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# Analysis of the Crystalline Phase Transformation of Poly(vinylidene fluoride)

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ABSTRACT: Infrared spectra have been obtained at various temperatures for poly(vinylidene fluoride) in the presence of electric fields up to 5.2 MV/cm in strength. Quantitative analysis of the spectroscopic data suggests that significant $\alpha \rightarrow \beta$ or $\alpha \rightarrow \gamma$ phase transformations can occur at electric fields as low as 1.2 MV/cm. The kinetics of these transformations have been studied. Our data show the degree of phase transformation also depends strongly on the temperature.

## Introduction

Poly(vinylidene fluoride) ($PVF_2$) is the most widely known polymer that exhibits piezoelectric or pyroelectric properties. At least four crystalline phases, $\alpha$, $\beta$, $\gamma$, and $\delta$, have been found for $PVF_2$, with one or two more under study.[1] It is now generally accepted that the existence or absence of a net polarization determines whether the crystalline phase is electrically active.[2,3] The $\beta$ phase, with a nearly planar zigzag conformation, has the highest piezoelectric constant.[1,4] Although the $\alpha$ phase, with a TGTG′ conformation, is electrically inactive, the $\delta$ phase, which is nearly identical with the $\alpha$ phase except that every other chain is effectively rotated, is electrically active.[3] The obvious connection between the crystalline structure and the resultant electrical property has led to many attempts to prepare different phases by various methods that include altering the thermal history,[5] mechanical deformation,[6] $\gamma$ radiation,[7] crystallization under high pressure,[8] crystallization under electric field,[9] and the application of a strong electric field.[10–12] The last method is fundamentally interesting because exact mechanisms have not yet been determined and is practically important because it is effective in the enhancement of $PVF_2$'s electrical properties.

The electrical-field-induced microstructural changes in $PVF_2$ may depend on field strength, temperature, and/or time. The transition that has received the most attention is probably the $\alpha \rightarrow \delta$ or $\alpha \rightarrow \beta$ transition. The initial report on the possibility of an $\alpha \rightarrow \beta$ transition is by Luongo for a field of 0.3 MV/cm.[13] The field strength is considerably weaker than those determined in later studies.[10–12] Davis and co-workers eventually concluded that the $\alpha \rightarrow \delta$ transition can occur at low field strengths ($\sim$1.5 MV/cm) while the subsequent transition to the $\beta$ phase can only occur at high field strengths of 4–5 MV/cm.[11] Several theoretical studies followed these experimental studies to consider the relative stability of each crystalline phase, their coupling to the applied field, the dynamics of structural change, and the critical field values.[14,15] However, the predictions of those theories have not been tested because of the difficulties involved in obtaining direct experimental evidence to characterize microstructural changes in the presence of an electric field.

In our laboratory we are using vibrational spectroscopy as the primary characterization technique. In the infrared spectra of $PVF_2$ there are absorptions that are characteristic of local conformations or environments that can be used to monitor microstructural changes induced by external electrical excitation.[16–23]. Using an experimental geometry suggested earlier,[18] we have used Fourier transform infrared spectroscopy to directly measure the electric field molecular motions of various phases of $PVF_2$ with high sensitivity, wide spectral response, and high time resolution.[19,20] In the present study we have carried out additional experiments as a function of field strength, temperature, and time and obtained a quantitative assessment of the relative fractions of different crystalline phases present. We found that the $\alpha \rightarrow \delta$ or $\alpha \rightarrow \beta$ phase transformation can take place at a much faster rate and lower field strength than previously reported theoretical or experimental values.[10–12,14,15]

Although a number of theoretical studies are under way,[19,20] details of the exact molecular mechanism associated with phase transformations in $PVF_2$ are still ill-understood; incorporation of experimental results such as the ones reported here is both interesting and relevant.

## Experimental Section

The 6-, 12-, and 24-$\mu$m-thick $PVF_2$ films used in our studies were obtained from Kureha Chemical Corp. Details of the experimental geometry used can be found in previous publications.[21,22] Gold–palladium electrodes 1.2 cm in diameter were deposited on both sides of the film. The deposited electrodes are sufficiently thick to conduct electricity, yet thin enough to transmit infrared radiation. We used a high-voltage power supply capable of providing 3000 V or the equivalent to a maximum field strength of 5 MV/cm for the 6-$\mu$m-thick samples. The entire sample was placed in a heating cell so that experiments could be carried out at temperatures between ambient and 150 °C in an inert atmosphere.

Infrared spectra were obtained with a Nicolet Fourier transform infrared spectrometer. Since we are mainly interested in the

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vibrational bands in the 1000–400-cm$^{-1}$ region (part of which has relatively low transmittance) we usually signal-average 200 scans of 4-cm$^{-1}$ resolution to obtain acceptable signal-to-noise ratios for analysis.

Typical infrared spectra obtained for PVF$_2$ film have been published previously. The complexity of spectroscopic analysis has been reduced considerably by previous theoretical and experimental vibrational analyses.[16,17,24] Spectral bands characteristic of each chain conformation in the infrared spectrum can be used for quantitative analysis. We found no noticeable differences among the three samples used. The electric field was applied at a specified temperature and length of time. However, all spectroscopic measurements were then taken at room temperature.

## Results and Discussion

The principal advantage of vibrational spectroscopy over other physical characterization techniques is its ability to selectively measure localized conformation, packing, and relative orientation changes. At least four PVF$_2$ crystalline structures ($\alpha$, $\beta$, $\gamma$, and $\delta$) are known to exist. The vibrational spectra of the two principal phases have been analyzed extensively.[16,17] The bands we used previously for structural characterization are as follows: $\alpha$ phase, 530 cm$^{-1}$ (CF$_2$ bending), 615 and 765 cm$^{-1}$ (CF$_2$ bending and skeletal bending), 796 cm$^{-1}$ (CH$_2$ rocking), and 976 cm$^{-1}$ (CH$_2$ twisting); $\beta$ phase, 510 cm$^{-1}$ (CF$_2$ bending) and 845 cm$^{-1}$ (CH$_2$ rocking). Furthermore, except for small frequency shifts, the infrared spectrum of the $\delta$ phase is essentially indistinguishable from the $\alpha$ phase.[11,21]

The $\gamma$ phase has been postulated to have a $T_3GT_3G'$ chain conformation intermediate between the $\alpha$ and the $\beta$ phase.[1,24] Its characteristic frequencies have been found at 1235, 1176, and 812 cm$^{-1}$. But it should be emphasized that vibrational spectra often show localized vibrations and are only characteristic of short-range order. Given the fact that the $\gamma$ conformation is intermediate between the $\alpha$ and $\beta$ forms, unless used in conjunction with other physical techniques such as X-ray diffraction, it is usually difficult to separate features arising from trans sequences in the $\beta$ or $\gamma$ forms. Although the 510-cm$^{-1}$ CF$_2$-bending or the 845-cm$^{-1}$ CH$_2$-rocking bands have been widely used to characterize the $\beta$ structure, in light of recent evidence[25] it would be more accurate to assign these bands to be characteristic of trans sequences in either the $\beta$ or $\gamma$ forms; instead only the 470-cm$^{-1}$ band is assigned to be characteristic of the $\beta$ form. In the present study, we will use the 510-cm$^{-1}$ band to represent the amount of trans conformation present associated with either the $\beta$ or the $\gamma$ form.

When an external electric field is applied, the frequency and intensity variations of characteristic bands are indicative of the changes both in orientation and in packing of chain segments in each phase that results from interaction with the external electric field.[18,21,22] Therefore, interpretation of the spectroscopic changes provides information regarding the degree and participation of each phase in the overall electric response of PVF$_2$. In our experiments, the field-induced change in the relative intensity of several vibrational bands, particularly at high temperature, may be due to two events: (1) a change in the dipole orientation relative to the field, and (2) a net transformation from one crystalline phase to another. The separation of the two often is difficult to accomplish and therefore seldom attempted.

At low temperatures, when most crystalline phase transitions are not expected to occur to any significant degree, the change in the band intensity as a function of field strength and polarity can be understood in terms of the dipolar orientation of the chain segments. For the PVF$_2$ films studied, initially the CF$_2$ dipoles are oriented mainly in the film plane. Therefore, when the external field is applied in our experimental geometry, most of the bands with transition moments perpendicular to the chain decrease in intensity. When the field is lowered back to zero the infrared absorption, or the dipole orientation, reaches a value that is lower than the original one. A finite reverse field is required to bring the intensity back to the initial value. Further increases in the reversal field strength will result again in a decrease in intensity. A second reversal of the electric field will result in a complete reversal of orientation. Since the intensity measured is multivalued as a function of the electric field, a hysteresis loop is formed. Of course, the electrical response is related to chain mobility; therefore, a strong temperature dependence is expected and observed. Such an example for the 510-cm$^{-1}$ band is shown in Figure 1. The absolute field value corresponding to the intensity maxima is the coercive field. These spectroscopic measurements are exactly analogous to the displacement field measured macroscopically.[26] Such curves generated from spectroscopic measurements for all the bands of interest have been shown in previous publications.[21,22]

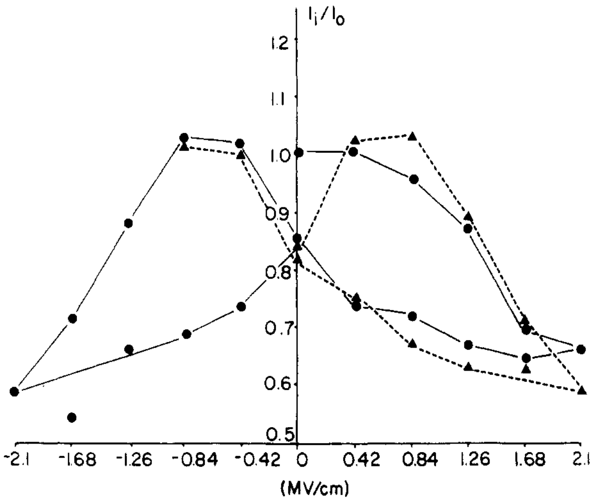

Figure 1. Hysteresis loop represented by intensity change of the 510-cm$^{-1}$ band, (measurement temperature 20 °C): (●) first cycle; (▲) second cycle.

The knowledge of such curves for all samples at various temperatures will then enable us to remove the orientation or polarization effects to obtain spectra of PVF$_2$ in essentially the depoled state in order to calculate the relative fractions of each crystalline phase present. In all our experiments, the samples are exposed to the electric field at specified temperatures and then depoled at room temperature. Such a sequence of infrared spectra is shown in Figure 2. It is clear then that much of the apparent band intensity change is actually due to changes in the orientation rather than real volume fraction changes of the various crystalline phases. Only by removing the effects of orientation can we quantitatively analyze the crystalline phases present. A representative sequence of spectroscopic change for depoled samples as a function of time in the presence of an electric field is shown in Figure 3. In these spectra it is evident that there is really a decrease in the helical conformation transforming to trans sequences. The apparently poor correlation between the morphology and macroscopic piezoelectric constants measured previously may be due to the fact that the orientation and volume fraction contributions in the infrared absorption intensity measurements were not separated.[27]

The absolute intensity of the 510-cm$^{-1}$ band increased tremendously as a function of time at high fields and

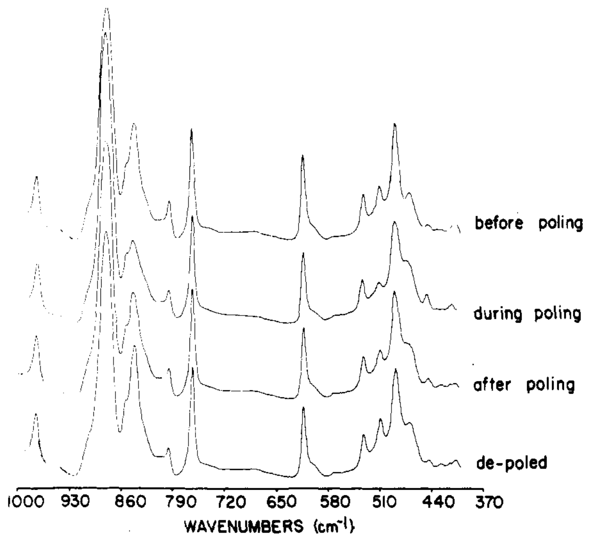

**Figure 2.** Infrared spectra obtained for $PVF_2$ film exposed to an electric field, (temperature of application 40 °C, maximum field ~3 MV/cm).

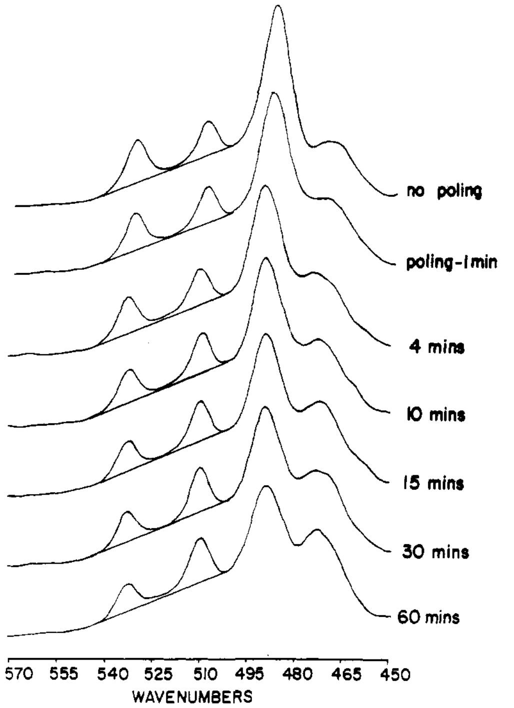

**Figure 3.** Infrared spectra obtained in the depoled state for $PVF_2$ film exposed to an electric field of 3.0 MV/cm as a function of time, (temperature 40 °C).

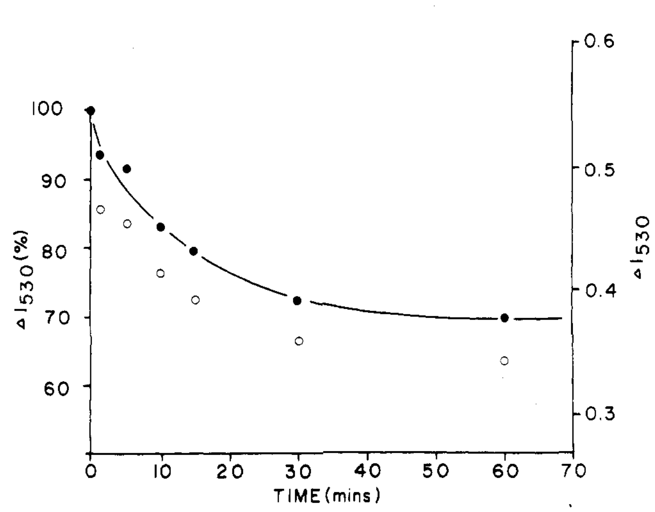

**Figure 4.** Change in the intensity of the 530-cm$^{-1}$ band relative to the sum of the 510- and 530-cm$^{-1}$ bands as a function of poling time. The field of 3 MV/cm was applied at 40 °C: (●) $(I_{510} + I_{530})/I_{530}$; (○) $I_{510} + I_{530}$.

particularly at high temperatures.[22] At the same time a decrease in the intensity of the $\alpha$ bands occurred. This change in band intensity for $PVF_2$ in the electric field is due to changing dipole orientation and the changing relative volume fractions of the various phases present. As mentioned previously, measuring the infrared intensity of bands before and after the application of the electric field is not sufficient to calculate quantitatively the amount of each phase present as has been done in previous studies. It is most important, as we have illustrated in Figures 2 and 3, to measure the relative intensity of infrared bands for $PVF_2$ samples in the depoled state in order to eliminate the contribution from remnant polarization or chain segmental orientation.

When $PVF_2$ film is exposed to a field of 2.1 MV/cm at 65 °C, the decrease in the $\alpha$ phase 530-cm$^{-1}$ $CF_2$ bending mode as a function of time in the depoled state is shown in Figure 4. In that figure, the intensity change is presented in two different ways, by the absolute value of $I_{530}/(I_{530} + I_{510})$ or the percentage of change (100% being $t = 0$). Even though some uncertainties exist for the assignment of the 510-cm$^{-1}$ band, there is little question that the 530-cm$^{-1}$ band is assignable to the helical phase.[16,17] The symmetry coordinates associated with these two bands are quite localized with essentially similar absorption coefficients expected. This intensity ratio is then used to represent the approximate volume fractions of the $\alpha$ phase remaining. By writing the intensity change in such a manner, we are assuming the integrated intensity of all forms is a constant. Except for a 10% drop for the period 0 to 1 min, the sum of the two bands indeed remained unchanged. Even after careful examination of the spectra obtained, no evidence of vibrational transitions characteristic of other phases has been found. As can be seen from Figure 4, the "steady-state" volume fraction of the $\alpha$ phase is usually reached in 60 min. Therefore, we adopted this as the standard length of time for $PVF_2$ to be exposed to the electric field. This poling time agrees quite well with the poling time needed to obtain the "steady-state" pyroelectric coefficient.[28]

The decrease of the $\alpha$ fraction cannot be described by the exponential function $f(x) = ae^{-bt}$ as we would expect from previous studies.[27] The data we obtained can be best fit to a power function of $at^b$ where $a = 0.98$ and $b = -0.08$. This time dependence needs to be considered carefully. Although Murayama found the piezoelectric constant to increase with poling time in an exponential manner,[27] the observed increase in the piezoelectric coefficient represented by one or two values of a highly anisotropic tensor may actually be due to chain-segment rotation or increasing sample uniformity. The exact molecular mechanism of that process is quite different from a crystalline phase transformation.

When low field strengths and temperatures are used, previous investigations indicate the increase in polarization of poly(vinylidene fluoride) ($PVF_2$) films occurs in two stages.[28-31] First a rapid increase in polarization occurs in as short as 6 s, followed by a much slower one. Corresponding X-ray studies have suggested that the rapid increase in the macroscopic electrical property is associated with the nonpolar $\alpha$ to the polar $\delta$ phase transition.[29] In those experiments, a weak field of no more than 1 MV/cm at room temperature was generally employed. Two mechanisms for this phase transition have been proposed,

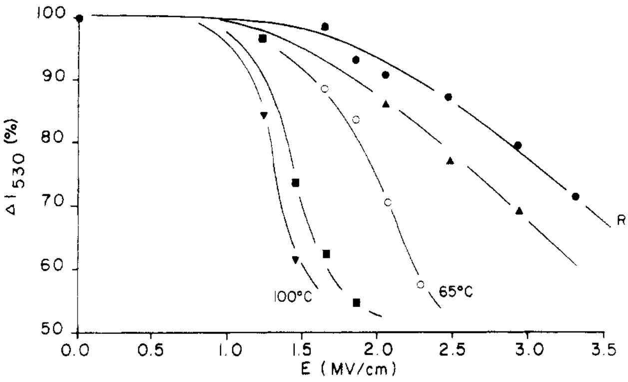

**Figure 5.** Change in the intensity of the 530-cm$^{-1}$ band for samples in the depoled state as a function of the electric field: (●) room temperature; (▲) 40 °C; (○) 65 °C; (■) 80 °C; (▼) 100 °C.

one involving cooperative rotation of the chains along the 010 plane[32,33] or a simpler one[1] requiring only small intramolecular rotations about all the G and G′ bonds of every second chain, causing the overall chain conformation to be altered from TGTG′ to TG′TG. The dynamics of this phase transition have also been studied theoretically.

Compared to the understanding achieved for the $\alpha \rightarrow \delta$ transition, the information obtained for the transformation of the $\alpha$ phase to one containing trans sequences at high field strengths is much more vague. But unlike the similarity found between the $\alpha$ and $\delta$ phases, both X-ray diffraction and infrared spectra of these poled samples contain explicit features differing from the $\alpha$ conformation. The relative amounts of different conformations can be quantitatively analyzed. Our data indicate that the rate of structural transformation may be significantly slower than the $\alpha \rightarrow \delta$ transition. The continually changing band intensities over long times shown in Figure 4 indicate this point clearly. Lovinger[34] and Takahashi and Tadokoro[35] have proposed possible mechanisms for the transformation from the $\alpha$ to the $\gamma$ phase. However, unlike the $\alpha \rightarrow \delta$ transition, no molecular mechanism is currently available to calculate the rate of change for the transformation in chain conformation. But the fact that the rate of transformation is both field strength and temperature dependent needs to be incorporated in any proposed model. Whether the phase transformation is a single-step or a multistep process involving the presence of an intermediate phase first cannot be answered at this moment.

For each poling temperature we can then plot the transformation from the $\alpha$ phase to the a phase containing trans sequences as a function of field. This is shown in Figure 5, which illustrates the dramatic field-strength dependence needed for the phase transformation. For low temperatures (<40 °C) the volume fraction of the $\alpha$ phase exhibits a monotonic decrease in intensity. For higher temperatures near 100 °C, the volume fraction decreased sharply, containing features of a sigmoidal curve. The data of others, as well as our own, show that a very small amount of conversion from the $\alpha$ phase would occur at low temperatures and field strength. We define the critical fields shown in Figure 5 to be associated with the approximated inflection point of each curve. The values obtained are then plotted as a function of temperature in Figure 6. As can be seen, for the sample poled at 80 °C or above, a considerable amount of phase transition already occurred when the applied field is near 1 MV/cm. A calculation of the free energy of both the polar and nonpolar forms of PVF$_2$ has been performed by means of a generalized mean-field approximation.[36] The estimates in that study for the lower bounds of the critical field as a function of temperature differ considerably from our experimental values. Previous theory greatly underestimates the effects of the applied electric field. The exact dependence of the fraction of the $\alpha$ form in the poled sample as a function of poling field strength and temperature is then of considerable interest.

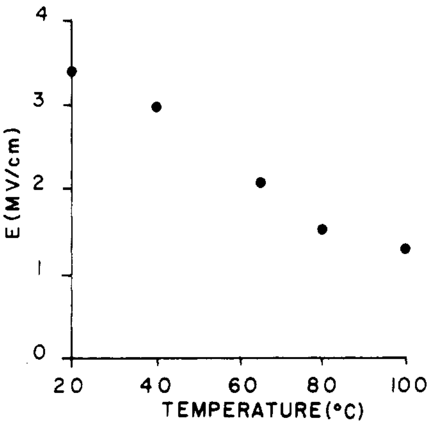

**Figure 6.** Measured critical fields for the phase transformation as a function of temperature.

## Conclusion

Poly(vinylidene fluoride) has been poled with an electric field of 0.5–4 MV/cm at temperatures from ambient to 100 °C. Infrared spectra were obtained for these samples in the presence of the electric field. In order to separate the changes in band intensity arising from changes in polarization from changes in actual volume fraction, the hysteresis curves were obtained so that remnant polarization could be removed to obtain spectra of the depoled state for quantitative analysis. We found that there was considerable conversion from the $\alpha$ phase to the $\gamma$ or $\beta$ phase at high temperatures. The time dependence of such phase transitions is not exponential in functional dependence but more like the power series $at^b$. Such conversions may take as long as an hour to reach the steady state. The critical fields obtained are also considerably lower than the theoretical values presented earlier. We propose that further theoretical studies should contain features of a cooperative transition.

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**Registry No.** PVF$_2$ (homopolymer), 24937-79-9.

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# Conformational Change, Chain Orientation, and Crystallinity in Poly(ethylene terephthalate) Yarns: Raman Spectroscopic Study

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ABSTRACT: A Raman spectroscopic study of five fibers of poly(ethylene terephthalate) is presented. These fibers are produced by annealing an original fiber under different temperatures and shrinkage conditions. The result is five spectra that are different in many ways. Included are results in the low-frequency region of the spectrum. Analysis of these results is approached in terms of three distinct types of events that take place in these fibers: conformational change, chain orientation, and crystallinity. The Raman data, in combination with data from X-ray, thermal analysis, density, and birefringence measurements on these same fibers, allow these three events to be separated. On the basis of this analysis, it is now possible to carry out this separation in PET fibers based on Raman spectroscopy alone. Raman polarization data are used to support the arguments.

The vibrational spectrum of poly(ethylene terephthalate) (PET or 2GT) has been extensively studied.[1-18] One of the main reasons for interest in the infrared and Raman spectra of PET is that the spectrum has been characterized as being sensitive to crystallinity. Indeed, such sensitivity is often mentioned in connection with the vibrational spectra of polymers.

In practice, the changes in the infrared and Raman spectra have only rarely been correlated with crystallinity, if we take that to mean the development of long-range, three-dimensional order. However, there have been some correlations with density, thermal analysis, and occasionally with X-ray data.

There have been attempts to explain the changes in the Raman spectrum that occur upon annealing of amorphous samples. These changes, though considered to be related to the development of crystallinity, are explained as being due to conformational changes in either the carbonyl groups or the glycol linkage. Since it is assumed that these conformational changes go hand in hand with crystallinity development, the extension is both logical and reasonable.

Relatively few studies have been carried out on the Raman spectrum of PET fibers or other oriented samples. These have usually focused on the assignment of Raman bands based on polarization.[3,11,19,20] Melveger[11] did show that certain changes in the Raman spectrum did not correlate well with density in the case of fibers and that this seemed to be a problem of orientation complicating the Raman intensities.

What appears to be needed is a study of the effect of conformational change, chain orientation, and crystallinity on the Raman spectrum. It is rarely possible to hold two of these variables constant while the third changes—they are not so independent. But by the use of a combination of varying the fiber and a range of characterization techniques, it should be possible to better understand the spectroscopic changes. As a consequence, this leads to the possibility of a variety of diagnostic techniques and physical understanding which can be derived from the Raman data.

In this paper, we approach this problem as follows: A PET yarn is prepared with a takeup speed of ca. 3300 m/min. This yields what is known as a partially oriented yarn (POY), which is oriented but still amorphous and in which the conformational disorder is great. This yarn is then annealed under a range of annealing conditions so that chain orientation, conformation, and crystallinity result in different combinations. In this way a set of five fibers, the original and four new ones prepared by annealing, is produced. Each of these is characterized by its Raman spectrum and by thermal analysis, birefringence, density, and wide-angle X-ray diffraction. It will be seen that the resulting data show that the Raman spectrum has great potential for separating the kinds of changes which are occurring, and, in the future, for following these changes as they occur. Raman polarization data on single filaments are used to support the analysis, but the basic

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