Ferroelectric properties of vinyl fluoride–trifluoroethylene copolymers

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Vinyl fluoride–trifluoroethylene copolymers were prepared by free-radical polymerization. The hysteresis loop of electrical displacement D *versus* electrical field E was obtained for 44 mol% vinyl fluoride copolymer. Values of the remanent polarization ranged from 20 to $50\,\mathrm{mC\,m^{-2}}$. The temperature dependence of the dielectric constant indicated a dielectric anomaly with frequency dependence. The reciprocal dielectric constant was thus plotted in conformity with the Curie–Weiss law. The remanent polarization gradually decreased from room temperature and completely disappeared at about 100°C. A discontinuous change in the linear thermal expansion coefficient was observed at 100°C. It was found that this vinyl fluoride copolymer is ferroelectric at the Curie point. It was also found that the copolymer has a phase transition in relaxation that resembles second order.

(Keywords: vinyl fluoride; trifluoroethylene; ferroelectricity)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has the crystalline structures of various polymorphisms[1,2]. In these polymorphic phases, the form I crystal has a structure with aligned dipoles and shows ferroelectricity. However, the Curie point (T_C) has never been observed in PVDF.

The ferroelectric transition in PVDF is made possible by copolymerization of VDF and trifluoroethylene (TrFE)[3,4] or tetrafluoroethylene (TFE)[5,6]. These copolymers have been studied by many research groups to elucidate the characteristics of structure and ferroelectricity[7–10]. The comonomers of TrFE and TFE have been shown to act as effective constituents in stabilizing planar zigzag conformations and they expand the unit cell of the crystal. The introduction of TrFE leads to the formation of polar crystals having dipole–dipole interactions that give rise to phase transitions.

We applied poly(vinyl fluoride)s (PVFs) to an attempt to obtain a novel ferroelectric. PVF has a polar crystal with a planar zigzag conformation[11,12], and its poled film shows piezoelectric activity[13,14]. However, no study on PVF has clarified its ferroelectric properties or T_C. Guerra *et al.*[15] reported that the copolymer of VF and VDF has no transition below the melting point. We obtained a VF copolymer with TrFE that possessed a van der Waals volume larger than that of VDF and a helical conformation in its homopolymer. TrFE was expected to control the dipole–dipole interactions in the PVF crystal. The possibility of ferroelectricity in P(VF–TrFE) was reported as a dielectric anomaly in previous work[16].

In the work described in this paper, the ferroelectric properties of P(VF–TrFE) with T_C were studied by examination of dielectric properties, Curie–Weiss plots, ferroelectric hysteresis, dielectric depolarization and structural changes in X-ray diffraction.

EXPERIMENTAL

Samples

PVF, P(VF–TrFE) and PTrFE were prepared by free-radical polymerization at 25°C in 1,1,2-trichloro-1,2,2-trifluoroethane with heptafluorobutylic peroxide as an initiator. After polymerization, these copolymers were washed with methanol and dried under vacuum.

Measurements

Differential scanning calorimetry (d.s.c.) was performed on a Mac Science DSC 3100 to observe the melting point of each sample. The relative dielectric constants were obtained with a 3520 LCR Hi tester (Hioki Ltd) at a heating rate of $2^\circ\mathrm{C\,min^{-1}}$. The measurement samples were fabricated by casting from methyl ethyl ketone solution onto an indium–tin oxide glass plate, and aluminium was evaporated on the surface of the cast film as an electrode. To increase crystallinity, the samples were annealed at 180°C for 2 h. The measurements were performed in a chamber oven under vacuum. The hysteresis loop of electrical displacement D *versus* electric field E was measured by using a triangular waveform at a frequency of 0.01 Hz. The temperature dependence of the remanent polarization was obtained by integrating the depolarization current in the sample after poling. X-ray diffraction by the symmetrical reflection method was performed on an MXP[18] from Mac Science Ltd, and the temperature dependence of the patterns was obtained by means of a sample set in a high-temperature cell equipped with a temperature controller.

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RESULTS AND DISCUSSION

Table 1 shows the polymer compositions and melting points for PVF, P(VF-TrFE) and PTrFE. Two compositions for P(VF-TrFE) were used in the present study. The melting points of the copolymers are higher than those of the homopolymers. In the study of ^{19}F n.m.r. spectra, we reported the sequence distribution of the copolymer to be almost random along the chain and the melting behaviour to be possibly related to the extent of alternation in the random chain[16]. Some alternating 1:1 copolymers possess higher melting points than homopolymers: Sibilia *et al.*[18] reported that the alternating 1:1 copolymer of ethylene (E) and chlorotrifluoroethylene (CTFE) has a higher melting point than PE and PCTFE. This was explained by the effect of intermolecular dipole association caused by strong packing of alternating chains.

The dielectric constants for the samples are shown as a function of temperature in *Figure 1*. The frequency used in the measurement was 1 kHz. The dielectric constant for PVF increases slightly with increasing temperature in the temperature range near the melting point. However, there is no transition. This indicates that molecular packing in the crystal of PVF is so strong that dipoles cannot rotate below the melting point. The copolymer with 78 mol% VF has a shoulder-like transition at 165°C with a higher dielectric constant than PVF. In P(VF-TrFE) with 44 mol% VF, the dielectric constant exhibits a peak around 140°C, similar to P(VDF-TrFE). This dielectric anomaly is considered to be an indication of ferroelectric transition. The decrease in dielectric constant above 140°C is thus due to the cooperative motion of dipoles. The frequency dependence of the dielectric peak temperature has been shown in the 44 mol% VF copolymer[16]. This frequency dependence is caused by a dielectric relaxation process. In Ba(Ti, Sn)O$_3$, the so-called 'ferroelectric relaxer'[17,19], a similar dielectric relaxation was noted with the disordered arrangement of the constituent ions.

Table 1 Copolymer compositions and melting points of P(VF-TrFE)

Polymer	VF (mol%)	T_m (°C)
PVF	100	198.8
P(VF-TrFE)	78	207.3
P(VF-TrFE)	44	216.2
PTrFE	0	198.1

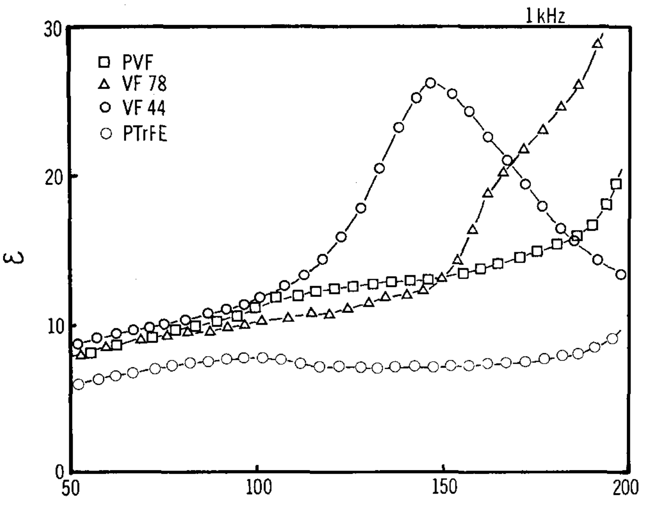

Figure 1 Temperature dependence of dielectric constant for PVF, P(VF-TrFE) and PTrFE

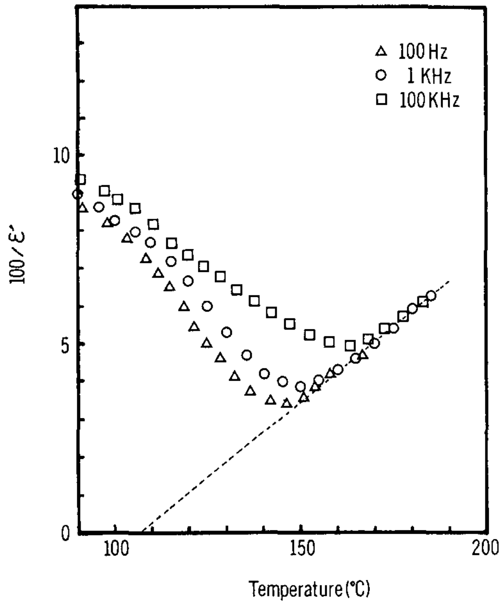

Figure 2 Temperature dependence of reciprocal dielectric constant at three frequencies for P(VF-TrFE) (44 mol% VF)

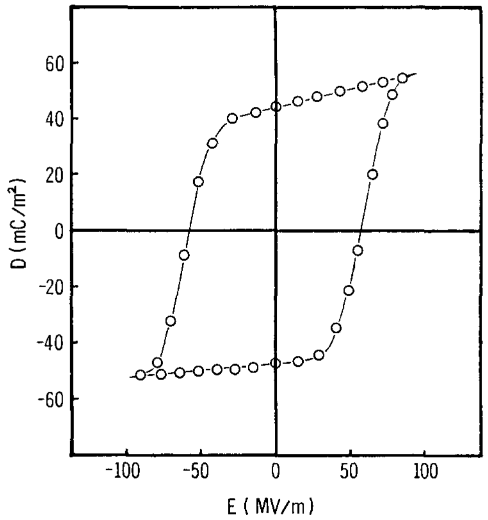

Figure 3 *D versus E* hysteresis loop for P(VF-TrFE) (44 mol% VF)

The reciprocal dielectric constants 1/ε at three frequencies are plotted against temperature for the 44 mol% VF copolymer in *Figure 2*. The plots at all frequencies give identical straight lines above the peak temperature. This conforms with the Curie-Weiss law. The extrapolated temperature, the intersection of a straight line and the *x*-axis, is about 107°C. A Curie constant of about 1200 K was estimated. This value is essentially the same as those of other ferroelectrics having order-disorder types of phase transition.

Figure 3 shows the *D versus E* hysteresis loop for the 44 mol% VF copolymer at 50°C. The hysteresis loop confirms that the copolymer is a ferroelectric. The intersections of the hysteresis loop with the *x* and *y* axes give a coercive field of 60 MV m^{-1} and a remanent polarization P_r of 44 mC m^{-2}, respectively. However, values of P_r ranged from 20 to 50 mC m^{-2}. P_r for this copolymer depends considerably on sample conditions such as crystallinity and molecular orientation. This P_r, smaller than those of PVDF and P(VDF–TrFE), is caused by low crystallinity and a small value of the average dipole moment per unit.

Figure 4 shows the temperature dependence of P_r for the 44 mol% VF copolymer after poling. The disappearance of P_r truly indicates that T_C is in the temperature range from 100 to 120°C. This is in good agreement with the value of 107°C for the extrapolated temperature in the Curie–Weiss plot. P_r at 50°C is about 16 mC m^{-2}, comparable to P_r obtained from the *D versus E* hysteresis loop. Furthermore, the point to be emphasized in this figure is the gradual decrease in P_r in the temperature range from room temperature to T_C. This gentle curve is similar to that of triglycine sulfate, which has a second-order phase transition. This type of decrease in P_r is associated with a large pyroelectric constant. In this copolymer, the pyroelectric constant calculated from the slope of P_r in *Figure 4* was about 17 nC cm^{-2} K^{-1} at room temperature, which is much larger than that of PVDF.

X-ray diffraction patterns for PVF, PTrFE and two copolymers are shown in *Figure 5*. PVF has a diffraction pattern with a main single peak at (110, 200). The main peak splits into two peaks and shifts to lower diffraction angle with increasing TrFE content. For PVF, Golike[11] proposed a hexagonal unit cell, whereas Natta[12] preferred on orthorhombic system. However, there is an agreement in both works that the chain conformation is planar zigzag. Our X-ray diffraction data suggest that the lattice is expanded by the introduction of the TrFE unit into the crystal.

Figure 6 shows the temperature dependence of the lattice spacing for the main peak of X-ray diffraction. A significant change in the slope of the lattice spacing *versus* temperature plot indicates a certain phase transition in T_C at about 100°C. The change in slope at 100°C is a continuous volume change. On the other hand, the change in the thermal expansion coefficient at this temperature is discontinuous. The thermal expansion coefficients calculated from the slopes below and above T_C are 2.27×10^{-4} K^{-1} and 4.95×10^{-4} K^{-1}, respectively. Furthermore, the phase transition showed no hysteresis during the heating or cooling cycles in the measurement of X-ray diffraction as a function of temperature.

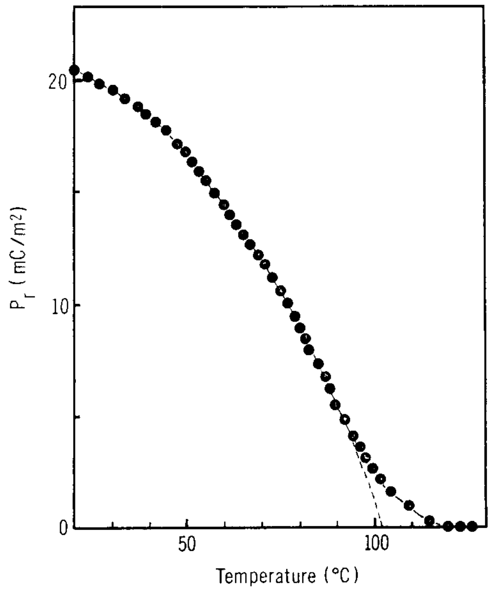

Figure 4 Temperature dependence of remanent polarization for P(VF–TrFE) (44 mol% VF)

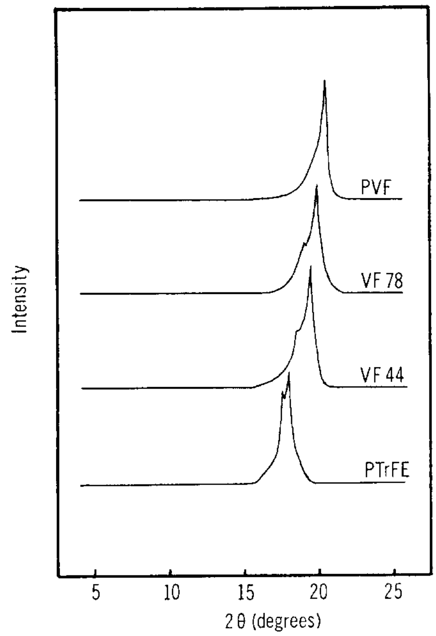

Figure 5 X-ray diffraction patterns of PVF, P(VF–TrFE) and PTrFE

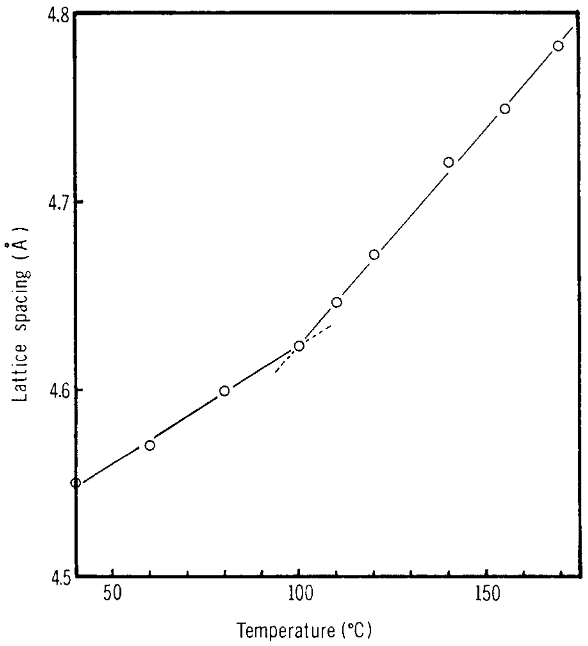

Figure 6 Temperature dependence of P(VF–TrFE) (44 mol% VF) lattice spacing as measured by X-ray diffraction

From the results of lattice spacing *versus* temperature, the copolymer appears to have a second-order ferroelectric–paraelectric phase transition. This agrees not only with the shapes of the plots of P_r and $1/\varepsilon$ *versus* temperature but also with the absence of latent heat in the d.s.c. measurements. The T_C of P(VDF–TrFE) with a high content of VDF behaves as a first-order phase transition because of the discontinuous change in lattice spacing, the presence of hysteresis for heating and cooling, and the observation of an enthalpy change. These features of the phase transition for P(VDF–TrFE) are completely different from those of P(VF–TrFE).

As seen in *Figure 2*, the phase transition of P(VF–TrFE) accompanies relaxation. We also observe in *Figures 4* and *6*, respectively, that P_r decreases gradually with increasing temperature and no change in crystal volume occurs at the transition temperature. Although these results lead us automatically to deduce a type of second-order transition, the ferroelectric phase transition of P(VF–TrFE) contains relaxation with a long relaxation time. Basically, the ferroelectric–paraelectric transition is a thermodynamic phase transition. The ferroelectric transition of the copolymer is thus possibly governed by non-equilibrium processes such as glass transition. It seems that the origin of relaxation is not only the disordered arrangement of the copolymer sequence with dipoles but also the large-molecule effects of the copolymer. Such large-molecule effects in polymeric materials make for dipoles which cannot move without much friction. Since the dipoles of ferroelectric polymers are bonded chemically to the main chain and are closely packed with each other, the transition requires 'free volume' to rotate the dipoles. There is similar behaviour in the glass transition of crystal glass[20].

The T_C and melting point of P(VF–TrFE) may depend on the crystal structure of the alternating sequence, even though this copolymer is basically composed of a random chain. The crystal formation, which leads to an increase in melting point, influences the ferroelectric phase transition. The ferroelectricity of the copolymer would thus be associated with the disordered arrangement of the alternating sequence in the crystal and the dipoles experiencing high friction. We should realize that the role of the chain sequence distribution in ferroelectric polymers is very important in determining the structure and properties. In fact, comonomer distribution affects T_C even in P(VDF–TrFE)[21].

CONCLUSION

In the present paper we have described the ferroelectric properties and phase transition of P(VF–TrFE) with 44 mol% VF. The ferroelectricity is confirmed by the *D versus E* hysteresis loop. P_r is about 20 to 50 mC m^{-2}, which is smaller than the values of P_r for PVDF and VDF copolymers. T_C in P(VF–TrFE) is observed at approximately 100°C through an anomaly in the dielectric constant, the Curie–Weiss plot, the disappearance of P_r, and the change in the slope of the lattice spacing *versus* temperature plot. In addition, the phase transition is of second order because of the gradual decrease in P_r and the continuous change in lattice spacing observed through the temperature dependence of the X-ray diffraction measurements.

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