Spectroscopic study of the electric field induced microstructural changes in poly(vinylidene fluoride)

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Infra-red spectra (4000–400 cm^{-1}) have been obtained for poly(vinylidene fluoride) films in the presence of high electric fields up to 2.6 MV cm^{-1} in strength. Both band intensity and polarization studies have revealed that dipolar re-orientation can be correlated with the macroscopic electric effect. The frequency shift as a function of field strength for the β phase bands can be attributed to the non-equivalent reorientation behaviour of the bands in the unit cell. However, the change in the frequency of the α bands shifted irreversibly with the applied electric field. These changes cannot be attributed to reorientation behaviour alone.

(Keywords: piezoelectricity; poly(vinylidene fluoride); infra-red spectroscopy; phase transformation)

INTRODUCTION

A considerable amount of effort has been directed at the structural characterization of poly(vinylidene fluoride) (PVF_2). These studies are important since PVF_2's extraordinary electrical properties are a direct consequence of its crystalline structures[1-5]. At least four PVF_2 crystalline structures (α, β, γ and δ) are known to exist with one or more still presently under scrutiny[1]. Two mechanisms, trapped charges and orientation of dipoles, have been offered to explain the relationship of these structures to the piezoelectric or pyroelectric effects associated with PVF_2. It is increasingly clear that orientation of dipole moments is by far the predominant mechanism, although, in some special cases, the trapped charge can play an important role[2-5].

From structural considerations it is highly likely that the β crystalline phase, with a planar zigzag chain conformation, can give rise to piezoelectric activity. However, the degree of participation of other crystalline phases is unclear. For instance, in the α phase the two chains in the unit cell are packed in an antiparallel fashion with no possibility of a net dipole. In order to account for the piezoelectric behaviour of PVF_2 containing this crystalline structure, phase transformation to the δ phase has been inferred from the changing X-ray diffraction intensities[6,7]. This transformation in a strong electric field (>1.2 MV cm^{-1}) involves intramolecular rotation about all G and G' bonds of every second chain in the unit cell causing the overall conformation to be altered from $TGTG'$ to $TG'TG$ with the overall chain direction and unit cell spacing preserved. At higher applied field (>5 MV cm^{-1}) it has been postulated that this δ phase can be further changed to the β structure. However, due to experimental difficulties, little direct evidence has been provided to substantiate these structural changes when the field is present. In the infra-red spectra of PVF_2, there are absorptions which are characteristic of local conformations or environments which can be used to monitor microstructural changes induced by external excitation. Recently, a unique spectroscopic study by Naegele and Yoon demonstrated that the β phase can be directly correlated to the piezoelectric effect[8]. The results from that experiment were not subject to large fluctuations arising from a number of processes to which the samples have been exposed between measurements, such as deposition and removal of electrodes and repositioning of samples.

In our laboratory we want to use Fourier transform infra-red spectroscopy in conjunction with the newly developed time resolved technique to directly measure the field induced molecular motions of various phases of PVF_2 with greater sensitivity, wider spectral response, and higher time resolution than previous experiments[8-10]. The results of the first part of this study, i.e. showing the feasibility of such a spectroscopic experiment, are reported here. In the subsequent paper we will present data relating to the dynamics of the structural changes.

EXPERIMENTAL

Biaxially oriented PVF_2 films used in our studies are capacitor-grade obtained from the Kureha Chemical Corporation. These films are available in 12 or 25 μm thickness. In order to eliminate any possibility of an air gap between the sample and electrodes, gold-palladium electrodes 1.2 cm in diameter were deposited directly on both sides of the film. The experimental geometry is shown in *Figure 1*. In this geometry the deposited electrodes should be sufficiently thick to conduct electricity, yet thin enough to transmit infrared radiation. When polarized radiation is used, this experiment can

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provide direct information regarding *in situ* PVF_2 structural changes caused by the electric field. Furthermore, by carefully coupling the application of the electric field to the *FT*i.r. interferometer movements, we can capture the dynamics of structural change by the use of time resolved spectroscopy with high temporal resolution and wide frequency response[11,12]. We used a high voltage power supply capable of providing a stepwise field across the film up to a maximum value of 3.3×10^6 volts cm^{-1}. Other circuits have also been designed to provide a programmable high voltage source.

Infra-red spectra were obtained with a Nicolet Fourier transform infra-red spectrometer. Since we are mainly interested in the vibrational bands in the 1000–400 cm^{-1} (a region of relatively low transmittance) we usually use at least 200 scans of 4 cm^{-1} resolution to obtain acceptable signal to noise ratio for analysis. A typical infrared spectrum of PVF_2 film is shown in *Figure 2*.

The field can induce microstructural changes in PVF_2 which are represented by changes in the relative intensity and frequencies of some vibrational bands. Examples are shown in *Figure 3*. To our knowledge, this is the first time that band frequency changes have been reported. Some of these frequency changes can be substantial; representative bands are listed in *Table 1*.

RESULTS AND DISCUSSION

The principal advantage of vibrational spectroscopy when compared to other physical techniques is its ability

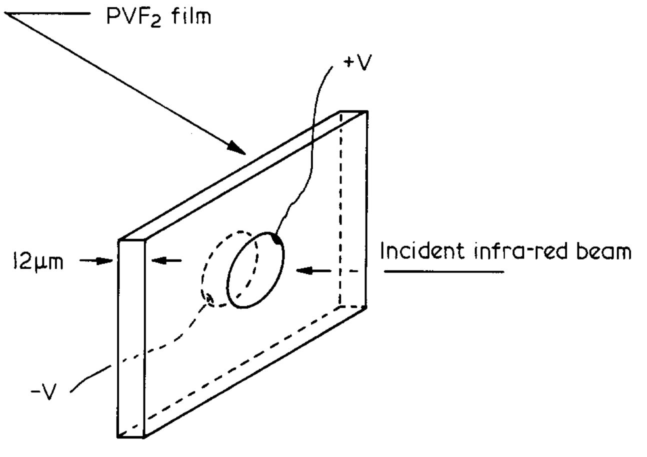

Figure 1 Experimental geometry

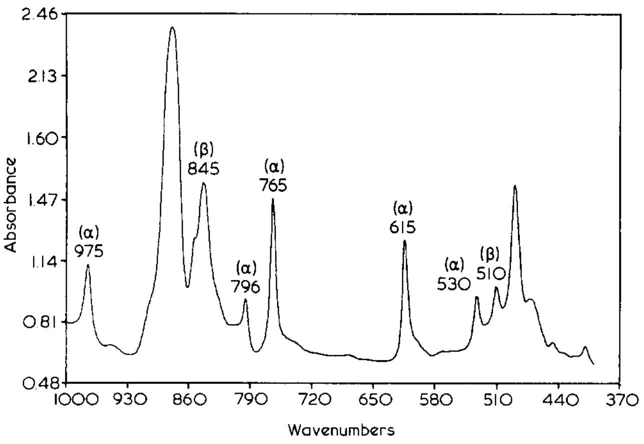

Figure 2 Infra-red spectrum of PVF_2 film; 4 cm^{-1} resolution, 600 scans

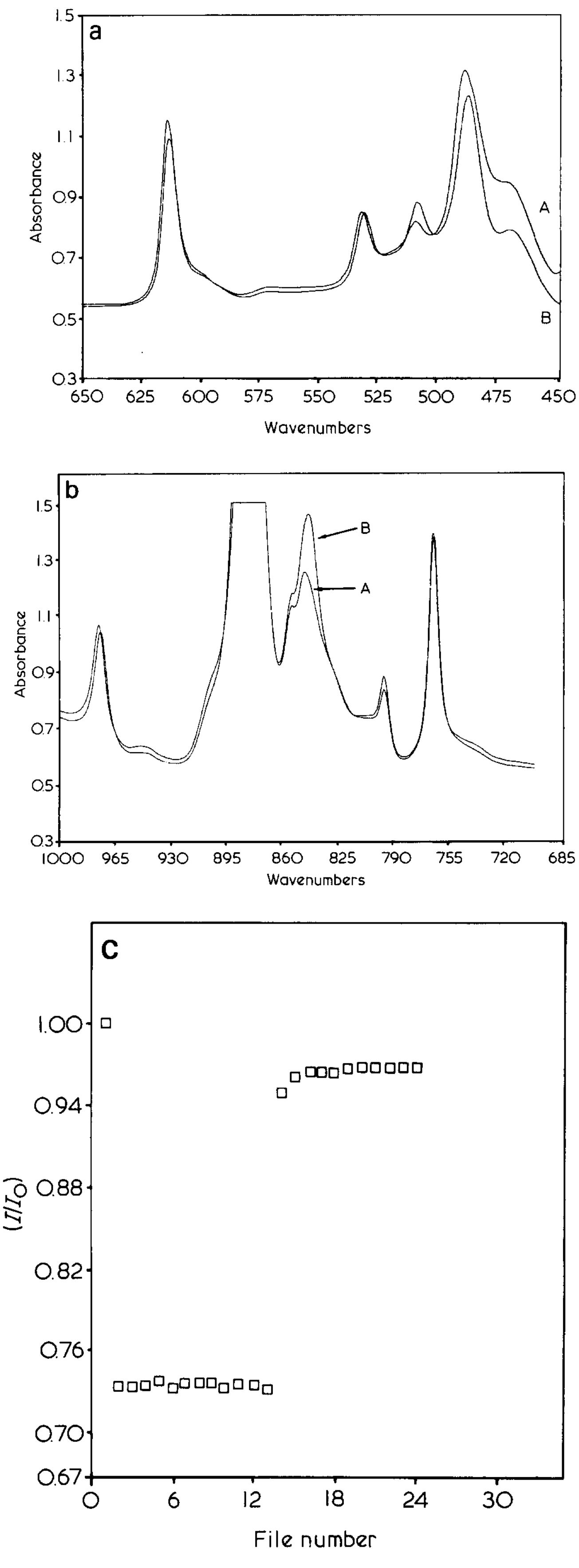

Figure 3 Electric field induced intensity and frequency changes of the vibrational bands in PVF_2. (B) 1000–685 cm^{-1} region, (A) 650–450 cm^{-1} region, (C) The intensity ratio (I/I_0) of the 510 cm^{-1} band when the electric field is applied. First file corresponds to the intensity measured with no field; files 2–12 correspond to the intensity measured with E=2.1 MV cm^{-1}; files 13–21 correspond to spectra obtained when the electric field is reduced to zero

Table 1 Electric field (E = 2.0 MV cm^{-1}) induced frequency changes for selected α and β bands in PVF$_2$

	before poling	during poling	after poling
		α form	
976 cm^{-1} [t(CH$_2$)]	975.9	974.8	975.8
796 cm^{-1} [γ(CH$_2$)]	796.4	796.3	796.3
765 cm^{-1} [δ(CF$_2$) + δ(CCC)]	765.1	764.3	764.0
614 cm^{-1} [δ(CF$_2$) + δ'(CCC)]	614.7	614.0	614.3
530 cm^{-1} [δ(CF$_2$)]	532.3	533.5	532.7
		β form	
845 cm^{-1} [γ(CH$_2$) + ν_a(CF$_2$)]	843.5	846.0	844.4
510 cm^{-1} [δ(CF$_2$)]	510.1	510.9	510.4

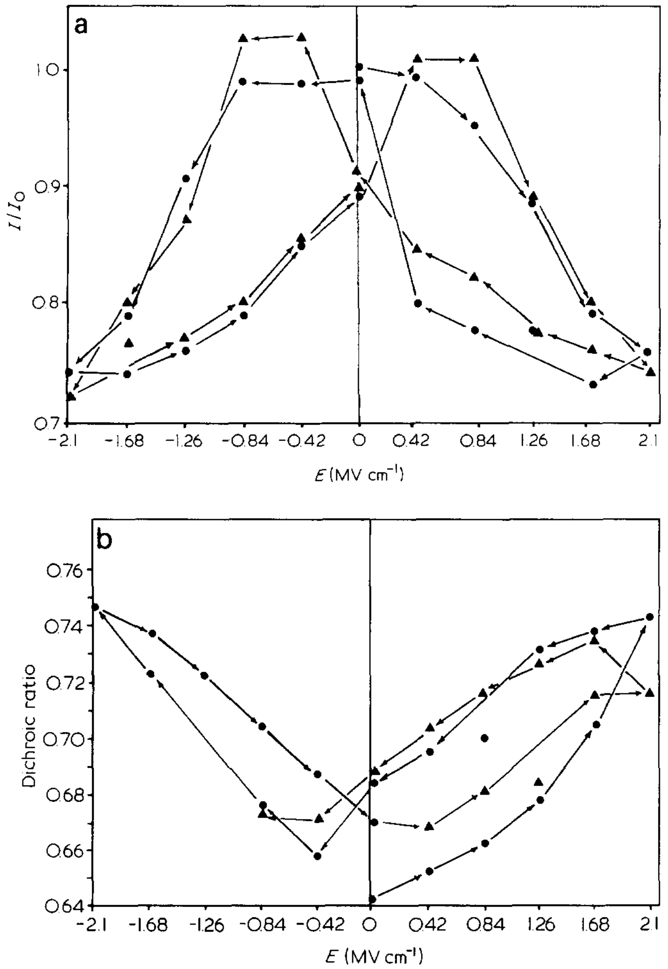

Figure 4 Hysteresis loop represented by the intensity changes of the β phase bands (●) the first cycle, (▲) the second cycle. (a) Intensity change of the 510 cm^{-1} band, (b) dichroic ratio measured for the 845 cm^{-1} band

to measure localized conformation, packing, and relative orientation changes. The vibrational spectra of various PVF$_2$ microstructures are relatively well understood[13,14]. The vibrational bands at 510 cm^{-1} (CF$_2$ bending) and 845 cm^{-1} (CH$_2$ rocking) are assignable to the β phase with others at 530 cm^{-1} (CF$_2$ bending), 615 cm^{-1} and 765 cm^{-1} (CF$_2$ bending and skeletal bending), 795 cm^{-1} (CH$_2$ rocking), and 976 cm^{-1} (CH$_2$ twisting) assignable to the α phase[13,14]. When an external electric field is applied, the frequency and polarization changes of these bands are indicative of the structural changes associated with the piezoelectric effect.

The participation of the β-phase PVF$_2$ in the piezoelectric effect is well established. As mentioned earlier, two major hypotheses have been advanced to explain the origin of this phenomenon. One attributes them to trapped charges, while the other supposes β-PVF$_2$ to be ferroelectric. The latter hypothesis is currently more generally favoured[3-5]. In the β-phase PVF$_2$, the transition moments of both the 510 and 845 cm^{-1} bands are perpendicular to the chain direction. Therefore, these two absorptions would exhibit the greatest sensitivity to the changes in chain orientation. With the experimental geometry shown in *Figure 1*, initially the CF$_2$ dipoles are oriented mainly in the film plane. Therefore, we would expect the intensity of both of these bands to decrease when an external field is applied. Due to the limited infra-red intensity available, without the use of specialized spectroscopic techniques, individual spectra of acceptable signal to noise ratio can only be collected at a time resolution of approximately 5.5 min. The intensity of the 510 cm^{-1} band measured as a function of time when a field is applied is shown in *Figure 3*. It is readily apparent that the orientation of the dipoles in the β-phase follow the input field within the time resolution of the present experiment.

The degree of the orientation achievable for the β chain is strongly dependent on the field strength. Extremely high orientation can be achieved when the field applied reaches 2.1 MV cm^{-1}. When the field is lowered back to zero the infra-red absorption, or the dipole orientation, reaches a value which is lower than the original one. This is due to the remnant polarization. A finite reverse field is required to bring the intensity back to the initial value, indicating complete depolarization. Further increases in the reversal field will result again in a decrease of intensity. A second reversal of the electric field will result in a complete reversal of orientation, thus completing a hysteresis loop. This hysteresis behaviour is shown in *Figure 4*. On this curve the effective polarizability is multivalued. Our experiments, similar to those carried out by Naegele and Yoon[8], show a clear relationship between the field applied and the orientation behaviour of the β PVF$_2$ chains, thus directly verifying the β phase as being ferroelectric in nature.

The advantages of using a Fourier transform infra-red instrument are its multiplex advantage, i.e. measuring all spectral elements at the same time, high throughput and inherent spectral accuracy. Therefore, we can obtain data of wider spectral range than dispersive instruments, making readily available the relative intensity and frequency changes. When an electric field is applied across the PVF$_2$ film, in addition to the relative intensity changes, we found that positions of vibrational bands can change as well. It is interesting to observe that the positions of some vibrational bands can change by as much as 2–3 cm^{-1} when the field is applied. This frequency change is equal to or larger than that which occurs when samples are mechanically stressed[15,16]. We found, as with chain orientation, the frequency change also follows a hysteresis loop, shown in *Figure 5*. Although the physical origin of the frequency change is unclear, several hypotheses can be considered. They are: (1) intermolecular packing change, (2) chain conformation change, and (3) the relative orientation changes of the optically active components arising from the intermolecular non-bonded crystalline field. Since the intrachain energy is so much higher than the non-bonded

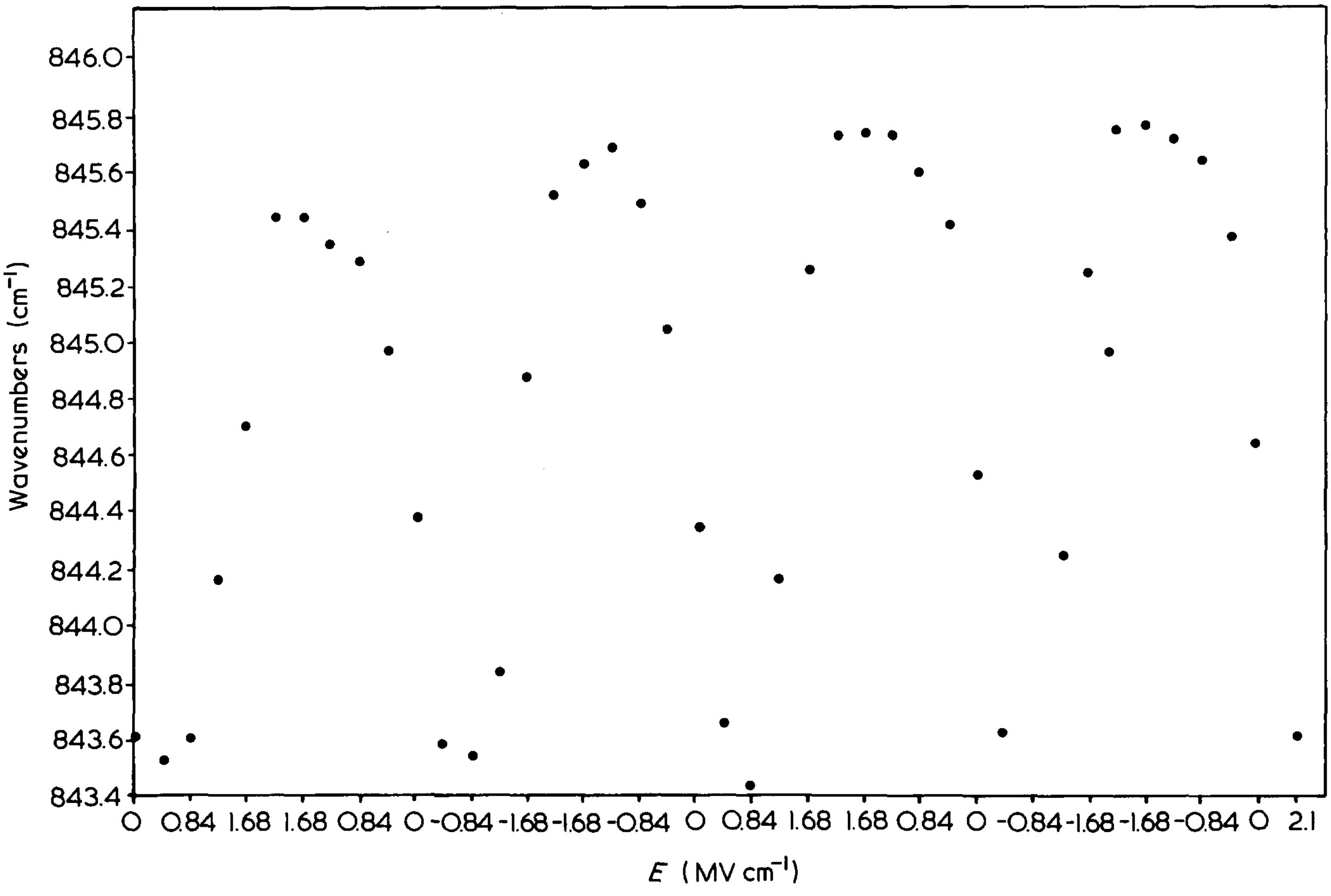

Figure 5 Frequency change of the 845 cm^{-1} as a function of electric field strength

interchain potential, the effects on the vibrational bands arising from changes of the first two possibilities may be considered to be separable.

Tadokoro and his coworkers have examined the vibrational spectra of various PVF_2 phases[13]. In their theoretical analysis a non-bonded van der Waals potential was incorporated into the intrachain potential developed earlier. Therefore, vibrational bands sensitive to the magnitude and specificity of intermolecular interactions can be established. Furthermore, in another crystalline form (γ phase), although the unit cell is quite similar to the β phase, its chain conformation contains features intermediate between the planar zigzag of the β phase and the $TGTG'$ conformation of the α phase forming a T_3GT_3G' chain conformation. Its vibrational spectra, when compared to the ones obtained from the α or β phases, should identify conformation sensitive bands.

It has been established that the especially strong piezoelectricity of the β form is attributable to a peculiar molecular chain structure: The molecular chain conformation is not exactly planar zigzag, but due to steric interactions, the chain units, CH_2–CF_2, deflect alternately from a perfect planar zigzag plane by an angle of about 7° [17–19]. In the presence of an electric field, spontaneous alignments of the CF_2 units cause a strain along the chain axis in order to diminish the FF steric interaction. This change in conformation can cause a change in the skeletal vibrations as observed. The characteristic times for the recovery may be much longer than the viscoelastic recovery, which would also explain the hysteresis behaviour of the frequency change. This type of behaviour has been seen in the phase transformation of other semi-crystalline polymers[20].

Because there are two chains present in the β phase unit cell, band splitting arising from non-bonded intermolecular crystalline fields should be present. Kobayashi *et al.* observed a shoulder on the high frequency side of the 845 cm^{-1} band[13]. This doublet was clearly resolved by Bachmann and his coworkers[21]. Although we could not resolve this splitting clearly at room temperature, two components, one at 842 cm^{-1} and the other at 850 cm^{-1}, were clearly observed at liquid nitrogen temperature. The relative intensity of the two components did change. Although we cannot rule out conformational changes as a function of electric field strength strength in the presence of the field, we feel the frequency change for the β phase is mainly attributable to the different reorientation behaviour of the bands in the unit cell.

In the previous experiment[8], a dispersive instrument was used to measure the band intensity when the field is applied. Since the instrument had limited spectral range per unit of measurement time, intensity measurement was generally carried out by moving the spectrometer to the peak position (no field) then turning on the field. Since we have demonstrated that peak position can shift significantly with applied field strength, the dynamics of structural transformation derived from the earlier data[8] may not be quantitatively correct. Details of our experiment will be published in a following publication[22].

Unlike the β phase, the participation of the α phase in the piezoelectric or pyroelectric behaviour has never been clearly established. As mentioned previously, since the chains are packed with dipoles in the opposite direction in the unit cell, α phase should exhibit no net polarization. One explanation for its piezoelectric behaviour is a structural transformation to the δ phase. Several mechanisms are available indicating the possibility that α to δ phase can occur with field strength above 1.5 MV/cm[23,24]. The δ phase can further transform to the β phase when applied field exceeds 5 MV cm^{-1}.

The assignment of several bands at 976 cm^{-1} (CH_2 twisting), 795 cm^{-1} (CH_2 rocking), 765 cm^{-1} and 615 cm^{-1} (CF_2 bending and skeletal bending), and 530 cm^{-1} (CF_2 bending) to the *TGTG'* chain conformation in the α phase is established from earlier normal vibrational analysis[13,14]. We found when an electric field is applied to the PVF_2 film, as long as the maximum field strength is below 1.5 MV cm^{-1}, the polarization changes of the above bands do not follow a uniform behaviour as a function of field strength. However, once the maximum field exceeds 2.0 MV cm^{-1}, a regular polarization of the α bands *versus* field strength relationship can be established. This is shown in *Figure 6*. In all cases, before the field reaches a critical value, the intensity changed in a very different manner during the first cycle when compared to all subsequent cycles. The intensity change which occurred in the first cycle is shown in *Figure 7*. The orientation behaviour of the α phase suggests that there is indeed an irreversible structural change at a critical field strength of approximately 1.5 MV cm^{-1} at room temperature. After this structural transformation has taken place, the α phase PVF_2 is ferroelectric in nature and can then interact strongly with the external field. Similar to the results we obtained for the β phase, the frequency of the vibrational bands in the δ phase can also vary with field strength.

The frequency change in this case cannot be explained easily. For the β phase when the sample is completely depoled, thus removing any residual polarization, the frequencies of the β bands are essentially unchanged when compared with the initial state. In contrast, the α bands at high field not only exhibit a hysteresis cycle, but also show an irreversible change as a function of the number of cycles applied. Even though dipolar reorientation in the δ phase is one explanation, these spectroscopic changes may be indicative of the permanent structural transformation from the α to the δ phase.

Two mechanisms have been proposed to interpret the structural transformation from the α to the δ phase[23,24]. The first one involves a physical rotation of 180° about the c-axis leaving the chain conformation essentially unchanged. This process should leave all the vibrational bands essentially unchanged except for intermolecular effects. The second possible mechanism involves small intramolecular rotations about all G and G' bonds of every second chain in the unit cell. When the electric field is applied across the film, various α bands changed positions permanently and in an irregular fashion, as shown in *Table 1*. Our observations would not be consistent with the first possibility.

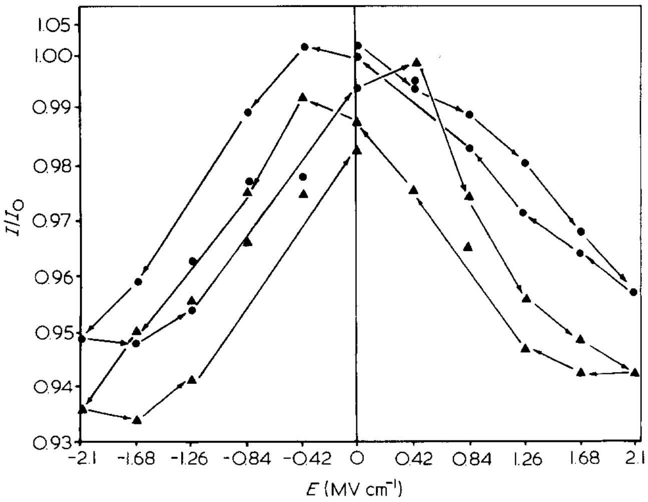

Figure 6 Intensity of the 765 cm^{-1} α band as a function of the applied electric field; (●) second cycle, (▲) third cycle

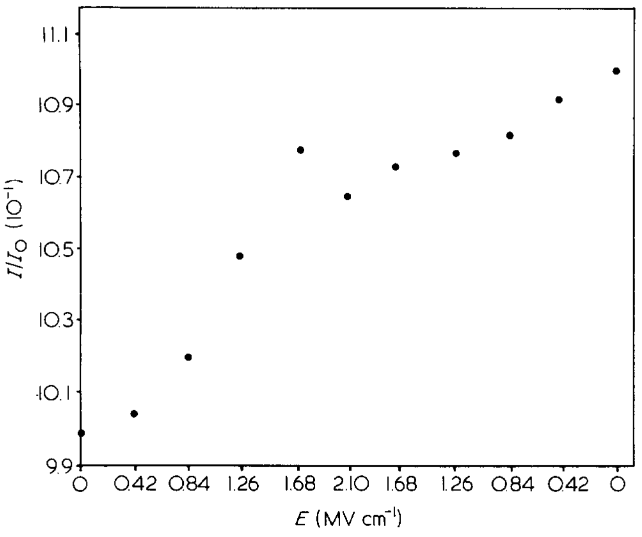

Figure 7 Intensity change of the 765 cm^{-1} α band when the electric field is first applied

In summary, we have demonstrated that the origin of the piezoelectric effect in PVF_2 may be inferred from the polarization and frequency changes of the vibrational bands. It has been definitely established that the β phase participates directly in the ferroelectric behaviour. The α phase must undergo an irreversible structural change at high field strength before participating in the piezoelectric effect. Our spectroscopic changes associated with structural change also suggest chain conformation can change for both the α and β forms when the field is applied. The dynamics of these structural changes are presented in another publication.

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