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Infrared Spectra of Amorphous and Crystalline Poly(tetrafluoroethylene)

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ABSTRACT: Infrared spectra for the crystalline and amorphous phases in poly(tetrafluoroethylene) were derived from spectra obtained by attenuated total reflectance from a series of samples covering a wide range of crystallinity as determined by differential scanning calorimetry. The data were treated by two-component factor analysis, which is equivalent to extrapolating a linear relationship between the normalized absorbance at each wavelength and the crystallinity. Groups of bands at 700-800 and 1400-1800 cm^{-1} are peculiar to the noncrystalline spectrum. While there are no easily separated crystalline bands, peaks at 502, 556, and 626 cm^{-1} are more prominent in the crystalline spectrum.

Introduction

It has long been known that the infrared spectrum of poly(tetrafluoroethylene) (PTFE) depends on the degree of crystallinity.[1] Several bands at 700-850 and 384 cm^{-1} decrease with increasing crystallinity. The absorbance at 778 cm^{-1} extrapolates to zero at the density of the crystalline unit cell.[2] Moynihan[2] based a method for determining crystallinity on the ratio between the absorbances at 778 cm and 2367 cm^{-1}. The objective of the present study was to determine the spectra of the pure crystal and amorphous phases.

Experimental Section

As polymerized, PTFE has a much higher degree of crystallinity than after recrystallizing from the melt. The crystallinity depends inversely on the rate of cooling and the molecular weight. A series of samples was prepared covering a wide range of crystallinity as determined from the heat of fusion.

Three resins were used in this study. Sample 1 was an experimental granular homopolymer of relatively low molecular weight noted for its ability to form void-free moldings. This polymer was used in our determination of the amorphous density of PTFE from the relationship between the heat of fusion and the specific volume.[3] Sample 2 was a standard, high molecular weight, granular homopolymer. Sample 3 was a granular resin containing 0.1% perfluoropropyl vinyl ether by weight. Each of these polymers was formed into bars 5 in. × $^{1}/_{2}$ in. × $^{1}/_{16}$ in. and specimens of each were given three thermal histories: preform (PF), made by compression molding virgin, unmelted polymer at room temperature: slow cooled (SC), cooled from the melt at 1 °C/min; and quenched (Q), cooled directly from the melt with dry ice. The heats of fusion for each of these nine samples are given in Table I. The percent crystallinity values were based on the value of 22.2 cal/g for the heat of fusion of the pure crystal determined by the use of the Clapeyron equation.[4] Conversions to volume percent were based on an amorphous density of 2.060 g/cm^3 and a crystalline density of 2.302 g/cm^3.

Infrared spectra were obtained by attenuated total reflection (ATR) with a Nicolet 7199 FTIR spectrometer. Data were obtained at a nominal 2-cm^{-1} resolution by using a weak apodization function,[5] and 64K data points were used in the Fourier transformation. Two hundred fifty-six interferograms were added to improve the signal-to-noise ratio. An Infrared Associates broad-band MCT detector was used in this study. A Harrick TMPRA variable-angle ATR attachment was used at an incident angle of 45°, and KRS-5 plates cut at 45° were used for the internal reflection elements.

The temperature of the samples in the spectrometer was 24 ± 1 °C. Thus, the polymer was in crystal phase IV, which lies between transitions around 19 and 30 °C.[1] At this temperature, the unit cell is hexagonal, and the conformation of the chains is a 15/7 helix.

Table I
Crystallinity of Samples of PTFE for Infrared Studies

		% crystallinity	
sample	ΔH_f, cal/g	by wt	by vol
1 PF	17.3 ± 0.7	78 ± 3	76
1 SC	10.5 ± 0.2	47 ± 1	45
1 Q	7.0 ± 0.1	32 ± 2	30
2 PF	19.3 ± 1.1	87 ± 5	86
2 SC	7.9 ± 0.3	36 ± 1	34
2 Q	6.9 ± 0.2	31 ± 1	29
3 PF	16.4 ± 0.4	74 ± 2	72
3 SC	10.0 ± 0.1	45 ± 0.3	42
3 Q	8.1 ± 0.1	36 ± 0.5	34

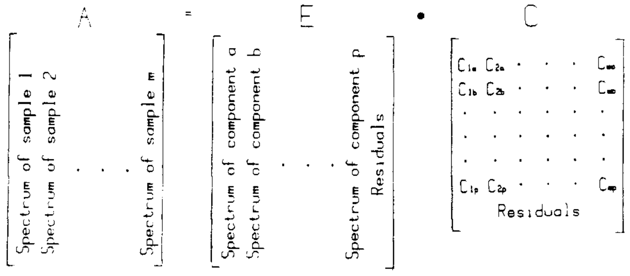
Statistical Analysis of FTIR Data

The raw interferograms were transmitted to a DEC-10 central computer and reprocessed. The base line for each spectrum was established by subtracting the minimum absorbance. The spectra were normalized on the peak absorbance in the 1150-1200-cm^{-1} range. Earlier work indicated that the bands in these regions are insensitive to percent crystallinity.[2] Factor analysis was applied to the full spectrum (400-4000 cm^{-1}) and to the region 400-2400 cm^{-1}. In each case, eigenvalue analysis indicated that the data could be adequately described by a two-component model, i.e., crystalline and amorphous phases. Inspection of the spectra indicated varying intensities of probable CH stretching modes at ca. 2900 cm^{-1}. As there were no hydrocarbon-containing species in the polymerization and isolation of the polymers, we attribute these vibrations to adventitious impurities incorporated in or on the surface of the specimens during sample preparation and handling.

For factor analysis, an *n* (absorbances) by *m* (samples) matrix, **A**, was formed from the absorbance vectors of the spectra. Assuming linearity (Beer's law), the basic factor analysis equation is

$$\mathbf{A} = \mathbf{E}\mathbf{C} \tag{1}$$

when **E** is the *n* row by *m* column absorptivity matrix, and **C** is *m* row by *n* column concentration matrix.



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In general, **E** and **C** are unknown. The purpose of the analysis is to obtain the absorptivity matrix, **E**, and concentration matrix, **C**, from **A**.

The first step in the analysis is to determine p, the apparent number of components contributing to the spectrum. This is accomplished by estimating the rank of **A**, i.e., the number of **A** columns needed to represent adequately the information in **A**. The matrices **A** and **C** may be determined to within a full-rank linear transformation **T** as follows:

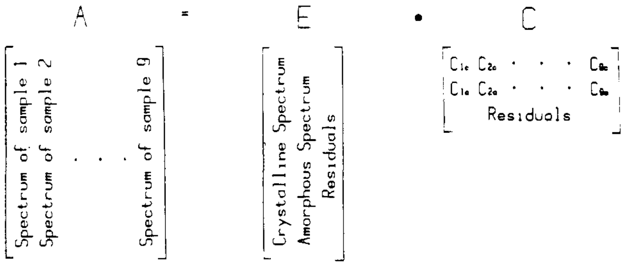
$$\mathbf{A} = \mathbf{EC}$$

$$\mathbf{A} = (\mathbf{ET})(\mathbf{T}^{-1}\mathbf{C})$$

$$\mathbf{A} = \boldsymbol{EC} \qquad (2)$$

Direct reduction of **A** to upper right triangular form reveals the rank of p.[6] Equivalent procedures have been described by others.[7,8]

The rank of **A** ($=p$) should be less than the number of samples. If not, more data are required, the problem is significantly nonlinear, or each data column is uniquely independent. Application of this procedure to the infrared data indicated that the system was linear and adequately described by $p = 2$ within statistical error. Thus, solution of eq 1 will give a 2-column by n-row absorptivity matrix and an n-column by 2-row concentration matrix, with $(m - p)$ columns of residual errors in **E** and $(m - p)$ rows of residual errors in **C**.



It is important to stress that **E** and **C** in the above analysis are not unique. Procedures have been developed to generate physically or chemically meaningful results, e.g., "target factor analysis".[7] In all cases, appropriate constraints and/or additional data are required.

If **E** or **C** are known, the unknown matrix can be calculated by standard statistical regression techniques, namely

$$\text{C known:} \quad \mathbf{E} = \mathbf{AC}'(\mathbf{CC}')^{-1} \qquad (3)$$

$$\text{E known:} \quad \mathbf{C} = (\mathbf{E}'\mathbf{E})^{-1}\mathbf{E}'\mathbf{A} \qquad (4)$$

If necessary, the fit can be improved by alternately calculating **E** and **C** until improvement in the estimates on successive iterations becomes insignificant.

In this work, the DSC data provided good estimates of crystallinity. A **C** matrix was generated from the volume percent crystallinities of the nine samples. The **E** matrix was then calculated by eq 3. Analysis of the residuals indicated that no significant improvement would follow from iterative application of eq 3 and 4.

The pure-crystalline- and -amorphous-phase spectra were then calculated by multiplying the corresponding absorptivity vectors by 100%. This procedure is equivalent to assuming that the absorbance at each frequency varies linearly with volume percent crystallinity and extrapolating the data to 0 and 100% crystallinity to obtain the amorphous- and crystalline-phase spectra. These pure-phase spectra are shown in Figures 1 and 2, with linear and logarithmic absorbance scales, respectively.

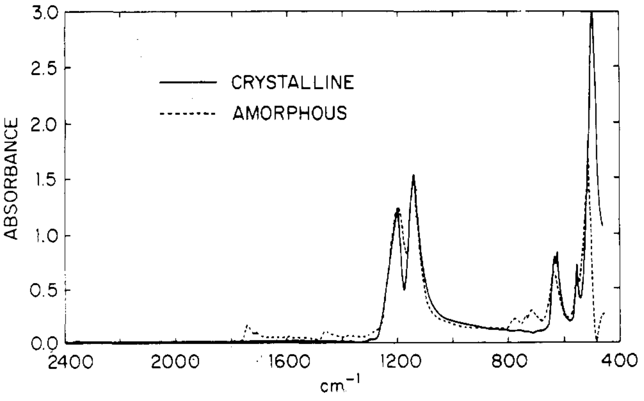


Figure 1. Infrared spectra: linear scale.

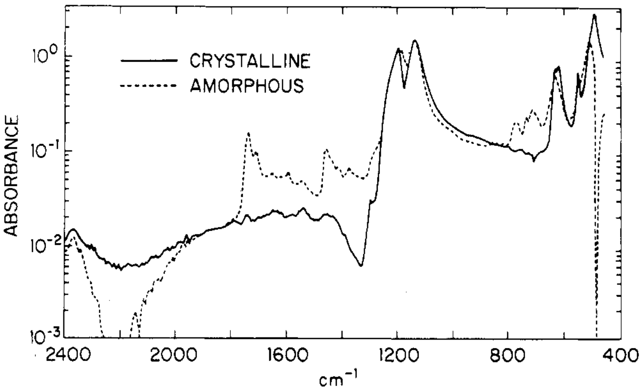


Figure 2. Infrared spectra: logarithmic scale.

The probable error introduced by the normalization procedure can be estimated by comparing the absorbances at 2367 cm^{-1} in Figure 2. Moynihan stated that the absorbance of this band is independent of crystallinity. In Figure 2, the absorbance of this band is about 25% higher in the crystalline spectrum than in the amorphous spectrum. Use of the "thickness" band at 553 cm^{-1} discussed by Vanni and Rabolt[9] would lead to a similar correction. This does not have a major impact on the assignment of the various bands to the two phases.

Amorphous Bands

It has long been recognized that a group of bands between 700 and 800 cm^{-1} are associated with the amorphous phase.[2,10,11] The band at 778 cm^{-1} is the basis for a standard infrared method for the determination of crystallinity.[2] The spectra in Figures 1 and 2 confirm that these bands are absent in the crystalline phase. In addition, we find a set of even weaker noncrystalline bands at 1400–1800 cm^{-1}.

There is a strong correlation between bands attributed to hydrocarbon and those of amorphous PTFE, and it was not possible to make a meaningful separation of the spectra in terms of three components. Bands near 1460, 1375, and 720 cm^{-1} have absorbances in a reasonable proportion to those near 2900 cm^{-1} for hydrocarbons. Vanni and Rabolt[9] attributed bands near 1800 cm^{-1} to carboxyl end groups and found bands near 1400 cm^{-1} in irradiated PTFE. While our samples were not irradiated, we did observe a number of bands in this region which were absent in the crystalline spectrum.

Our extrapolated amorphous spectrum is strongly influenced by the properties of the quenched samples. X-ray studies[12] have shown that quenching produces a high degree of planar orientation in the surface layer with the polymer chains parallel to the quenched surface. In ATR spectra from oriented samples, the relative absorbance of

Table II
Assignment of Infrared Peaks

our observns		Cutler et al.[15]				
ν, cm^{-1}	phase	ν, cm^{-1}	pol	branch	descrip	symmetry
1201 ± 2	C, A	1213	$\perp$	B_1	sym CF_2 str	E_1
1144 ± 3	C, A	1154	$\perp$	B_2	asym CF_2 str	E_1
		1154	$\perp$	B_3	CC str	E_1
784 ± 2	A					
776 ± 4	A					
742 ± 3	A	746		B_3	CC str	E_2
		735		B_3	CC str	A_1
721 ± 2	A				hydrocarbon	
639 ± 2	C, A	642	$\parallel$	B_4	CF_2 rock	A_2
626 ± 2	C				helix reversal (Brown)	
556 ± 2	C	555	$\perp$	B_4	CF_2 rock	E_1
514	A	516	$\perp$	B_5	CF_2 wag	E_1
502	C	502	$\parallel$	B_5	CF_2 wag	A_2

the bands may be affected even if the spectrometer radiation is unpolarized.

One can speculate about the nature of the amorphous bands. One possibility is that they are associated with conformations other than the 15/7 helix which occurs in the crystal above 19 °C. This was considered by Zerbi and Sacchi,[13] who concluded that, unlike the case of polyethylene, the spectrum of PTFE is not greatly changed by conformational variations. They did state the "helix reversal" band 626 cm^{-1}[14] could be assigned to a planar zigzag, but this is clearly a crystalline feature. The band at 776 cm^{-1} could possibly be associated with a gauche conformation.

Another possibility is that the amorphous bands are normally Raman-active modes that appear in the infrared through a lifting of the selection rules. As indicated in Table II, it seems possible that the amorphous band at 742 cm^{-1} is related to Raman-active bands at 746 and 735 cm^{-1}.[15] These possibilities could be explored further through a study of the far-infrared beyond the limit of the ATR.

Crystalline Bands

In common with earlier studies, we do not see any uniquely crystalline bands that can readily be separated from neighboring bands for quantitative work. There are, however, several features that are more prominent in the crystalline spectrum. The strongest band in the crystalline spectrum is at 502 cm^{-1} and appears to shift toward higher frequencies with decreasing crystallinity, reaching a limiting value of about 514 cm^{-1} in the amorphous spectrum. Masetti et al.[16] reported a similar contrast between the virgin powder and a film. There is a sharply defined band at 556 cm^{-1} in the crystalline spectrum, which is reduced to a shoulder in the amorphous spectrum. This is also true of the band at 526 cm^{-1}, which has been associated with helix reversals by Brown.[14]

A number of papers have discussed the assignments of the bands in the infrared and Raman spectra of PTFE.[2,10,15–17] The status of this subject has recently been summarized by Cutler and co-workers.[15] The peaks in our spectra are related to these assignments in Table II. The strong peaks near 1200 and 1150 cm^{-1}, which are believed to be independent of crystallinity, are assigned to symmetric and asymmetric CF_2 stretch and CC stretch. All have perpendicular polarization. The band at 556 cm^{-1}, which was more prominent in the crystalline spectrum, is assigned to a CF_2 rocking mode. The amorphous band at 514 cm^{-1} and the crystalline band at 502 cm^{-1} are both assigned to CF_2 wagging modes with perpendicular and parallel polarizations, respectively.

We did not observe the band at 1242 cm^{-1}, which has been discussed in several papers.[2,10,15–17] This peak has been assigned to an asymmetric CF_2 stretch with A_2 symmetry.[15] Moynihan[2] has already reported that it is not observed by reflection. It may, however, be present as a shoulder on the 1201-cm^{-1} peak in Figure 2.

Conclusions

With the approach taken here, it has been possible to arrive at a good idea of the infrared spectra of the pure crystalline and amorphous phases. Use of a transmission technique would have avoided some of the uncertainties associated with the normalization procedure, but it is more difficult to prepare very thin samples covering a wide range of crystallinity. It would be desirable to extend the study into the far-infrared, where many important bands occur in poly(tetrafluoroethylene) and amorphous bands have been identified at 384[2,18] and 277 cm^{-1}.[18]

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