An infra-red spectroscopic study of structural reorganization of a uniaxially drawn VDF/TrFE copolymer in an electric field

Kap Jin Kim*
Department of Textile Engineering, Kyung Hee University, 1 Seochun-ri, Kiheung-eup, Yongin-kun, Kyunggi-do 449-701, South Korea

and Shaw Ling Hsu
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA
(Received 24 May 1993; revised 3 December 1993)

A spectroscopic study has been conducted for the analysis of electric field induced microstructural changes in a uniaxially drawn 75/25 vinylidene fluoride/trifluoroethylene copolymer. Based on the relative intensities of the infra-red active bands measured, changes in the average orientation of the CH_2 dipoles after poling could be determined. Upon applying an electric field of 1.0 MV cm^{-1} to the sample, the mean-squared value of cos α for the CH_2 dipoles in the crystalline domain with respect to the film plane was found to change irreversibly from 0.46 to 0.34. Additionally, an increase in the degree of crystallinity of approximately 8% was observed after poling. Factor analysis was utilized in our spectroscopic analysis. Infra-red spectra for both the crystalline and amorphous regions have been constructed. These spectra are identical to those previously measured for isotropic samples. The conformational distribution for samples after poling contains a larger fraction of *trans* segments than unpoled samples.

(Keywords: VDF/TrFE copolymers; infra-red spectroscopy; poling)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) are of interest because of the piezoelectric and pyroelectric properties principally associated with the crystalline regions. PVDF has a number of well-defined chain conformations such as α, β, γ and δ in the crystalline phase[1]. The chain conformations and packing of the VDF/TrFE copolymers are also complex. The microstructure of these copolymers are strongly perturbed by processing conditions. The chain conformation distribution, i.e. all-*trans* planar zigzag or helical in nature, can also depend on the relative molar concentrations of VDF and TrFE[2-5]. The ferroelectric–paraelectric transition, or Curie transition, of the PVDF homopolymer has been speculated to be near or above the melting temperature. Curie temperatures are known to be below the melting temperatures for some copolymers, although the exact values have at times proven difficult to define[6-8]. The chain conformation of the copolymer is all-*trans* planar zigzag in the ferroelectric phase, while the paraelectric phase above the Curie transition is known to be helical, containing a number of *gauche* linkages[4,6,9-12]. Other structures prepared by varying the VDF/TrFE molar ratio and thermal history have also been found[3,13-16].

It is also known that chain conformation, packing and macroscopic electrical response can change significantly as a function of temperature and/or in the presence of an electric field[3,4,6,10,11,13,16-24]. An understanding of field-induced structural changes is of importance in order to establish the molecular mechanisms associated with macroscopic electrical properties. The exact relationship connecting the piezoelectric property to the structure of these homopolymers and copolymers has been the subject of many studies[1,8,24-27]. If the electrical property originates from the crystalline units, information on chain conformation, packing, degree of crystallinity, crystal orientation and crystal size is of importance. For these electrically active polymers, crystal orientation, orientation of individual dipoles along the chain and the relative chain orientation in the unit cell are equally important for determination of the overall electrical properties. Thus, chain orientation by mechanical orientation, crystallization by annealing and CF_2 dipole orientation by poling are necessary in order to achieve high piezoelectric and pyroelectric constants for both PVDF homopolymer and its copolymers[8,24,27-29]. However, there have been only a few papers[30-34] to study the changes in the degree of dipole orientation in the presence of an applied electric field. The coupling of CF_2 dipoles with the electric field, i.e. rotation of the dipoles towards the electric field, is also expected to produce structural

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* To whom correspondence should be addressed

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changes at different levels. For example, the sequence length of specific conformations, packing of segments in the crystalline unit cell, degree of crystallinity, individual dipole orientation and the overall segmental orientation are all influenced by the electric field[4,6,8,11,19,21,22,30–34]. All of these structural changes directly influence the overall electrical properties of VDF polymers. Büchtemann and coworkers[30–33] have calculated the mean dipole orientation in highly oriented PVDF films during the application of an electric field from the absorbances of the infra-red bands at 510 and 445 cm^{-1}. Day *et al.*[34] have found direct evidence supporting the six-site model of dipolar orientation in the ferroelectric phase of VDF/TrFE copolymer upon poling from wide-angle X-ray diffractometry. However, they did not find any changes in crystallinity, chain conformation or segmental chain orientation which the rotation of CF_2 dipoles may produce cooperatively in the presence of the field.

In previous papers[19,20], infra-red spectroscopy was employed to characterize the chain conformation of a 75/25 VDF/TrFE copolymer. We are particularly interested in the distribution of chain conformations and orientation of the CF_2 dipoles along the chain as a result of the poling procedure. Infra-red spectroscopy can accurately determine localized structures. When the vibrations are well characterized, the orientation of chemical groups can be determined. Specific vibrations have been used to characterize chain conformations for the PVDF homopolymer. Owing to the uncertainty in band assignment, extensive spectroscopic studies have not been carried out for the copolymers[16,20,35,36]. Even though the copolymers are known to have a large fraction of amorphous phase, there are few vibrations which can be definitely assigned to either the amorphous phase or crystalline phase. By using the technique of factor analysis in conjunction with the ratio method, it is now possible to isolate both the amorphous and crystalline spectra, and to obtain explicit evidence of transformation from the amorphous to the crystalline phase as a function of thermal annealing[20].

For poled samples, significant changes in the infra-red band intensities are usually observed[19,30–33,37,38]. However, some of these changes are only associated with the orientation of dipoles with respect to the incident infra-red radiation and cannot easily be related to the volume fractions of the different phases, i.e. all-*trans* and helical phases. In this paper, factor analysis is employed for a series of polarized spectra obtained from oriented copolymers, poled or unpoled, in order to separate the spectroscopic features of the amorphous and crystalline phases. Field-induced structural changes not easily observed for isotropic samples can be more conveniently analysed for the drawn samples. The overall dipolar orientation is analysed and an assessment is made of the changes in the degree of crystallinity and chain conformation distribution as a function of field strength.

EXPERIMENTAL

All analyses in this study were performed with samples of 75/25 mol% VDF/TrFE, obtained in pellet form from the Pennwalt Corporation. For infra-red studies, 10 μm thick films were cast from a 2 wt% acetone solution. After removing the glass substrate, the films were dried in vacuum for one week at room temperature. These cast films had a degree of crystallinity of approximately 30–35%, determined using factor analysis and thermal data described in an earlier publication[20]. Polarized absorption spectra from highly oriented samples proved to be extremely useful for an understanding of average dipolar orientation. However, uniaxially oriented commercial films were too thick for spectroscopic analysis. Therefore, uniaxially oriented films were obtained by drawing the cast films at room temperature to a draw ratio of 5. These drawn films of 3–4 μm thickness were annealed at fixed length at 135°C for 3 h and poled at room temperature. Poling was achieved by placing the sample film between aluminium foil electrodes with a commercial 6 μm PVDF spacer to prevent electrical breakdown. All poling experiments were carried out with six cycles of bipolar poling. The maximum field applied across the copolymer film was 1.0 MV cm^{-1}. Depoling to remove remnant polarization was carried out as before[19]. The drawn films of 3–4 μm thickness were also annealed at various temperatures (ca. 25–140°C) for 3 h to obtain samples with various crystallinities and chain orientations for factor analysis. Infra-red spectra were obtained with an IBM model IR38 Fourier transform infra-red spectrometer. In all cases, 200 scans of 2 cm^{-1} resolution were signal averaged and the data obtained transferred to other workstations for further analysis. Factor analysis programs to deconvolute amorphous and crystalline spectral features have been described elsewhere[20]. Differential scanning calorimetry (d.s.c.) measurements were performed on a Perkin–Elmer DSC4 using a heating rate of 10°Cmin^{-1}.

RESULTS AND DISCUSSION

The principal focus of this study was to characterize electric field induced microstructural changes in the VDF/TrFE copolymer by infra-red experiments. Unlike the PVDF homopolymer, the 75/25 VDF/TrFE copolymer always has the β conformation in the crystal at room temperature, regardless of mechanical drawing. Therefore, we can eliminate at least the effect of the field-induced α–β crystal phase transition, frequently observed in the PVDF homopolymer, from the changes in the infra-red spectrum in the presence of an electric field for the copolymer. Polarized infra-red spectra of unpoled, poled and depoled drawn films in the 1500–700 cm^{-1} region are shown in *Figures 1* and *2*.

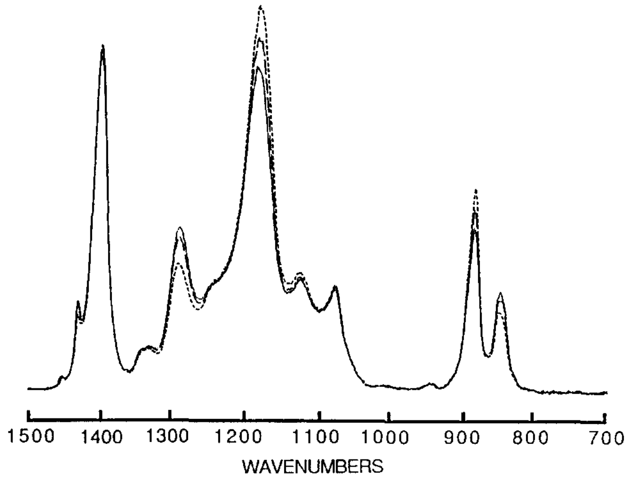

Figure 1 Perpendicularly polarized infra-red spectra of the drawn and annealed 75/25 VDF/TrFE copolymer film as a function of poling: (——) before poling; (----) after poling; (– – –) after depoling

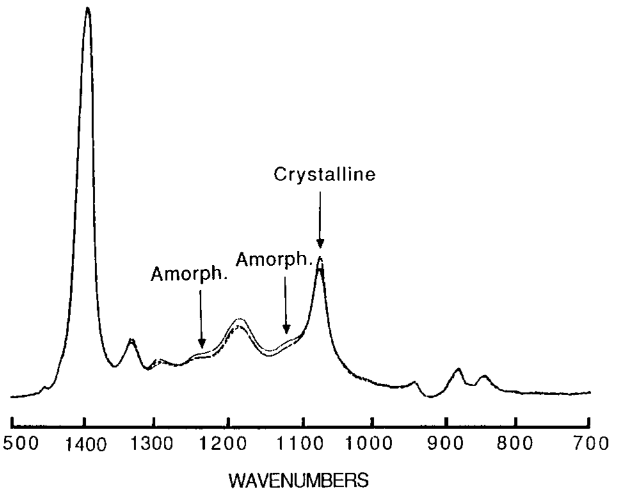

Figure 2 Parallel-polarized infra-red spectra of the drawn and annealed 75/25 VDF/TrFE copolymer film as a function of poling: (——) before poling; (- - - -) after poling; (— — —) after depoling

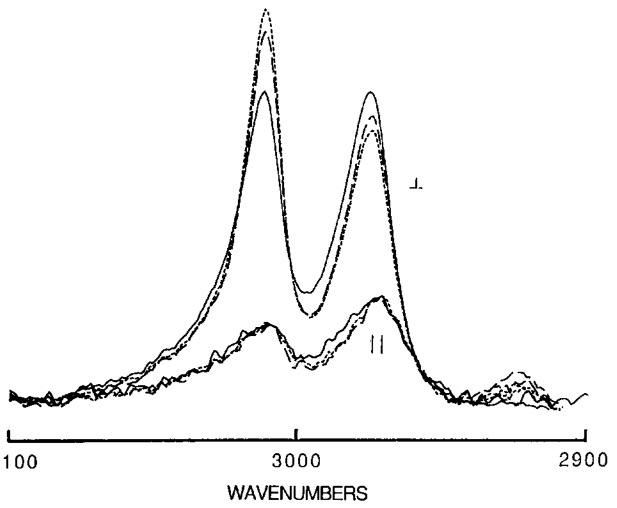

Figure 3 Polarized infra-red spectra of the drawn and annealed 75/25 VDF/TrFE copolymer film as a function of poling in the CH_2 stretching region: (——) before poling; (- - - -) after poling; (— — —) after depoling

Because of the large dipoles present in the copolymer, the electric field is expected to reorient chemical units along the chain, if not entire chain segments. The realignment of CF_2 dipoles with respect to the applied electric field can also induce changes in crystallinity, average chain orientation function, rotational isomer (*trans* and *gauche*) content and packing density.

In our experiments the applied electric field was parallel to the incident infra-red radiation. Therefore, variations in infra-red absorption because of changes in crystallinity, segmental chain orientation, conformation, etc. must be separated from the simple CF_2 dipole orientation in order to discern various aspects of field-induced microstructural changes. For example, the CH_2 stretching region before poling and after poling at room temperature and after depoling is shown in *Figure 3*. It is readily apparent that both the CH_2 asymmetric and symmetric stretching vibrations change signfiicantly in the perpendicularly polarized spectra in the presence of the electric field.

Because the chains are highly oriented, the spectroscopic changes are mainly associated with the rotation of crystallite chains with respect to the electric field and are less related to structural transformation. Similarly, the changes in intensity at 1290 ($t_m(m>4)$, $\nu_s(CF_2)+\nu_s(CC)+\delta_s(CCC)$), 884 ($t_1$, $\rho(CH_2)+\nu_{as}(CF_2)+\rho(CF_2)$) and 848 ($t_m(m>3)$, $\nu_s(CF_2)+\nu_s(CC)$) cm^{-1} with perpendicular polarization as a function of poling are attributed to the alignment of CF_2 dipoles in the electric field direction rather than to an increase or decrease in the *trans* sequences as interpreted earlier[19]. Poling increases the intensity at 884 cm^{-1} but decreases the intensities of both 1290 and 848 cm^{-1} (see *Figure 6*). This inconsistency in the change in *trans* isomer content shows that many of the observed changes in perpendicularly polarized bands can be attributed to changes in the local dipolar orientation distribution rather than structural reorganization or transformation.

In order to remove dipolar orientation effects, we tried to remove the remnant polarization by using the depoling technique. However, as shown in *Figure 3*, depoling does not return band intensities to their initial values before poling, which means that, after depoling, the sample still has preferential dipolar orientation even though its macroscopic net polarization is zero. Therefore, with depoling it is impossible to separate completely the dipolar orientation changes from conformation and crystallinity changes in the infra-red spectra. Band intensity changes, especially in the perpendicularly polarized spectrum, reflect the overall dipole orientation for the poled or depoled sample, and are not solely associated with changes in chain conformation or packing.

Instead, a conformational and structural analysis separate from the effect of transition dipole orientation can be accomplished with the use of parallel-polarized data, which are much more likely to indicate irreversible changes in chain conformation distribution or crystalline phase. As an example, the reduced intensity of the amorphous bands and the increased intensity of the 1076 cm^{-1} crystalline band are much more reliable indicators for showing an increase in the degree of crystallinity after poling (see *Figure 2*)[20].

Quantitative analysis of polarized infra-red data

Based on previous studies, there are several bands characteristic of crystalline and amorphous conformations[20]. Transition dipole directions associated with some of these vibrations are known well. It is thus possible to calculate explicitly the changing orientation distribution of the crystalline units and the increase in the degree of crystallinity as a function of poling field strength, time and temperature.

It is convenient to refer to sets of mutually orthogonal coordinate systems, one defined with respect to the macroscopic axes and the other attached to the plane containing the chain backbone. This arrangement is shown in *Figure 4*. If the drawn sample film is assumed to be uniaxially oriented, then the spatial averages of directional cosines can be expressed as

$$\langle\cos^2\theta\rangle+\langle\cos^2\beta\rangle+\langle\cos^2\gamma\rangle=1 \qquad (1)$$

$$\langle\cos^2\phi\rangle+\langle\cos^2\alpha\rangle+\langle\cos^2\beta\rangle=1 \qquad (2)$$

Since $\langle\cos^2\beta\rangle$ and $\langle\cos^2\gamma\rangle$ are identical for a uniaxially oriented sample, we have

$$\langle\cos^2\phi\rangle+\langle\cos^2\alpha\rangle=(1+\langle\cos^2\theta\rangle)/2 \qquad (3)$$

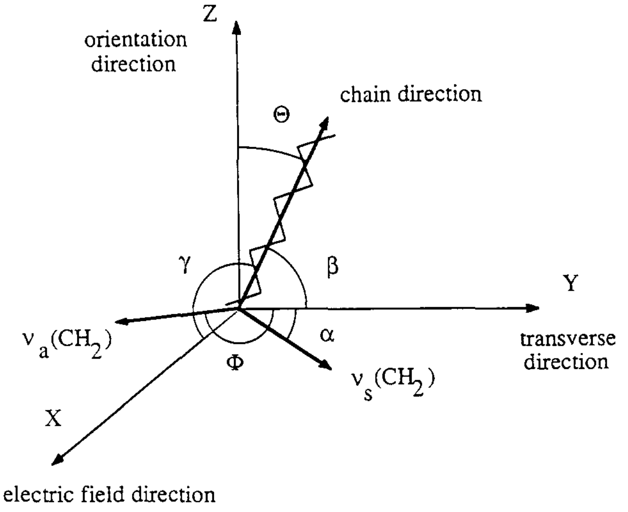

Figure 4 Angles α and θ specifying chain orientation and dipolar orientation with respect to the macroscopic laboratory Cartesian coordinates X, Y and Z

The absorption coefficient k of an individual transition is proportional to the number of oscillators present, the magnitude of the transition moment and the relative orientation of the transition moment with respect to the polarization of the incident radiation. The CH_2 symmetric ($2987\ cm^{-1}$) and asymmetric ($3012\ cm^{-1}$) stretching vibrations are employed for dipolar orientation analysis since their transition moments can be assumed to be perpendicular to the chain axis.

For an isotropic sample, we can define a parameter C_1 as follows

$$C_1 = k_a/k_s = P_a^2/P_s^2 = I_a/I_s \tag{4}$$

where the subscripts a and s refer to the asymmetric and symmetric CH_2 stretching vibrations, respectively, P is the transition moment magnitude and I is the observed absorption intensity. The value of C_1 can be determined experimentally from the corresponding absorbance ratio of the isotropic sample.

When perpendicularly polarized radiation is used for the uniaxially drawn sample, the transverse direction of the sample film coincides with the incident electric field direction. Since we must consider the possibility that crystalline (cr) and amorphous (am) regions have different distributions of orientation, k_s and k_a for a uniaxially drawn sample can be written as follows

$$\begin{aligned} k_s &= N_{am}P_s^2\langle\cos^2\alpha\rangle_{am} + N_{cr}P_s^2\langle\cos^2\alpha\rangle_{cr} \\ &= NP_s^2[(1-X_{cr})\langle\cos^2\alpha\rangle_{am} + X_{cr}\langle\cos^2\alpha\rangle_{cr}] \end{aligned} \tag{5}$$

$$k_a = NP_a^2[(1-X_{cr})\langle\cos^2\phi\rangle_{am} + X_{cr}\langle\cos^2\phi\rangle_{cr}] \tag{6}$$

where N_{am} and N_{cr} are the number of CH_2 groups per unit volume in the armophous and crystalline regions, respectively, N is the total number of CH_2 groups per unit volume in the sample, i.e. $N = N_{am} + N_{cr}$, and X_{cr} is the degree of crystallinity. Since the CH_2 groups in amorphous regions are assumed to be randomly distributed around the stretch direction Z, we have from equation (3)

$$\langle\cos^2\alpha\rangle_{am} = \langle\cos^2\phi\rangle_{am} = (1 + \langle\cos^2\theta\rangle_{am})/4 \tag{7}$$

The value of k_s is then defined as

$$k_s = NP_s^2[(1-X_{cr})(1+\langle\cos^2\theta\rangle_{am})/4 + X_{cr}\langle\cos^2\alpha\rangle_{cr}] \tag{8}$$

An expression similar to equation (8) can also be written for the asymmetric stretching vibration.

Using perpendicularly polarized spectra for the uniaxially drawn samples, the I_a/I_s intensity ratio C_2 can be defined as

$$C_2 = C_1\frac{(1-X_{cr})(1+\langle\cos^2\theta\rangle_{am})/4 + X_{cr}\langle\cos^2\phi\rangle_{cr}}{(1-X_{cr})(1+\langle\cos^2\theta\rangle_{am})/4 + X_{cr}\langle\cos^2\alpha\rangle_{cr}} \tag{9}$$

In this expression the segmental orientation associated with the chain must be considered. The average value of the segmental orientation function[39], $f_{av}(1-X_{cr})f_{am} + X_{cr}f_{cr}$, can be obtained from the dichroic ratio of a vibration which does not exhibit strong dipolar orientation, such as the parallel-polarized $1402\ cm^{-1}$ band that shows both amorphous and crystalline characteristics. Now

$$f_{av} \approx (D-1)/(D+2) \tag{10}$$

where D is the dichroic ratio of the $1402\ cm^{-1}$ band. Therefore

$$\begin{aligned} \langle\cos^2\theta\rangle_{am} &= (1+2f_{am})/3 \\ &= [2(f_{av}-X_{cr})/(1-X_{cr})+1]/3 \end{aligned} \tag{11}$$

Since $\langle\cos^2\theta\rangle_{am} = (1+2f_{am})/3$, the average value of dipolar orientation in the crystalline regions with respect to the film plane can then be obtained from equations (3), (9) and (11), giving

$$\begin{aligned} \langle\cos^2\alpha\rangle_{cr} = {} & \frac{C_1}{2(C_1+C_2)X_{cr}} \\ & \times [(1-X_{cr})(1-C_2/C_1)(1+\langle\cos^2\theta\rangle_{am})/2 \\ & + (1+\langle\cos^2\theta\rangle_{cr})X_{cr}] \end{aligned} \tag{12}$$

Using equation (12), from the spectroscopic data it is possible to obtain the average orientation of functional groups caused by poling if the crystallinity of each sample is known. In our calculations, the crystallinity after poling and depoling was obtained from the equation for the average segmental orientation function with the initial f_{cr} value in the range 0.85–1.0, assuming that f_{cr} and f_{am} remain constant upon poling and depoling. The degree of crystallinity and the dipolar orientation angle were not highly dependent on the value of the crystal orientation.

Analysis of microstructural change as a function of poling

In addition to the increase in the orientational order, another aspect of poling is the increase in the degree of crystallinity. From d.s.c. the drawn sample exhibits a Curie transition at 115.4°C with an enthalpy of $6.40\ cal\ g^{-1}$ (1 cal = 4.2 J). However, after poling these values increased to 117.7°C and $7.08\ cal\ g^{-1}$, respectively. These observed changes are directly related to the increase in packing density and structural stability of the ferroelectric phase through structural reorganization upon poling. They also suggest that the total amount of ferroelectric crystal phase is increased as a function of poling. From the factor analysis technique developed earlier[20], we determined the degree of crystallinity to be 0.5 before poling, 0.56 with poling and 0.55 with depoling.

We assumed the segmental orientation, both crystalline and amorphous, to remain constant when the poling field was applied perpendicular to the stretch/draw direction. We did observe, however, an increase in the average overall orientation function f_{av} calculated from the dichroic ratio of the parallel-polarized $1402\ cm^{-1}$ band

Table 1 Changes in various parameters of a uniaxially drawn and annealed 75/25 VDF/TrFE copolymer film during poling

	f_{av}	X_{cr}	$\langle\cos^2\alpha\rangle_{cr}$	f_α
Before poling	0.727	0.500		
$f_{cr}=1$			0.473	0.210
$f_{cr}=0.95$			0.465	0.197
$f_{cr}=0.90$			0.457	0.185
$f_{cr}=0.85$			0.448	0.172
After poling	0.756			
$f_{cr}=1$		0.552	0.350	0.026
$f_{cr}=0.95$		0.564	0.345	0.018
$f_{cr}=0.90$		0.583	0.342	0.013
$f_{cr}=0.85$		0.616	0.341	0.012
After depoling	0.749			
$f_{cr}=1$		0.540	0.362	0.044
$f_{cr}=0.95$		0.549	0.357	0.035
$f_{cr}=0.90$		0.563	0.352	0.028
$f_{cr}=0.85$		0.588	0.351	0.027

$C_1=0.9377$. C_1 value experimentally measured from the isotropic sample was used to calculate $\langle\cos^2\alpha\rangle_{cr}$ from equation (12)

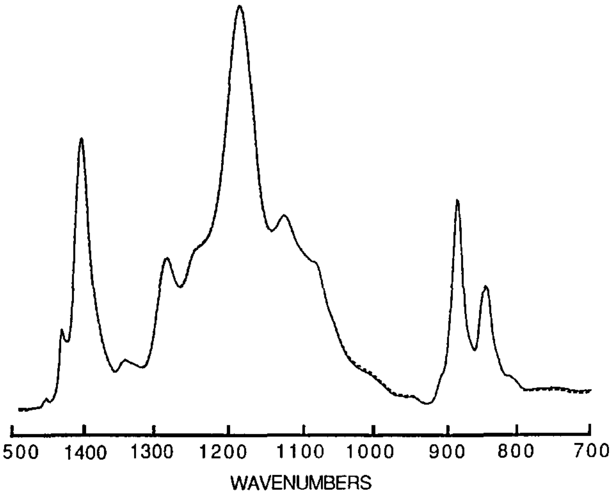

Figure 5 Infra-red spectra of cast 75/25 VDF/TrFE copolymer film before and after poling at room temperature: (——) before poling; (- - - -) after poling

after poling. This implies that there is an increase in the degree of crystallinity. The degree of crystallinity we calculated in the case of $f_{cr}=0.9$ was 0.58 after poling, which agrees quite well with the factor analysis result and the increase in the enthalpy of the ferroelectric–paraelectric transition obtained from d.s.c. results.

Therefore, substituting the X_{cr} determined from the equation for the average segmental orientation function and the C_2 values measured from the perpendicularly polarized spectra after poling or depoling into equation (12) yields the $\langle\cos^2\alpha\rangle_{cr}$ value in the crystalline region. The expression for $\langle\cos^2\alpha\rangle_{cr}$ can be incorporated into the commonly used orientation expression for f_α

$$f_\alpha=(3\langle\cos^2\alpha\rangle_{cr}-1)/2 \qquad (13)$$

The results of these calculations are listed in *Table 1*. It is clear that the poling process has increased the degree of crystallinity and has changed the $\langle\cos^2\alpha\rangle_{cr}$ value from 0.46 to 0.34.

Annealing also has an effect on microstructural changes which occur under an applied field. In our earlier study, we clearly showed that copolymer microstructures can be perfected by thermal annealing[20]. The amount of microstructural change in terms of increasing crystallinity is strongly dependent on the annealing temperature and time. The overall increase in crystallinity with temperature shows a sigmoidal plot with the greatest change occurring at the Curie transition[20].

It is interesting to note that the microstructures of the isotropic cast copolymer films do not seem to be altered by the applied electric field. For the cast film, there is virtually no difference, as shown in *Figure 5*, between the spectra obtained before and after poling with a field strength as high as 1.0 MV cm^{-1}. In contrast, for the isotropic film annealed at 135°C for 3 h, significant differences were observed as a consequence of the poling process. These differences are shown in *Figure 6*. Although the exact mechanisms are not well understood, the data for the cast *versus* a more ordered annealed sample clearly demonstrate that the electrical response of the 75/25 VDF/TrFE copolymer is dependent upon the degree of crystallinity. This result is consistent with an earlier study showing that the dipole-switching characteristics of VDF/TrFE copolymers are greatly improved by thermal annealing[23].

From factor analysis in conjunction with the ratio method, separate spectra for the crystalline and amorphous phases can be obtained for the oriented film. These pure component spectra are shown in *Figures 7* and *8*. The

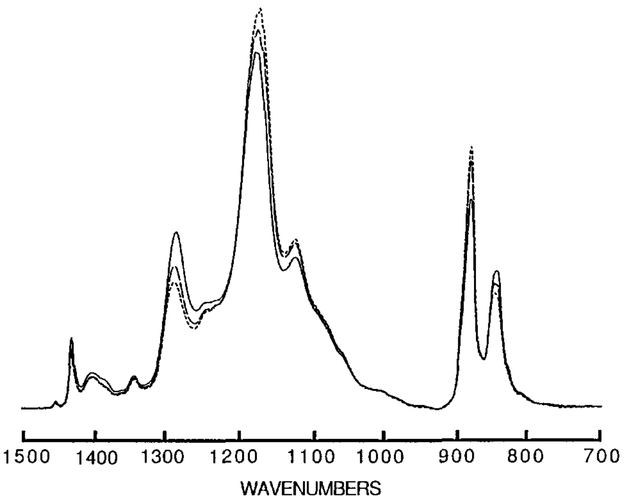

Figure 6 Infra-red spectra of the annealed 75/25 VDF/TrFE copolymer film before and after poling at room temperature: (——) before poling; (- - - -) after poling; (– – –) after depoling

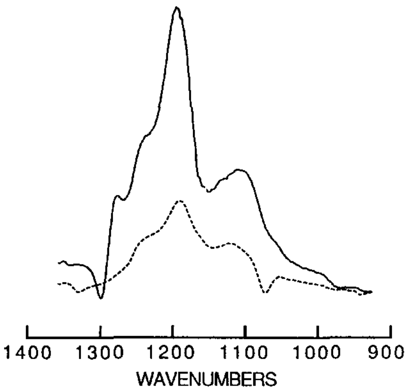

Figure 7 Polarized infra-red spectra of the pure amorphous phase of uniaxially drawn and annealed VDF/TrFE copolymer film: (——) perpendicular; (– – –) parallel

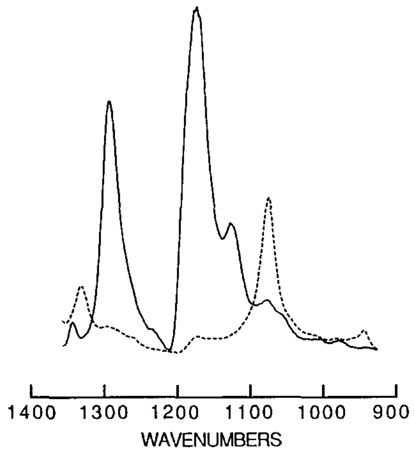

Figure 8 Polarized infra-red spectra of the pure crystalline phase of uniaxially drawn and annealed VDF/TrFE copolymer film: (——) perpendicular; (- - - -) parallel

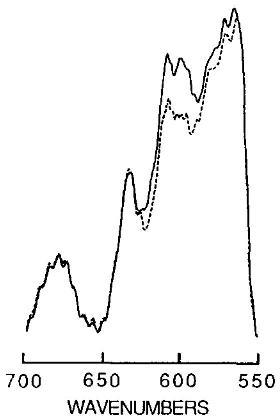

Figure 9 Parallel-polarized infra-red spectra of the drawn and annealed 75/25 VDF/TrFE copolymer film as a function of poling in the 700–550 cm^{-1} region: (——) before poling; (- - - -) after poling

reduced structure factor A_0, which is independent of orientation, can be calculated from $(A_{\parallel}+2A_{\perp})/3$ for both the crystalline and amorphous phases under the assumption that the pole diagram of the uniaxially drawn film used in this experiment is rotationally symmetrical around the Z (stretching) direction, in which case $A_X=A_Y$, i.e. there is no degree of biaxiality such that $A_X \neq A_Y$. The calculated A_0 values for both the crystalline and amorphous phases are the same as obtained for the cast film[20]. This suggests that the crystalline and amorphous regions of the drawn copolymer at room temperature have the same chain conformation distribution as the cast film. It should be emphasized again that the relative amounts of crystalline and amorphous features are indicative of the degree of sample crystallinity. From our factor analysis results, the bands at 1120 and 1243 cm^{-1} were assigned to the amorphous phase. These bands and other amorphous phase bands exhibit considerable polarization characteristics.

In an earlier study[19], we deduced that poling reduced the number of long *trans* sequences in the 75/25 VDF/TrFE copolymer from the decrease in intensity at 1290 cm^{-1} after poling. Our present study suggests that this is not the case. A comparison between the spectra obtained for the ferroelectric and paraelectric phases suggests that the introduction of structural disorder at high temperature below melting is characterized by the presence of an extremely weak 612 cm^{-1} band ($\delta(CF_2)+\delta(CCC)$, crystalline *trans–gauche* conformation) in the 700–550 cm^{-1} region. This band disappears completely in the melt. We found that this peak was observed only in parallel-polarized infra-red spectra when the VDF/TrFE copolymer was measured in the ferroelectric state at room temperature. After poling there was a definite intensity reduction at 612 cm^{-1}, as shown in *Figure 9*. As discussed earlier, significant intensity changes in the 1290, 884 and 848 cm^{-1} bands are dominated by polarization or dipolar orientation changes and, in fact, cannot be used reliably to characterize the irreversible segmental orientation increase or changes in the degree of crystallinity and *trans* isomer content. The analysis presented in the current study shows that when dipolar orientation is taken into consideration there is an increase in the number of *trans* sequences at the expense of the decreasing *gauche* content during poling. Such an increase in the number of *trans* sequences was also found in the PVDF homopolymer under repeated poling cycles[33]. This conclusion is also supported by the observed increase in intensity for the 1076 cm^{-1} band after poling, which is insensitive to dipolar orientation but sensitive to structural regularity as our annealing studies have shown[20,23]. Previous X-ray diffraction has found no significant structural changes upon poling a 75/25 copolymer[6]. Diffraction is sensitive to long range order, while infra-red spectroscopy is only sensitive to localized structural changes. Thus the small increase in *trans* isomer content may be too small to be observed by X-ray diffraction.

CONCLUSIONS

The difficulty in analysing microstructures of annealed or poled VDF/TrFE copolymers is directly related to the large transition moments of the CF_2 dipoles and their relative orientations. It is often tempting to correlate the observed infra-red band intensities with the volume fractions of the microstructural units present. The relative band intensities measured depend on the transition moment magnitude, the transition moment orientation with respect to the incident polarized radiation and the number of dipoles in the beam. In our earlier studies we overcame this difficulty with some success when structural analysis was only carried out for samples without remnant polarization. In the current study, we were able to deconvolute the contributions from dipolar and segmental orientations by considering parallel-polarized and perpendicularly polarized spectra separately. This type of analysis is best suited for highly oriented samples obtained by drawing or extrusion. Upon poling, the degree of crystallinity increased, and this was accomplished by a small increase in the number of long sequences of *trans* conformers. The $\langle\cos^2\alpha\rangle_{cr}$ value for the CH_2 dipoles with respect to the film plane was changed from 0.46 to 0.34 after poling.

ACKNOWLEDGEMENTS

The financial support from the National Science Foundation Polymers Program (grant DMR 89-89105) is deeply appreciated. We are also grateful to the Pennwalt Corporation for supplying the samples used in this study. Partial support (postdoctoral grant 87-117) from the Korean Science and Engineering Foundation is greatly appreciated (K.J.K.).

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