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Spectroscopic Analysis of the Crystalline and Amorphous Phases in a Vinylidene Fluoride/Trifluoroethylene Copolymer

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ABSTRACT: The structure of a random copolymer of 75 mol % vinylidene fluoride and 25 mol % trifluoroethylene has been studied by infrared spectroscopy. Spectra of samples containing varying degree of crystallinity have been analyzed by factor analysis, and from this the spectra of pure amorphous and pure crystal phases have been isolated. The amount of the crystalline phase was determined as a function of annealing temperature, and a significant increase was found for annealing near the Curie transition temperature. We have also analyzed spectra obtained at varying temperatures, and the spectra of the isolated low-temperature and high-temperature phases were obtained. The low-temperature-phase spectra appeared very similar to that of the isolated crystalline phase. The high-temperature-phase spectra differed from that of the amorphous, showing fewer sequences of four or more trans isomers and a greater amount of TG or TG′ isomers. The low-temperature-phase content during a heating/cooling cycle was also analyzed.

Introduction

Poly(vinylidene fluoride) (PVDF) is a well-studied piezoelectric polymer.[1] It may also be ferroelectric with the Curie transition above the melting point. Copolymers of PVDF with trifluoroethylene (TrFE) or tetrafluoroethylene (TFE) units are known to be ferroelectric with well-defined Curie transitions.[2,3] These copolymers show a higher piezoelectric activity than PVDF.[4,5] Several crystalline phases, α, β, δ, and γ, are known to exist for PVDF with the β phase (fully trans planar zigzag conformation) showing the greatest piezoelectric activity.[1] Chain conformation of the copolymer depends on both composition and thermal history. It has been speculated that only the β phase exists for VDF/TrFE copolymers containing greater than 65% of VDF at room temperature.[2,3] It is also clear that chain conformations for all the copolymers can change significantly at high temperature.[2,3]

The structure of VDF/TrFE copolymers depends strongly on the composition of the polymer, thermal history of the sample, and poling (time and temperature).[3,6–8] The Curie transition, T_c, found for these copolymers also depends on the composition and processing conditions. A range from 65 to 130 °C has been measured for copolymers containing 52–90 mol % of VDF.[2] The structures below and above this temperature differ significantly, changing from ferroelectric to paraelectric at T_c. Several X-ray and spectroscopic studies have been performed to determine the structure of these copolymers at various temperatures and the changes that occur under a high strength electric field.[3,6,7,9–16] These studies have basically established the trans structure for the copolymer and have shown the conformational disordering that occurs at the Curie temperature. In order to enhance the amount and stability of the β phase, high-temperature drawing or the application of a high-strength electric field is necessary.[13] In our previous spectroscopic study, we have shown the spectroscopic features associated these structural changes.[17]

The use of the spectroscopic method is limited by the lack of definitive band assignments. Even though the copolymer is known to have a large fraction of amorphous phase, there are few quantitative studies to characterize the amorphous and crystalline phases. By using the technique of factor analysis we have isolated spectra of the amorphous and crystalline phases and found explicit evidence of transformation from the amorphous to the crystalline phase as a function of annealing. By applying the factor analysis technique to spectra obtained at various temperatures, we have been able to obtain spectra of the low- and high-temperature phases and to monitor the relative amount of these phases upon heating and cooling through the transition. Our results are reported here.

Experimental Section

VDF–TrFE copolymer samples in the form of 9-μm-thick films have been obtained from Pennwalt Corporation. Samples were also provided in the form of pellets. For annealing experiments, films were cast in aluminum pans from a 2% solution of copolymer pellets in acetone. Films containing varying amounts of ordered and disordered phases were prepared by annealing in vacuum for

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3 h at various temperatures. In order to obtain spectra at various temperatures, samples were mounted in a heating cell and spectra were recorded with a Bruker IFS 113v FTIR spectrometer. All spectra were obtained with 200 scans at a resolution of 2 cm^{-1}. All the spectroscopic data were transferred from the spectrometers to IBM 9000 computers for further analysis.

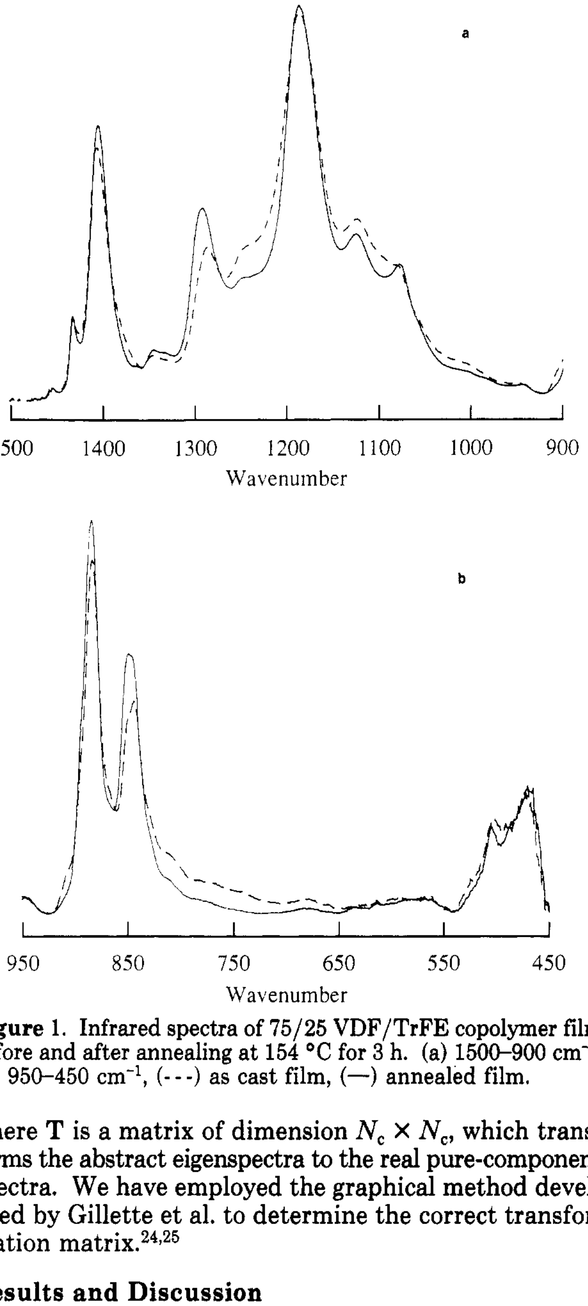

Figure 1. Infrared spectra of 75/25 VDF/TrFE copolymer film before and after annealing at 154 °C for 3 h. (a) 1500–900 cm^{-1}; (b) 950–450 cm^{-1}, (- - -) as cast film, (—) annealed film.

Factor Analysis

Factor analysis has been widely used to identify the number of independent components in a mixture and to determine the concentration of each pure component present in the mixture.[18-25] In this study, factor analysis is employed to extract the infrared spectra of pure amorphous and crystalline phases and to separate features due to the ferroelectric and paraelectric phases.

Beer's law for a series of mixture spectra can be written in matrix form as

$$\mathbf{A} = \mathbf{KC} \tag{1}$$

where **A** is the normalized mixture absorbance matrix, **K** is the extinction coefficient matrix, and **C** is a concentration matrix. Each column in the **A** matrix represents the absorbance values for one particular mixture spectrum. Each spectrum has N_w data points in the frequency space. The concentration matrix is an $N_c \times N_s$ matrix, where N_c is the number of pure components and N_s is the number of mixtures studied. Usually each spectrum given in terms of N_w data points in the frequency space is difficult to analyze. However, the **Q** matrix, a much smaller matrix of dimension $N_s \times N_s$ contains the number of linearly independent components. The value of N_c is equal to the rank of the covariance matrix **Q** given by

$$\mathbf{Q} = \mathbf{A}^{\mathrm{T}}\mathbf{A} \tag{2}$$

where $\mathbf{A}^{\mathrm{T}}$ is the transpose of **A**. Since the **Q** matrix is real and symmetric, the rank of the matrix can be easily determined to obtain the nonzero eigenvalue matrix. The eigenvalue matrix **L** and the eigenvector matrix **E** are therefore obtained by the following

$$\mathbf{E}^{-1}\mathbf{QE} = \mathbf{L} \tag{3}$$

In order to determine the number of nonzero eigenvalues, we employed the Malinowski indicator function[26-28] given by the following expression

$$(\mathrm{IND})_k = (\mathrm{RE})_k/(N_s - k)^2 \tag{4}$$

where $(\mathrm{RE})_k$ is the real error for k components. This function reaches a minimum when the correct number of factors are employed, which occurs when the error is random and uniformly distributed throughout the data set. Thus if N_c is determined on the basis of Malinowski's indicator function, abstract eigenspectra are constructed by using the real data matrix, **A**, and the "real" eigenvectors, $\mathbf{E}'$, with dimension $N_s \times N_c$, by

$$\mathbf{U}' = \mathbf{AE}' \tag{5}$$

The regenerated data matrix, $\mathbf{A}'$, in which extracted error (XE) is removed from real error (RE) and in which only imbedded error (IE) exists, is obtained from the following equation

$$\mathbf{A}' = \mathbf{U}'(\mathbf{E}')^{\mathrm{T}} \tag{6}$$

where $\mathbf{U}'$ is the abstract eigenspectra matrix of dimension $N_w \times N_c$. The pure-component spectra and their concentrations are given by the **K** and **C** matrices, respectively, which are determined by

$$\mathbf{K} = \mathbf{U}'\mathbf{T} \tag{7}$$

and

$$\mathbf{C} = \mathbf{T}^{-1}(\mathbf{E}')^{\mathrm{T}} \tag{8}$$

where **T** is a matrix of dimension $N_c \times N_c$, which transforms the abstract eigenspectra to the real pure-component spectra. We have employed the graphical method developed by Gillette et al. to determine the correct transformation matrix.[24,25]

Results and Discussion

Crystalline and Amorphous Phases. The infrared spectra of a 75/25 copolymer in the as-cast state and after annealing at 154 °C for 3 h are shown in Figure 1. Annealing is known to produce a significant increase in the degree of crystallinity, and we observe large increases in the intensities of the 1402-, 1290-, 883-, and 844-cm^{-1} bands and a decrease in the 1247- and 1124-cm^{-1} bands. These intensity changes reflect changes in the chain conformation upon annealing and were observed in our previous study.[17] It is difficult to identify bands due solely to the amorphous phase, since most bands sharpen and increase in intensity with annealing as they are associated with the ordered trans conformation. The overlapping of crystalline and amorphous bands makes it difficult to identify bands of each phase, and samples of purely amorphous or crystalline structure cannot be produced. Another method such as digital subtraction or a numerical technique such as factor analysis must be used to separate the phases. The subtraction method requires the existence of at least one nonoverlapping band characteristic of each phase, a requirement not met for this system. Therefore factor analysis was the only alternative method of analysis.

Table I
Factor Analysis Results for the Annealed 75/25 VDF/TrFE Copolymer System

component	annealing temp, °C	eigenvalue	10^4IND
1	20	15.9564	0.0981
2	68	0.0379	0.0424
3	92	0.0034	0.0323
4	102	0.0011	0.0290
5	110	0.0004	0.0294
6	113	0.0003	0.0288
7	117	0.0003	0.0223
8	122	0.0001	0.0227
9	126	0.0000	0.0227
10	128	0.0000	0.0270
11	132	0.0000	0.0305
12	136	0.0000	0.0407
13	142	0.0000	0.0626
14	146	0.0000	0.1310
15	150	0.0000	0.4900
16	154	0.0000	

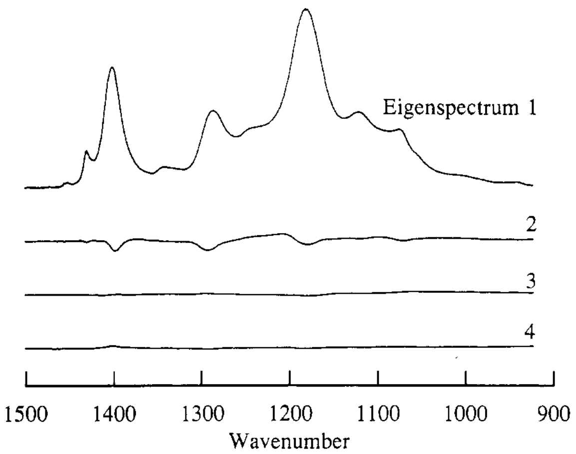

Figure 2. Abstract eigenspectra for the annealed 75/25 VDF/TrFE copolymer system.

For factor analysis, 16 samples were prepared by annealing cast films at temperatures ranging from 29 to 154 °C for 3 h. Usually, samples of different degree of crystallinity can be prepared in such fashion. A frequency range of 1500–900 cm^{-1} containing 597 data points was used in the analysis. The data were corrected with a straight baseline connecting the first and last data point, and then the spectrum intensity was normalized by dividing the baseline-corrected spectrum by the square root of the sum of the squared absorbances. The results of factor analysis are shown in Table I. The initial assumption was made of two factors being necessary to describe the data, one representing the amorphous phase and the other describing the crystalline phase. Malinowski's indicator function reached the first minimum at a k value equal to four, indicating that four factors were present.

The magnitude of the eigenvalues is a measure of the relative importance of corresponding eigenvectors in data regeneration expressed in eq 6. However, it is seen in Table I that the third and fourth eigenvalues are both nearly zero. For the normalized data the eigenvalues are equal to the sum of the squares of the corresponding abstract eigenspectra, and the four abstract eigenspectra are shown in Figure 2. From this figure it is observed that the third and fourth eigenspectra are not significant, and thus the first two eigenvectors were used to extract the pure-component spectra.

In order to determine the pure spectra, the **T** matrix can be determined from a graphical method[24,25] shown schematically in Figure 3. A quadratic relationship $E_1 = aE_2^2 + bE_2 + c$ is fitted to the 16 eigenvector pairs. From the cross product of the eigenspectra, the minimum and maximum peaks are chosen as characteristic points. Boundary lines are constructed with slope equal to the ratio of the eigenvectors at the characteristic frequencies. The intersection of the quadratic curve with the boundaries gives the transformation matrix **T**.[24,25] The 1399- and 1207-cm^{-1} bands were our initial choice for characteristic bands as they were the minimum and maximum, respectively, in the product spectrum. However, this produced negative absorbances in the pure-component spectra. Therefore the secondary minimum at 1293 cm^{-1} was employed. The other charateristic point was obtained by trying values near 1207 cm^{-1} until acceptable absorbance values were obtained for the pure components. This occurred at a characteristic point of 1214 cm^{-1}.

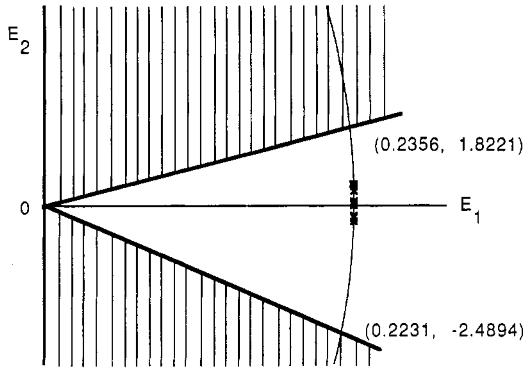

Figure 3. Plot of "real" eigenvector pairs and the boundary lines for the annealed 75/25 VDF/TrFE copolymer system.

The pure-component spectra are shown in Figure 4. The spectroscopic features obtained from such a factor analysis are consistent with our expectations. The crystalline bands are narrow and well defined. The breadth of the amorphous-phase bands reflects the wide distribution of conformations present. From our previous results, we can conclude that the pure-component spectra 1 and 2 correspond to that of pure amorphous (disordered) phase and pure crystalline (ordered) phase, respectively. Previous studies[29,30] have suggested crystalline bands representing the β phase of PVDF to be at 1278, 1185, 1074, 882, and 842 cm^{-1}. In the pure crystalline spectra we find bands at 1293, 1181, 1076, 884, and 848 cm^{-1}. The 1181-, 1124-, and 1075-cm^{-1} bands for the pure crystalline phase overlap with the broad disordered-phase bands in this region and cannot be used to measure sample crystallinity. Although the 1124-cm^{-1} band is a true crystalline band, its intensity in the annealed sample spectrum decreased with increasing crystallinity because the intensity decrease for the disordered-phase band at 1120 cm^{-1} was much greater. Several bands are unique to the crystalline-phase spectrum. The intense 1399-cm^{-1} band overlaps with a relatively weak disordered-phase band, while the 1293-cm^{-1} band, assigned to sequences of four or more trans isomers,[3,6,14] does not overlap with any disordered-phase band. Thus these two bands show large intensity increases with increasing crystallinity. There are also bands that are characteristic of trans sequence length. These are found at 1293 and 848 cm^{-1}. One of the bands we found to be associated with the crystalline component at 848 cm^{-1} has been assigned to be associated with trans sequences longer than three or more units.[3,6,14] The infrared spectrum shown in Figure 1a does not show any features clearly assignable to the amorphous phase except the 1247-cm^{-1} shoulder. A similar band at 1230 cm^{-1} in PVDF has been observed by Cortili and Zerbi and by Kobayashi et al. and is thought to be associated with amorphous regions.[31,32] One of many amorphous

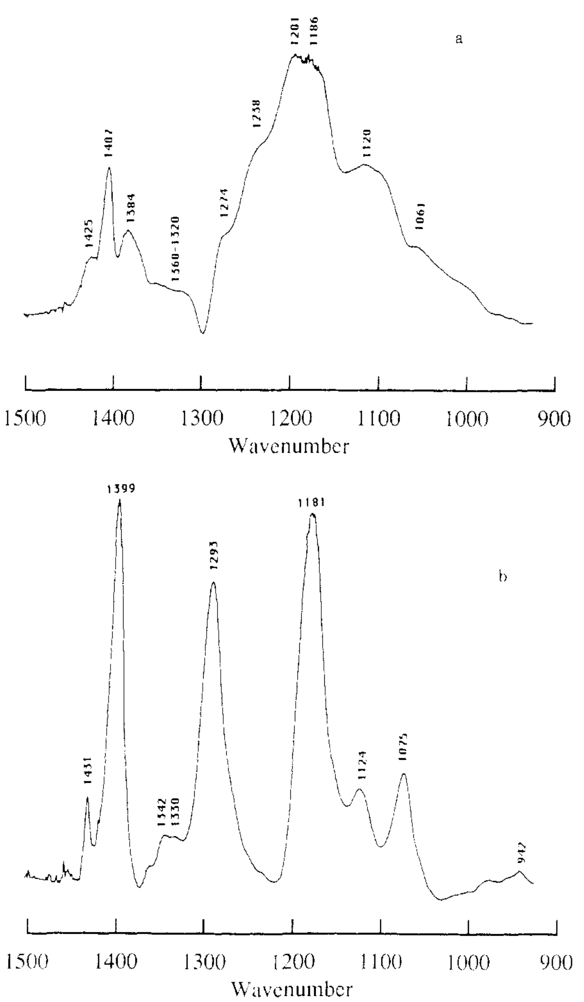

Figure 4. Extracted pure-component spectra from the annealed 75/25 VDF/TrFE copolymer system. (a) pure 1 (=0.2356 × eigenspectrum 1 + 1.8221 × eigenspectrum 2):pure amorphous phase; (b) pure 2 (=0.2231 × eigenspectrum 1 − 2.4894 × eigenspectrum 2):pure crystalline phase.

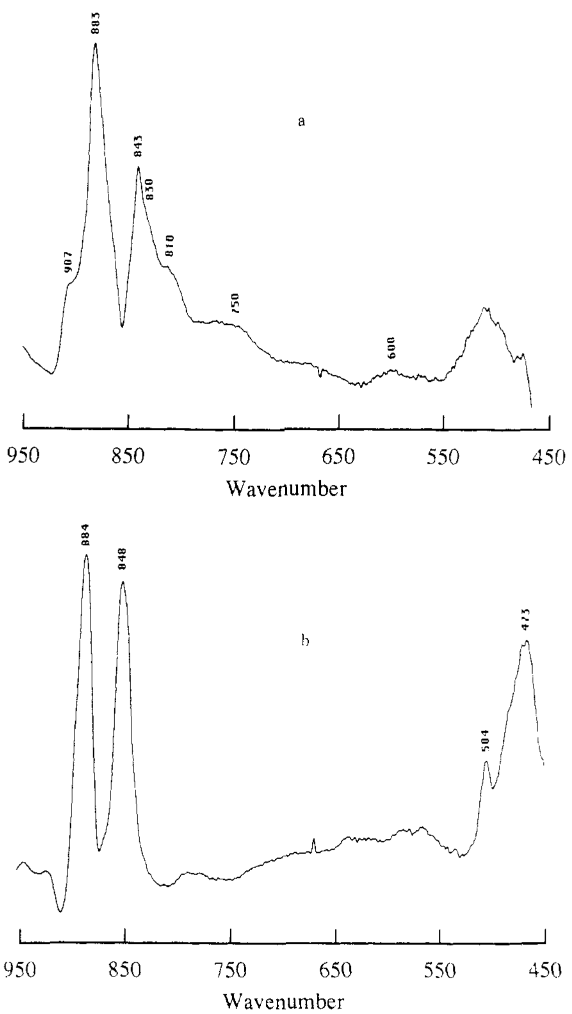

Figure 5. Difference spectra: (a) isolated amorphous phase, cast film spectrum minus the spectrum of the film annealed at 154 °C for 3 h; (b) isolated crystalline phase, the spectrum of the film annealed at 154 °C for 3 h minus the spectrum of the cast film.

bands found by the factor analysis, the 1238-cm^{-1} band, is consistent with the assignment of the 1230-cm^{-1} peak.[31,33] Other new amorphous bands found here have never been reported. For the first time a full spectrum representing the disordered phase has been found.

From the factor analysis results, the 1293-cm^{-1} peak and the 1214-cm^{-1} shoulder band have been found to be nonoverlapped characteristic bands for the pure crystalline and pure amorphous phase, respectively. When reference peaks for two components are known, the pure-component spectra can also be obtained by spectral subtraction. The spectrum of the as-cast film containing the lowest degree of crystallinity was subtracted from the spectrum of the film annealed at 154 °C for 3 h with the criterion being to remove the contribution from the 1214-cm^{-1} amorphous shoulder. Similarly, the pure amorphous spectrum was obtained by subtracting the highly crystalline sample spectrum from the less crystalline, reducing the 1293-cm^{-1} band to the baseline. These deconvoluted spectra are shown in Figure 5. The isolated amorphous- and crystalline-phase spectra in the 1500–925-cm^{-1} range obtained by spectral subtraction are nearly identical with those obtained from factor analysis.

In the region 925–400 cm^{-1} there were no nonoverlapped peaks characteristic of the two phases, and therefore factor analysis could not be applied. However, the crystalline and amorphous bands in this range could be obtained from spectral subtraction by using the two reference bands previously mentioned. The 884-, 848-, 504-, and 472-cm^{-1} bands are crystalline-phase bands, while those at 907 (sh), 883, 843, 830 (sh), 810 (sh), 750, 600, and 515 cm^{-1} represent amorphous structure. The presence of the 843- and 810-cm^{-1} bands in the isolated amorphous phase at room temperature suggests that there is a significant amount of sequences of three or four trans isomers in the amorphous phase, since the 844- and 811-cm^{-1} peaks can be assigned to sequences of three or more trans units and T_3G or T_3G' isomers, respectively,[14,16] and the absence of the 1293-cm^{-1} band suggests the absence of sequences of five or more trans isomers. The crystalline bands at 884 and 848 cm^{-1} overlap with the amorphous bands found at 883 and 843 cm^{-1}. Although spectra of the amorphous and crystalline phases for the copolymer have not previously been reported, bands have been assigned to specific conformations by Kobayashi et al.,[3,6,14,16] based on the normal coordinate analyses of α-, β-, and γ-phase PVDF.[29,32] Our results are consistent with their findings. Band assignments for the copolymer are listed in Table II.

By use of the transformation matrix **T** and "real" eigenvector matrix **E**′, the crystalline phase content in the annealed sample can be calculated from eq 8. Figure 6 shows a plot of crystalline-phase content versus annealing temperature. The amount of crystalline phase remains essentially unchanged below 110 °C, increases significantly in the range 112–128 °C, which is equal to the Curie transition range of this copolymer, and then levels off at

Table II
Band Assignments of a 75/25 VDF/TrFE Copolymer

obsd freq[c]	species	approx normal mode assignt	phase[a] ordered	phase[a] disordered	obsd freq in semicrystalline sample	sensitivity to crystallinity[b]	chain conformation	ref
1431	A1	$\delta_s(CH_2)$	++		1431	↑		29, 30, 32
1425				++	buried			
1407				+++	buried			
1399	B1	$\omega(CH_2) + \nu_a(CC)$	+++++		1401	↑↑↑		29, 30, 32
1384			++		buried			
1360–1320			+	+	1343	→		
1293	B2	$\nu_a(CF_2) + r(CF_2) + r(CH_2)$	++++		1284–1291	↑↑↑	t_m ($m > 4$)	32
	A1	$\nu_s(CF_2) + \nu_s(CC) + \delta_s(CCC)$				(shift to higher frequency)		29, 30
1274[sh]				++	buried			
1238[sh]				+++	1247	↓		
1201[br]				++++	buried			
1186[br]			++++	buried				
1181	A1	$\delta_s(CCC) + \nu_s(CF_2) + \nu_s(CC)$						32
	B2	$\nu_a(CF_2) + r(CF_2) + r(CH_2)$	++++		1183	→ (sharper)		29, 30
1124			+		1124	↓ (sharper)		
1120[br]				+++	buried			
1075	B1	$\nu_a(CC) + \omega(CH_2) + \omega(CF_2)$	++		1076	↑ (sharper)	t	29, 30, 32
1061[br]			++		buried			
942			+		945	→		
907[sh]				++	buried			
884	B2	$r(CH_2) + \nu_a(CF_2) + r(CF_2)$	++++	++	884	↑	t	29
	A1	$\nu_s(CF_2)$						30, 32, 33
848	A1	$\nu_s(CF_2) + \nu_s(CC)$	+++		848,844	↑↑	t_m ($m > 3$)	29
	B2	$r(CH_2) + \nu_a(CF_2)$						30, 32, 33
843				++	buried			
830[sh]				+	buried			
810[sh]				+	buried			
750				+	buried			
600				+	buried			
515				+	buried			
504	A1	$\delta_s(CF_2)$	++		505	↑		29, 30, 32, 33
		F_3 unit						11
473	B1	$\omega(CF_2)$	++		473	↑		31, 32

[a] +, very weak intensity; ++, weak intensity; +++, medium intensity; ++++, strong intensity; +++++, very strong intensity. [b] →, very small increase; ↓, small decrease; ↑, small increase; ↑↑, medium increase; ↑↑↑, large increase. [c] sh, shoulder; br, broad.

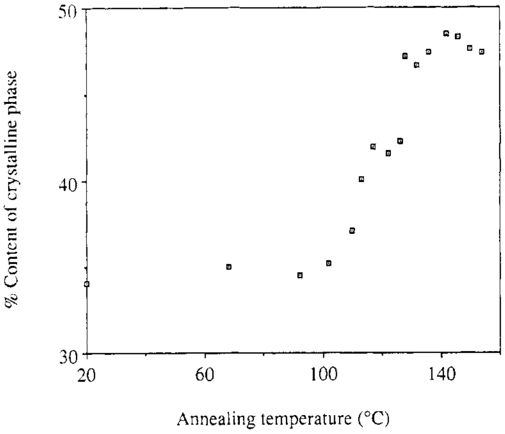

Figure 6. Changes in the content of crystalline phase with annealing temperature.

higher annealing temperatures. The overall trend representing the increase in the degree of crystallinity with annealing temperature is similar to that seen in previous studies, although the degree of crystallinity determined from our spectroscopic method is somewhat lower than that determined from X-ray diffraction.[2,34] The sigmoidal behavior observed is unusual, a characteristic only expected for polymers with a solid–solid crystal-phase transition.

During this phase transition, polarization is lost through an order–disorder transition and the material becomes paraelectric. Recent studies have suggested these copolymers, which have an all-trans conformation in the ferroelectric phase, transform to a paraelectric phase consisting of a statistical combination of TG, TG′, T_3G, and T_3G' isomers packed in a disordered lattice.[3,6,14,16] Therefore the Curie transition must involve significant increases in chain mobility. NMR relaxation data show that both amorphous and crystalline regions show an increase in mobility at the transition, thus increasing the content of paraelectric crystalline phase.[35] Cooling after annealing above the Curie temperature converts paraelectric crystallites into ferroelectric crystallites. In this case, more paraelectric crystalline phase produces more ferroelectric crystalline phase. Therefore annealing at or above the Curie temperature results in an increase of the ferroelectric crystalline phase at room temperature. In addition to the crystallization of the amorphous phase, annealing increases the size and positional order of crystalline domains as well as removing crystalline defects. The reduction of conformation defects produces the narrow crystal-phase bands observed.

Phase Transition. For VDF/TrFE copolymers containing more than 55% VDF, a clear Curie transition has been observed by X-ray diffraction, vibrational spectroscopy, and thermal analysis.[2–4,6–16] Lovinger has suggested that the Curie transition is caused by intramolecular changes through the introduction of *G* and *G′* conformations into the all-trans structure, with an increase in the size of the crystal lattice.[12] However, the spectra of the pure crystalline ferroelectric and paraelectric phases have not been reported. In Figure 7, the infrared spectra of a

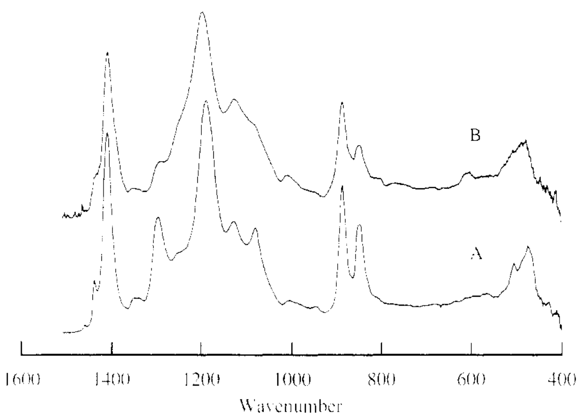

Figure 7. Infrared spectra of 75/25 VDF/TrFE copolymer film as a function of temperature: (a) 25 °C; (b) 135 °C.

75/25 copolymer film at room temperature and at 135 °C are shown. This temperature is above the Curie temperature and below the melting point of 155 °C. As we have previously observed at 135 °C, bands assigned to trans isomers, 1431, 1401, 1290, 1076, 884, and 844 cm^{-1}, decreased greatly in intensity. Bands characteristic of the α-phase PVDF, 800 and 602 cm^{-1}, appeared above the Curie temperature. These bands were not as intense or sharp as they appear in α-phase PVDF. Also bands sensitive to sequences of three or more trans units were still present above the Curie temperature. This suggests that the chain conformation of the paraelectric phase is not as regular as that of α-phase PVDF and that some trans sequences still exist. These conclusions are supported by the Raman data of Tashiro et al. in which they conclude that the high-temperature phase consists of TGTG′ sequences with some TT isomers remaining.[15,16]

In this study, 19 spectra were recorded during a heating and cooling cycle and analyzed by factor analysis in order to separate spectral features of the high- and low-temperature phases. The 1500–925- and 925–400-cm^{-1} regions were again chosen for analysis, which was performed as described in the previous section. The extracted pure high-temperature-phase spectrum obtained from factor analysis of spectra obtained at different temperatures is shown in Figure 8. The high-temperature-phase spectrum in the 1500–925 cm^{-1} range is similar to the pure amorphous-phase spectrum at room temperature shown in Figure 4a. Bands at 1274, 1238, and 1201 cm^{-1} present in the amorphous phase at room temperature disappear in the high-temperature disordered phase, while the 1425, 1407, and 1384-cm^{-1} bands appear as a single peak at 1399-cm^{-1} in the high-temperature-phase spectrum. In the 925–400-cm^{-1} region the high-temperature-phase spectrum differs greatly from that of the isolated amorphous phase shown in Figure 5a. The 884-, 843-, 810-, and 515-cm^{-1} bands in the isolated disordered phase disappear in the high-temperature phase and bands at 876, 800, 762, 615, 602, 523, and 489 cm^{-1} appear. The disappearance of bands at 843 and 810 cm^{-1} and the appearance of the 800- and 602-cm^{-1} bands in the high-temperature-phase spectrum suggest that long trans sequences are no longer present in the high-temperature phase, but only the TG or TG′ sequences seen in α-phase PVDF exist. There is some amorphous phase present, which will contribute to the high-temperature-phase spectrum. However, it is impossible to distinguish between amorphous and paraelectric crystalline phases at high temperature. The low-temperature-phase spectrum is nearly identical with the room temperature crystalline phase spectrum over the entire frequency range studied.

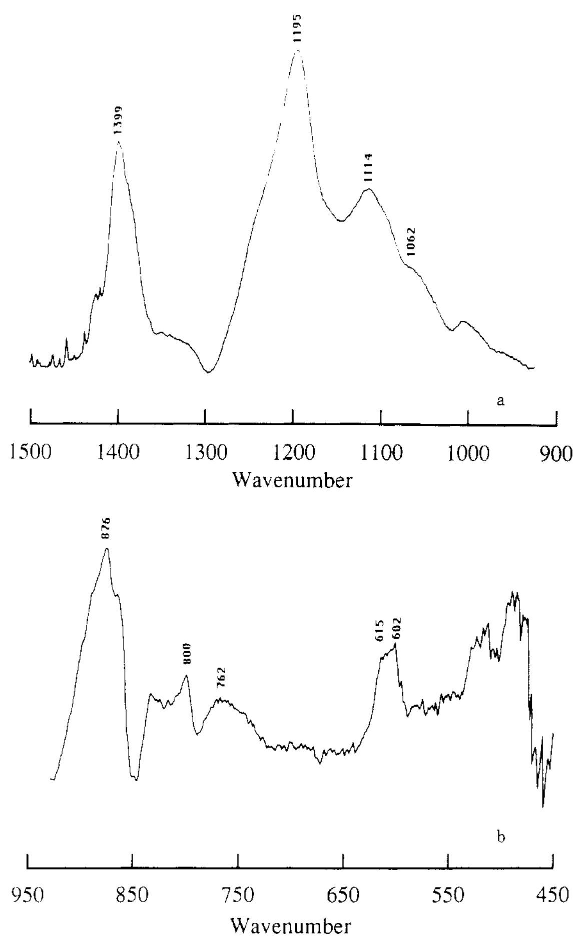

Figure 8. Extracted pure high-temperature-phase spectra from the spectra of 75/25 VDF/TrFE copolymer at different temperatures upon heating and cooling: (a) 1500–900 cm^{-1}; (b) 950–450 cm^{-1}.

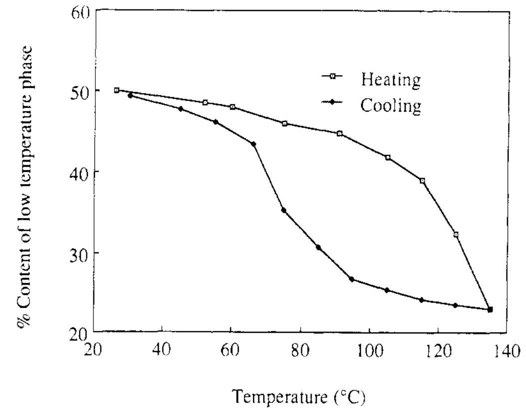

Figure 9. Temperature dependence of the content of low-temperature phase for 75/25 VDF/TrFE copolymer.

The variation in low-temperature phase with temperature is shown in Figure 9. The transition from the low-temperature phase to the high-temperature phase and its hysteresis have been observed. This is consistent with the X-ray, infrared, and Raman results of Lovinger et al.[12] and Tashiro et al.[6] for a 72/28 copolymer. The phase transition is observed to be reversible, although thermal hysteresis exists, with the transition occurring at 116 and 84 °C on heating and cooling, respectively. The hysteresis curve is similar to those of infrared and Raman intensities of conformation-sensitive bands.[6,16] The phase-transition temperatures observed in this study are nearly equal to those shown in the previous DSC measurements.[9]

Conclusions

The microstructure of the amorphous and crystalline regions of a 75 mol % VDF–25 mol % TrFE copolymer has been studied by infrared spectroscopy. Samples of differing degree of crystallinity were analyzed by factor analysis in order to separate the spectra of the amorphous and crystalline phases. Features associated with each phase have been clearly identified. The crystalline phase spectra show sharp bands at frequencies that agree with previous assignments, while the amorphous-phase spectrum shows broad bands as expected, with a substantial amount of short trans sequences present. Many amorphous-phase bands overlap with the crystalline-phase bands. Spectral subtraction was performed for comparison, with the reference bands determined from the cross product of the eigenspectra, and virtually identical results were obtained. The amount of crystal phase was determined as a function of annealing temperature and was constant below 112°, but underwent a large increase in the Curie transition region. Therefore the mobility of the amorphous phase is significantly increased at the Curie transition to allow crystallization and the significant loss of the intermolecular interaction in the crystalline lattice also facilitates the reorganization of the paraelectric crystalline phase formed in the early stage.

The factor analysis technique was also applied to spectra collected at different temperatures in order to isolate spectra of the pure high- and low-temperature phases. The low-temperature-phase spectrum was nearly identical with that of the pure crystalline phase at room temperature. The spectrum of the high-temperature phase was similar to that for the amorphous phase, although bands were broader due to the effect of temperature. In the 925–400-cm^{-1} region, the high-temperature-phase spectrum differed from that of the amorphous and suggests that fewer long trans sequences exist above the Curie temperature, with TG and TG′ sequences present as in α-phase PVDF. The transition between the high- and low-temperature phases was monitored and a hysteresis was observed similar to that seen from infrared and Raman intensities of conformation-sensitive bands.

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