Temperature Effect on the Infrared Absorption of Ferroelectric Copolymer Poly(vinylidene fluoride-trifluoroethylene)

Y. W. Wong, C. M. Leung, N. M. Hui, H. L. W. Chan, C. L. Choy

Department of Applied Physics and Materials Research Center, Hong Kong Polytechnic University, Hung Hum, Hong Kong, China

ABSTRACT: The intensity of two infrared absorption bands of annealed ferroelectric copolymers [poly(vinylidene fluoride-trifluoroethylene)] in the mid-infrared high-frequency region was found to be strongly related to the annealing temperature. The vibration modes in the amorphous phase of the copolymers were considered to account for these two bands. On the other hand, the temperature dependence of the absorption spectra of the copolymers in the heating and cooling cycle was investigated. In the vicinity of the Curie transition, the absorption bands associated with the CH_2 vibrations exhibited a shift in frequency. Two bands were identified as shifting to a high frequency, and one band shifted to a low frequency with heating. These three bands were restored to their room-temperature frequency with cooling. In addition, copolymers of a higher vinylidene fluoride content exhibited a more pronounced thermal hysteresis in terms of a shift in frequency. This was consistent with the electrical behavior of the copolymers. The trends of the frequency shifts suggested that dipole–dipole coupling existed between two adjacent chains in the all-trans conformation, which originated from the interaction of the CH_2 and CF_2 dipoles. The coupling diminished as the copolymers underwent a change in phase above the transition temperature. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1662–1666, 2005

Key words: ferroelectricity; FT-IR; fluoropolymers

INTRODUCTION

Fluoro-polymer poly(vinylidene fluoride) and its copolymer with trifluoroethylene, poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)], have been widely studied in the last 2 decades because of their piezoelectric and ferroelectric properties.[1–5] These copolymers, with an increasing vinylidene fluoride (VDF) molar content, have higher ferroelectric phase-transition temperatures. From X-ray diffraction results and from studies of the vibrational spectra, it has been determined that the copolymers experience a conformational change in the ferroelectric phase transition.[1,6] The all-trans (TT) polymer chains below the Curie temperature (T_c) change into the trans–gauche (TG) conformation above T_c. As a result of the structural change, most of their physical properties, such as their mechanical stiffness and thermal expansion, also exhibit an abrupt change in temperature at the phase transition.[7,8] For copolymers with a VDF molar content of more than 60%, these physical properties exhibit a significant thermal hysteresis in a heating and cooling cycle. The thermal lag, a manifestation of a first-order phase transition, is proportional to the VDF content.

Although the temperature dependence of the vibrational spectra, particularly the infrared (IR) absorption, has been well examined by many authors,[6,9,10] most such work has been concentrated on the far-IR region (1000–100 cm^{-1}). In these studies, it has been observed that as the temperature increases above T_c, the skeletal torsional mode of the TT conformation continuously transfers to the torsional mode of the gauche type, and this suggests a phonon-softening behavior in the phase transition. However, apart from the far-IR region, not much research has been focused on the high-frequency range (4000–2000 cm^{-1}), as the corresponding active absorption bands are weak and far fewer. For practical purposes, the sample thickness is usually only several micrometers to avoid absorption saturation in the far-IR region; this sacrifices those high-frequency bands of relatively low absorbance. In this investigation, we used thick copolymer samples to enhance the absorption in the high-frequency range. The correlation of the intensity of the absorption band to the sample annealing temperature and the temper-

ature dependence of the frequency of the absorption bands in the vicinity of the phase transition were observed and studied in detail.

EXPERIMENTAL

Copolymer pellets provided by Piezotech (Saint-Louis, France), with VDF molar contents of 56, 70, and 77%, were used in this study; they are called 5644, 7030, and 7723, respectively. The pellets were hot-pressed at 190°C for 1 h and then quenched in ice water. The thickness of the obtained films was approximately 200 μm. The ferroelectric phase-transition temperature of the samples was determined with a differential scanning calorimeter (DSC-7, PerkinElmer, Wellesley, MA). The 5644 and 7030 quenched samples were annealed at 100, 120, 130, and 140°C for 4 h to obtain various crystallinities. Wide-angle X-ray diffraction (WAXD) patterns of the samples were obtained with Ni-filtered Cu Kα radiation. They were employed to determine the degree of crystallinity (χ_c). The crystalline and amorphous peaks, assumed to be Gaussian, were least-square-fitted and separated after the subtraction of the background.[11] χ_c was then obtained with the following equation:

$$\chi_c = \int I_c(\theta) \, d\theta \bigg/ \left(\int I_c(\theta) \, d\theta + \int I_a(\theta) \, d\theta \right) \quad (1)$$

where I_c and I_a are the fitted crystalline and amorphous intensities, respectively, and θ is the diffraction angle.

The IR absorption spectra were measured with a Nicolet Magna-760 Fourier transform infrared spectrometer (Madison, WI) equipped with a Graseby variable-temperature cell with a stability of ± 0.5°C. The temperature of the cell was calibrated with a K-type thermocouple. The resolution of the spectrometer was set to 4 cm^{-1}, and the scan was averaged to 32, whereas the data spacing was 1.9 cm^{-1}.

RESULTS AND DISCUSSION

The ferroelectric phase-transition temperatures of the quenched 5644, 7030, and 7723 samples, as determined from the differential scanning calorimetry heating measurements, were 65, 108, and 130°C, respectively. In the cooling temperature scanning, the three samples were found to have a phase change at lower temperatures of 59, 62, and 78°C, respectively. Evidently, a copolymer with a high VDF content has a higher transition temperature. From the difference in the transition temperature in the heating and cooling cycle, it is clear that copolymers with a high VDF content have more significant thermal hysteresis. As a matter of fact, thermal hysteresis is a result of the

TABLE I
χ_c of 5644 and 7030 Copolymers at Various Annealing Temperatures

Annealing temperature (°C)	χ_c	
	5644	7030
Quenched	0.45	0.55
100	0.49	0.58
120	0.58	0.71
130	0.63	0.78
140	0.72	0.85

coexistence of the ferroelectric phase and paraelectric phase of the copolymers in the vicinity of the transition temperature. This is a typical characteristic of a first-order phase transition. The coexistence of the two phases in the transition temperature range has been elucidated in a study of X-ray diffraction.[12]

The degree of the crystallinities of the quenched and annealed 5644 and 7030 samples, as determined by WAXD, are given in Table I. From the tabulated results, it can be seen that the quenched samples had a crystalline phase of more than 40% and that the crystallinity increased along with increases in the annealing temperature.

At temperatures higher than T_c, the crystallization process is dominated by the growth of crystals in the consumption of the amorphous phase at the two-phase interface.[13] This feature can also be revealed from the IR absorption spectra of the copolymers. Figures 1(a,b) depicts the IR absorption spectra in the range of 4000–3500 cm^{-1} for the 5644 and 7030 samples, respectively. The intensity of the absorption at 3708 and 3624 cm^{-1} clearly decreased as χ_c increased. A plot of χ_c versus the absorbance is shown in Figure 2. Although the assignment of these two bands is as yet unclear, the correlation between χ_c and the absorbance is evident. The 5644 sample was highly dependent on χ_c, whereas the 7030 sample changed modestly; the absorbance of these bands for both copolymers decreased to the extent that they nearly disappeared. The vibration modes in the amorphous phase account for the existence of these two bands. They diminished with the reduction of the amorphous phase of the copolymers as a result of recrystallization at high temperatures.

Another unusual effect in the high-frequency range that has not attracted much attention is the temperature dependence of the band frequency. The example shown in Figure 3 is the IR spectrum of the quenched 7723 sample in the region of 3500–1500 cm^{-1}. The intense absorption bands at 3012 and 2977 cm^{-1} were assigned to the asymmetric and symmetrical stretching of CH$_2$ of the TT conformation, respectively. The frequencies of these two bands are temperature-sensitive. The temperature dependencies of the peak fre-
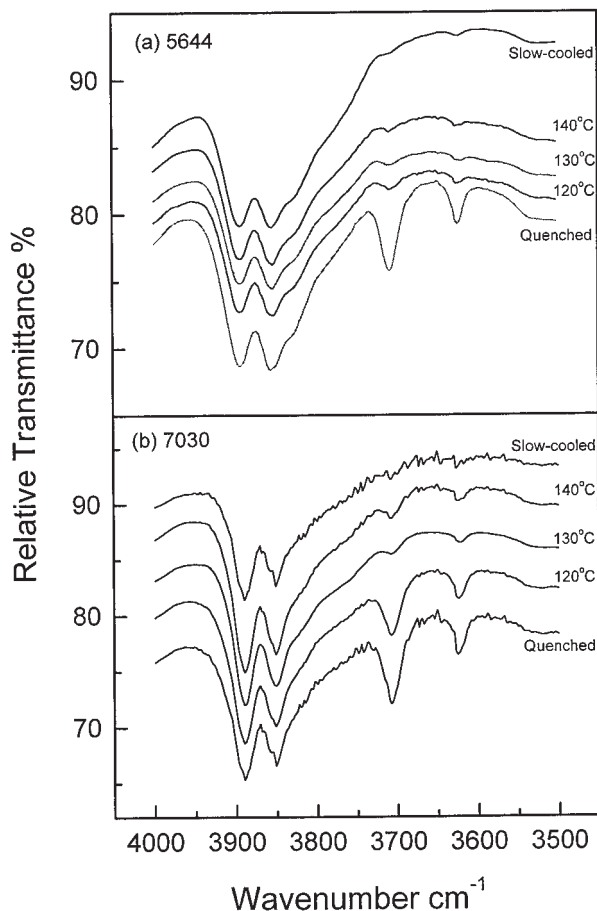
Figure 1 IR absorption spectra of quenched and annealed P(VDF-TrFE) copolymers (a) 5644 and (b) 7030 in the frequency range of 4000–3500 cm^{-1}. The transmittance of the samples has been shifted for clarity to show the change in the intensity.
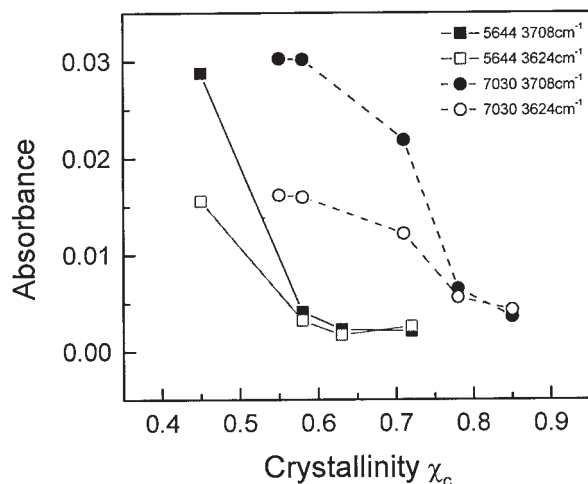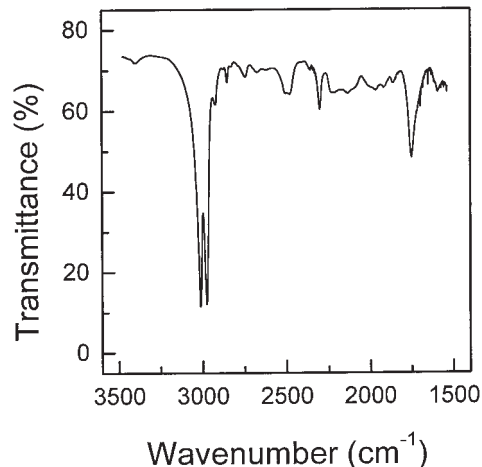

Figure 3 IR absorption spectrum of quenched P(VDF-TrFE) copolymer 7723 in the frequency range of 3500–1500 cm^{-1}.

quency in the heating and cooling process are evident in the expanded diagram shown in Figure 4. Both bands shift to a higher frequency with heating and are restored to the original frequency with cooling. The asymmetric mode (3012 cm^{-1}) manifests a more significant shift. Similar features in the frequency shift were also found for the 5644 and 7030 copolymers. The peak frequencies of the two bands of the 5644, 7030, and 7723 samples, plotted against the temperature, are given in Figures 5–7, respectively. Copolymer 5644 showed a modest shift in frequency with respect to the temperature change, as shown in Figure 5. For the 7030 and 7723 samples, as shown in Figures 6 and 7, there was a critical temperature, above which with heating and below which with cooling the peak fre-
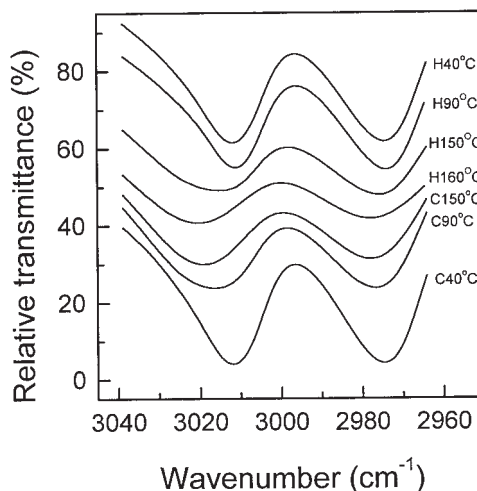

Figure 2 Dependence of the absorbance of the bands at 3708 and 3624 cm^{-1} for P(VDF-TrFE) copolymers 5644 and 7030 on χ_c.

Figure 4 IR absorption spectra of P(VDF-TrFE) copolymer 7723 obtained at various temperatures in a heating (H) and cooling (C) cycle. The transmittance has been shifted for clarity to show the peak frequency shift.
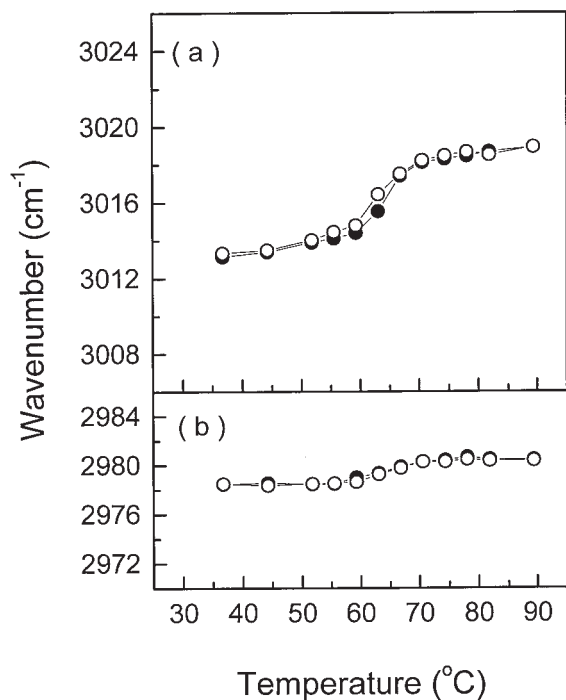
Figure 5 Dependence of the peak frequency on the temperature of the bands at (a) 3012 and (b) 2977 cm^{-1} of P(VDF-TrFE) copolymer 5644. The solid and open circles are the data obtained in heating and cooling, respectively.

Figure 7 Dependence of the peak frequency on the temperature of the bands at (a) 3012 and (b) 2977 cm^{-1} of P(VDF-TrFE) copolymer 7723. The solid and open circles are the data obtained in heating and cooling, respectively.
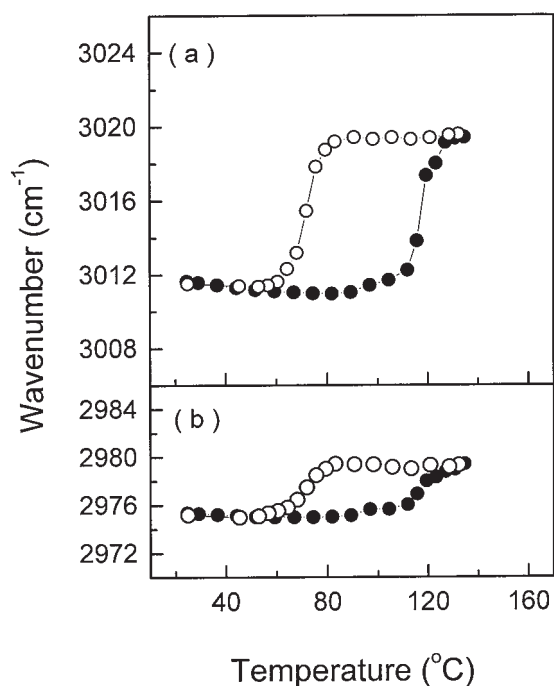

Figure 6 Dependence of the peak frequency on the temperature of the bands at (a) 3012 and (b) 2977 cm^{-1} of P(VDF-TrFE) copolymer 7030. The solid and open circles are the data obtained in heating and cooling, respectively.
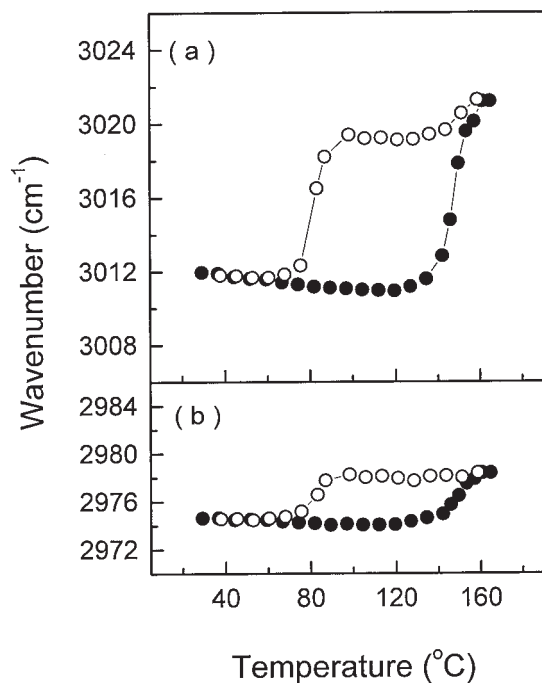
quencies changed abruptly. The onset was found to be close to their respective ferroelectric phase-transition temperatures with both heating and cooling. In other words, the shift in the frequency also exhibited thermal hysteresis. The thermal lag of copolymer 7030 was about 44°C, whereas for copolymer 7723, it was about 63°C. Another lower frequency band at 1428 cm^{-1}, which was assigned to the TT bending mode of CH$_2$, also exhibited a shift in frequency, but toward a lower frequency, as the temperature was raised above T_c. The band returned to a high frequency as the temperature was reduced to room temperature. The temperature dependence of the peak frequency is shown in Figure 8(a,b) the copolymers 5644 and 7030, respectively. A summary of the magnitude of the shift in the frequency of the copolymers is also given in Table II.

A study of the far-IR spectra of the copolymers indicates that the trans band at 116 cm^{-1} shifted to the gauche band at 108 cm^{-1} continuously as the temperature increased from room temperature to a temperature near the transition. This shift in frequency was probably due to an increase in the anharmonicity of the skeletal torsional mode of the copolymers' CF$_2$ groups.[14] However, in this study, no shift in frequency was found for the vibrations related to CF$_2$ in this frequency range. On the other hand, the absorption bands that exhibited a shift in frequency were attributed to the high-frequency vibrations of CH$_2$ groups. The drastic shift in frequency occurred above T_c with

both heating and cooling, unlike the skeletal torsional shift, which was accomplished below the transition temperature.

In polymers, the formation of hydrogen bonds accounts for the shift in the stretching vibration mode to a lower frequency and for the shift in the bending mode to a higher frequency. The shift in frequency that was observed for the CH_2 groups in the phase transition was attributed to the formation of hydrogen bonding in the copolymers. At low temperatures in the ferroelectric phase, for a copolymer of an orthorhombic structure ($a = 9.12$ Å, $b = 5.25$ Å, and $c = 2.55$ Å),[14] the trans–trans conformation helps the CF_2 and CH_2 dipoles to form the H$\cdots$F hydrogen bond. At temperatures above the Curie transition, the copolymer transforms into a monoclinic structure ($a = 9.75$ Å, $b = 5.63$ Å, and $c = 4.6$ Å), the TT chains in the crystallites change into the TG chains of TG^+TG^- or $TTTG^+TTTG^-$, interchain distances a and b both increase, and a change in the dipole orientation results because of the chain rotation. The result is the dissociation of the H$\cdots$F bonding. Therefore, the stretching vibration of the CH_2 dipole shifts to a higher frequency, whereas the bending vibration shifts to a

TABLE II
Magnitude of the Shift in the Band of the Copolymers at the Phase Transition

Band (cm^{-1})	Shift magnitude (cm^{-1})		
	5644	7030	7723
3012	5	7	7.5
2977	2.5	5	3
1428	2.5	5	—

lower frequency. Both vibrations are restored to the original frequency as the CF_2 and CH_2 dipoles again recouple in the ferroelectric phase.

CONCLUSIONS

In this study of the IR absorption of copolymers, we have found that the intensity of two adjacent absorption bands in the high-frequency range is related to χ_c. These absorption bands diminish in samples with higher crystallinity. This suggests that these two bands originate from the molecular vibrations in the amorphous phase of the copolymers.

An examination of the absorption band frequency of the CH_2 groups has identified three bands undergoing a shift in frequency as the temperature changes, and a drastic shift has been observed at the phase transition for all three samples. This trend for the shift in frequency suggests that it is the result of interactions between the CH_2 and CF_2 dipoles of the ferroelectric copolymer.
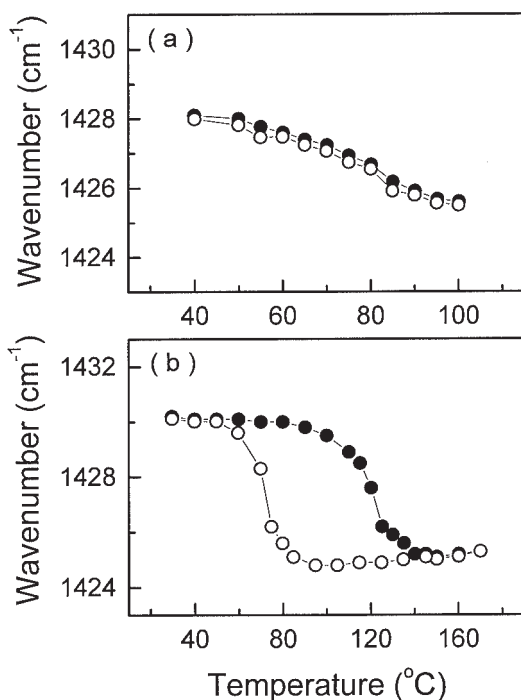

Figure 8 Dependence of the peak frequency on the temperature of the bands at 1428 cm^{-1} of P(VDF-TrFE) copolymers (a) 5644 and (b) 7030. The solid and open circles are the data obtained in heating and cooling, respectively.

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