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Study of irradiation effect on poly(vinylidene fluoride-trifluoroethylene) copolymers

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Abstract In order to get the nature of the ferroelectric relaxor behavior, the structural changes of electron irradiated of P (VDF-TrFE) copolymer have been investigated through IR spectra, X-ray, DSC, and AFM. The irreversible transformation from the ferroelectric copolymer to the relaxor state induced by irradiation is related to the creation of polar clusters, consisting of a variety of short range coherence of trans-conformation, stabilized by random fields of C=C and C=O bonds. And the existence of nanometer scale crystals embedded in an amorphous matrix may be the base of the relaxor behavior and high performance in these polymers.

Introduction

Poly(vinylidene-fluoride) (PVDF) and its copolymers with trifluoroethylene, P (VDF-TrFE) hereafter, have been studied widely [1–3], since the materials are interesting for high performance actuators and transducers. These polymers can crystallize into four types of crystals forms: form (β), form (α), form (γ), and form (δ). It is well-known that the α phase consists of anti-parallel $TGTG'$ chains and the β phase consists of all-trans chains, and the α phase is an intermediate conformation T_3GT_3G' [4]. Among the four types, only the β phase is the polar phase. Recently, different radiations such as gamma rays, X-ray and UV were applied to modify the properties of these materials [5–7]. It has been found that after irradiation the ferroelectric copolymer exhibited characteristic of ferroelectric relaxors, giant electrostrictive response, high and dispersive dielectric anomaly. Although extensive research has been carried out to understand the irradiation effect [8, 9], the nature of the irreversible transformation of ferroelectric P (VDF-TrFE) copolymer into the relaxor state induced by irradiation is still unclear. On the other hand, scanning probe microscopy techniques have been used widely to investigate local structures and electrical properties of ferroelectrics. So in this work the structural modification of P (VDF-TrFE) induced by electron irradiation is to be investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and atomic force microscopy (AFM). Similar with the phenomenon in those inorganic ferroelectric relaxors [10], the effect of polar nanosize clusters and random fields in nonpolar matrix are presented to interpret the microcosmic process during irradiation. It will be helpful to make clear the microscopic mechanism, understand the ferroelectric relaxor behavior and establish structure–property relationships.

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

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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 CuK$_\alpha$ radiation at a scanning speed of 0.005° 2θ/s. The IR spectra were obtained using a Shimadzu (FT-8201PC) Fourier transform infrared spectrometer. DSC was performed with a (Perkin-Elmer) Sapphire DSC thermal analyzer at a heating rate of 10 °C/min. The images of AFM were gotten by the Nanoscope III Multi-mode Scanning Probe Microscopy (Veeco Instruments) using tapping mode at the room temperature.

Results and discussion

IR transmission spectra of P (VDF-TrFE) at different irradiation doses are presented in Fig. 1. For unirradiated film, the spectrum shows two bands at 3,012 and 2,975 cm^{-1} that are the asymmetric stretching vibration of C–H bond [11]. It can be used as an internal standard here, just like the same analyses in our previous work [12]. The data in Fig. 2 is the relative absorbance after correction. According to Hector and Kabayashi's study, the bands at 1,286 cm^{-1} and 505 cm^{-1} are the vibration of all-trans sequences and the bands at 601 cm^{-1} and 768 cm^{-1} correspond to the trans-gauche sequence from paraelectric α and β phase [6, 13]. From Fig. 2, it can be found that the bands at 1,286 cm^{-1} and 505 cm^{-1} decrease gradually and nearly disappear when the dose is 110 Mrad. However, the bands at 601 cm^{-1} 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 by irradiation.

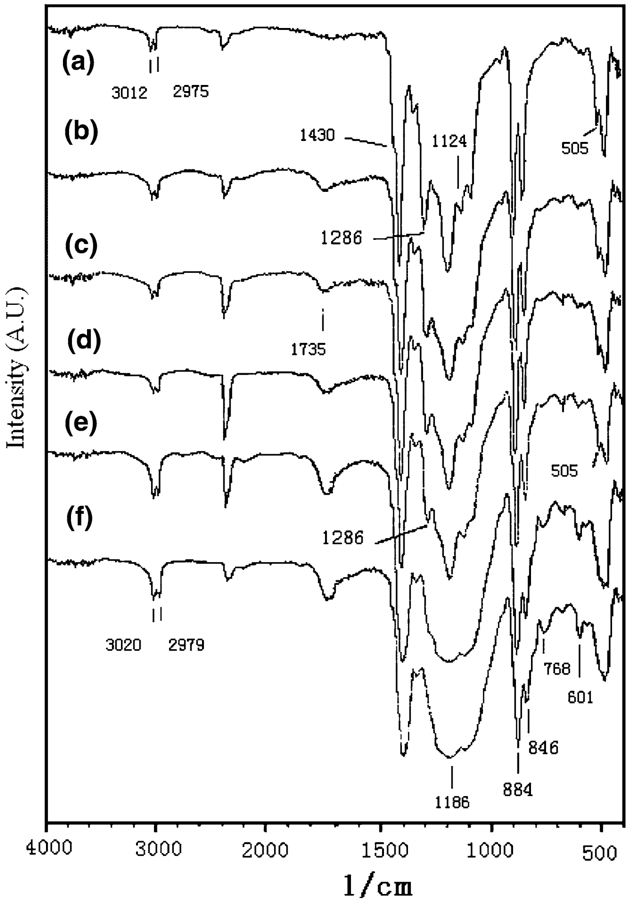

Fig. 1 IR transmission spectra of P(VDF-TrFE) at different radiation doses in the 400–4,000 cm^{-1}: (**a**) 0 Mrad, (**b**) 60 Mrad, (**c**) 70 Mrad, (**d**) 80 Mrad, (**e**) 100 Mrad, and (**f**) 110 Mrad

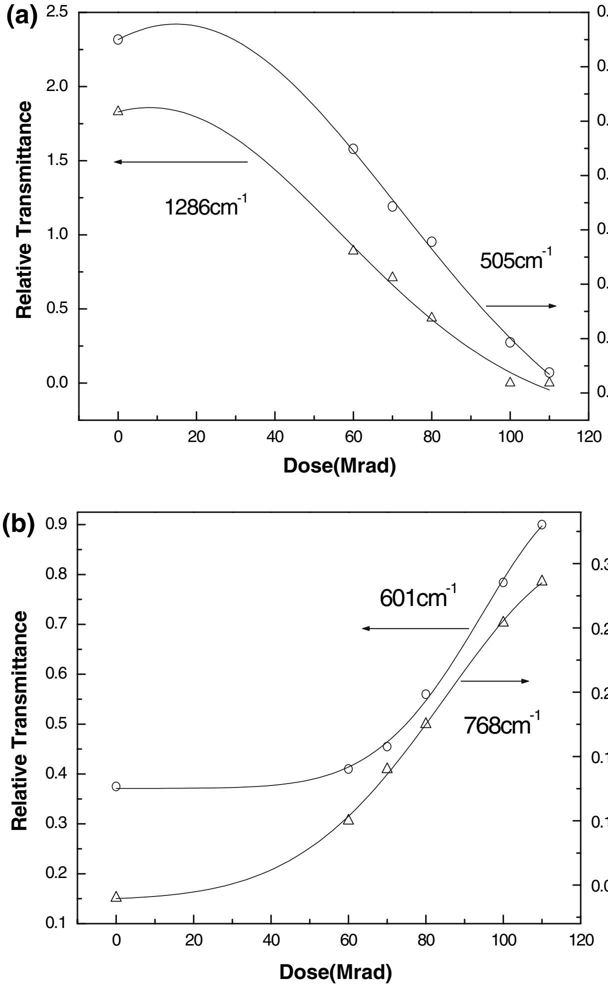

Fig. 2 The relative transmittance of different bands as a function of radiation doses. (**a**) 1,286 cm^{-1} and 505 cm^{-1}; (**b**) 768 cm^{-1} and 601 cm^{-1}

As shown in Fig. 3, the band at 1,735 cm^{-1} is characteristic of C=C bonds [14], and the band at 1,717 cm^{-1} is ascribed to C=O bonds or conjugated C=C bonds, according to Hilczer et al. study [15]. The intensity of these

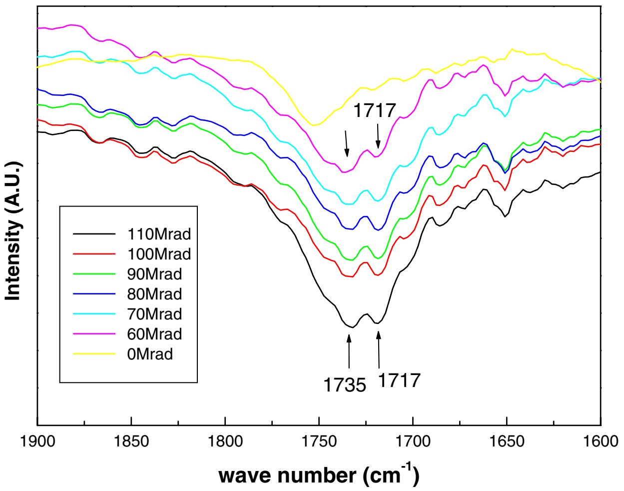

Fig. 3 IR transmission spectra of bands at 1,735 cm^{-1} and 1,717 cm^{-1} as a function of radiation doses

two bands was found to increase linearly with the dose of radiation. These microscopic defects (double bond) produced in P (VDF-TrFE) during the irradiation are basically related to dehydrofluorination reaction and scission of long-range all-trans chain conformation, which results of the decreasing of spontaneous polarization. It should be point out Stephanovich et al. [16] have calculated the dielectric response, which fit the experimental results well, when the C=C bonds and conjugated C=C bonds are treated as the sources of random field.

The electromechanical activity of the copolymer mainly comes from the crystalline regions. So it is important to investigate the crystalline change after irradiation. X-ray data taken at room temperature after exposure to different radiation doses are presented in Fig. 4. For unirradiated film, only one reflection at $2\theta = 19.8°$ is observed, which is from the ferroelectric β phase and represents the Bragg diffraction of (110) and (200) [17]. For the 60 Mrad irradiated film, a new peak appears at 18.4°, corresponding to the nonpolar phase. This means the polar phase 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 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.

Using Gaussian function to fit the X-ray peaks, the degree of crystallinity is estimated by calculating the volume ratio of crystal and noncrystal fraction, as shown in Fig. 5. From Fig. 5, we can see the reduction of β phase volume fraction after irradiation. At the 110 Mrad dose, the polar phase nearly disappears. And the degree of crystallinity changes from the 75% (0 Mrad) to 22% (110 Mrad). So it clearly proves the phase transition from polar phase to nonpolar phase and the breakage of crystalline phase. It is also noticed from the XRD results that the full width at half maximum of the polar phase peak increases with irradiation dosage while the intensity decreases. This also indicates the decrease of both the volume fraction of lamella crystalline phase and the average size of the polar crystalline phase in the irradiated copolymer films.

DSC data of the irradiated copolymers are presented in Fig. 6. 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 146 and 128 °C. The peak at the lower temperature (T_C) is associated with (F–P) phase transition in the crystalline regions,

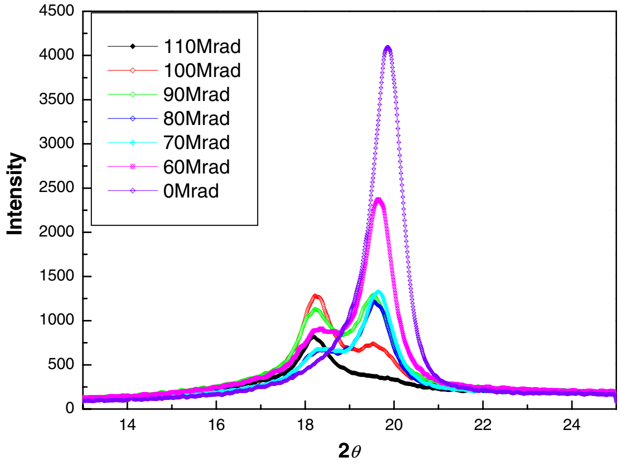

Fig. 4 X-ray diffraction curve of P (VDF-TrFE) (80/20), as a function of radiation doses

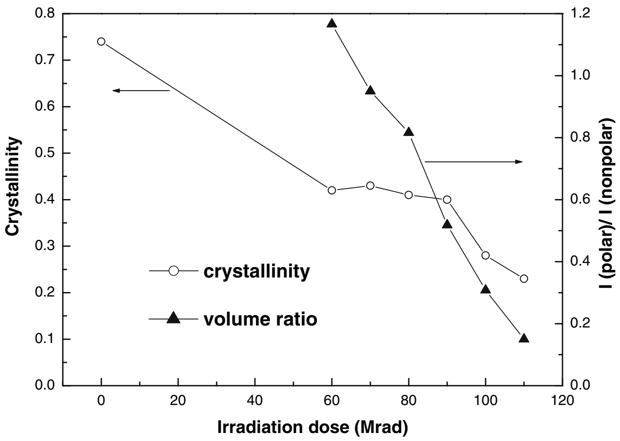

Fig. 5 The crystallinity (hollow circle) and volume ratio of the polar and nonpolar phase (solid triangle) with different radiation doses

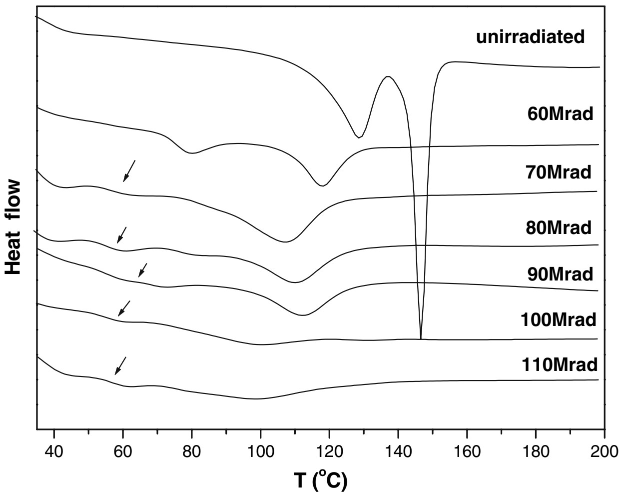

Fig. 6 DSC curves of P (VDF-TrFE) (80/20) with different radiation doses

while the one at the higher temperature (T_m) reflects the melting behavior of the crystalline regions in the materials [18]. It is found that the position of both peaks shifts to lower temperature and the peak of F–P phase transition nearly disappears. As shown in the Fig. 7, 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 cross-linking in the copolymer.

The topography of P (VDF-TrFE) by AFM using tapping mode are shown in the Fig. 8 with the scan range 1,000 × 1,000 nm. It is found the crystalline grains with size of 50–100 nm array tightly and orderly on the surface of unirradiated copolymers. After irradiation the number of grains increase obviously, but the size lessens gradually, up to 30–50 nm at 70 Mrad. Further more, with radiation dosage increasing, the number of grains decreases and the boundaries of grains get illegible. For 100 Mrad-irradiated sample, the surface exhibits amorphous state with few grains, which was proved to be nonpolar phase by IR and X-ray data. It can be interpreted that the crystalline regions of the copolymers are broken into ''nanocrystals'' (polar nanosize cluster) gradually by the high-energy electron irradiation. The ''nanocrystals'' are distributed in an amorphous phase so as to form a special microstructure consisting of nanocrystalline-amorphous regions. Ang and Yu call this microstructure is a nanometer scale structure [19]. The dipoles within such regions cannot form macrodomains due to their nanometer size. On this condition, the F–P transition peak in DSC curves reflecting the

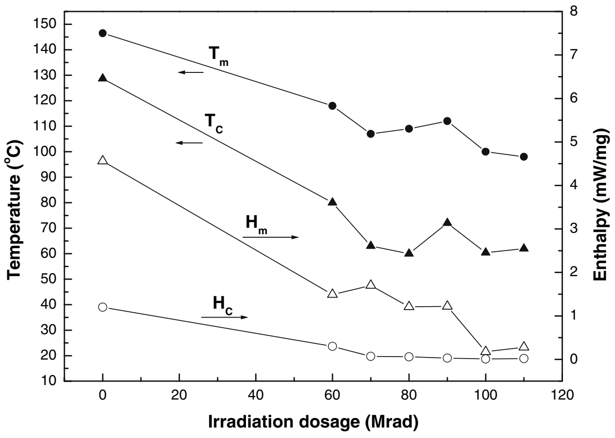

Fig. 7 The temperature and enthalpy curves of P (VDF-TrFE) with different radiation doses

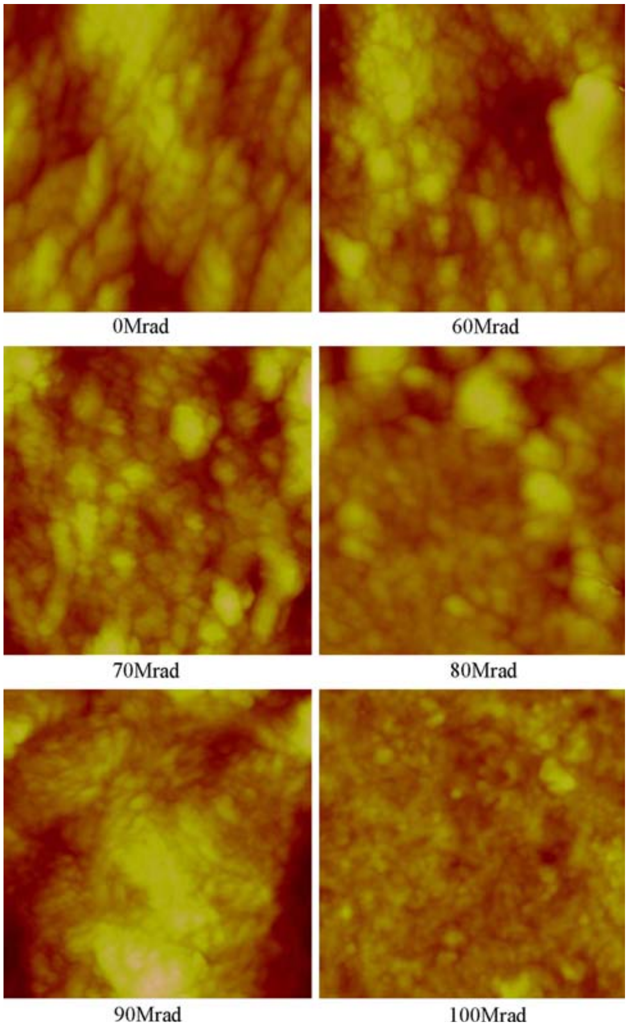
0Mrad 60Mrad
70Mrad 80Mrad
90Mrad 100Mrad

Fig. 8 The topography of P (VDF-TrFE) by AFM tapping mode, 1,000 × 1,000 nm. (**a**) 0 Mrad, (**b**) 60 Mrad, (**c**) 70 Mrad, (**d**) 80 Mrad, (**e**) 90 Mrad, and (**f**) 100 Mrad remaining crystalline regions is not seen again. According to the report of Cross [10], the relaxor properties (high dielectric coefficient) in some ferroelectric perovskites are related to the existence of polar nanosize cluster and random fields in nonpolar matrix. So, it can be concluded that in P (VDF-TrFE) copolymers the ferroelectric relaxor behaviors, high and dispersive dielectric anomaly induced by irradiation should be related to thermal fluctuation and orientations under electric fields of polar nanosize clusters in such structure. These polar nanosize clusters are in a dynamic disorder state and the interacting of them can be canceled out, so as that the copolymers are nonpolar at macroscopic state. But they can be united into macrodomains when being cooled below Curie point (T_c) or applied an electric fields. And this also may be one good interpretation of our previous results about the reversible phase transition in irradiated copolymer induced by thermal and electric field [20].

Conclusion

The influence of electron irradiation on structure has been investigated through IR spectra, X-ray, DSC, and AFM. It is found that after irradiation polar phase and nonpolar phase can exist in P (VDF-TrFE) copolymer, the polar phase change into nonpolar phase gradually; the trans-gauche (*TG*) sequence replaces the all-trans (*TT*) sequence; the Curie point (T_c) and the melting point (T_m) shift to the lower temperature. The result that the radiation-induced irreversible transformation of the ferroelectric copolymer to the relaxor state is related to the creation of polar clusters, consisting of a variety of short range coherence of trans-conformation, stabilized by random fields of C=C and C=O bonds. The C=C and C=O bonds induced by irradiation cut the ferroelectric all trans conformation into polar clusters of short-range coherence of trans conformation. The data of AFM shows that crystalline regions of the copolymers are broken into ‘‘nanocrystals’’ gradually by the high-energy electron irradiation. The ‘‘nanocrystals’’ are distributed in an amorphous phase so as to form a nanoscale structure consisting of nanocrystalline-amorphous regions. The thermal fluctuation and orientations under electric fields of ‘‘nanocrystals’’ or polar nanosize clusters in these nanocrystalline-amorphous regions may be the mechanism of ferroelectric relaxor behaviors and dispersive dielectric anomaly.

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