Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 2124–2129

polymer

www.elsevier.com/locate/polymer

Structural and ferroelectric response in vinylidene fluoride/trifluoroethylene/hexafluoropropylene terpolymers

Haisheng Xu [a,*], Dong Shen [a], Qiming Zhang [b]

[a] Department of Physics, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China
[b] Materials Research Laboratory, The Pennsylvania State University, PA 16802, USA

Received 15 November 2006; received in revised form 1 February 2007; accepted 14 February 2007

Abstract

Poly(vinylidene fluoride/trifluoroethylene/hexafluoropropylene) terpolymers were synthesized by bulk polymerization process at ambient temperature based on alkyl borane/oxygen initiator. The ferroelectric and dielectric properties were investigated and compared with those of poly(vinylidene fluoride/trifluoroethylene) copolymer. The DSC, X-ray and FT-IR results suggest that the third comonomer in the polymer chain breaks the large polar domains into smaller domain size and reduces the crystallinity of terpolymer. As a result, both the ferroelectric–paraelectric phase transition and melting process take place at lower temperature. The smaller domain makes the dipoles reversal at lower electric field and reduces the polarization hysteresis as well as polarization level. High electrostrictive strain (2.5%) was obtained at low electric field for terpolymer with small quantity of HFP. The polarization and dielectric behaviors imply that the terpolymer is a typical ferroelectric relaxor. The terpolymer also shows higher room temperature dielectric constant than that of copolymer due to the lower phase-transition temperature.

Keywords: P(VDF-TrFE) copolymer; P(VDF-TrFE-HFP) terpolymer; Ferroelectric polymer

1. Introduction

Polymers that exhibit large electromechanical response have attracted a great deal of attention in recent years. Extensive research has been focused on poly(vinylidene fluoride/trifluoroethylene) copolymers, P(VDF-TrFE), because of their relatively high piezoelectric response as well as thermal and chemical stabilities compared with those of other known polymers [1]. A large change of conformation of polymer chains and a large lattice strain associated with conformational change were observed during ferroelectric–paraelectric (F–P) transition, which will have applications in transducer, sensor, and actuator technologies [2–4]. One drawback of this large strain associated with the transition is the large hysteresis [5–7]. We reported that with a proper high energy electron irradiation treatment, P(VDF-TrFE) copolymers exhibit a high electrostrictive response and improved electromechanical coupling factors due to the reduction of hysteresis [8–10]. These results demonstrated that the properties and structures of P(VDF-TrFE) copolymer can be modified and improved markedly by the introduction of “defects” structure. Another possible method inducing defects is to introduce a third comonomer, such as chlorotrifluoroethylene (CTFE) [11] and hexafluoropropylene (HFP), into the polymer chain. In this article, we will report the synthesis of P(VDF-TrFE-HFP) terpolymers by bulk polymerization process and discuss the relationship between the structural and the electrostrictive response as well as ferroelectric behavior. We will show that a small amount of HFP units have a significant effect on the polymer morphology and ferroelectric response.

2. Experiment

2.1. Synthesis of P(VDF-TrFE-HFP) terpolymers and sample preparation

The terpolymers were synthesized by bulk polymerization process at ambient temperature using the triethyl borane/

---

[*] Corresponding author. Tel.: +86 21 68622262; fax: +86 21 64252018.
E-mail address: hsxu@ecust.edu.cn (H. Xu).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.02.035

oxygen initiator. The products were washed by methanol under stirring for 4 h. After filtration, the terpolymer was dried at 70 °C under vacuum for 12 h. The films were prepared by solution casting by first dissolving P(VDF-TrFE-HFP) terpolymer in dimethyl formamide (DMF). The films were subsequently annealed under vacuum at the temperature 10 °C below the melting temperature of each terpolymer for 12 h and then cooled down under vacuum to room temperature. The thickness of the films is around 15 μm. The samples used for electric measurements were sputtered with gold electrodes on both surfaces.

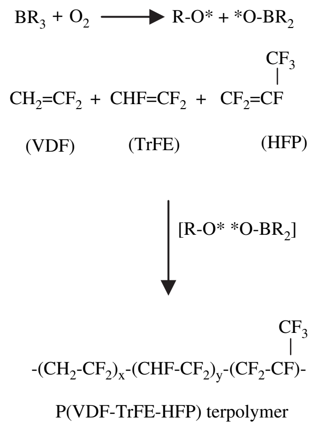
2.2. Measurement

The polarization hysteresis loops were measured using the Sawyer–Tower technique. An external electric field was applied in the form of triangular waveform with a frequency of 10 Hz and different amplitude of field. The electrostrictive strain was measured with bimorph-based cantilever dilatometer, a lock-in amplifier and a high voltage source [12]. The temperature dependence of dielectric properties was measured in the temperature range from 20 to 120 °C and in a frequency range from 100 Hz to 100 kHz. The heating rate employed was 2 °C/min. The molecular weight was measured by GPC on Waters 710 B delivery system with 410 refractive index detector and calibrated with monodisperse polystyrene. The solvent was tetrahydrofuran. ^{19}F NMR was recorded using 20% polymer solution in dimethylsulfoxide (DMSO). Chemical shifts are referenced to an external standard, trimethylsilane (TMS). The DSC measurements were taken using a differential scanning calorimeter (TA Instruments, Model No. 2010) at a scanning rate of 10 °C/min under a nitrogen atmosphere. The X-ray patterns were taken at room temperature using a Scintag diffractometer with Ni filter Cu Kα radiation. The FT-IR spectra were obtained using an Bio-Rad Win Fourier transformation IR spectrophotometers in the wave-number range 4000–400 cm^{-1}.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the polymerization process. All of the monomer gases were purified freshly by freeze–thaw process before synthesis. The triethyl borane was added into the stainless reactor in a dry-box filled with argon. The measured amount of monomers (VDF, TrFE and HFP) was vacuum distilled into the reactor at the liquid nitrogen temperature. After a known amount of oxygen was added, the polymerization was carried out at ambient temperature under vigorous stirring for 20 h. The final composition of terpolymers was evaluated from ^{19}F NMR [13] and the weight-average molecular weight (M_w) was measured by GPC. To facilitate the discussion and comparison with P(VDF-TrFE) copolymer, the composition of the terpolymer is labeled as VDF$_x$–TrFE$_{1-x}$–HFP$_y$, where the mole ratio of VDF/TrFE is x:$(1-x)$ and y is the mol% of HFP in the terpolymer. The terpolymers with three different compositions, i.e., (1) 64/36/0.8, $M_w = 180{,}000$, (2) 61/39/2.0, $M_w = 34{,}000$ and (3) 62/38/2.5, $M_w = 52{,}000$, were investigated. The traditional terpolymerization carried out in emulsion or suspension process usually leads to a terpolymer with inhomogeneous molecular structure and broad composition distribution. The preliminary results of bulk polymerization process, in which all the three monomers were condensed into homogeneous liquid phases and well mixed with a low-temperature initiator, show that a uniform terpolymer structure was obtained when the content of ‘‘bulky’’ monomer was low. However, the relationship between HFP content and molecular weight implied that the polymerization procedure needs to be optimized with further study as the content of monomer with large side group size increases.



Scheme 1. Synthesis of P(VDF-TrFE-HFP) terpolymer.

3.2. Polarization hysteresis and electrostrictive strain

For many electronic device applications utilizing ferroelectric polymers, the polarization response in the films is of prime importance. Fig. 1(a) compares the polarization hysteresis loops measured at room temperature under 100 MV/m and 10 Hz for P(VDF-TrFE-HFP) terpolymers with different HFP contents and P(VDF-TrFE) copolymer. The polarization hysteresis is reduced markedly after the HFP was introduced into the polymer chains. The coercive field (E_c) of terpolymers is about 20 MV/m, whereas the E_c of commercial copolymer is around 60 MV/m. Fig. 1(b) shows the polarization level of terpolymers and variation with the content of HFP, which was replotted from Fig. 1(a). The remanent polarization (P_r) and maximum polarization decrease gradually as the content of HFP increases and the ratio of P_r/P_{max} also decreases. These results imply that the third comonomer breaks large polar domains into smaller domain size and makes the dipoles reversal at lower electric field and also reduces the polarization level since the crystallinity decreases. At higher temperature (e.g., 60 °C), E_c decreases since the motion of dipoles becomes easier at higher temperature.

One of the most important properties of the electroactive polymer is the electrostrictive strain in electromechanical applications. Fig. 2 shows the longitudinal electric field induced strain measured on P(VDF-TrFE-HFP) terpolymer film with different contents of HFP. Comparing with the strain of

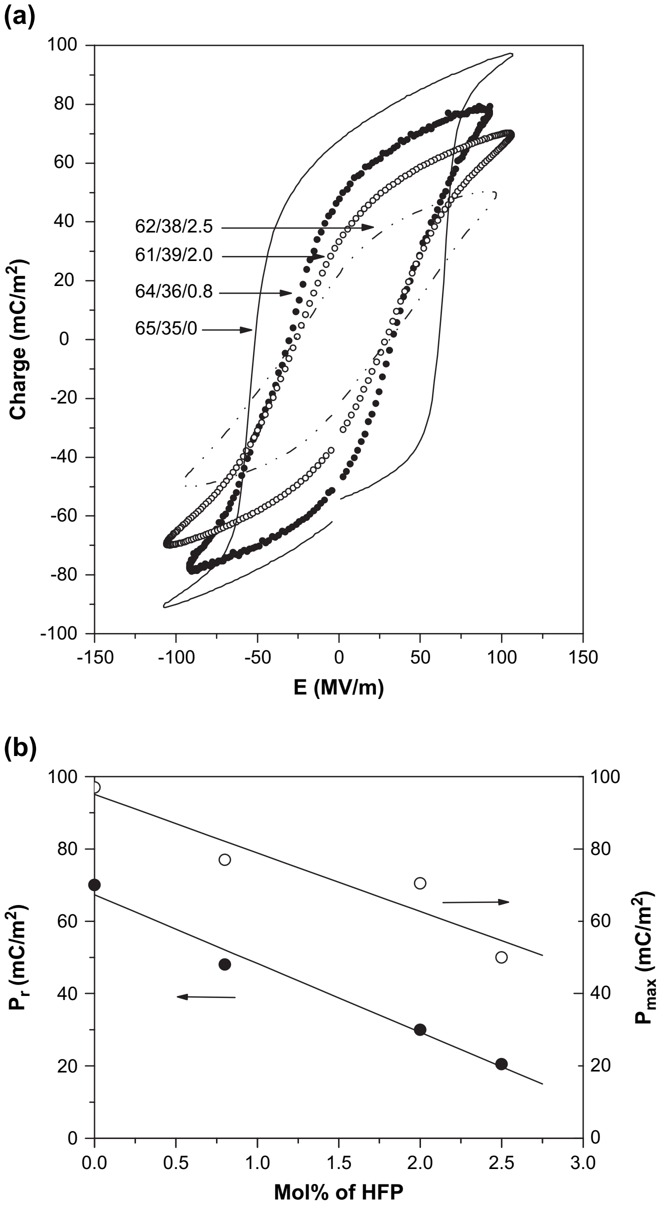


Fig. 1. (a) Polarization hysteresis loops of P(VDF-TrFE-HFP) terpolymers and P(VDF-TrFE) copolymer measured at 100 MV/m and 10 Hz. (b) Variation of polarization with the content of HFP [obtained from (a)].

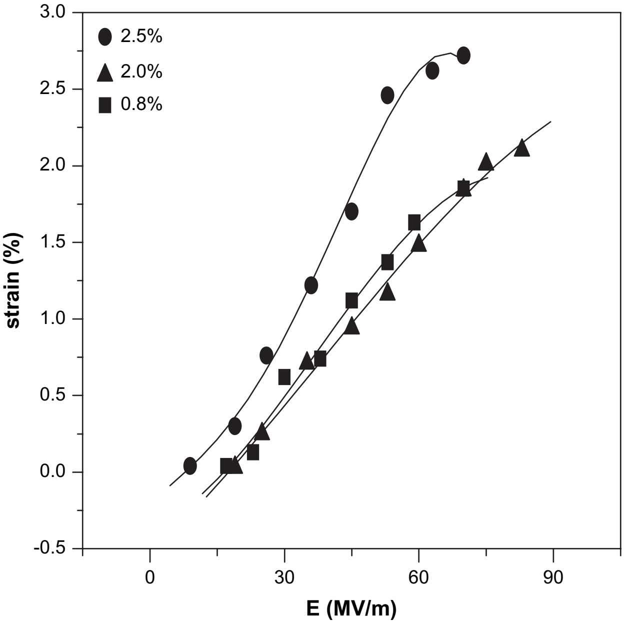


Fig. 2. Longitudinal electric field induced strain of P(VDF-TrFE-HFP) terpolymers: 64/36/0.8, 61/39/2.0 and 62/38/2.5.

copolymer, which is less than 0.1% [14], the terpolymers show much higher strain. The figure shows that the strain of terpolymer increases with the HFP content. For the terpolymer with 2.5 mol% of HFP, high strain was obtained at 50 MV/m, which is more than enough for most electromechanical applications. It is well known that the existence of hysteresis in ferroelectric materials is due to the energy barrier during polarization switching or phase transition. The energy barrier can be reduced or eliminated by introducing "defects" into the polymer chains.

3.3. Dielectric behavior

To investigate the change for the ferroelectric related properties in the terpolymer films, the weak field dielectric constant of terpolymer film was measured. Fig. 3(a) shows the temperature dependence of dielectric properties measured on P(VDF-TrFE-HFP) 62/38/2.5 terpolymer film and compared with P(VDF-TrFE) 65/35 copolymer film. The dielectric properties were recorded during cooling. As shown in the figure, after the introduction of HFP, the dielectric peak of terpolymer film shifts towards a lower temperature. The peak becomes broader and its position shifts progressively with frequency towards higher temperature. It is understandable that the ferroelectric transition will be broadened and the ferroelectric–paraelectric (F–P) transition temperature will be lowered as the bulky and less polar termonomer HFP is randomly introduced into P(VDF-TrFE) normal ferroelectric crystals. It should also be noted that the terpolymer possesses a high room temperature dielectric constant because of the lower F–P transition temperature. For example, at 1 kHz the dielectric constant of terpolymer is about 30, whereas that of the corresponding copolymer is 15. Fig. 3(b) shows the dielectric constant measured on terpolymer and copolymer films at both heating and cooling cycles. No thermal hysteresis in the dielectric data was observed for terpolymer, i.e., the broad dielectric peak stays at the same temperature when measured in heating and cooling cycles. In contrast, the copolymer shows thermal hysteresis in the dielectric data. The results from polarization and dielectric behaviors of terpolymer suggest that the introduction of HFP into P(VDF-TrFE) copolymers converts the normal ferroelectric P(VDF-TrFE) copolymer into a material closely resembling ferroelectric relaxor [15].

3.4. DSC results

To understand the change of the morphology and the transitional behavior as the third comonomer introduced in the polymer chain, a DSC measurement was carried out on these P(VDF-TrFE-HFP) terpolymer and P(VDF-TrFE) copolymer samples and the results are shown in Fig. 4 and Table 1. The

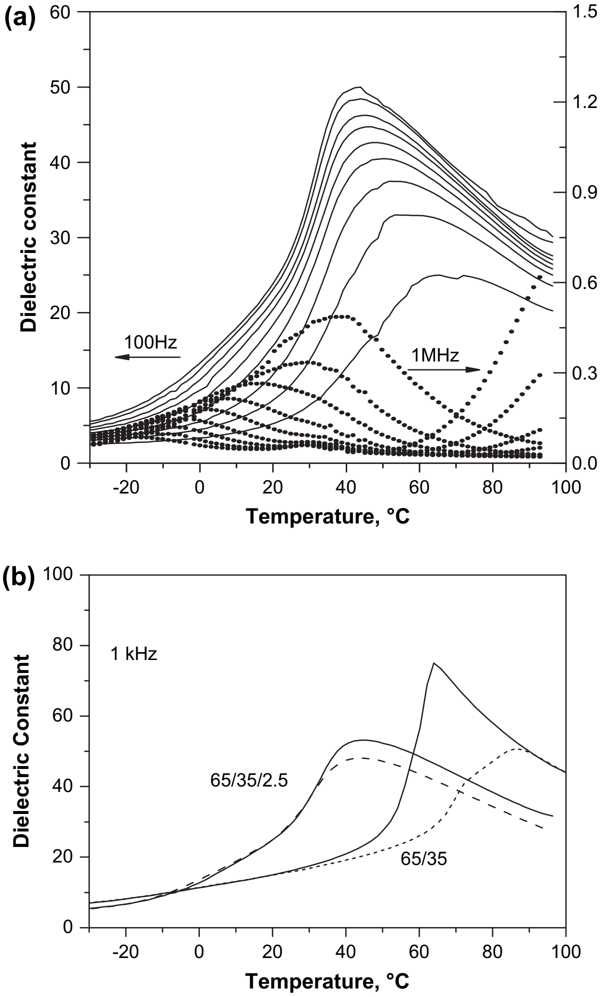


Fig. 3. Terpolymer P(VDF-TrFE-HFP) 62/38/2.5 (a) dielectric constant (solid curves) and dielectric loss (dashed curves) as a function of temperature at frequencies (from top to bottom for dielectric constant and from bottom to top for dielectric loss) 100 Hz, 300 Hz, 1, 3, 10, 30 kHz, 0.1, 0.2 and 1 MHz. (b) Dielectric constant at 1 kHz of the P(VDF-TrFE-HFP) 62/38/2.5 terpolymer and P(VDF-TrFE) 65/35 copolymer for both heating (dashed curves) and cooling (solid curves) cycles.

film samples were annealed before measurement and the heating cycle was recorded.

The DSC results show clearly that after HFP being introduced into the P(VDF-TrFE) copolymer chain, both the Curie temperatures (T_c) and melting temperatures (T_m) of terpolymers decreased markedly. For terpolymers, T_c and T_m decreased continuously as the HFP molar content increased. In addition, the enthalpy of both Curie transition and melting process decreased for terpolymers. These results suggest that the size of polar crystalline domain and crystallinity decreased after HFP being introduced into the polymer chain. Since the CF_3 group in HFP monomer has much bigger size comparing with F atom in VDF and TrFE, the HFP monomer in the polymer chain will break down the long sequences of β-phase into several short sequences in crystalline region. The smaller polar domains result in the lower energy for the conformational transition and therefore reduce the polarization hysteresis of materials.

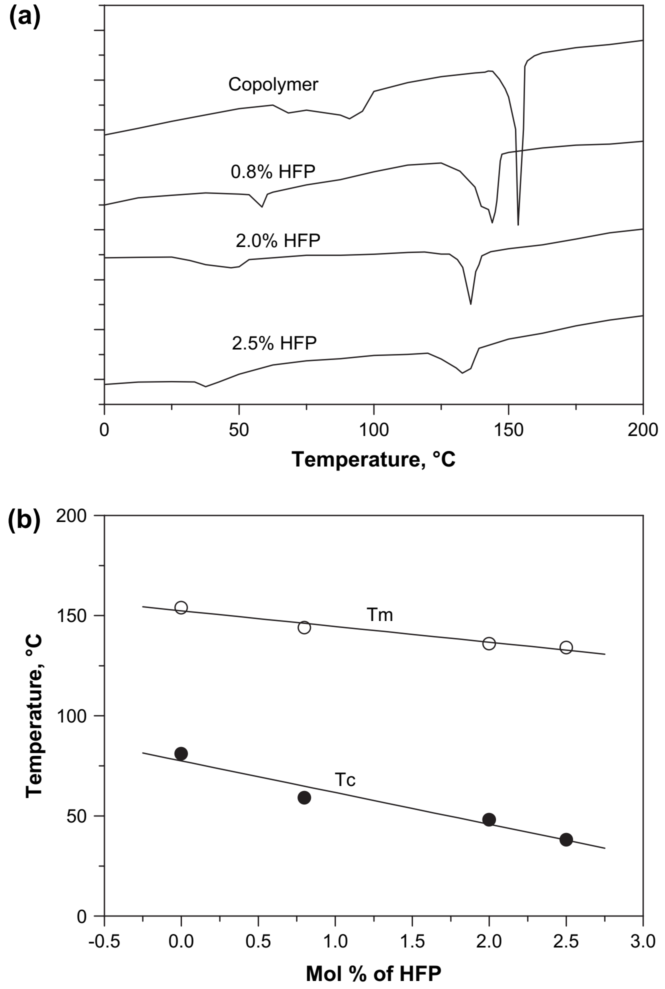


Fig. 4. (a) DSC curves of P(VDF-TrFE-HFP) terpolymers with various HFP contents and the P(VDF-TrFE) (65/35) copolymer. (b) Melting temperature (upper line) and Curie temperature (lower line) vs. mole fraction of HFP.

3.5. X-ray and FT-IR results

X-ray data of (200) and (110) reflections taken at room temperature on both unstretched and stretched terpolymer films compared with the copolymer film are presented in Fig. 5(a) and (b). In addition to this sharp peak in the X-ray data, there is a broad peak with a much lower intensity that is due to the amorphous phase in the films. By separating and fitting the amorphous and crystalline regions, the change of the crystallinity due to the introduction of HFP can be estimated from the area of crystalline diffraction peak and

Table 1
Thermal properties of terpolymers and copolymer from DSC

Sample no.	Composition (%)			T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
	VDF	TrFE	HFP				
1	65	35	0	103	22.5	152	33.1
2	64	36	0.8	43	4.6	140	22.7
3	61	39	2.0	41	4.7	138	19.6
4	62	38	2.5	35	2.6	129	15.6

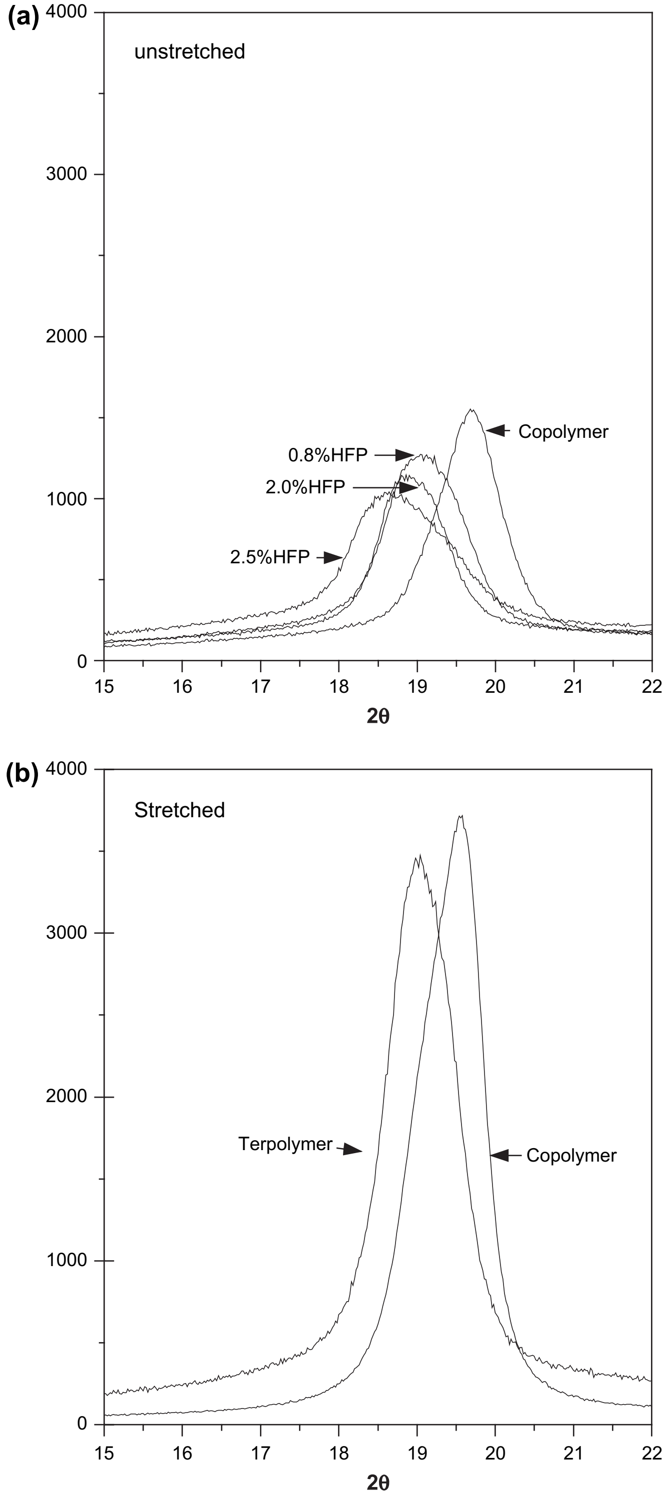


Fig. 5. X-ray diffraction pattern of P(VDF-TrFE-HFP) terpolymer and P(VDF-TrFE) 65/35 copolymer (a) unstretched film and (b) stretched film.

amorphous hola contribution and comparing the peak area from the crystalline diffraction with the total area (crystalline plus amorphous phase) [16]. For example, the crystallinity for the stretched and annealed copolymer film is 80%, whereas for the stretched and annealed terpolymer with 0.8% HFP, it is reduced to 60%. After the introduction of HFP into the polymer chain, the peak shifts to lower angle for both stretched and unstretched films and therefore indicates clearly the expansion of the lattice. For example, the peak of stretched copolymer 65/35 film appears at 4.50 Å ($2\theta = 19.69°$), whereas the terpolymer with 2.5% HFP has a peak at 4.77 Å ($2\theta = 18.61°$). For terpolymers, the higher the HFP content, the lower the peak locates. The expanded lattice spacing is close to the paraelectric phase.

Fig. 6 shows the FT-IR spectra in the wave-number range between 1500 and 400 cm^{-1} for the P(VDF-TrFE-HFP) terpolymer with 2.5% content of HFP. P(VDF-TrFE-HFP) terpolymers with 2.0% and 0.8% show similar FT-IR spectra. The spectra of P(VDF-TrFE) copolymer were also shown for comparison. It is well known [7,17–23] that P(VDF-TrFE) copolymers can crystallize into at least four types of crystal forms, named forms I(β), II(α), III(γ), and IV (polar form II, IIp). There exist three basic chain conformations, i.e., all-*trans* planar zigzag ($T_{m>3}$), *trans–gauche–trans–gauche*′ (TGT$\overline{G}$), and $T_3GT_3\overline{G}$, in crystalline phases. Among these crystalline forms, the β-phase (or form I), which has all-*trans* chains packed with their dipoles pointing in the same direction exhibits a strong ferroelectric behavior. As shown in Fig. 6, for the copolymer, the spectrum is characterized by a strong absorbance peak at 1288 cm^{-1}, which is ascribed to the long *trans* sequence ($T_{m\geq4}$) of the ferroelectric β-phase. Weak absorbance peaks corresponding to the TGT$\overline{G}$ (614 cm^{-1}) and $T_3GT_3\overline{G}$ (510 cm^{-1}) conformations are also observed. After introducing HFP into the polymer chain, the absorbance from ferroelectric phase decreases dramatically even with low HFP content, meanwhile the absorbance from $T_3GT_3\overline{G}$ increases. Fig. 7 shows the dependence of the relative absorbance of these two bands on the percent of HFP. In this analysis, the method by Osaki and Ishida was used to calculate the fraction F_i of the each chain conformation, $F_i = A_i/(A_I + A_{II} + A_{III})$, where i = I, II, III, and A_I, A_{II}, A_{III} are the absorbencies of the chain conformations with all-*trans* (absorbance peak at 1288 cm^{-1}), $T_3GT_3\overline{G}$ (510 cm^{-1}), and TGT$\overline{G}$ (610 cm^{-1}), respectively [24]. Each individual component of the bands has been fitted and separated from others by assuming a Lorentzian function peak shape. Since the samples with different HFP contents have small variations in thickness and moreover, the absorbance of even the same type of chain conformation may be different due to the different crystallinity of different samples, an internal standard was used to compare the relative absorbance of different conformational sequences. The absorbance at 3022 cm^{-1} is the asymmetric stretching vibration of the C–H bond [25], and as it is almost proportional to the thickness of the sample and does not depend on the state of the sample, it was used as an internal standard here. The data in Fig. 7 are the relative absorbance after this correction. The relative absorbance intensity of the all-*trans* peak decreases monotonically with the HFP content in terpolymers while the peak of $T_3GT_3\overline{G}$ sequence shows a monotonic increase. Although the absorbance peak corresponding to TGT$\overline{G}$ sequence also increases with HFP content, it is still weak within the range of HFP content studied in this article.

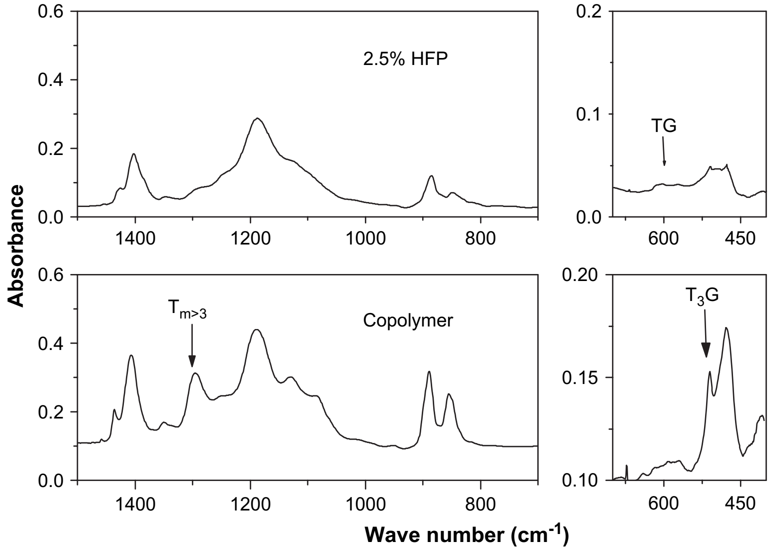


Fig. 6. FT-IR spectra of P(VDF-TrFE-HFP) terpolymer film with 2.5 mol% of HFP. The spectrum of P(VDF-TrFE) copolymer is also presented for comparison.

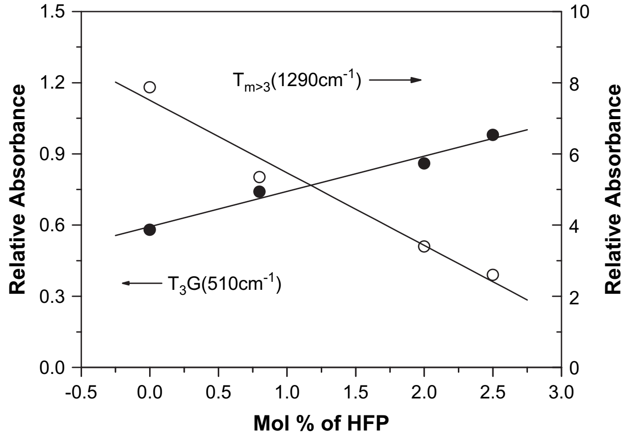


Fig. 7. Relative absorbance of the *trans* ($T_{m>3}$) and *gauche* ($T_3GT_3\overline{G}$) bands change with HFP%.

4. Summary

The structural and polarization properties of poly(vinylidene fluoride/trifluoroethylene/hexafluoropropylene) terpolymers synthesized by bulk polymerization process at ambient temperature were investigated and compared with those of poly(vinylidene fluoride/trifluoroethylene) copolymer. As the third comonomer with large side group size, such as HFP, is introduced into P(VDF-TrFE) polymer chain, the large polar domains are broken into smaller domain size. This reduces the crystallinity of terpolymer. Both the ferroelectric–paraelectric phase transition and melting process take place at lower temperature as suggested by DSC and dielectric measurements. The X-ray results indicate the expansion of the lattice due to the introduction of HFP in the crystalline phase. Therefore, the polarization hysteresis is reduced as well as polarization level. High electrostrictive strain (2.5%) was obtained at low electric field for terpolymer with small amount of HFP. The terpolymer shows typical behaviors of ferroelectric relaxor.

References

[1] Tashiro K. In: Nalwa HS, editor. Ferroelectric polymers. New York: Dekker; 1995. p. 63.
[2] Lovinger AJ, Furukawa T, Davis GT, Broadhurst MG. Polymer 1983;24:1225.
[3] Yagi T, Tatemoto M, Sako J. Polym J 1980;12:209.
[4] Herbert JM. Ferroelectric transducers and sensors. New York: Gordon and Breach Science Publishers; 1982.
[5] Furukawa T. Phase Transition 1989;18:143.
[6] Lovinger AJ, Davis DD, Cais RE, Kometani JM. Polymer 1987;28:617.
[7] Tashiro K, Takano K, Kobayashi M, Chatani Y, Tadokoro H. Ferroelectrics 1984;57:297.
[8] Zhang QM, Bharti V, Zhao X. Science 1998;280:2101.
[9] Xu HS, Shanthi G, Bharti V, Zhang QM. Macromolecules 2000;33:4125.
[10] Bharti V, Xu HS, Shanthi G, Zhang QM. J Appl Phys 2000;87:452.
[11] Xu HS, Cheng Z-Y, Olson D, Mai T, Zhang QM, Kavarnos G. Appl Phys Lett 2001;78:2360.
[12] Su J, Moses P, Zhang QM. Rev Sci Instrum 1998;69:2480.
[13] Isbester PK, Brandt JL, Kestner TA, Munson EJ. Macromolecules 1998;31:8191.
[14] Zhang QM, Cheng Z-Y, Bharti V, Xu T, Xu HS, Mai T, et al. Proceedings of SPIEs seventh annual international symposium on smart structures and materials 3987, 34 Newport Beach, CA; 2000.
[15] Cross LE. Ferroelectrics 1994;151:305.
[16] Zhang QM, Xu HS, Fang F, Cheng Z-Y, Xia F, Hou Y. J Appl Phys 2001;89:2613.
[17] Lovinger AJ. Science 1983;220:1115.
[18] Tashiro K, Takano K, Kobayashi M, Chatani Y, Tadokoro H. Polymer 1984;25:195.
[19] Lovinger AJ, Davis GT, Furukawa T, Broadhurst MG. Macromolecules 1982;15:324.
[20] Lovinger AJ, Davis DD, Cais RE, Kometani JM. Macromolecules 1988;21:78.
[21] Tashiro K, Kobayashi M. Polymer 1988;29:426.
[22] Tashiro K, Kaito H, Kobayashi M. Polymer 1992;33:2915.
[23] Tashiro K, Tanaka R, Ushitora K, Kobayashi M. Ferroelectrics 1995; 171:145.
[24] Osaki S, Ishida Y. J Polym Sci Part B Polym Phys 1975;13:1071.
[25] Kobayashi K, Tashiro K, Tadokoro H. Macromolecules 1975;8:158.