# Studies of Chain Conformation above the Curie Point in a Vinylidene Fluoride/Trifluoroethylene Random Copolymer

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ABSTRACT: A 60/40 mol % vinylidene fluoride/trifluoroethylene random copolymer was found to undergo a ferroelectric-to-paraelectric phase transition over a broad temperature region centered at ~70 °C. This Curie transition was studied by thermal analysis, X-ray diffraction, and Raman scattering measurements. It was found that the initial trans planar conformation of the copolymer transforms into a structure similar to the TGTG′ conformation of $PVF_2$. Raman studies have shown that the structure of the copolymer undergoes a hysteresis as it returns to its room-temperature conformation when the temperature is lowered through the Curie point. The mechanism of this transition and possible origins of the hysteresis are discussed.

## Introduction

Recently, renewed interest in poly(vinylidene fluoride) ($PVF_2$) has been generated by the discovery of a well-defined Curie transition in random copolymers of vinylidene fluoride and trifluoroethylene.[1] Since its piezoelectric properties were first discovered by Kawai in 1969,[2] the homopolymer, $PVF_2$, has commanded considerable attention in the scientific literature. It exists in at least four crystalline forms,[3-5] of which the planar zigzag modification (form I) has been shown to be ferroelectric on the basis of *D–E* hysteresis studies and infrared and X-ray measurements.[6-9]

A ferroelectric material is polar and has the additional property that its polarity can be reversed when placed in a sufficiently large electric field.[10] Another important characteristic of such a material is the existence of a Curie point, the temperature at which it undergoes a transition to a paraelectric phase, in which a random orientation of dipoles is present. This phase transition is manifested by changes in the crystal structure, thermal properties (as evidenced by DSC measurements), and dielectric constant,[1,6-9] which can also lead to changes in relative permittivity and remnant polarization.

Although $PVF_2$ is considered to be ferroelectric, a Curie point has not yet been observed, possibly because melting intervenes before the onset of the transition.[11,12] In order to avoid this problem, $PVF_2$ has been copolymerized with several different fluorocarbons, including trifluoroethylene (TrFE), producing a ferroelectric copolymer with a planar structure similar to that of $PVF_2$ (form I) and with a well-defined Curie transition significantly below the melting point.[1] As the $PVF_2$ content is increased, the Curie point shifts toward the melting point,[13] which further suggests that melting may intervene with this transition in the homopolymer.

Considerable thermal, X-ray, and IR measurements have been performed on a wide variety of $VF_2$–TrFE copolymer compositions[13] in order to determine the nature of this transition. Some investigators believe that the transition occurs intermolecularly by randomization of dipole vectors along polar chains[14,15] while others have suggested that the transition involves conformational changes that result in a nonpolar chain structure. Considerable discrepancy exists among the latter group regarding the exact conformation of the copolymer in the paraelectric state. Some have predicted that the initial planar zigzag conformation transforms into a random combination of TG, TG′, $T_3G$, and $T_3G'$ sequences,[16-18] while others have suggested that the copolymer assumes a conformation similar to that of $PVF_2$ (form III).[19] It has also been proposed that the conformation in the paraelectric phase is analogous to that of poly(trifluoroethylene) (PTrFE), which is a disordered 3/1 helix.[20-24]

To further characterize the Curie transition, Raman spectroscopic methods have been employed to analyze a 60/40 mol % $VF_2$–TrFE copolymer, as well as the $PVF_2$ (forms I and II) and PTrFE homopolymers. Thermal analysis and X-ray measurements were also obtained on the copolymer and homopolymers in order to elucidate the nature of this transition and present a mechanism consistent with all the data obtained.

## Experimental Section

**$VF_2$–TrFE Copolymer.** The $VF_2$–TrFE random copolymer used in this study was obtained from ATOCHEM Co. (France) and was used without further purification. The $VF_2$–TrFE comonomer ratio was 60/40 and the sample provided was in the form of a semicrystalline white powder. For Raman studies, the powdered sample was packed into a melting point capillary and then inserted into the laser beam. For comparison, the spectrum of a melt-crystallized sample was run and found to be identical with that of the as-received powder.

**$PVF_2$ Homopolymer.** The homopolymer used in this study was a commercial sample, Kynar, provided by Pennwalt Chemical Co. as a small-particle resin. The as-received sample was found by IR and Raman measurements to be in the form II crystalline modification. To obtain form I, the form II powder was ground for several hours at room temperature.[3] No specific effect on the degradation of the molecular weight of the sample was observed.

**Raman Scattering.** Raman spectra were recorded with a Jobin-Yvon HG-2S double monochromator equipped with concave holographic gratings and a spatial filter to enhance stray light rejection. A cooled RCA 31034A-02 photomultiplier tube was used to detect the scattered photons because of its high sensitivity and low dark count. Laser excitation was supplied by either the 514.5- or the 488.0-nm line of a Spectra Physics 165-08 argon ion laser. All data were collected and processed digitally by a Nicolet 1180 Data System. Typical spectra were recorded at 4-$cm^{-1}$ resolution, using 200 mW of laser power. The coaddition of 20 scans was usually sufficient to achieve spectra with a high *S*/*N* ratio.

Variable-temperature measurements were made in a vertical Harney–Miller cell by blowing nitrogen over an attached cartridge heater. The temperature was maintained to within ±2 °C of the desired value by adjusting the voltage applied to the heater and the flow rate of the nitrogen. A typical experiment employed a delay of 15 min after the temperature was changed to allow the sample to reach thermal equilibrium before the next set of measurements was made.

## Results and Discussion

**A. Thermal Measurements.** A thermogram for the 60/40 mol % $VF_2$–TrFE copolymer is shown in Figure 1. The melting endotherm at 154.3 °C is fairly sharp and intense ($\Delta H$ = 31.6 J/g), reflecting a high degree of crystallinity. The homopolymers $PVF_2$ forms I and II also have fairly sharp melting endotherms at 160.1 and 159.2 °C, respectively. However, these melting points are somewhat lower than expected for $PVF_2$ (~170 °C), possibly due to an increased percentage of head-to-head

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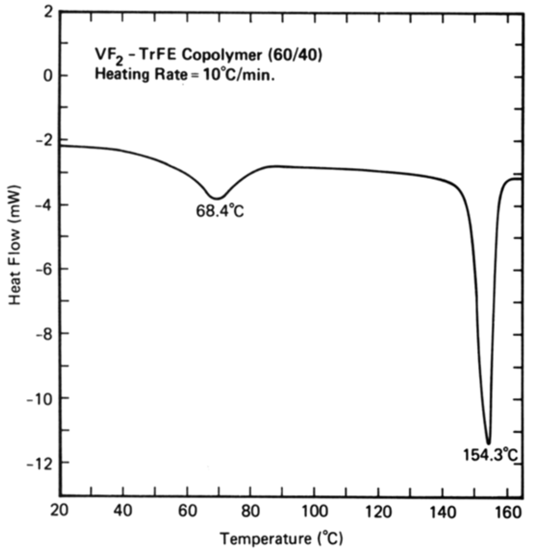
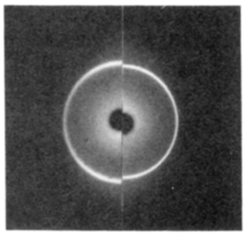


**Figure 1.** DSC trace of the VF$_2$–TrFE copolymer (60/40) recorded at a heating rate of 10 °C/min.



$T$ = 20 °C $d$ = 4.57 Å

$T$ = 100 °C $d$ = 4.86 Å

**Figure 2.** X-ray diffraction patterns for the 60/40 mol % copolymer (a) at room temperature ($T$ = 20 °C) and (b) at 100 °C.

defects.[18] The homopolymer PTrFE melted over a broad region centered at 195.0 °C, reflecting the disorder and low crystallinity associated with an atactic material. Furthermore, only 18.5 J/g was required to melt atactic PTrFE whereas 40.8 J/g was required to melt the more highly crystalline PVF$_2$. The choice of representing the heat of fusion in units of J/g was made in order to allow for comparison between the homopolymers and the random copolymer, in which the exact nature of the repeat unit is unknown.

In addition to the melting endotherm, a weaker, broader endotherm was observed at 68.4 °C in the copolymer. This corresponds to a transition from the ferroelectric to paraelectric phase, which is usually observed in this region for certain copolymers of at least ~55 mol % VF$_2$.[13,18,19] The DSC thermograms of the homopolymers PVF$_2$ (forms I and II) and PTrFE revealed only melting endotherms.

**B. Wide-Angle X-ray Diffraction (WAXD).** The as-received copolymer sample was also investigated by WAXD at ambient and elevated temperatures using the 1.542-Å line of Cu K$_\alpha$ radiation. At room temperature, a medium-strong reflection was observed corresponding to a $d$ spacing of 4.57 Å. This is characteristic of the pseudohexagonal lattice commonly found for PVF$_2$ copolymers exhibiting a structure similar to the $\beta$ phase (planar zigzag) of the homopolymer and has been observed for a number of VF$_2$–TrFE copolymers[21-24] exhibiting a range of comonomer concentrations. As shown in Figure 2, at 100 °C, which is above the Curie transition temperature, a single $d$ spacing is also observed at 4.86 Å, corresponding to the paraelectric phase and resulting from the introduction of G and G′ bonds into the all-trans structure.[23]

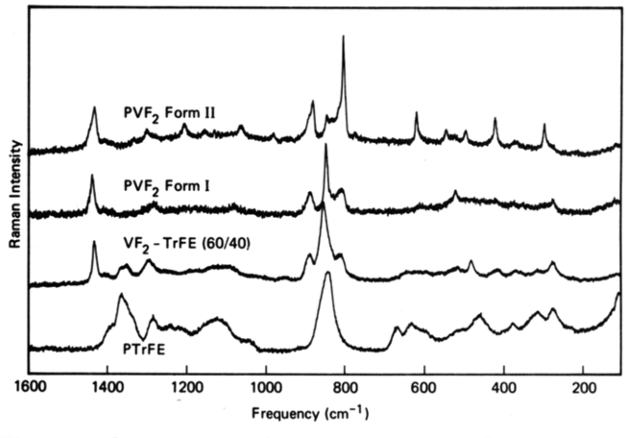


**Figure 3.** Comparison of the room-temperature Raman spectra of PVF$_2$ form II (TGTG′), PVF$_2$ form I (planar zigzag), 60/40 mol % copolymer, and PTrFE.

**C. Structure of Homopolymers and VF$_2$–TrFE Copolymers.** Room-temperature Raman measurements of the copolymer, each of the homopolymers (PVF$_2$, forms I and II), and PTrFE are shown in Figure 3. The overall appearance of the strong bands in the 900–800-cm$^{-1}$ region of the copolymer suggests that its conformation is most similar to that of PVF$_2$ (form I). The 884-cm$^{-1}$ peak present in the spectrum of the copolymer is almost identical with the 885-cm$^{-1}$ peak of PVF$_2$ (form I) and involves stretching of the CF$_2$ groups coupled with rocking of the CH$_2$ groups. However, the 849-cm$^{-1}$ CF$_2$ symmetric stretching peak of the copolymer is much broader than its corresponding 841-cm$^{-1}$ band of PVF$_2$ (form I), reflecting the presence of TrFE comonomeric units since the PTrFE homopolymer contributes an intense Raman band in the vicinity of 840 cm$^{-1}$ as shown in the bottom spectrum of Figure 3. The band at 808 cm$^{-1}$ in the copolymer is also very similar to the 805-cm$^{-1}$ peak of PVF$_2$ (form I) and may also be attributable to the presence of a residual amount of TGTG′ (form II) conformational sequences.

The Raman spectrum of the copolymer also closely resembles that of PVF$_2$ (form I) in other spectral regions. The band at 1430 cm$^{-1}$, attributable to CH$_2$ bending,[3] is present in PVF$_2$ (forms I and II) and in the VF$_2$–TrFE copolymer. The doublet at 1363 and 1350 cm$^{-1}$ in the copolymer is apparently derived from the strong Raman bands of PTrFE in the 1390–1330-cm$^{-1}$ region since there is no corresponding feature in PVF$_2$ form I or form II, suggesting that these modes involve coupling between bending motions of the lone CH and stretching of the CC backbone. The 1293-cm$^{-1}$ band of the copolymer is stronger and broader than either the 1296-cm$^{-1}$ band of form II or the 1283-cm$^{-1}$ band of form I. The homopolymer, PTrFE, shows a similar, somewhat broad band at 1282-cm$^{-1}$, which can be attributed to the antisymmetric CF$_2$ stretching and CH$_2$ rocking vibration similar to that assigned in PVF$_2$.[5]

A weak broad Raman band is observed in the 1100-cm$^{-1}$ region of the copolymer and corresponds to the more intense but equally broad band centered at 1113-cm$^{-1}$ in the spectrum of PTrFE. Both the broad background in this region of the copolymer and that in PTrFE have a shoulder in the vicinity of 1040-cm$^{-1}$. This shoulder, although very weak in the copolymer, is more intense in PTrFE. In this region, form II shows a weak, fairly sharp peak at 1055 cm$^{-1}$, which has been attributed to a combined motion of symmetric CF$_2$ stretching, CH$_2$ wagging, and CC stretching.[5] Since the band in this region of the copolymer is extremely broad, it is probably more closely related to that of PTrFE than PVF$_2$.

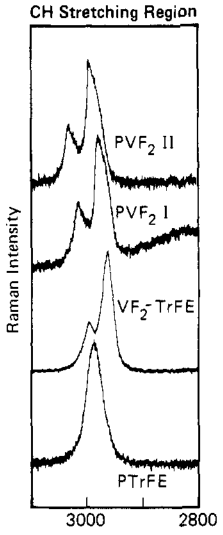


**Figure 4.** Raman spectra in the CH$_2$ stretching region (3100–2800 cm$^{-1}$) for PVF$_2$ form II, PVF$_2$ form I, 60/40 mol % copolymer, and PTrFE taken at room temperature.

The Raman spectrum of the copolymer can also be compared with those of homopolymers in the low-frequency region. A small amount of scattering occurs in the 640–600-cm$^{-1}$ region in the copolymer, most likely attributable to the features shown at 663 and 628 cm$^{-1}$ in PTrFE. The small band located at 509 cm$^{-1}$ in the copolymer, which appears as a peak superimposed on a shoulder, is most likely derived from the combination of the peak at 514 cm$^{-1}$ in form I and the shoulder at 513 cm$^{-1}$ in PTrFE. In addition, the copolymer shows a sharp peak at 476 cm$^{-1}$ which does not appear in any of the homopolymers. There are also a number of weak features at 413, 365, and 309 cm$^{-1}$ in the copolymer, which are probably derived from the 373- and 313-cm$^{-1}$ bands of PTrFE. Typically bands in this region of the spectrum are assignable to nonlocalized vibrations of the backbone, with some additional contribution from CF$_2$ rocking motion.[5]

The overall appearance of the copolymer spectrum closely resembles that of form I primarily because of the intense bands in the 900–800-cm$^{-1}$ region but also due to the coincidence of other weaker bands previously mentioned. This suggests that the copolymer is in a trans planar conformation at room temperature. The broad bandwidth of the 849-cm$^{-1}$ peak of the copolymer reflects the presence of the 839-cm$^{-1}$ band due to the TrFE comonomeric units, which may be somewhat disordered since PTrFE is known to be atactic.

The CH stretching region, 3100–2800 cm$^{-1}$, for the copolymer and each of the homopolymers is shown in Figure 4. The spectra for the two forms of PVF$_2$ are nearly identical with both the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ vibrations of form II being ~10 cm$^{-1}$ higher than their counterparts in form I as predicted by normal coordinate calculations.[5] As expected, PTrFE shows only one peak in this region since there is only one CH bond per repeat unit. Thus, this peak is not a doublet as is the case of the copolymer and PVF$_2$. The CH stretching region of the copolymer is qualitatively similar to that of PVF$_2$ (form I) but the peaks of the two bands occur at slightly lower frequencies, reflecting the spectral superposition of contributions from both VF$_2$ and TrFE units.

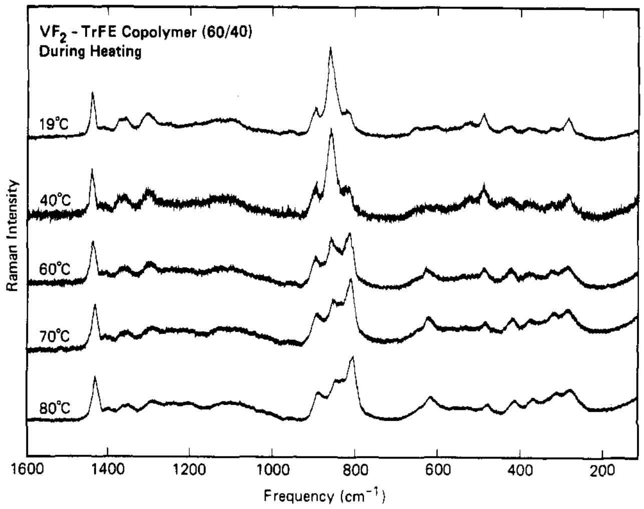


**Figure 5.** Raman spectral changes that occurs as the 60/40 mol % copolymer is heated through the Curie transition.

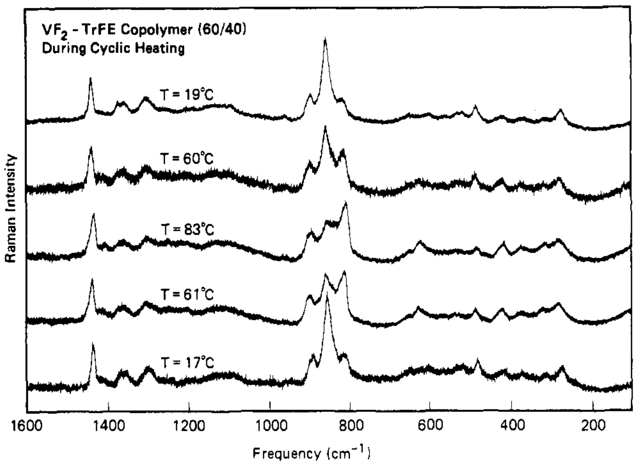


**Figure 6.** Cyclic heating of the 60/40 mol % copolymer.

**D. Structure of the VF$_2$–TrFE Copolymer above the Curie Point.** The relative intensities of several bands changed dramatically at the phase transition temperature as shown in Figure 5. At 40 °C the spectrum had scarcely changed from that at room temperature. However, by 60 °C, the 808-cm$^{-1}$ peak had grown significantly at the expense of its neighbor at 849 cm$^{-1}$. This trend continued until 80 °C when the transition appeared to be complete since no changes resulted upon further heating. This is consistent with the thermal measurements where the transition was observed to begin at about 55 °C and was completed at approximately 85 °C.

In the high-frequency region, a very weak peak at 1400 cm$^{-1}$ increased with temperature and its position appeared to correspond with a similar band observed in the spectrum of the form II homopolymer. Scattering in this region has been correlated with the wagging and bending of CH$_2$ groups.[5] On the other hand, the 1430-cm$^{-1}$ peak, attributable to CH$_2$ bending and wagging, did not change with temperature and its intensity was therefore used to normalize the spectra shown in Figures 5 and 6. The background level between 1400 and 1000 cm$^{-1}$ and the overall bandwidth of the peaks increased as the sample temperature was raised. The doublet at 1363 and 1350 cm$^{-1}$ coalesced into one peak and became less distinct from the 1293-cm$^{-1}$ band at higher temperatures.

Vibrations in the lower frequency region also change significantly with heating. At 60 °C, a peak at 612 cm$^{-1}$, initially observed in the IR and linked to the introduction of gauche bonds,[4] was observed. This broad peak at 612 cm$^{-1}$ in the copolymer gains significant intensity above 60 °C and shows a distinct resemblance to the 610-cm$^{-1}$ band observed in the Raman spectrum of form II. In fact, broad vibrations also found at 411 and 300 cm$^{-1}$ in the high-temperature spectrum resembled in both frequency and intensity (relative to that at 808 $cm^{-1}$) the Raman bands found at 414 and 290 $cm^{-1}$ in form II.

Solid-to-solid phase transitions in other polymers such as poly(tetrafluoroethylene) typically show only slight Raman spectral changes.[25] However, the ferroelectric-to-paraelectric transition in $VF_2$–TrFE clearly causes dramatic changes as evidenced by the Raman measurements shown in Figure 4. Initially, the copolymer appears to be trans planar similar to $PVF_2$ (form I). After the transition to the paraelectric phase, it would appear from the intensity changes observed for the vibrations in the 900–800-$cm^{-1}$ region and the growth of other new bands mentioned previously that the conformation is most nearly similar to that of $PVF_2$ (form II). However, it should be emphasized that a differentiation between the existence of TGTG′ sequences and isolated TG and/or TG′ defects within the chain has not been possible in this work. Even though there is some thermal broadening, the peaks at 808, 612, 411, and 300 $cm^{-1}$ remain reasonably sharp and relatively intense above the Curie transition in contrast to the IR changes observed previously[16] for a 55/45 $VF_2$–TrFE copolymer and assigned to a chain conformation constructed from a random combination of TG, TG′, $T_3G$, and $T_3G'$ sequences. This suggests that the paraelectric phase is not highly disordered but most likely incorporates some TGTG′ sequences.

**E. Cyclic Temperature Studies.** Cyclic heatings were performed to determine if the transition is completely reversible or if it shows hysteresis-like behavior (Figure 6). Although the spectrum taken at 60 °C while heating differs considerably from that taken at 61 °C while cooling, the room-temperature spectra taken before and after heating are nearly identical. Up to four heating–cooling cycles were performed and the room-temperature spectrum remained unchanged. The dramatic difference in the 60 °C spectrum taken while heating and the 61 °C spectrum taken while cooling may reflect the high sensitivity to slight shifts in temperature near the maximum in the endotherm. However, this is unlikely because the actual temperatures are only known to within ±2 °C, meaning that the readings of 60 and 61 °C are within experimental error. It is therefore more probable that the observed difference between measurements taken during heating and those taken during cooling is due to hysteresis as has been observed previously.[13,15,16,19,22-24] It is interesting to note that the spectra shown in Figure 6 represent a time resolution of at least 1 h between each measurement. Typically, after the temperature was changed, a 15-min interval was allowed for the specimen to come to thermal equilibrium. This was then followed by the actual measurement, which took approximately 45 min. Thus, the difference between the 61 °C spectrum on cooling and that recorded at 60 °C upon heating represents a considerable temporal lag of the molecule in returning to its initial conformation at a given temperature. This behavior may therefore be analogous to the supercooling phenomena commonly observed in polymers since the re-formation of the ferroelectric phase can only occur at a certain rate which most certainly is a function of chain mobility and thus the TrFE concentration.

## Conclusion

Spectroscopic studies of $PVF_2$ homopolymers and a copolymer with TrFE has revealed that the Curie transition of the $VF_2$–TrFE copolymer results in a change in the conformation of the backbone from a planar structure to one that more nearly resembles the TGTG′ conformation adopted by $PVF_2$. Since this conformation is the most energetically favorable at room temperature, it is not unlikely for the polymer chain to adopt such a structure above the Curie point.

Insights provided by this study and others[16,21] suggest that both the melting process and the order–disorder transition that occurs at the Curie point involve an intermolecular expansion of the lattice. In planar zigzag $PVF_2$ (form I) the crystal lattice packing is very efficient and at elevated temperatures the increase in intermolecular distance required to transform from the ferroelectric to paraelectric state creates a lattice instability leading to total disorder or melting. In the $VF_2$–TrFE copolymer on the other hand, the incorporation of TrFE units into the crystal lattice as defects serves to increase the intermolecular separation between chains. Thus the barrier of transformation (via the rotation about bonds) from the ferroelectric to the paraelectric phase is lower and can be reached before the occurrence of the melting point. Support for this interpretation has recently come from the observation of a Curie transition in a random copolymer of $VF_2$ (81 mol %) and TFE by Lovinger et al.[26]

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**Registry No.** $VF_2$–TrFE (copolymer), 28960-88-5.

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