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Thermal study on structural changes and phase transition in high-energy electron-irradiated blends of P(VDF–TrFE) copolymers

S. S. Guo · C. L. Sun · T. S. Wu ·
X. Z. Zhao · Helen L. W. Chan

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Abstract Thermal study of high-energy electron-irradiation binary blends of ferroelectric P(VDF–TrFE) copolymers has been investigated by X-ray diffraction, differential scanning calorimetry (DSC) and thermally stimulated depolarization current (TSDC). X-ray diffraction shows some degree of mixing inside a crystal lattice due to significant changes in the ferroelectric-to-paraelectric phase transition behavior from all-trans to trans-gauche conformation in nanometer range after irradiation. In DSC thermograms, it is found that both the Curie temperature and melting temperature decrease with the dose and that the F–P transition temperatures and enthalpies of two individual copolymers and the blend merge into one with the increase of dose, indicating that there exists a strong lattice coupling between the two copolymers. The peaks observed in TSDC spectra of the blends exhibit the phase transitional characters of the parent copolymers which demonstrates that the miscibility in the crystalline region for their large compositional discrepancy. The distribution of temperature peaks in TSDC also show that the existence of two types of crystallite in the blend which become more clear after irradiation, confirming the X-ray and DSC results.

S. S. Guo (✉) · T. S. Wu · X. Z. Zhao
Department of Physics, Wuhan University, Wuhan, Hubei 430072, China
e-mail: gssyhx@whu.edu.cn

C. L. Sun · H. L. W. Chan
Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

Introduction

Ferroelectric copolymers of vinylidene fluoride and trifluoroethylene [P(VDF–TrFE)] and their blends have been studied for many years from both the theoretical and the experimental points of views [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]. For PVDF and their copolymers, the structure and phase transitions of the copolymer crystals mainly depend on the VDF (or TrFE) content in the molecules [5, 6]. The copolymers are considered to have a planar-zigzag conformation [7, 8], similar to the β-phase of PVDF, and display ferro-paraelectric phase transition before the melting of the crystalline phase [9, 10]. In order to improve the performances of these materials, it is an effective method by using high-energy particle irradiation [11–13]. Lovinger found that the ferro-paraelectric phase transition could be induced by electron-irradiation at room temperature in P(VDF–TrFE) copolymers both in intra-molecular and inter-molecular fashions [14]. Similar behavior was also found in P(VDF–TrFE) 65/35% by using γ-rays by Odajima et al. [15]. 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 responses. Longitudinal strain over 4% and transverse strain over 3% were observed in electron-irradiated P(VDF–TrFE) copolymers [16, 17]. That is, the electromechanical performance of the copolymers can be effectively enhanced through high-energy irradiation. For the polymer binary mixtures without irradiation, the major endeavors are put onto the miscibility and cocrystallization where both components are crystallizable in the solid states. The majority of such blends is incompatible and undergoes phase separation between crystalline polymers and monomers or low-MW organics [18, 19]. However, Tanaka et al. found that the blend of P(VDF–TrFE) 52/48 and 73/27 mol% consist of two separate ferroelectric and paraelectric phases, indicating the existence of two types of crystal in the mixture for their large compositional difference (21 mol% in their VF_2 contents) [1, 3]. So it is interesting to study the blends for the changes of structural and phase transition associated with the isomorphic cocrystallization and miscibility in VDF/TrFE composites after electron-irradiation.

In this paper, we employed thermally stimulated depolarization current (TSDC) technique, 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) before and after different high-energy electron-irradiation doses.

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 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. The doses are in the range of 30–110 Mrad for 56/44 mol%, 60–120 Mrad for 80/20 mol% and 50–110 Mrad for their blend, respectively.

TSDC of the samples has been measured on a modified apparatus of thermal electric analyzer [20]. Before the measurement, aluminum electrodes with a diameter of 8 mm are vacuum deposited on the surface of each side of the films. The poling temperature and poling field for the blends are 135 °C and 9 MV, respectively. The poling time is 20 min followed by keeping the sample in a short-circuited state for 20 min. Then the TSDC is performed with a heating rate of 2 °C/min. Differential scanning calorimetry (DSC) is performed with a Perkin-Elmer DSC7 thermal analyzer with a heating or cooling rate of 10 °C/min from 0 to 170 °C. X-ray diffraction is carried out with Philips Dual X'Pert system by using Ni-filtered CuK_α radiation at a scanning speed of 0.01° 2θ/s.

Results and discussion

X-ray Diffraction (XRD)

As is well known, P(VDF–TrFE) copolymer is semicrystalline polymer, i.e., there are crystalline lamellae imbedded in amorphous matrix [21, 22]. X-ray diffraction, shown in Fig. 1, 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 √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) [23]. For the un-irradiated 56/44 and 80/20 mol% copolymers the diffraction peak reflection is observed at $2\theta = 18.9°$ and $2\theta = 19.8°$, respectively, corresponding to the polar phase [24]. For the blend, the diffraction peak becomes broad are divided into two peaks which closely approach those of the individual copolymers in the profile. After electron-irradiation with the dose of 70 Mrad, the blend shows two peaks at $2\theta = 18.2°$ and $2\theta = 19.6°$, respectively. It can been seen that the peak in non-irradiated blend is somewhat sharper than a

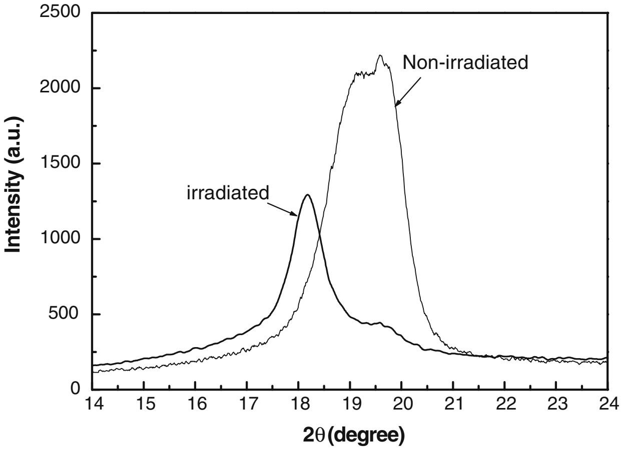

Fig. 1 X-ray diffraction profiles of P(VDF–TrFE) blends non-irradiation and after 70 Mrad irradiation

simple summation of the two constituent peaks, indicating that the original copolymers crystallize is not in a common lattice and that a small degree of mixing occurs in the crystals; after irradiation, the blend shows two peaks which also present the characteristics of parent copolymers, coinciding with the unirradiated one.

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. Figure 2 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} at low angle of the blend increases from 6.56 nm to about 11.23 nm after irradiation from 60 to 110 Mrad shown. 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 [24]. 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, similar to the upper two copolymers. The domain size of the blend at high angle before irradiation is about 9.92 nm. 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. [26]. The results indicate 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 VF_2 contents after high-energy electron-irradiation. It is suggested here that the existence of mixing crystalline phase play an important role in the X-ray diffraction.

Differential scanning calorimetry (DSC)

The results of the DSC measurements are shown in Fig. 3 from 0 to 170 °C for unirradiated copolymer blends. The original P(VDF–TrFE) 56/44 mol% without irradiation exhibits two endothermic peaks at 64.5 °C and 155.2 °C, respectively, and P(VDF–TrFE) 80/20 mol% also exhibits two peaks of 129.3 °C and 149.1 °C. These peaks represent the ferro-paraelectric phase transition T_c and the melting T_m of the crystalline region [24, 27]. The blend without irradiation exhibits four endothermic peaks; each two peaks coincide with those from the two copolymers. The above phenomena are also observed 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

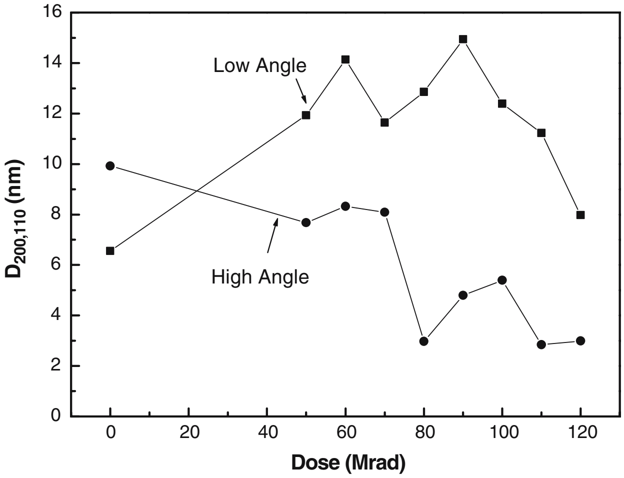

Fig. 2 The coherent size D_{hkl} dependence of irradiation dose at room temperature for P(VDF–TrFE) blends

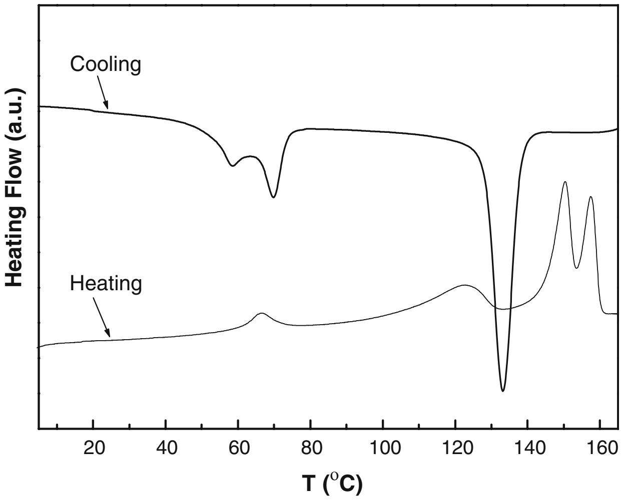

Fig. 3 DSC heating and cooling thermograms of P(VDF–TrFE) blends without irradiation

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.

After irradiation with the dose of 70 Mrad, as shown in Fig. 4, the blend shows two broad endothermic peaks intermediate between the transition temperatures of the two copolymers for heating or cooling process. It should be point out that the P(VDF–TrFE) 80/20 mol% shows three endothermic peaks during heating process for polar and non-polar phases coexisting in the crystalline regions after irradiation as discussed in X-ray results[24]. However, all the T_c and T_m decrease 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 non-irradiated copolymers.

It is believed that the crystalline regions with small and distributed size of cocrystallite region in the irradiated blend are responsible for the change of phase transition temperatures and enthalpies. For the blend, as the electron dose increases beyond 70 Mrad, more cross-linking will be induced by irradiation, which leads to the reduction of the size of crystalline region and thus the irradiated sample has very weak ferroelectric property. The blend shows characteristics of the two copolymers, which exhibits some degree of the miscibility and cocrystallization in the structure of molecular conformation from microscopic mechanism. The F–P transition temperatures and enthalpies of two individual copolymers and the blend merge into one with the increase of dose indicate that there exists a strong lattice coupling between the two copolymers. Thus it is possible for the existence of a very limited isomorphic cocrystallization in the blend because of the large lattice mismatch and chemical difference, indicating the possibility of effective compatibility.

Thermally stimulated depolarization current (TSDC)

The TSDC spectra of P(VDF–TrFE) blend before and after electron-irradiation are shown in Fig. 5. Before irradiation the peak temperatures for 56/44, 80/20 mol% are at about 70 and 141 °C, respectively, which corresponds to the peak found in DSC analysis [24, 28], while for their blend a relative broad peak appears at 116.3 °C. After 70 Mrad electron-irradiation, the blend shows two peaks; one is at low temperature T_l (about 55.7 °C) and the other is at high temperature T_h (about 120.9 °C), both of which obviously approach those of the two original components (49.2 °C for 56/44 mol% and 129 °C for 80/20 mol%). The TSDC current in the poled, short-circuited films comes mostly from the depolarization and no current is found when heating the unpoled ones. Because the charge can be injected around the ferroelectric crystalline region during the poling process and trapped in a non-uniform fashion [29], a small contribution from the space charge cannot be ruled out, though the poling field is much lower than the coercive field of the copolymer. The appearance of peaks is corresponding to phase transition as illustrated in the DSC measurement, which demonstrates changes in the molecular conformation of the copolymers [30].

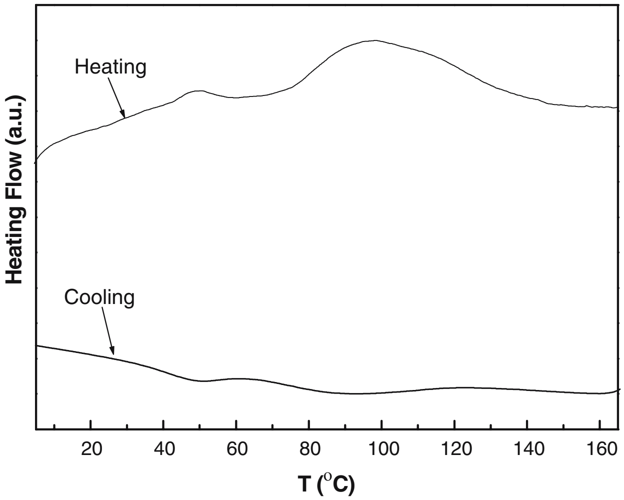

Fig. 4 DSC heating and cooling thermograms of P(VDF–TrFE) blends after 70 Mrad irradiation

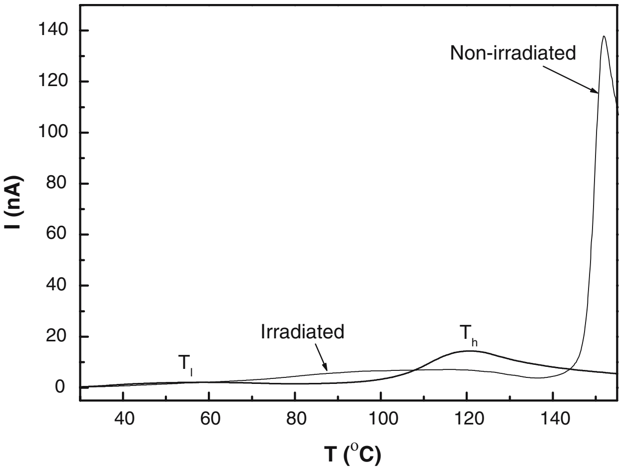

Fig. 5 TSDC spectra for P(VDF–TrFE) blends without irradiation and 70 Mrad irradiation

The depolarization current reaches a maximum at the phase transition including a large number of charges are detrapped from the crystalline domains during the phase transition.

Relationships of T_h and T_l of the blend with dose are plotted in Fig. 6. It can be seen that the peak temperatures for the two copolymers decrease when the doses increase. The peaks for blend after irradiation are divided into two parts of T_h and T_l, which corresponds to the peaks of irradiated 80/20 and 56/44 mol%, respectively. It is reasonable to believe the difference in chemical and lattice mismatch for their large compositional discrepancy (24 mol% in their VF_2 contents), introducing some mixing between the two copolymers, i.e., the existence of a little isomorphic cocrystallization [3]. The peaks observed in TSDC is also a first-order process similar to the peaks in DSC, as they will shift to lower temperatures during the cooling process which is characteristic of first-order transition. The irradiated blend with two peaks associating with those of two parent components suggests that a small amount of the 56/44 mol% copolymer is contained in the crystals of the 80/20 mol%, thus introducing additional disorder, which is fully consistent with the above XRD and DSC results.

Conclusions

The binary blend of P(VDF–TrFE) blend exhibits some degree of miscibility and cocrystallization in the crystalline region both before and after high-energy electron-irradiation. X-ray diffraction shows both the unirradiated and irradiated blends have two peaks that closely approach those of parent copolymers, which indicates the crystal structure of the blend is not in a common lattice for their large compositional difference (24 mol% in their VF_2 contents), indicating some degree of mixing in the crystals. In DSC thermograms, the blends consist of two separate ferroelectric and paraelectric phases, exhibiting the features of the two original copolymers. The F–P transition temperatures and enthalpies of two individual copolymers and the blend merge into one with the increase of dose indicate that there exists a strong lattice coupling between the two copolymers. In TDSC spectra the phase transitional temperatures at low and high temperature clearly approach those of the two component copolymers after irradiation, demonstrating the miscibility in the crystalline region. The distribution of peak temperature also confirmed that the blend presents the characteristics of original components, demonstrating that the miscibility in the crystalline region.

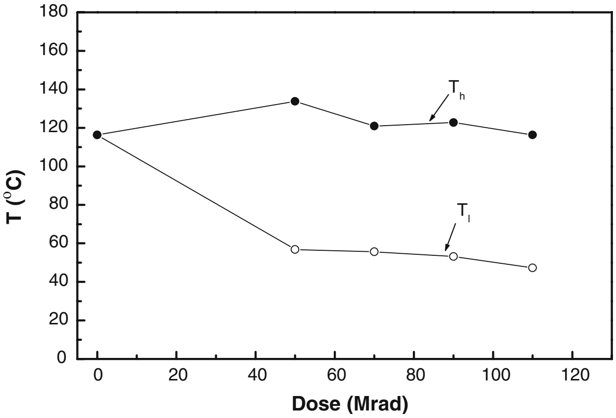

Fig. 6 The peak temperatures in TSDC as a function of electron-irradiation dose for P(VDF–TrFE) blends

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References

1. Tanaka H, Lovinger AJ (1987) Macromolecules 20:2640
2. Natta G, Allegra G, Bassi IW, Sianesi D, Caporiccio G, Torti E (1965) J Polym Sci A 3:4263
3. Tanaka H, Lovinger AJ, Davis DD (1990) J Polym Sci Polym Phys Ed 28:2183
4. Doll WW, Lando JB (1970) J Macromol Sci B 4:897
5. Lovinger AJ, Furukawa T, Davis GT, Broadhurst MG (1983) Polymer 24:1225
6. Chen G, Fouracre RA, Banford HM, Tedford DJ (1991) Radiat Phys Chem 37:523
7. Lovinger AJ, Davis GT, Furukawa T, Broadhurst MG (1982) Macromolecules 15:323
8. Tashiro K, Tanka K, Kobayashi M, Chatani Y, Tadakoro H (1981) Ibid 22:1312
9. Furukawa T, Johnson GE (1981) J Appl Phys 52:940
10. Lovinger AJ, Davis DD, Cais RE, Jometani JM (1988) Macromolecules 21:78
11. Daudin B, Dubus M, Legrand JF (1987) J Appl Phys 62:994
12. Kepler RG, Anderson RA (1978) J Appl Phys 49:1232
13. Furukawa T, Wen JX, Suzuki K, Takashina Y, Date M (1984) J Appl Phys 56:829
14. Lovinger AJ (1985) Macromolecules 18:910
15. Odajima A, Takase Y, Ishibashi T, Yusa K (1985) Jpn J Appl Phys 24(Suppl):881
16. Zhang QM, Bharti V, Zhao X (1998) Science 280:2101
17. Zhao X-Z, Bharti V, Zhang QM (1998) Appl Phys Lett 73:2054
18. Wittmann JC, Manley RSJ (1977) J Polym Sci Polym Phys Ed 15:1089
19. Hodge AM, Kiss G, Lotz B, Wittmann JC (1982) Polymer 23:985
20. Peng Z, Liu D, Hu S, Zhou Y, Zhang X (1998) Comp Appl Chem 15:248
21. Lovinger AJ (1983) Science 220:1115

22. Ohigashi H, Koga K, Suzuki M, Nakanishi T, Kimura K, Hashimoto N (1984) Ferroelectrics 60:263
23. Fermandez MV, Suzki A, Chiba A (1987) Macromolecules 20:1806
24. Guo SS, Sun XH, Wang SX, Xu S, Zhao XZ, Chan HLW (2005) Mater Chem Phys 91:348
25. Warren BE (1990) X-ray diffraction. Dover Publication, New York
26. Cheng Z-Y et al (2002) Macromolecules 35:664
27. Gregorio JRR, Botta MM (1998) J Polym Sci Polym Phys Ed 36:403
28. Zhang XY, Peng Z, Chan HLW (2001) Ferroelectrics 264:15
29. Womes M, Bihler E, Eisenmenger W (1989) IEEE Trans Electron Insul 24:461
30. Faria RM, Neto JMG, Olivelra ON Jr (1994) J Phys D Appl Phys 27:611