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Structural modification of electron-irradiated poly (vinylidene fluoride-trifluoroethylene) copolymer

W. P. LI*, S. S. GUO, Y. W. TANG, C. L. SUN, X. Z. ZHAO
Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China
E-mail: wp_li2003@hotmail.com

Since the discovery of ferroelectricity in the copolymer poly (vinylidene-fluoride-trifluoroethylene) (P (VDF-TrFE) hereafter) extensive research has been carried out to understand the ferroelectric behavior, to enhance the electromechanical properties, and to establish structure-property relationships [1, 2]. These polymers can crystallize into four types of crystals: I (β), II (α), III (γ), and IV (δ). It is well-known that the α phase consists of anti-parallel TGTG′ trans-gauche chains, the β phase consists of all-trans chains, the γ phase is an intermediate conformation T_3GT_3G' and the δ phase is a parallel version of the α phase [3]. Of the four types, only the β phase is polar. After Lovinger found that the ferroelectric-paraelectric (F-P) phase transition could be induced by electron irradiation at room temperature in P (VDF-TrFE), different radiations such as gamma rays, X-rays and ultraviolet radiation have been used to modify the properties of these materials [4–6]. The aim of this work is to investigate the structural modification of P (VDF-TrFE) induced by electron irradiation using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC).

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 one 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. XRD was carried out using a Philips Dual X'Pert XRD system with Ni-filtered Cu K_α radiation at a scanning speed of 0.005 ° 2θ/s. 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 Perkin-Elmer DSC7 thermal analyzer at a heating rate of 10 °C/min.

X-ray data taken at room temperature after exposure to different radiation doses are presented in Fig. 1. For unirradiated film, only one reflection at $2\theta = 19.8\,^\circ$ is observed, which is from the ferroelectric β phase and represents the Bragg diffraction of (110) and (200) [7]. For the 60 Mrad irradiated film, a new peak appears at 18.4 °, corresponding to a nonpolar phase that is thought to be the metastable paraelectric phase [8]. This means that the polar and nonpolar phase coexist in crystalline regions after irradiation. With increasing radiation dosage, the intensity of the peak corresponding to the ferroelectric phase decreases while the new peak from the nonpolar phase gradually becomes more intense. When the radiation dose reaches 110 Mrad the ferroelectric peak has nearly disappeared. Additionally, the position of the peak associated with the nonpolar phase moves to lower angles, and the corresponding lattice spacing is close to that of paraelectric phase. The XRD results indicate that the crystalline phase is predominantly nonpolar at this dose.

In the ferroelectric copolymer there are polarization domains in which the electric moments are aligned. The size of the domain D_{hkl} in the direction normal to the *hkl* plane can be evaluated on the basis of Scherrer's equation [9].

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

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. In the polar phase the coherent X-ray reflection region is determined by the polarization domain size; in the nonpolar phase, it corresponds to the crystallite size [10]. The results are shown in Fig. 2. With increasing radiation dosage, the domain size of the nonpolar phase increases to 11 nm, but that of the polar phase decreases from 10.8 to 6.9 nm. This indicates the ferroelectric domains changes to the nonpolar phase. It is also noted that the peak width of the (110, 200) diffraction increases greatly, due to the disappearance of the ferroelectric domains. For a ferroelectric material in equilibrium, the domain size is determined by the domain wall energy, the coupling between domain walls, and the crystallite size. Cheng and co-workers state that the domain size is controlled mainly by defects in the crystallites and the crystallite-amorphous boundary conditions [10]. Therefore, with increasing irradiation, the concentration of defects (such as chain ends and pendant groups generated by chain scission) in

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*Author to whom all correspondence should be addressed.

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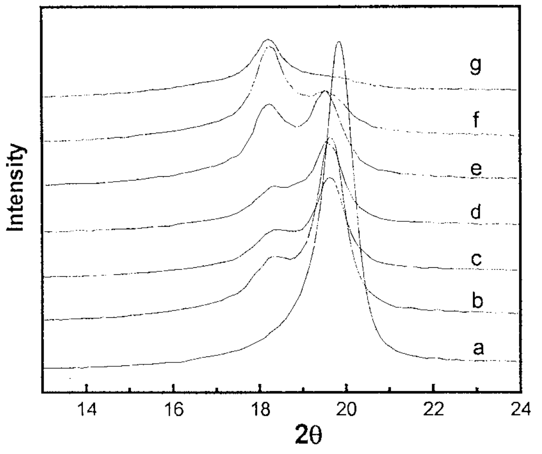

Figure 1 X-ray diffraction diagram of P (VDF-TrFE)(80/20), as a function of the radiation doses: (a) 0 Mrad, (b) 60 Mrad, (c) 70 Mrad, (d) 80 Mrad, (e) 90 Mrad, (f) 100 Mrad and (g) 110 Mrad.

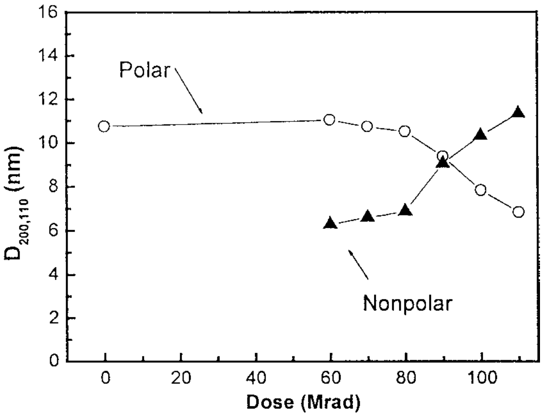

Figure 2 Dose dependence of crystalline size $D_{200,110}$.

the crystallites also increases, resulting in the observed reduction of the polarization domain size.

Fig. 3 shows the IR transmission spectra of P (VDF-TrFE) copolymers after different radiation doses. For unirradiated film, the peaks at 3012 and 2975 cm^{-1} are the asymmetric stretching vibration of C—H bond [11]. After irradiation, these two peaks shift slightly to a higher wavenumber region (3020 and 2979 cm^{-1} at 110 Mrad dose), which is due to the decreasing concentration of comomer unit (—CHF—CF_2—) in the irradiated copolymer structure. The absorbance of C—H bond is related to the thickness of sample and does not depend on the state of the sample [12]. So it can be used as an internal standard here. The data in Fig. 4 is the relative absorbance after correction.

According to Hector and Masamichi's study, the peaks at 1286 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 [5, 13]. From Fig. 4a and b, it can be seen that the peaks at 1286 cm^{-1}, 505 cm^{-1}, decrease gradually and nearly disappear when the dose is 110 Mrad. Conversely, the peaks at 601 and 768 cm^{-1} increase in intensity. So after irradiation, the all-trans conformation disappears and is replaced by a trans-gauche sequence. Thus it is suggested that there is a gradual phase transformation from polar to nonpolar induced

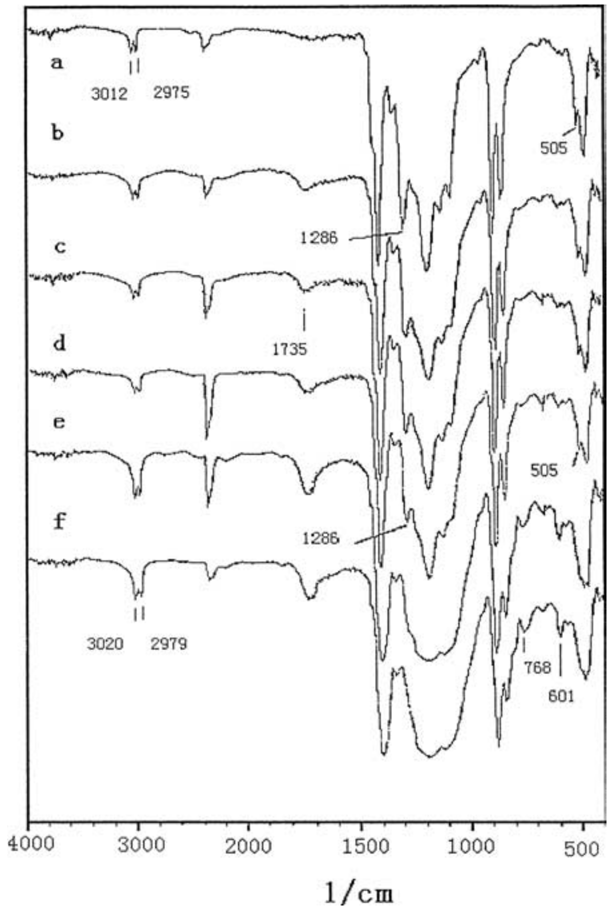

Figure 3 IR transmission spectra of P (VDF-TrFE) at different irradiation doses in the 400–4000 cm^{-1}: (a) 0 Mrad, (b) 60 Mrad, (c) 70 Mrad, (d) 80 Mrad, (e) 100 Mrad and (f) 110 Mrad.

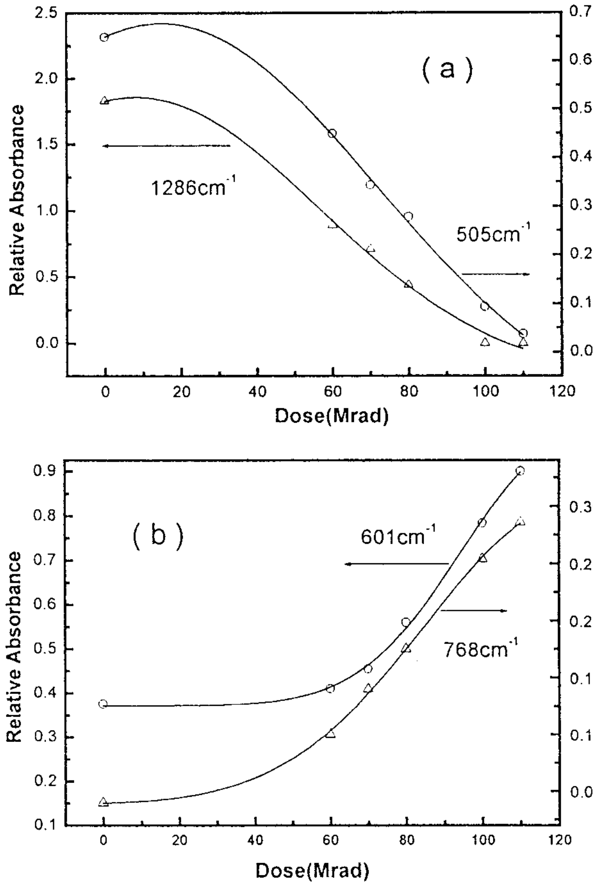

Figure 4 The relative absorbance of different bands as a function of the radiation doses: (a) 1286 and 505 cm^{-1} and (b) 768 and 601 cm^{-1}.

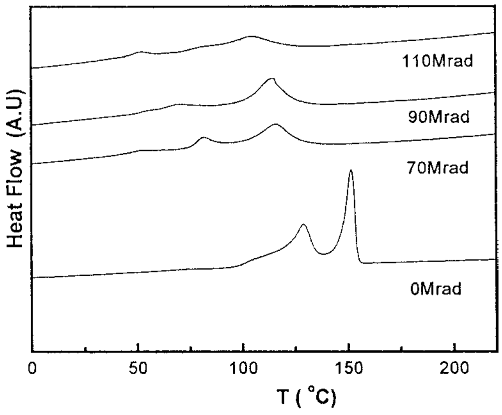

Figure 5 DSC curves of P (VDF-TrFE)(80/20) with different radiation doses.

by irradiation. This is in agreement with the results of XRD that demonstrated that the crystalline phase is nonpolar above 110 Mrad irradiation.

The band at 1735 cm^{-1} appearing after irradiation can be assigned to a carbon-carbon double bond [14]. The intensity increases greatly with irradiation. These microscopic defects (double bond) produced in P (VDF-TrFE) during the irradiation are basically related to the dehydrofluorination reaction and may affect the domain size.

DSC data of the irradiated copolymers are presented in Fig. 5. Clearly, the electron irradiation results in significant changes in both the phase transition and crystallization behaviors of the copolymer samples. The unirradiated sample exhibits two endothermic peaks located at 151 and 129 °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 temperature (T_m) reflects the melting behavior of the crystalline regions in the materials [15]. It is found that the position of both peaks shifts to lower temperature and the peak of F-P phase transition nearly disappears. The temperature and the enthalpy of the melting peak decrease continuously with irradiation dose, in agreement with the destruction of crystalline domains and the decrease in the degree of crystallinity. Additionally, the DSC peak associated with the melting of crystals also broadens with irradiation dose. This indicates the presence of broad distribution in crystalline sizes and crystal ordering, which is due to the lattice defects and crosslinking in the copolymer.

In summary, it is found that there is a gradual phase transition from polar to nonpolar with increasing radiation dosage. The XRD and DSC results show the loss of ferroelectric property, and decrease of the degree of crystallinity after irradiation. As suggested by FT-IR data, the structure of crystalline regions changes from polar, characterized by the all-trans configuration in the molecular chains, to a nonpolar state, represented by the trans-gauche conformations in molecular chains.

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