

THERMALLY STIMULATED DEPOLARIZATION CURRENT IN FERROELECTRIC BLENDS OF COPOLYMERS OF VINYLIDENE FLUORIDE WITH TRIFLUOROETHYLENE

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Abstract

Ferroelectric blends of vinylidene fluoride (VDF) /trifluoroethylene (TrFE) copolymer with different molar ratio of 56/44, 60/40, 63/37, 67/33, 70/30, 73/27 and 77/23 were fabricated by casting from methyl ethyl ketone solution. Thermally stimulated depolarization current (TSDC) of the samples has been measured using a modified thermal electric analyzer. Wide angle X-ray diffraction shows two peaks in the region of $2\theta = 18-20^\circ$ for all the blends, which indicates that the blends have the same crystal lattice structures as the copolymers. DSC results show that the blends display the phase transition characteristics of both copolymers of 77/23 and 56/44. TSDC spectra of the blends also exhibits the characters of both components at different polarization temperatures.

Introduction

Although numerous studies have been published regarding the ferroelectric phase transition in vinylidene fluoride-trifluoroethylene copolymer crystals[1-5], it has been generally recognized that the structure and phase transitions in the copolymer crystals critically depend on the VDF(or TrFE) content in the molecules. The copolymers are considered to assume a planar-zigzag conformation [6,7], similar to the β phase of PVDF. But unlike the pure PVDF, they display ferro-paraelectric phase transition before the melting of the crystalline phase[8,9], which allows their ferroelectric properties to be experimentally investigated in detail. The crystal structure and its dependence on temperature and molar ratio for the VDF/TrFE copolymers has undergone scrutiny[10-12], but agreement remains incomplete[13] regarding the crystal structure change occurring at the Curie temperature. In order to study the change associated with the VDF/TrFE composition, we blend the copolymers 77/23 and 56/44 to obtain other compositions between them. 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 the blends with different molar ratio of VDF and TrFE contents.

Experiments

The samples used here were VDF/TrFE copolymers with compositions of 56/44mol%, 77/23mol% and 70/30mol%, supplied by Piezotech France. The ferroelectric blends with different VDF/TrFE molar ratios of 60/40, 63/37, 67/33, 70/30 and 73/27 are obtained by physical blending the two copolymers 56/44 and 77/23 according to theoretical calculation of the VDF and TrFE molar ratio. Films of average thickness of 40 μ m are prepared by casting from methyl ethyl ketone solution, and then kept in vacuum for 2 days to let out the residual solvent. The annealed films are obtained by keeping the as-cast films at a temperature of 125-130°C for 2 hours, and then cooled to room temperature naturally.

TSDC of the samples has been measured on the modified apparatus of thermal electric analyzer[14], before which aluminium electrode of diameter 10mm was vacuum deposited on the center of each side of the films. All TSDC spectra were performed under the condition of 20kV/cm poling electric field and 20min poling time. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC7 thermal analyzer with a heating or cooling rate of 10°C/min. X-ray diffraction was

carried out with Philips Dual X'Pert XRD system.

Results and discussion

Fig.1 shows the DSC curves for various copolymers and blends of VDF/TrFE under a cooling rate $10^{\circ}\text{C}/\text{min}$. Fig.1(a) shows that the copolymer of VDF/TrFE 56/44 exhibits two endothermal peaks corresponding to the ferro-paraelectric phase transition and the melting[15] of the crystalline region with the peak values of 75°C and 155°C respectively, and so does the copolymer of VDF/TrFE 77/23 with the peak values of 116°C and 148°C . The blends exhibit four endothermal peaks, the values of

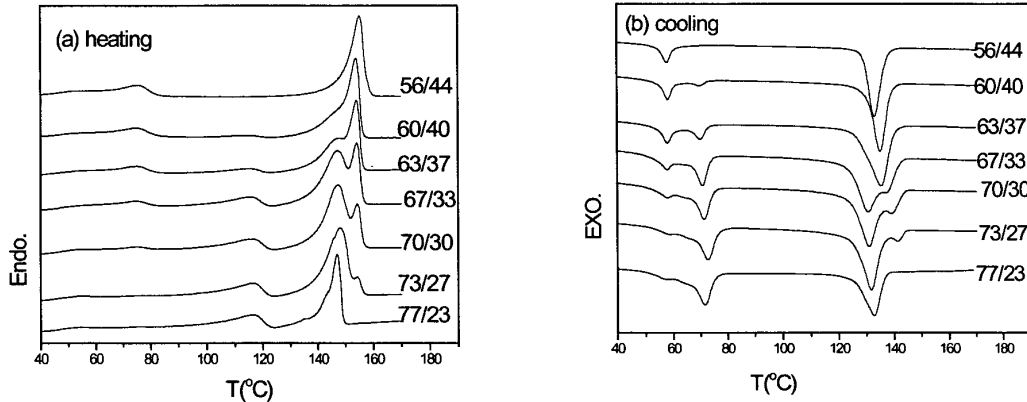


Fig.1 DSC spectra of copolymers of VDF/TrFE and their blends
(Here 56/44 and 77/23 are referred as to the copolymers, others are their blends, which is applied in the whole papers)

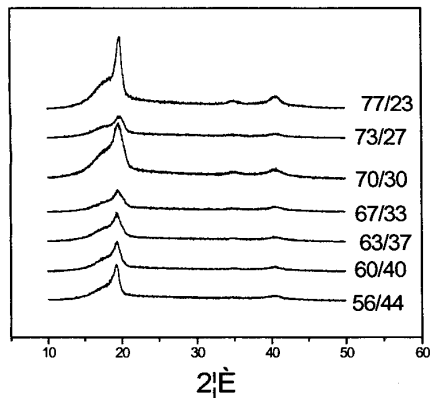


Fig. 2 X-ray spectra of different compositions of VDF/TrFE copolymers and blends

we obtain a multiple peak from all the samples. The peak can be divided into two peaks of about $2\theta=19^{\circ}$ and 19.5° associating with the (110) and (200) reflections[16]. The X-ray diffraction of the copolymers and the blends are all alike. We attribute this to the fact that the copolymers of different compositions all assume a planar-zigzag conformation [6,7], and they remain independent in the blend, introducing no new crystal structure.

Fig.3(a) shows the TSDC spectra of annealed samples with different compositions of VDF/TrFE copolymers and blends with $T_p=60^{\circ}\text{C}$. We can see all the blends show a peak whose value is about 63°C , which we suggest as a contribution from the copolymer VDF/TrFE 56/44. But we can see

each two peaks coincide with that from the two copolymers. And we also find that with a decrease of VDF content, the two peaks with the peak values of 75°C and 155°C , which are relating to the copolymer VDF/TrFE 56/44, weaken gradually and disappear at last in the copolymer VDF/TrFE 77/23, while the other two peaks with the peak values of 116°C and 148°C , which are relating to the copolymer VDF/TrFE 77/23, strengthen and become the strongest in the copolymer VDF/TrFE 77/23. The above phenomena are also observed in Fig.1(b) during the cooling process. We suggest that the two components have little or no interaction and maintain their own properties in the blend. X-ray diffraction, shown in Fig.2, was also employed to study the lamellar structure. In the region $2\theta=15-25^{\circ}$,

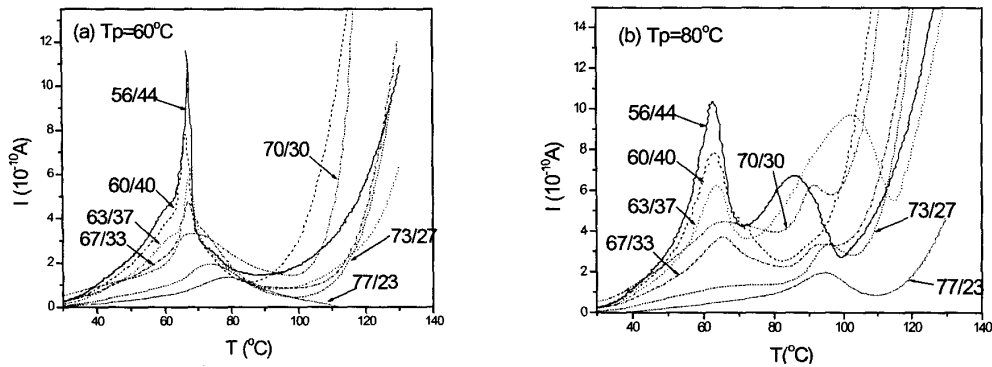


Fig.3 TSDC spectra of annealed samples of different VDF/TrFE copolymers and blends

no obvious contribution from the copolymer VDF/TrFE 77/23 in the blends except in sample 73/27. We attribute this to the relatively lower TSDC current of the latter to the former. Fig.3(b) shows TSDC spectra of annealed samples with different compositions of VDF/TrFE copolymers and blends with $T_p = 80^\circ\text{C}$. We can see, when poled at a higher temperature, the TSDC current of copolymer VDF/TrFE 77/23 increases significantly, and all the curves corresponding to the blends show two peaks, which we consider as the contribution from the two copolymers respectively. As we cannot see any new peaks formed in the TSDC spectra of the blends contrasting to that of the copolymers, we conclude that the copolymers act independently in the crystalline region in the blend, which agrees with DSC results of the blends.

We also compare the annealed samples of the blends and the as supplied copolymers with the same molar ratio 70/30 showed in Fig.4, and find they are quite different. The TSDC spectra of the copolymer always exhibits two peaks, and the second peak appears at a temperature about 113°C for $T_p = 60^\circ\text{C}$ and 121°C for $T_p = 80^\circ\text{C}$, which are much higher than that of the blend. And we can hardly see the second peak in the spectra of the blend.

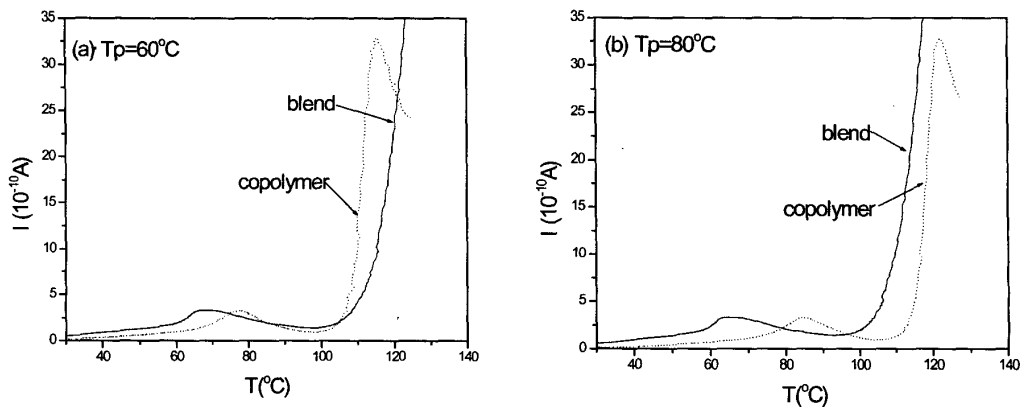


Fig.4 TSDC spectra of the annealed blend and the copolymer sample with the same molar ratio of VDF/TrFE 70/30mol% poled at different temperature.

Fig.5 Shows the TSDC spectra of annealed sample of 63/37 blend at different poling temperatures. We can see the curve doesn't change much with the increased poling temperature except for an increase in the TSDC current. All curves exhibit two peaks as discussed above, and no new peaks are

found as

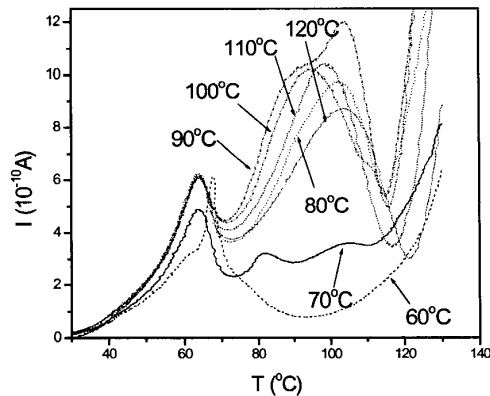


Fig.5 TSDC spectra of annealed sample of blend of VDF/TrFE 63/37mol% with different poling temperature.

the poling temperature increased.

Conclusion

1. X-ray diffraction shows that the crystal structure of the copolymers remains unchanged in the blends.
2. In DSC spectra, the blends exhibit the features of the two copolymers and no new peaks is observed, suggesting that in the blends, the copolymers have little or no interaction.
3. In TSDC spectra, the blends also exhibit the features of the two copolymers, which is in agreement with the DSC results. This indicates that blending doesn't introduce any change to the conformation of crystalline region of the copolymers.

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