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Relaxor ferroelectric behavior and structural evaluation in electron-irradiated *P* (vinylidene fluoride-trifluoroethylene) copolymer blends

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The effect of high-energy electron-irradiation on binary ferroelectric blends of poly(vinylidene fluoride-trifluoroethylene) 56/44 and 80/20 mol% has been studied in a broad dose ranging from 0 to 120 Mrad. It was found that the blends transformed from a normal ferroelectric to relaxor ferroelectric, obeying the Vogel-Fulcher law, after a proper electron dose by dielectric constants and loss measurements. X-ray diffraction shows significant changes in the ferroelectric-to-paraelectric phase transition behavior from all-trans to trans-gauche conformation after irradiation. In differential scanning calorimetry (DSC) thermograms, the Curie temperature and melting temperature decrease with the dose, indicating that there exists a strong lattice coupling between the two copolymers.

1. Introduction

Ferroelectric copolymer blends of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] have come under intense study in these decades [1, 2]. It has been demonstrated that very close chemical and structural similarities required for coexistence of two different macromolecules within a single crystalline lattice [3, 4]. In order to improve the performances of these materials, it is an effective method by using high-energy particle irradiation [5, 6]. Lovinger found that the ferroelectric to-paraelectric (F-P) phase transition could be induced by electron irradiation at room temperature in P(VDF-TrFE) copolymers both in intra-molecular and inter-molecular fashions [7]. Similar behavior was also found in P(VDF-TrFE) 65/35% by using γ-rays by Odajima *et al.* [8]. More recently, Zhang *et al.* found that the 2.55–3.0 MeV electron irradiated P(VDF-TrFE) 65/35 and 50/50 mol% copolymers exhibit exceptionally high electrostrictive strain ($\sim$4%) after they transformed from a normal ferroelectric to relaxor ferroelectric (RFE) [9, 10]. In addition, the dielectric constant of irradiated copolymers exhibited strong frequency dispersion which can be fitted well by the Vogel-Fulcher (V-F) law that holds for RFE [11, 12]. The V-F law is an empirical relation that can describe temperature dependence of relaxation time observed in many glass systems and in relaxor ferroelectric ceramics. For the polymer binary mixtures, the major endeavors are put onto the miscibility and cocrystallization where both components are crystallizable in the solid states without high-energy irradiation [13, 14]. So it is interesting to study the dielectric relaxor behavior and structural changes in P(VDF-TrFE) copolymer blends after electron irradiation.

In this paper, we employed dielectric constant and loss measurements together with differential scanning calorimetry (DSC) and X-ray diffraction to study the properties of binary blends of P(VDF-TrFE) copolymers 56/44 and 80/20 mol% (with constituents differing by 24 mol% in their VF_2 contents) over a broad electron dose ranging from 0 to 120 Mrad.

2. Experimental

The random copolymer of P(VDF-TrFE) (Piezotech, France) in the present study, has a comonomer ratio, VDF/TrFE, of 56/44 mol% in pellets form and 80/20 mol% in powder form, respectively. The ferroelectric blends are prepared by physical blending the two copolymers according to theoretical calculation of the VDF and TrFE molar ratio. Equal weights of the two copolymers are stirred in dimethylformamide (DMF) at 70°C for 24 h in order to fully dissolved. Thin films (about 20–30 μm in thickness) are made by solvent casting method, followed by vacuum

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drying. To remove residual solvent and improve the crystallinity, films are directly annealed at 120°C in oven for 12 h and then at 135°C for 2 h after casting. The electron irradiation is carried out at about 80°C in air condition with 3 MeV electrons using a BF-5 electron-beam accelerator in the range from 0 to 120 Mrad.

The dielectric constant and loss dependence of temperature ranging from –60 to 140°C were evaluated using an impedance/gain-phase analyzer (HP 4194A), equipped with a temperature chamber (Delta 9023). X-ray diffraction measurement was carried out using an X-ray diffractometer with nickel-filter Cu K_α irradiation (D8 Advance, Bruker analytical X-ray system) at a scanning speed of 0.005° 2θ/s. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC7 thermal analyzer at a heating rate of 10°C /min from 0 to 170°C.

3. Results and discussion

3.1. Dielectric behavior

The dielectric constants of P(VDF-TrFE) blend films were measured as a function of temperature at a rate of 4°C/min. All the data were taken as the films were heated up from –60°C. Fig. 1 presents the dielectric constants of unirradiated and irradiated (80 Mrad) copolymer films at different frequencies. It can be seen that the dielectric constant peak becomes broadened and decreases with the electron dose. Just as expected, the temperature of the dielectric constant maximum T_p shifts to lower temperature after irradiation at various doses. It is interesting to point out that there is no obvious shifting in T_p for the unirradiated copolymer films as shown in Fig. 1a. For films irradiated with 80 Mrad as illustrated in Fig. 1b, T_p gradually moves to higher temperatures as the frequency increases. These experimental results are typical features of relaxor ferroelectrics and the results observed here also correspond to first-order transitions [15]. Therefore, it is reasonable to believe that P(VDF-TrFE) blends can be transformed from a normal ferroelectric to a RFE with the high-energy electron irradiation.

The data of dielectric loss (tan δ) vs temperature were collected during the heating process as shown in Fig. 2. It is interesting to note that a broad transition was observed at a temperature above the peak temperature T_p of the real part of the dielectric constant. As the frequency increases, this small transition disappears at high frequency (>1 MHz). Such behavior was also experimentally observed in electron-irradiated P(VDF-TrFE) 68/32 mol%, which is quite similar to what is observed in inorganic materials in which a spontaneous RFE to ferroelectric transition was observed [15, 16]. It can be interpreted that this broad transition above T_p is another typical characteristic of

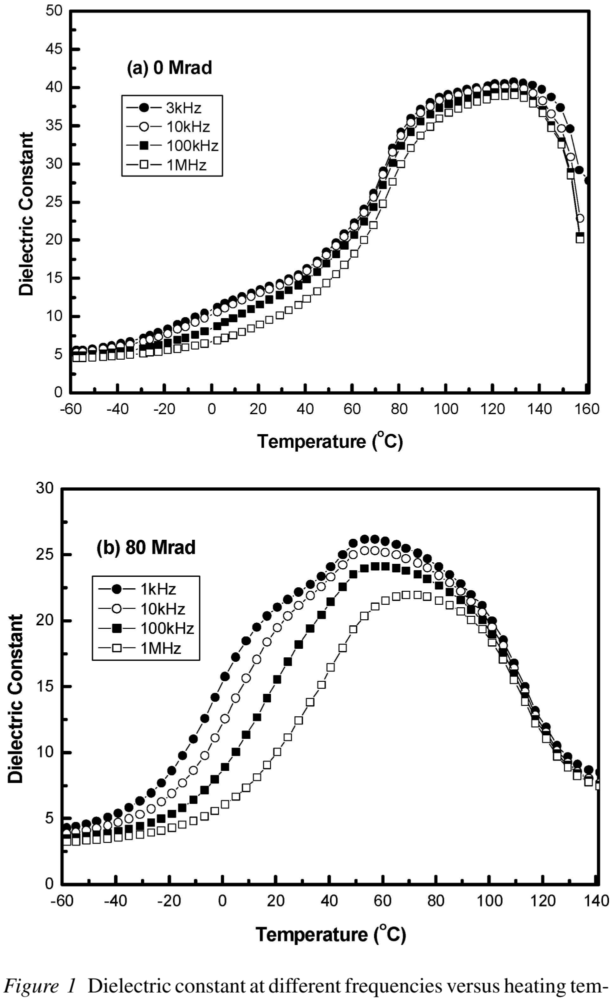

Figure 1 Dielectric constant at different frequencies versus heating temperature for P(VDF-TrFE) blend films at (a) unirradiated and (b) 80 Mrad during the heating run.

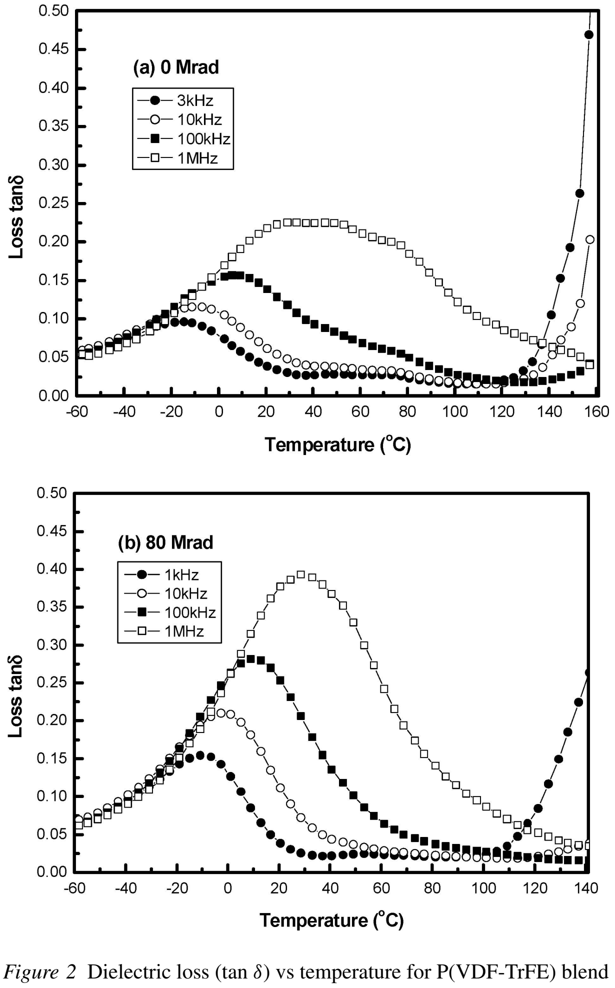

Figure 2 Dielectric loss (tan δ) vs temperature for P(VDF-TrFE) blend films of (a) unirradiated and (b) 80 Mrad during the heating run.

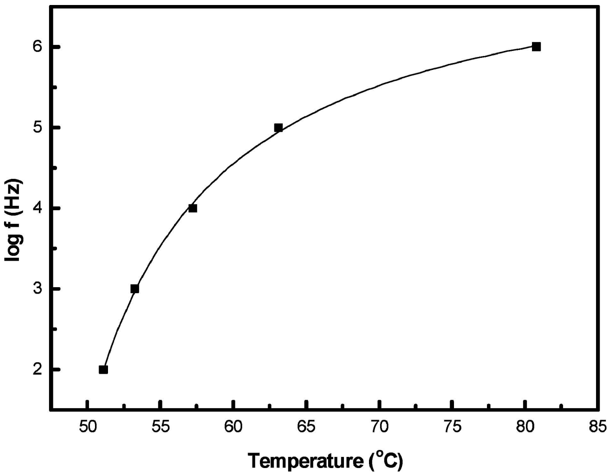

Figure 3 The fitted results between f and T_m for irradiated P(VDF-TrFE) blend film with the dose of 80 Mrad.

the transition between RFE and normal ferroelectric observed in these irradiated P(VDF-TrFE) copolymer blends.

We can use Vogel-Fulcher (V-F) law to describe the relaxor behavior in these irradiated blend films. The relation between the frequency f and T_p of the relaxor ferroelectric is given by [17]:

$$f = f_0 \exp \frac{-U}{k(T_p - T_f)}$$

where U is a constant related to the activation energy, k is the Boltzmann constant, f_0 is a constant associated with the relaxation frequency, and T_f can be interpreted as the freezing temperature. Applying the V-F law to fit the experimental data of 80 Mrad in Fig. 1(b), we obtain the results of $T_f = 41.43°\text{C}$, $f_0 = 20.95$ MHz and $U = 0.01021$ eV, as shown in Fig. 3. It can be seen that the experimental results are well fitted by the V-F law.

In P(VDF-TrFE) copolymers, electron irradiation can induce several types of defects in the crystalline region, some of which act as random fields to the dipoles in the crystalline regions [18, 19]. And there are irregular changes in the interchain and intrachain spacings due to the presence of those defects, resulting in a random interaction between dipoles and limiting of the growth of the polar region. Therefore, the system can be regarded as a dipolar glass [15, 20]. The observed V-F behavior of P(VDF-TrFE) blend after irradiation can also be interpreted as a direct consequence of freezing of the system into the polar glass state, similar to its parent compounds. It is also widely accepted that the frequency dispersive dielectric characteristics of the relaxor ferroelectric ceramics are mainly due to the nanometer-size polar regions [17, 21]. By analogy, it is supposed that the irradiated copolymer blends contain polar regions of different sizes, and the distribution of both the size and polarization strength of these polar regions cause the diffuse dielectric response with frequency. The influence of small polar region plays an important role in the RFE transition.

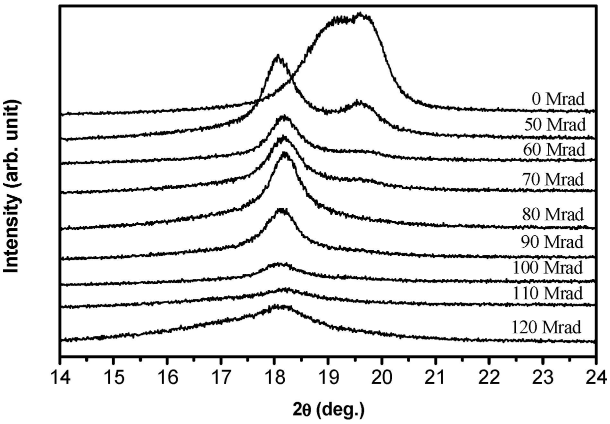

Figure 4 X-ray diffraction profiles of P(VDF-TrFE) blend films with different dose ranging from 0 to 120 Mrad.

3.2. X-ray diffraction (XRD)

As is well known, P(VDF-TrFE) copolymer is semi-crystalline polymer, i.e., there are crystalline lamellae imbedded in amorphous matrix [22, 23]. X-ray diffraction, shown in Fig. 4, is employed to study the lamellar structure. The P(VDF-TrFE) has an orthorhombic unit cell in the crystalline phase in which the lattice a and b axes are perpendicular to the chain. Because the ratio of the lattice constants of the unit cell along the two axis is close to $\sqrt{3}$, the lattice has a quasi-hexagonal structure, resulting in the overlap of the (110) and (200) reflections. Thus the peak represents Bragg diffractions of (110) and (200) [24]. For the unirradiated blend film, only a single broad reflection peak ($2\theta = 18.9°$ to $19.8°$) is observed, corresponding to the all-trans ferroelectric phase (polar phase). After irradiation, the peak at low angle grows at the expense of the broad peak of the polar phase, corresponding to the trans-gauche paraelectric phase (nonpolar phase). As can be seen, the relative intensity of the peak associated with the polar phase subsides and the one associated with the nonpolar phase increases with the dose.

We estimated the size of the coherent X-ray reflection region D_{hkl} according to the Scherrer equation [25],

$$D_{hkl} = \frac{0.9\lambda}{B \cos\theta}$$

where λ is the X-ray wavelength (1.5406 Å), B is the full width at half-maximum (FWHM) of the reflection peak (hkl), and θ is the peak position. The D_{hkl} in the polar phase is determined by the polarization domain size while in the non-polar phase it corresponds to the crystallite size. Fig. 5 shows the relationship between the coherent size D_{hkl} and electron irradiation dose for polar and non-polar phase at high and low angles, respectively. The D_{hkl} of nonpolar phase increases from 6.56 nm to about 11.23 nm after irradiation from 0 to 110 Mrad. The expansion in the coherent size indicates that the partial polar domain has changed into a non-polar phase in the crystalline region of the blend. A reduction of the D_{hkl} will occur after 110 Mrad, which is caused by the reduction of the crystallite size due to increased cross-linking density. The domain size of

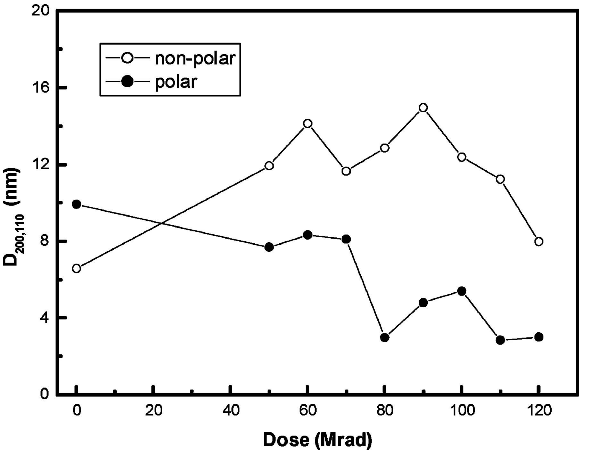

Figure 5 The coherent size $D_{200,110}$ dependence on irradiation dose at room temperature.

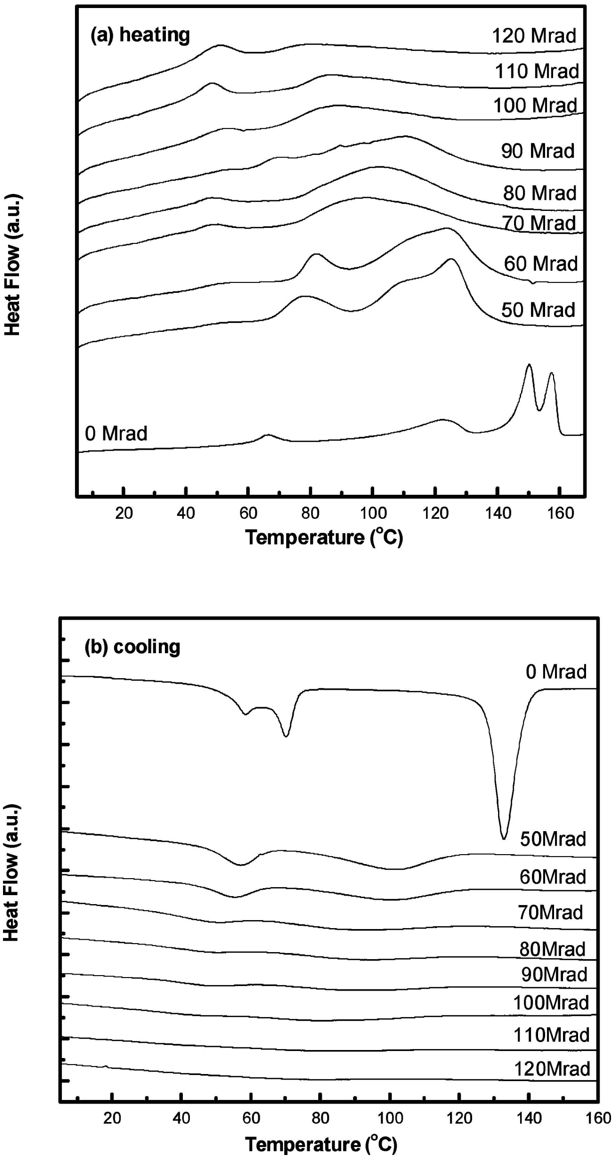

Figure 6 DSC thermograms of copolymer P(VDF-TrFE) blends during: (a) heating process and (b) cooling process.

polar phase before irradiation is about 9.92 nm shown in Fig. 5. This value decreases with the dose and it is less than 3 nm beyond 110 Mrad, which indicates the electron irradiation introduced defects in the crystalline region and broke up the domain size of polarization. The coherent size D_{hkl} of the crystalline domain continuously changes with the irradiation dose which reflects strong lattice spacing coupling between the two componential copolymers. It should be noted here that the results coincide with those obtained in electron-irradiated P(VDF-TrFE) 68/32 mol% by Cheng *et al.*, which also show two-phase coexistence and a critical domain size of about 5 nm for unstable ferroelectric phase after electron-irradiation [26]. It indicates that the lattice expansion perpendicular to the chain and contraction along the chain, respectively, showing a similar characters in the pure copolymer with 32 mol% of TrFE contents after high-energy electron irradiation.

3.3. Differential scanning calorimetry (DSC)

The results of the DSC measurements of P(VDF-TrFE) blends are shown in Fig. 6 from 0 to 170°C for different dose. The blend without irradiation exhibits four endothermic peaks; each two peaks coincide with those from the two copolymers [27]. These peaks represent the F-P phase transition T_c and the melting T_m of the crystalline region. The above phenomena are also observed in Fig. 6(b) with three peaks observed during the cooling process. We should note here that DSC results from the blend without irradiation are similar to the blend of P(VDF-TrFE) 52/48 and 73/27 mol% presented by Tanaka and Lovinger [1, 3], which has a compositional difference of 21 mol% in their VF_2 contents. The fact that these components are miscible in the melt implies their compatibility in the amorphous regions, so that the observed phase separation in the crystalline regions is attribute to the lattice mismatch arising from the large (24 mol%) compositional difference. It should be point out that all theT_c and T_m decrease and broaden with the dose and there are no obvious endothermic or exothermic peaks above 70 Mrad for the blend. The results indicate that high-energy electro-irradiation can decrease the cocrystallization and induce an amorphous, cross-linked structure in the blend similar to that in unirradiated copolymers.

There is another effective way to confirm the conformational changes by means of Fourier transform infrared spectroscopy (FTIR). In order to investigate the change in the chain conformation of irradiated P(VDF-TrFE) copolymer blends due to the phase transition from a nonpolar to a polar phase, FTIR measurements will be carried out and reported later.

4. Conclusions

The binary blend of P(VDF-TrFE) 56/44 and 80/20 mol% exhibit ferroelectric relaxor character and obvious structural changes after high-energy electron irradiation. It will be transformed from a normal ferroelectric to a relaxor ferroelectric (RFE) with the coexistence of polar and nonpolar phases. The change during the ferroelectric relaxation can be interpreted by the fact that the defects induced by irradiation in the nanometer-size polar regions, which exhibit typical characteristics of relaxation following the Vogel-Fulcher law. X-ray diffraction shows both the unirradiated and irradiated blends have two peaks that closely approach those of parent copolymers, which indicate the crystal structure of the blend transformed from all-trans to trans-gauche conformation. In DSC thermograms, the blends consist of two separate ferroelectric and paraelectric phases, exhibiting the features of the two original copolymers. The Curie temperature and melting point decrease of the blend become broaden and merged with the increase of dose indicate that there exists a strong lattice coupling between the two copolymers for their large compositional difference (24 mol% in their VF_2 contents).

Acknowledgments

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