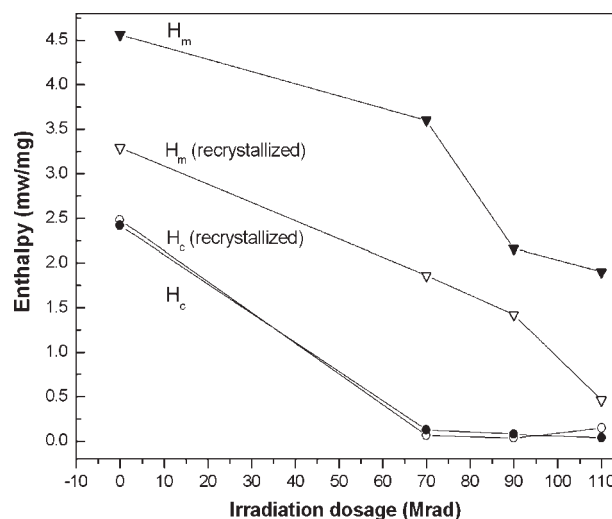

Figure 8 The enthalpy curves of irradiated (solid) and recrystallized (hollow) P(VDF-TrFE) copolymers with different radiation doses.

perature (T_m) reflects the melting behavior of the crystalline regions in the materials.[21] It is found that after irradiation the position of both peaks shifts to lower temperature and the peak of F-P phase transition nearly disappears. But in the recrystallized sample, the peak of phase transition is very strong, and the melting peaks are broader than that in irradiated samples. Since the melting temperature is related to the size of crystal regions, so the crystalline regions in recrystallized samples have a broader size distribution than the irradiated sample, and the size distribution broadens with irradiation dose.

As shown in the Figures 7 and 8, the temperature and the enthalpy of the melting peak decrease with irradiation dose, in agreement with the destruction of crystalline domains and the decrease in the degree of crystallinity. But the enthalpy of the melting peak in recrystallized samples is less than that in irradiated samples. It indicates the degree of crystallinity is lower than that of corresponding irradiated samples.

CONCLUSIONS

The structure of recrystallized-irradiated P(VDF-TrFE) (80/20) copolymer was studied using XRD, FTIR, and DSC. It was found during recrystallization, trans-gauche sequence is replaced by all-trans conformation, and the influence that causes the appearance of nonpolar phase during irradiation was recovered. The average crystallite size of polar phase is larger than that in irradiated samples, and the difference between recrystallized and irradiated samples reduces gradually with increasing irradiation. Combining with Chen and coworker's report about the nanostructure of P(VDF-TrFE) induced

Figure 7 The temperature curves of irradiated (solid) and recrystallized (hollow) P(VDF-TrFE) copolymers with different radiation doses.

irradiation,[22] here one reasonable picture can be drawn to interpret the changes during irradiation and recrystallizaiton. The crystalline regions of the copolymers are broken into ''nanocrystals'' (polar nanosize cluster) gradually by the high energy electron irradiation. And the ''nanocrystals'' are distributed in an amorphous phase so as to form a special microstructure consisting of nanocrystalline–amorphous regions. So here the nanocrystals size in such regions can form macrodomains due to recrystallization effect and the copolymers change back to polar phase partly. Because of existence of defects, such as C=C and conjugated C=C bonds, it cannot be recovered completely to the original state before irradiation and exhibit a flat diffraction peak with broader crystallite size distribution

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