Structural Changes of 80/20 Poly(vinylidene fluoride–trifluoroethylene) Copolymer Induced by Electron Irradiation

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ABSTRACT: The electron irradiation effect on 80/20 poly-(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] copolymers was studied by FTIR spectra and X-ray diffraction. Infrared spectra showed decreasing intensity of bands at 1430, 1286, 846, and 505 cm^{-1}, the appearance and intensity increasing with irradiation doses of bands at 768, 601, and 1735 cm^{-1}, which revealed the conformational change after irradiation. The X-ray diffraction patterns exhibited a decrease of volume fraction of ferroelectric phase and expansion of the lattice space. The electron-irradiated P(VDF–TrFE) films showed structural changes and polar phase to nonpolar phase transformation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2903–2907, 2004

Key words: X-ray; FTIR; electron beam irradiation; poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)]; films

INTRODUCTION

Heightened interest continues to be focused on ferroelectric polymers as functional materials. Among them poly(vinylidene–fluoride) (PVDF) and its copolymers with trifluoroethylene [P(VDF–TrFE) hereafter] have been studied widely because they exhibit high electrostrictive response and ferroelectric polarization.[1–3] These polymers can crystallize into four types of crystal forms: form I (β), form II (α), form III (γ), and form IV (δ). It is well known that the α-phase consists of antiparallel TGTG' chains and the β-phase consists of all-*trans* chains, and the γ-phase is an intermediate conformation T_3GT_3G' and the δ-phase is a parallel version of the α-phase.[4] Among the four types, only the β-phase is the polar phase. In contrast to pure PVDF, P(VDF–TrFE) copolymer crystallizes directly into β-phase when the molar ratio of VDF(x) and TrFE($1 - x$) is within an adequate range.

Ferroelectric to paraelectric phase transformation in P(VDF–TrFE) induced by irradiation has been demonstrated in the last few years.[5–7] X-ray, DSC, gel content analysis, and FTIR spectra have been used to investigate the influence of irradiation on the structure of ferroelectric P(VDF–TrFE) copolymers.[5,8,9] Recently Xu investigated the structural and conformational changes with irradiation of 50/50 P(VDF–TrFE) by means of IR spectra.[8] Because the copolymer with molar ratio of 50/50 is most sensitive to electron irradiation among the P(VDF–TrFE) copolymers studied to date and the electron irradiation was carried out at a quite high temperature of 120°C under a nitrogen atmosphere using electrons of 2.55 MeV, the ferroelectric to paraelectric-like phase transition induced by the irradiation accelerated significantly in their study. As can be seen in Figure 2 of Xu's article, even at the smallest dose of 30 Mrad used in their study the characteristic peak of the ferroelectric phase at 1288 cm^{-1} was already reduced to a small shoulder. Moreover, the resolution power was not adequate to recognize many weak absorbance peaks (except for a few strong absorbance peaks) and no IR spectra with different irradiation doses were presented in the range between 1500 and 4000 cm^{-1}. The film for 30-Mrad irradiation showed substantial change compared with the nonirradiated sample. With further irradiation, however, there were no obvious changes in IR spectra with different irradiation doses. Because of the high irradiation temperature, the irradiation effect on P(VDF–TrFE) (50/50) was so great that we could not accurately determine results of the changes below 30 Mrad. In this study, the irradiation was carried out at 70°C in vacuum with 3 MeV electron irradiation. From 60 to 110 Mrad a gradual change with different levels of irradiation can be seen. It will help to elucidate the phase transformation and the structural change induced by electron irradiation. The present article introduces detailed and accurate results of IR spectra in the wavenumber range between 400 and 4000 cm^{-1}. Additionally, X-ray was also used to analyze the change during irradiation. We sought to clarify the
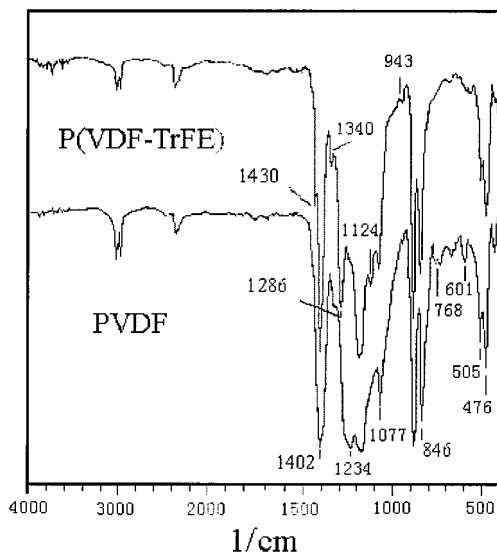
Figure 1 IR transmission spectra of PVDF and P(VDF–TrFE) in the range 400–2000 cm^{-1}.

microscopic mechanism and further improve electromechanical properties of the copolymers.

EXPERIMENTAL

The P(VDF–TrFE) (80/20) was obtained from Piezotech (France) in the form of white pellets. These pellets were dissolved in dimethylformamide at a concentration of 20 wt % by ultrasonic stirring for 3 h at room temperature. The film samples were then formed by solution casting onto a glass substrate, followed by evaporation of the solvent and drying in a vacuum oven at 120°C for 1 day. To improve the crystallinity of the sample, the films studied here were isothermally treated at 135°C for 12 h. The samples were then cooled to room temperature and removed from the substrate by immersion in distilled water. For X-ray measurements, the thickness of samples ranged between 20 and 30 μm. The electron irradiation was carried out at 70°C in vacuum with 3 MeV energy level electrons. X-ray diffraction patterns were performed at room temperature using Cu–K$_\alpha$ radiation, on a Shimadzu (XD-3A; Kyoto, Japan) diffractometer. The IR spectra were obtained using a Shimadzu (FT-8201PC) FTIR spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 presents the IR transmission spectra of PVDF and P(VDF–TrFE) in the 400–4000 cm^{-1} range. The spectrum of the P(VDF–TrFE) (80/20) films clearly shows many strong absorbance peaks at 1402, 1286, 1186, 1124, 1077, 883, 844, and 476 cm^{-1}, and many weak absorbance peaks at 1430, 943, 678, 505 cm^{-1}, and so on. Compared with PVDF, the P(VDF–TrFE)

exhibits the appearance of a new strong absorbance peak at 1286 cm^{-1}, which is characteristic of the ferroelectric β-phase.[8] At the same time, the peaks at 1234 and 768 cm^{-1} disappear and the peaks at 1077 and 601 cm^{-1} become weaker. All these peaks are attributed to the TG sequence of the paraelectric α-phase. The peak at 812 cm^{-1} is characteristic of the γ-phase (T$_3$G), which is seen in PVDF but not in P(VDF–TrFE) copolymer.[9,10] It can therefore be concluded that P(VDF–TrFE) (80/20) directly crystallizes into the ferroelectric β-phase from melting temperature.

IR transmission spectra of P(VDF–TrFE) at different irradiation doses are presented in Figure 2. The absorbance at 2360 cm^{-1} is attributed to vibration of CO$_2$ existing in the sample chamber. For nonirradiated film, the spectrum shows a broad and very weak band at the region of 1730 cm^{-1} and two peaks at 3012 and 2975 cm^{-1}, which are the asymmetric stretching vibration of the C—H bond.[11] With increasing irradiation, the bands at 3012 and 2975 cm^{-1} shift slightly to a high wavenumber region (3020 and 2979 cm^{-1} at 110-Mrad dose), which is attributed to the decreasing concentration of comomer unit (–CHF—CF$_2$–) in the irradiated copolymer structure.[5] The absorbance at 3020 cm^{-1}
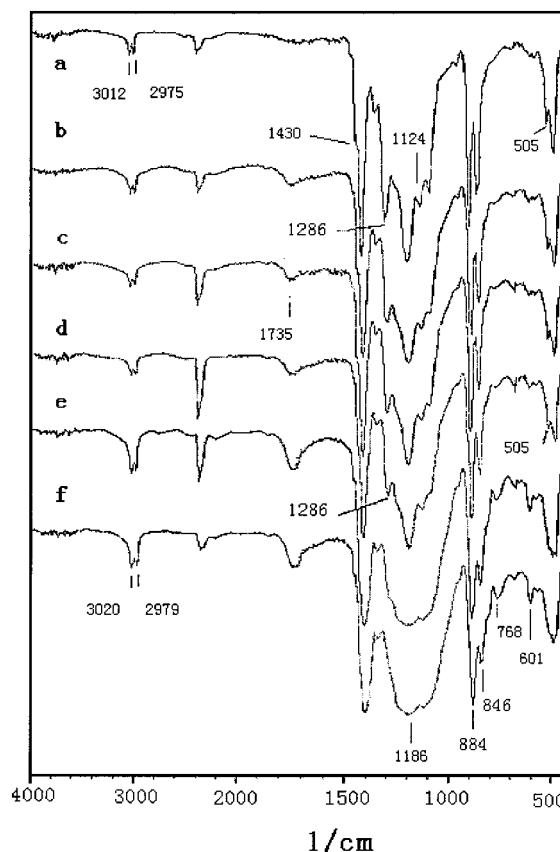
Figure 2 IR transmission spectra of P(VDF–TrFE) at different irradiation doses in the range 400–4000 cm^{-1}: (a) 0 Mrad, (b) 60 Mrad, (c) 70 Mrad, (d) 80 Mrad, (e) 100 Mrad, (f) 110 Mrad.

(3012 cm^{-1} in the nonirradiated sample) is almost proportional to the thickness of the sample and does not depend on the state of sample; thus it can be used as an internal standard here.[8] The data in Figure 3 represent the relative absorbance after correction.

According to the study by Hector et al.[5] and Kabayashi et al.,[9] the peaks at 1286, 1430, 846, and 505 cm^{-1} are attributed to the vibration of all-*trans* sequences. From Figures 2 and 3, we can clearly see that the peaks at 1286, 846, and 505 cm^{-1}, decrease gradually and can still be recognized below a 100-Mrad irradiation dose, whereas in the report by Xu et al.[8] the peak at 1288 cm^{-1} (the characteristic peak of the ferroelectric phase) disappears quickly after irradiation at 120°C. The process of change can thus be seen in detail here. In the present investigation, the peaks at 1286, 1430, and 505 cm^{-1} nearly disappeared at 110-Mrad irradiation. On the contrary, the absorbance peaks at 601 and 768 cm^{-1}, corresponding to the TG sequence from the paraelectric α-phase, appeared again and substantially increased in intensity with increasing irradiation; they were also observed in the spectra of PVDF, which distinctly suggests phase transformation from ferroelectric to paraelectric induced by irradiation. It must be mentioned that the curve of relative absorbance of the TG sequence reported by Xu et al.[8] does not show monotonic change with irradiation dose. The data in Figure 3 denote the gradual change before the completed phase transition occurs.
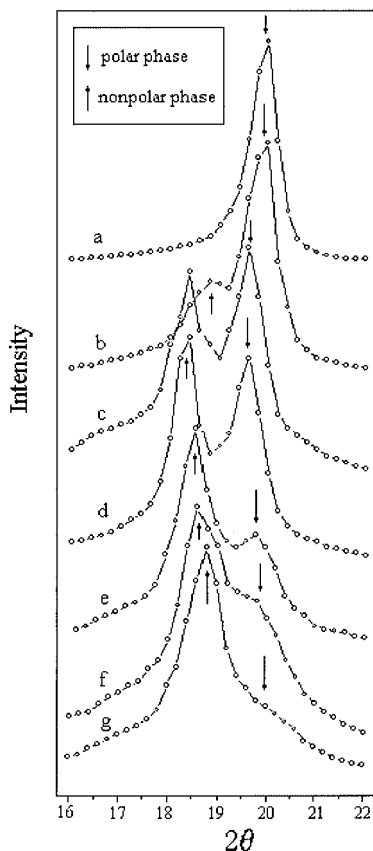
The band at 1735 cm^{-1} appearing after irradiation can be assigned to a carbon–carbon double bond according to the study by Odajima et al.[6] and the intensity increases significantly with irradiation. These microscopic defects (double bonds) produced in P(VDF–TrFE) during irradiation are basically related to a dehydrofluorination reaction. This phenomenon was also found in P(VDF–TrFE) induced by X-ray and γ-ray irradiation.[5,12]

With further irradiation, the absorbance peak at 1122 cm^{-1} increased greatly in intensity. At higher irradiation doses, the weak peak at 1234 cm^{-1} was observed again. At the region of 1186 cm^{-1} there appeared a broad and strong absorbance band above the 100-Mrad irradiation dose, which also confirmed the increase of volume fraction of the nonpolar phase.

The electromechanical activity of the copolymer mainly comes from the crystalline regions. It is thus important to investigate the crystalline change after irradiation. Figure 4 presents X-ray patterns of nonirradiated and irradiated copolymer films. These measurements were taken at room temperature. For nonirradiated film, only one reflection at $2\theta = 20.2°$ is observed, corresponding to the polar phase, which represents the Bragg diffraction of (110) and (200).[12] Like the IR data, this phenomenon also indicates P(VDF–TrFE) (80/20) copolymer is ferroelectric β-phase before irradiation. For film irradiated at 60
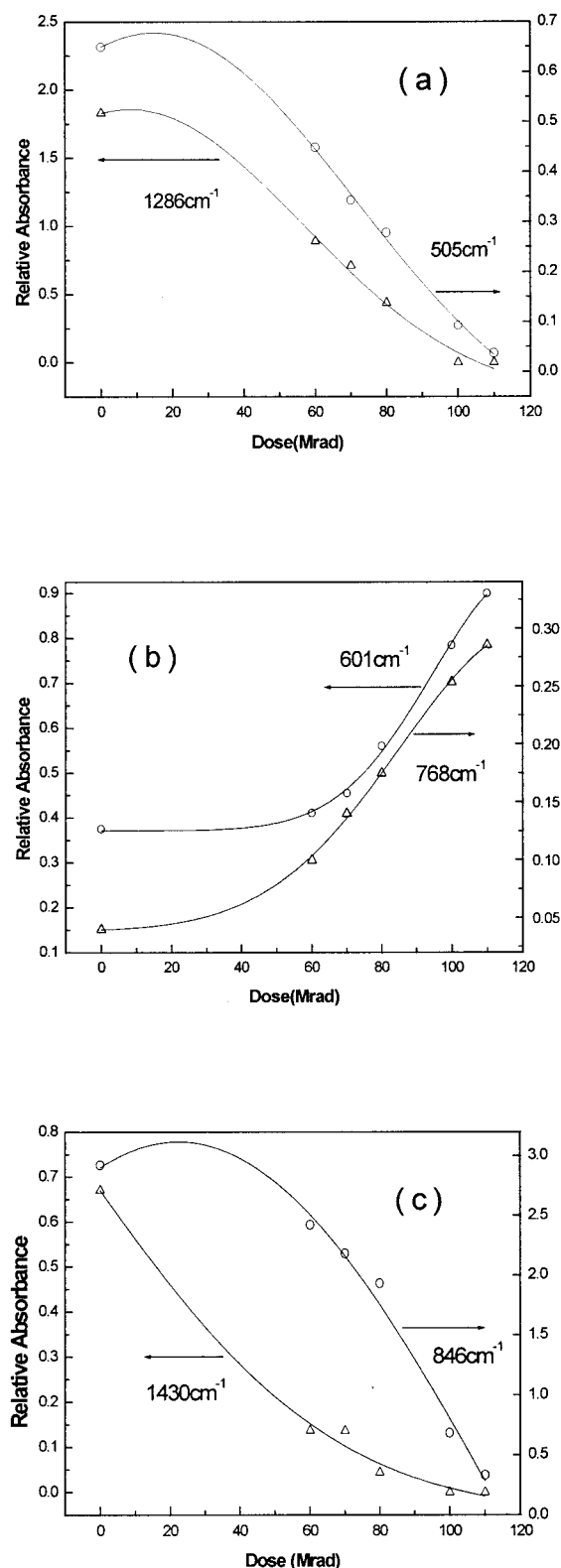
Figure 3 Relative absorbance of different bands as function of irradiation dose: (a) 1286 and 505 cm^{-1}; (b) 768 and 601 cm^{-1}; (c) 1430 and 846 cm^{-1}.

Figure 4 X-ray diffraction diagram of P(VDF–TrFE) (80/20), as a function of the doses of the irradiation: (a) 0 Mrad, (b) 60 Mrad, (c) 70 Mrad, (d) 80 Mrad, (e) 90 Mrad, (f) 100 Mrad, (g) 110 Mrad.

defects induced during irradiation, depending on the boundary conditions of the crystalline–amorphous interface and crystalline size. It can also be interpreted as a partial recovering to local *trans* bonds from *trans–gauche* bonds at that dose level.[15]

It is also noticed from the X-ray diffraction results that the full width at half-maximum of the polar phase peak increases with irradiation dosage whereas the intensity decreases, thus indicating 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. The intensity ratio of the polar and nonpolar phases is shown in Figure 5, from which we can observe the reduction of β-phase volume fraction after irradiation. At the 110-Mrad dose, the polar phase nearly disappears, which clearly confirms the phase transition from polar phase to nonpolar phase, thus providing evidence of structural change during irradiation.

CONCLUSIONS

The ferroelectric P(VDF–TrFE) (80/20) copolymers were irradiated at relatively low temperature in vacuum by electron beam. The influence of electron irradiation on the structure was investigated through IR spectra and X-ray analysis. The appearance of a carbon–carbon double bond was found in irradiated copolymer from IR spectra data, and the intensity increased with further irradiation. Additionally, with increasing irradiation doses, the intensity of the characteristic absorbance peaks from β-phase gradually decreased, whereas the intensity of peaks from the nonpolar phase increased. These phenomena indicated the phase change during irradiation, which is an evidence of conformational change induced by electron irradiation. With increasing irradiation, the inten-

Mrad, a new peak appears at 18.9°, corresponding to the nonpolar phase, which means that the polar phase and nonpolar phase coexist in the crystalline regions after irradiation. It can thus be concluded that irradiation has a strong influence on the structure of the crystalline regions. At the same time, the position (2θ) of the two peaks shifts to a lower angle with irradiation dosage, which proves the lattice expansion attributed to the introduction of defects in the crystalline phase during irradiation.
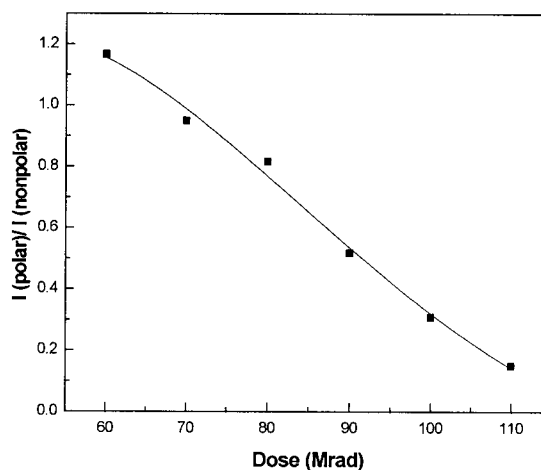
It is believed that the large strain response observed in the irradiated copolymer is related to the electron field–induced phase transition of the crystal regions between nonpolar and polar phase.[1,13] After 80 Mrad irradiation, the peak appears at 18.3°. According to the equation $2d \sin \theta = \lambda$, the corresponding lattice spacing is about 4.84 Å, which is close to that of the paraelectric phase measured above Curie temperature for nonirradiated copolymer films,[14] and which indicates the conversion of ferroelectric to a paraelectric-like phase at this dose. Interestingly, at higher doses, the X-ray peaks shift back to a higher angle, indicating the reduction of the crystalline size. The contraction in the lattice spacing might be related to the nature of

Figure 5 Area ratio of the polar phase and nonpolar phase, as a function of irradiation dose.

sity of the polar peak from β-phase in the X-ray pattern decreased substantially, and vanished at a dose of 110 Mrad. Simultaneously, the nonpolar peak appeared after irradiation, the intensity of which gradually increased. The position of the diffraction peaks changing with irradiation dose implies the expansion of lattice space (there is slight contraction in the lattice space after 80-Mrad irradiation). Based on X-ray and IR spectra data, it is concluded that the change from the ferroelectric phase (polar phase) to the paraelectric phase (nonpolar phase) occurs during electron irradiation.

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