

Fourier-Transform Infrared Study of Uniaxially Oriented Polytetrafluoroethylene

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Synopsis

Infrared measurements of the dichroic ratio of polytetrafluoroethylene absorption bands provide a valuable method of determination of the orientation of chains as well in crystalline regions as in amorphous ones. The 1452 cm^{-1} , 1545 cm^{-1} , and 2362 cm^{-1} combination bands are convenient for measuring crystalline orientation while the 703 cm^{-1} , 740 cm^{-1} , and 786 cm^{-1} bands lead to amorphous orientation. The 1795 cm^{-1} (crystalline), 720 cm^{-1} , and 774 cm^{-1} (amorphous) absorption bands are shown to be complex ones and thereby unusable for measuring orientation.

INTRODUCTION

Polytetrafluoroethylene (PTFE) has proved to be an outstanding material of great importance. Results from different fields of research have led to a better understanding of its structure and its mechanical and thermal behavior. This polymer owes its remarkable properties to the stability of the C—F bond and the high electron negativity value of fluorine. Among its unusual properties are its very high melting point, extreme resistance to solvents and corrosive agents, unique nonadhesion, and very low coefficient of friction. A summary of its physical and chemical properties has already been given by Sperati and Starkweather.¹

While this polymer offers an immense technological interest, special techniques of processing are required since it is not possible to process the polymer by conventional extrusion or injection molding because of its high melt viscosity. One of the techniques employed consists of compacting the powder of this polymer and calendering into sintered or unsintered films. The quality of the film depends on the temperature of the rollers and the velocity at which they turn. These two factors determine the extent of crystallinity and introduce an orientation in the final product, giving it directional characteristics.

The orientation results in an anisotropy in the physical properties of the material and enhances its mechanical resistance in certain direction. A study of such an orientation in terms of the deformation will be a good help for optimizing the processing conditions to obtain products of various qualities. Wecker et al.,^{2,3} having investigated the mechanism of orientation of the crystallites in PTFE films under uniaxial deformation by X-ray diffraction, found that the crystallites undergo plastic deformation and that the axis of the chains orient to the draw direction. Davidson et al.^{4,5} have studied the orientation in the crystalline and amorphous phases of PTFE films under uniaxial deformation by IR dichroism and NMR. They obtained different values of orientation function from different

fundamental absorption bands. In the following study we look for other possibilities for measuring orientation in commercial films of PTFE by IR dichroism and compare the results with those obtained by the above-mentioned authors.

THEORETICAL BACKGROUND

Although the use of vibrational spectroscopy to measure orientation in a polymer was recently reviewed,⁶ it is worthwhile to sum up briefly the information available from infrared dichroism measurements. The orientation of a single unit of a polymer chain can be described by the three Eulerian angles θ , ϕ , and ψ , which define the three rotations required to bring into coincidence a set of Cartesian axes in the unit with a reference set of Cartesian axes in the oriented polymer. The orientation is then described by an orientation distribution function $f(\theta, \phi, \psi)$.⁷ In the case of uniaxially oriented systems the orientation distribution of structural units is random with respect to ϕ and ψ and the orientation distribution function can be expressed as

$$f(\theta) = \sum_{n=0}^{\infty} (n + 1/2) \langle P_n(\cos \theta) \rangle_{\text{av}} P_n(\cos \theta)$$

where $P_n(\cos \theta)$ are the Legendre polynomials:

$$P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2,$$

$$P_4(\cos \theta) = (35 \cos^4 \theta - 3 \cos^2 \theta + 3)/8, \quad \text{etc.}$$

As far as IR spectroscopy is concerned, the dichroic ratio $R = A_{\parallel}/A_{\perp}$ (A_{\parallel} and A_{\perp} being the measured absorbance for electric vector parallel and perpendicular, respectively, to the draw direction) is related to the second-order moment of the orientation function $\langle P_2(\cos \theta) \rangle_{\text{av}}$ by

$$\langle P_2(\cos \theta) \rangle_{\text{av}} = (3 \langle \cos^2 \theta \rangle_{\text{av}} - 1)/2 = \frac{R - 1}{R + 2} \cdot \frac{R_0 + 2}{R_0 - 1}$$

where $R_0 = 2 \cot^2 \alpha$, α being the angle between the dipole moment vector M and the chain axis, and θ is the angle between the chain axis and the draw direction. The angle α can usually be determined from theoretical considerations⁸ and dichroic ratio measurements allow the calculation of $\langle P_2(\cos \theta) \rangle_{\text{av}}$. Alternatively, if the value of the second-order moment is known by using either another method of measurement or a well-assigned absorption band, the orientation of the dipole moment vector relative to the chain axis can be determined for any other absorption band.

VIBRATIONAL SPECTRUM AND STRUCTURE OF PTFE

The use of vibrational spectra to determine the second-order moment of the orientation function requires a reliable assignment of absorption bands. Many studies indicate that PTFE is highly crystalline.⁹⁻¹⁵ A 13/6 helical structure was proposed by Bunn and Howells¹⁶ and recognized as the most stable conformation for this polymer.¹⁷⁻²⁰ PTFE undergoes a phase transition at 19°C. Recently Zerbi et al.^{21,22} have shown that this transition is characterized by an increase of the amount of all trans conformations (2/1 helix) with respect to the

13/6 helices, with no change in the lattice structure. As far as amorphous regions are concerned, it seems that they are constituted of chains with different conformational structures (2/1, 10/3, 4/1 helices).²²

Few fundamental absorption bands are expected in the IR spectrum of PTFE. The 13/6 helix belongs to the dihedral point group D_{13} with $4A_1$, $3A_2$, $8E_1$, and $9E_2$ vibrational modes. Only the A_2 and E_1 modes are active in IR. According to the selection rules, the combination bands correspond to the same species. The 2/1 helix which belongs to the D_{2h} point group, gives rise to a B_{3u} absorption band near 627 cm^{-1} . The different absorption bands observed in the range $4000\text{--}400\text{ cm}^{-1}$, and their assignments are listed in Table I.

Another interesting point to discuss is how to define a chain axis in PTFE. As far as the crystalline regions are concerned, we choose the helix axis as chain axis. In that case the transition moment associated with A_2 vibrations is parallel to the helix axis and therefore to the chain axis, while the transition moment associated with E_1 mode is perpendicular to this axis.²³ On the other hand, all the absorption bands related to the amorphous regions possess a parallel character, and, according to Davidson et al.,⁴ we will arbitrarily assume an angle $\alpha = 0$ in that case.

TABLE I
PTFE Infrared Absorption Bands

cm ⁻¹	From Refs. 26, 27, and 22 resp.	Zone ^a	Polarization ^b	Mode
516	516, 516, 503	C	π	A_2
556	553, 553, 553	C	σ	E_1
627	625, 625, 626	C	π	B_{3u} (D_{2h})
640	638, 638, 638	C	π	A_2
703	703, 703, —	A	π	
720	720, 718, —	A	π	
740	740, 738, —	A	π	
774	780, 778, —	A	π	
786		A	π	
850	850, 850, —	A	π	
940	932, 932, —	C	σ	$E_1 \times A_1 = E_1$
1157	1152, 1152, 1153	C	σ	E_1
1214	1210, 1213, 1213	C	$\pi?$	A_2
1242	1242, 1242, 1242	C	σ	E_1
1300	—, —, 1298	C	σ	E_1
Combination bands ²⁶				
1415	$1210(A_2) + 203(E_1) = 1413(E_1)$			
1450	$1242(E_1) + 203(E_1) = 1445(A_2)$			
1545	$1242(E_1) + 304(A_1) = 1546(E_1)$			
1792	$1152(E_1) + 638(A_2) = 1790(E_1)$			
1859	$1242(E_1) + 625(A_2) = 1867(E_1)$			
1883	$1152(E_1) + 730(A_1) = 1882(E_1)$			
1935	$1380(A_1) + 553(E_1) = 1933(E_1)$			
2365	$1210(A_2) + 1152(E_1) = 2362(E_1)$			
2390	$1242(E_1) + 1152(E_1) = 2394(A_2)$			
2450	$1242(E_1) + 1210(A_2) = 2452(E_1)$			

^a C: crystalline; A: amorphous.

^b π : Parallel; σ : perpendicular.

EXPERIMENTAL

All the experiments were performed between 21°C and 23°C in order to minimize structural or/and conformational changes.

Preparation of Samples

Films of different thickness were kindly provided to us by Sirem Co. (Langres, France). Two of them were quenched from 380°C in order to increase the amorphous content. The third one was dispersion cast and used as obtained. The characteristics of the samples are given in Table II.

Rectangular strips (50 × 5 mm) of each sample were stretched at room temperature at a draw rate of 2 mm/min using a DY 14 Adamel-Lhomargy stretching machine. After drawing, samples were allowed to relax under stress for 2 min. The draw ratio was defined as $\lambda = l/l_0$ (l_0 , initial length of the sample, 1 cm; l is the length after drawing) and measured by the way of two ink marks previously printed on the sample before stretching.

Infrared Dichroism

The polarized spectra were recorded using a Nicolet 7199 Fourier transform infrared spectrometer. Single beam spectra were run with 200 scans at a 2 cm^{-1} resolution. The absorbance spectra were calculated by the computer using a stored polarizer spectrum as reference. The polarization of the incident beam was obtained by the use of a Perkin-Elmer gold wire-grid polarizer. Samples rather than the polarizer were rotated 90° in order to obtain the two perpendicular polarization measurements. Infrared dichroism was calculated as $R = A_{\parallel}/A_{\perp}$ with A_{\parallel} and A_{\perp} the optical densities at the absorption maximum.

Overlapping absorption bands regions were resolved using a Dupont 310 Curve Resolver and Gaussian line shape. The position and the width of each band were determined from a nonpolarized spectrum of PTFE. These were then kept fixed, and the intensities of the absorption bands in the polarized spectra were obtained on adjusting the height of the bands to get the best fit. The difference between independent trials was less than 5%. Examples of such resolutions in the ranges 1350–1650, 1650–2050, and 2050–2750 cm^{-1} are shown in Figures 1, 2, and 3. Weak absorption bands (2300 cm^{-1} and 2530 cm^{-1}) or broad ones (1710 cm^{-1}

TABLE II
Characteristics of PTFE Films

Sample	Origin	Treatment	Thickness (μm)
1	Dispersion cast		22
2	Industrial	Quenched	30
3	Industrial	Quenched	80

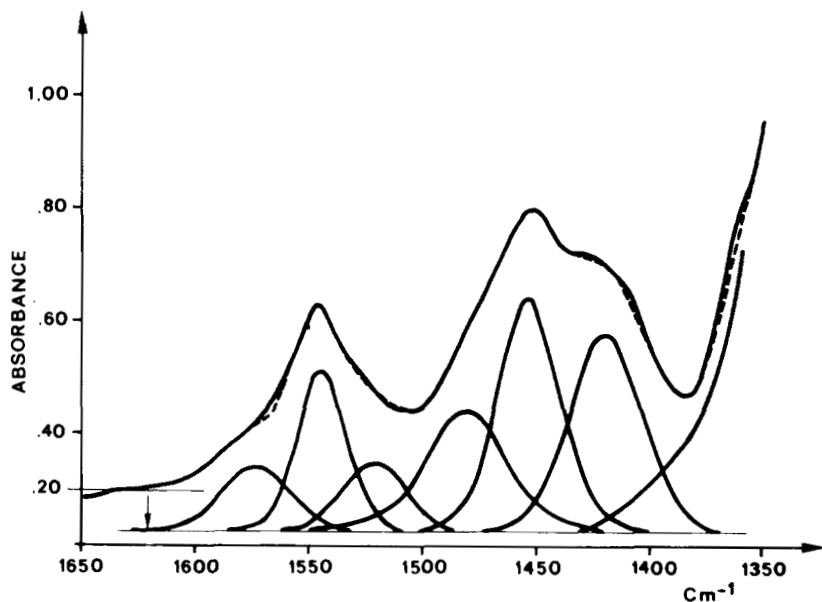


Fig. 1. PTFE spectrum analysis in the crystalline $1350\text{--}1650\text{ cm}^{-1}$ range: (—) original spectrum; (---) best fit with elementary bands.

and 2530 cm^{-1}) which are suspected to be complex bands have been rejected for the calculation of the orientation.

RESULTS

We will examine successively crystalline and amorphous orientation.

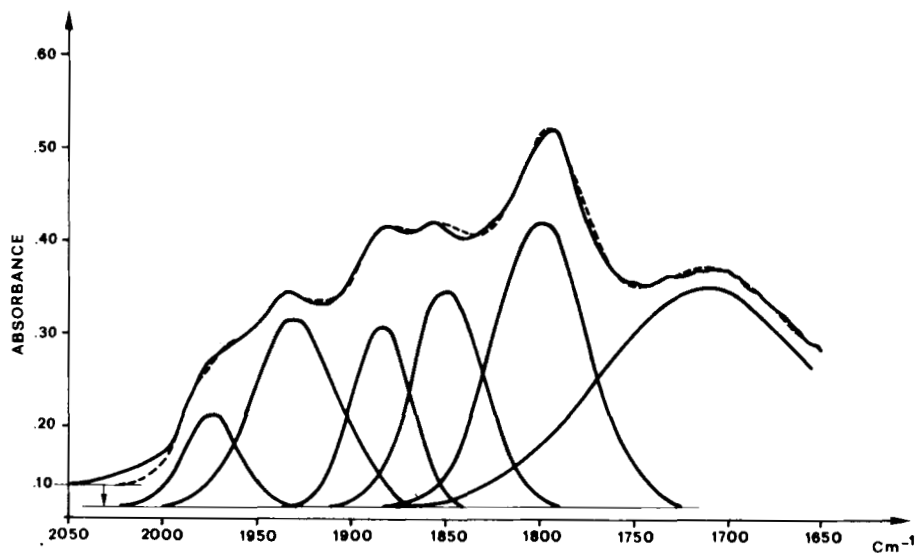


Fig. 2. PTFE spectrum analysis in the crystalline $1650\text{--}2050\text{ cm}^{-1}$ range: (—) original spectrum; (---) best fit with elementary bands.

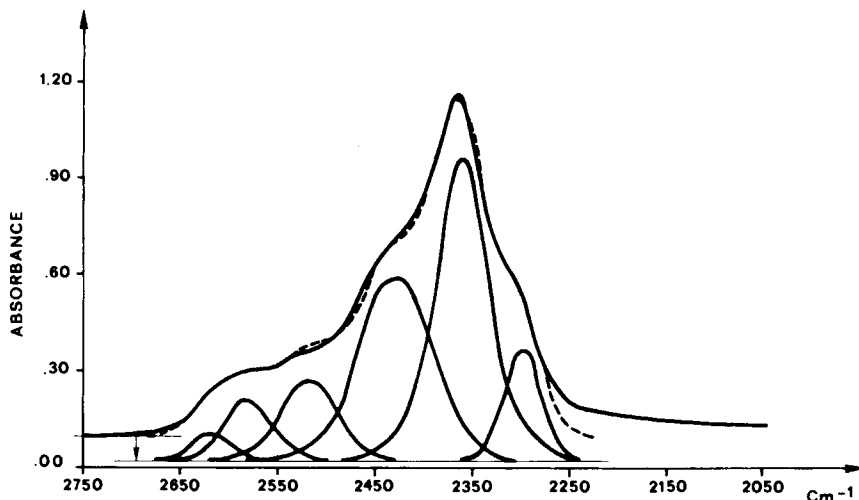


Fig. 3. PTFE spectrum analysis in the crystalline 2050–2750 cm^{-1} range: (—) original spectrum; (---) best fit with elementary bands.

Crystalline Orientation

It is very difficult to determine crystalline orientation in PTFE samples using fundamental vibrational modes on account of too high absorbance values which do not obey the Lambert–Beer law. Values not higher than 0.7 absorbance units should be used.²⁴ Very thin films are difficult to prepare, and only sample 1 was suitable for the use of the CF_2 rocking fundamental mode at 556 cm^{-1} . But the combination bands of this sample were too weak to be used. The change of orientation as a function of draw ratio is shown in Figure 4.

As far as sample 2 is concerned, the 556 cm^{-1} absorption band is too strong. Alternatively the orientation can be measured using the 1452, 1545, and 2362 cm^{-1} combination bands. Because of the small thickness difference between sample 1 and sample 2, one can expect that in the crystalline regions the chains orient in a similar fashion. The results shown in Figure 4 indicate that the concerned combination bands are suitable for measuring such an orientation.

Orientation in sample 3, whose thickness is similar to those of industrial tapes, was measured using the 1452 cm^{-1} (π), 1545 cm^{-1} (σ), 1795 cm^{-1} (σ), 1858 cm^{-1} (σ), 1885 cm^{-1} (σ), 1933 cm^{-1} (σ), and 2362 cm^{-1} (σ) combination bands. The change of orientation as a function of draw ratio is shown in Figure 5. All these absorption bands but one (1795 cm^{-1}) give the same result. One can explain this discrepancy by the fact that the 1795 cm^{-1} band is not pure; in perpendicularly polarized light the wavenumber of the absorption maximum changes slightly, as shown in Figure 6. Krimm²⁵ has assigned this band to the following combination: 1152 cm^{-1} (E_1) + 640 cm^{-1} (A_2) = 1792 cm^{-1} (E_1). We also suggest as a possible combination: 1242 cm^{-1} (E_1) + 556 cm^{-1} (E_1) = 1798 cm^{-1} (A_2). Overlapping of these two σ and π bands leads to wrong calculated values of orientation. One can notice that a slightly lower orientation level is attained in sample 3. Such a behavior could be assigned to a different morphological structure in this sample.

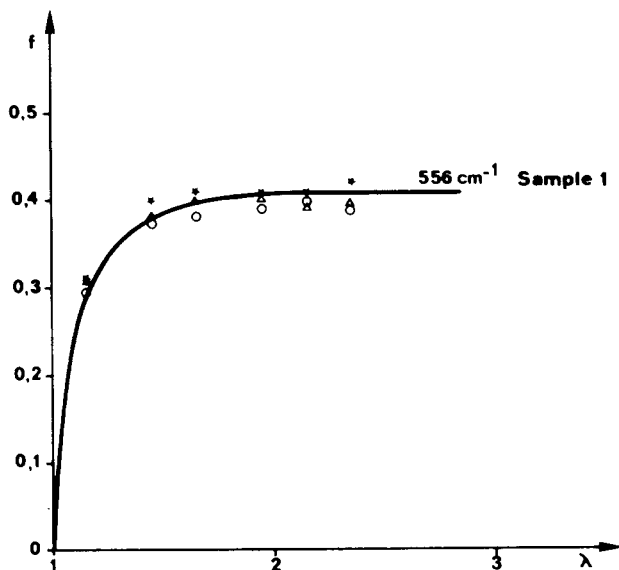


Fig. 4. Crystalline orientation function as a function of draw ratio in samples 1 and 2. The full line is the orientation function for sample 1 measured from the 556 cm^{-1} absorption band. Sample 2: (O) 1452 cm^{-1} (π); (★) 1545 cm^{-1} (σ); (Δ) 2362 cm^{-1} (σ).

Amorphous Orientation

Among the amorphous absorption bands which appear in the range $650\text{--}950\text{ cm}^{-1}$ (Fig. 7) we have used the 703 , 720 , 740 , 774 , and 786 cm^{-1} absorption bands to measure the $\langle P_2(\cos \theta) \rangle$ orientation function. The results are given in Figure 8. One can notice that three absorption bands lead to the same value of the or-

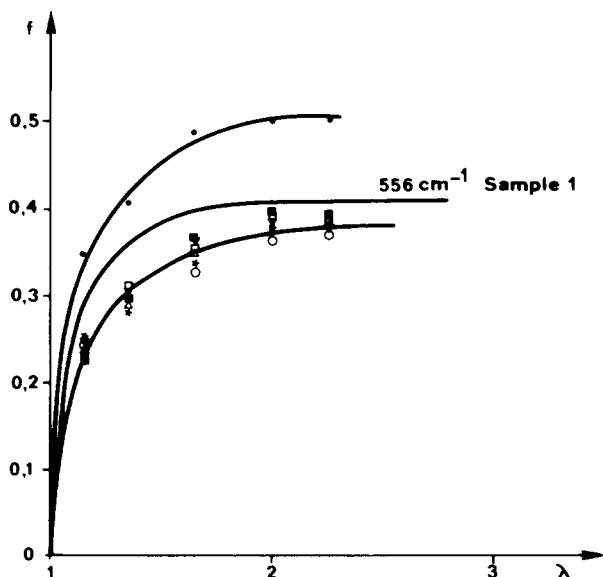


Fig. 5. Crystalline orientation functions as a function of draw ratio in sample 3, using different absorption bands: (O) 1452 cm^{-1} (π); (★) 1545 cm^{-1} (σ); (●) 1795 cm^{-1} (σ); (■) 1858 cm^{-1} (σ); (Δ) 1885 cm^{-1} (σ); (\square) 1933 cm^{-1} (σ); (▼) 2362 cm^{-1} (σ).

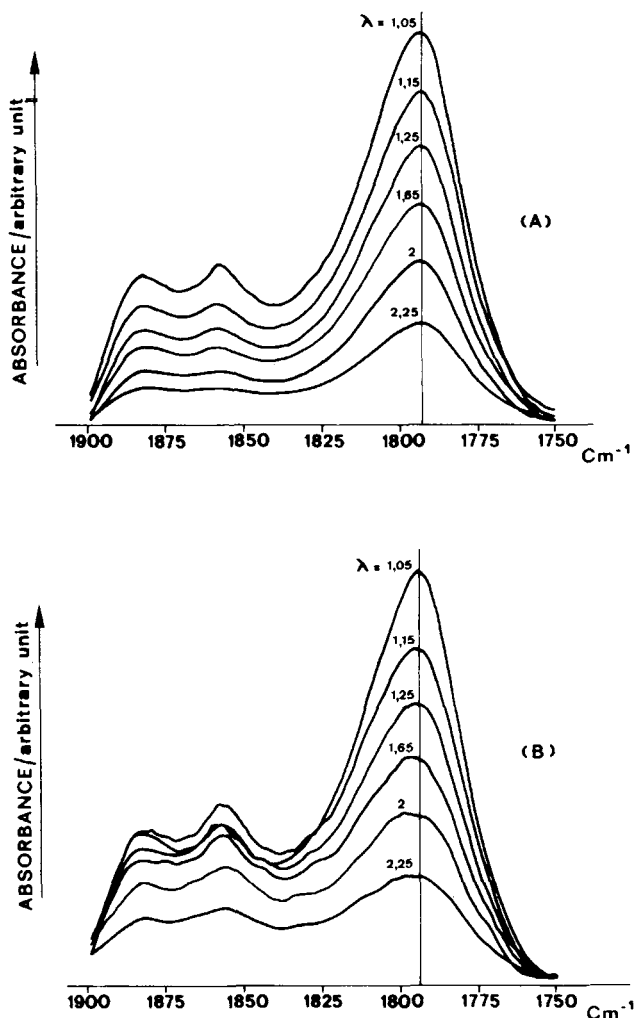


Fig. 6. Wavenumber shift of the maximum of the 1795 cm^{-1} absorption band in oriented PTFE as a function of draw ratio. Electric vector: (A) parallel; (B) perpendicular, to the stretching direction.

ientation function. The 720 cm^{-1} band which gives higher values is usually considered as amorphous. However, careful examination of the spectrum shows that this band is not symmetrical and could be consisted of two overlapping bands of different origins. Furthermore, we observed in the spectrum of a highly crystalline sample a weak absorption band around 720 cm^{-1} , which can be assigned to the combination $203\text{ cm}^{-1} + 516\text{ cm}^{-1} = 719\text{ cm}^{-1}$. Overlapping of this crystalline band and the amorphous band leads, as expected, to higher values of the orientation function.

The 774 cm^{-1} absorption band gives lower values of the orientation function. A tentative explanation could be to assign this band to a less oriented particular conformational structure of the chain in the amorphous regions.

Similar results were obtained by Davidson et al.^{4,5} However, these authors considered the doublet $774\text{-}786\text{ cm}^{-1}$ as a sole band at 780 cm^{-1} , which led to lower values of the orientation function.

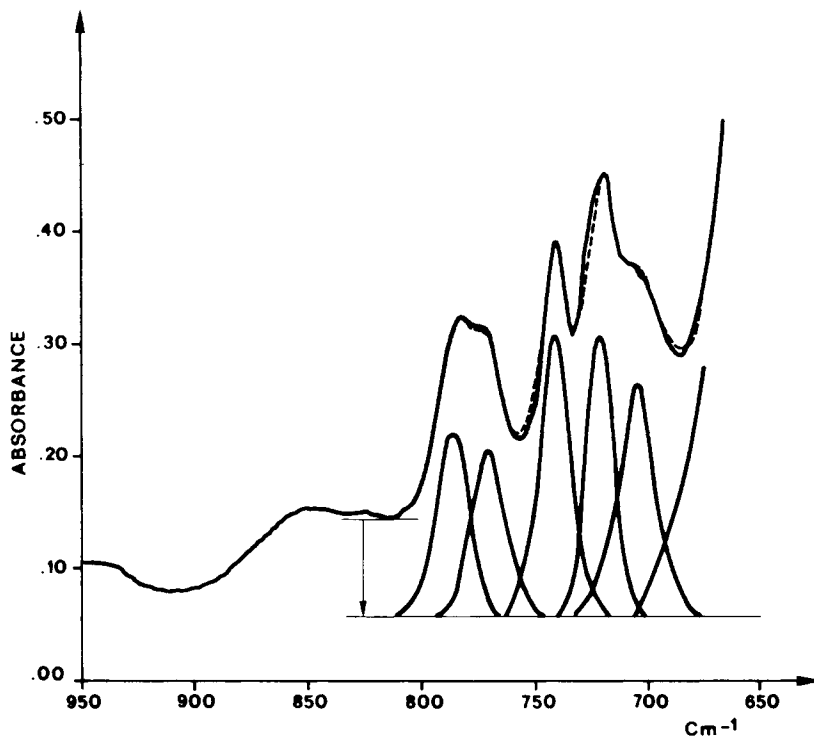


Fig. 7. PTFE spectrum analysis in the amorphous 650–950 cm^{-1} range: (—) original spectrum; (---) best fit with elementary bands.

DISCUSSION

The present results show that the 1452 cm^{-1} , 1545 cm^{-1} , 2362 cm^{-1} (crystalline) and 703 cm^{-1} , 740 cm^{-1} , 786 cm^{-1} (amorphous) absorption bands can be used to obtain reliable results for the value of crystalline and amorphous orientation functions in PTFE. Davidson et al.^{4,5} obtained orientation values similar

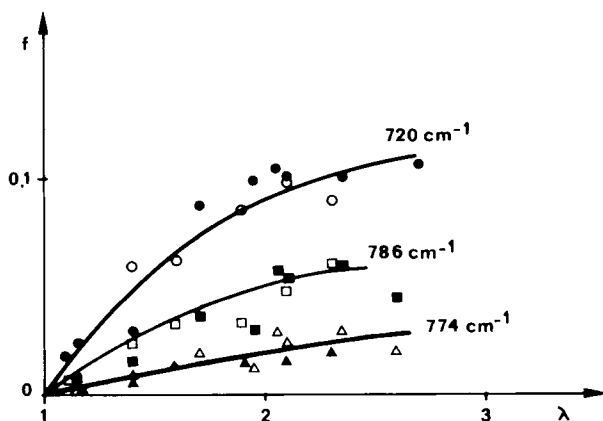


Fig. 8. Amorphous orientation functions as a function of draw ratio in samples 1 and 2 using different absorption bands: (●, ■, ▲) sample 1; (○, □, △) sample 2.

to ours using the 553 cm^{-1} absorption band for the crystalline regions and the 740 cm^{-1} absorption band for the amorphous regions. They, however, observed different values of crystalline orientation from the 516 cm^{-1} , 625 cm^{-1} , and 638 cm^{-1} absorption bands. These authors assigned this discrepancy either to specific effects produced on each vibrational motion of the PTFE chain when subjected to applied deformation or to a deviation from 0° or 90° of the angle between the transition moment vector and the chain axis. One can, however, expect that any pure crystalline absorption band should lead to the same result. As a matter of fact, some of the so-called crystalline bands are affected by the presence of amorphous components. Figure 9 shows the spectrum of sample 2 before and after quenching from 380°C . Besides the appearance of amorphous absorption bands one can notice an important broadening of the bands in the range $500\text{--}700\text{ cm}^{-1}$, in particular the 516 cm^{-1} absorption band. Such an effect has to be assigned to the appearance in the amorphous phase of different chain conformations introduced by the amorphisation process. One can particularly expect the presence of trans planar conformation sequences (2/1 helices) which give rise to a $B_{2u}(\sigma)$ absorption band around 548 cm^{-1} .²¹ The presence of different conformational structures related to the amorphous phase makes such absorption bands inadequate to measure crystalline orientation in PTFE. Furthermore, the high absorbance values of the 625 cm^{-1} and 638 cm^{-1} absorption bands suggest that these two bands do not obey any more the Lambert-Beer law.

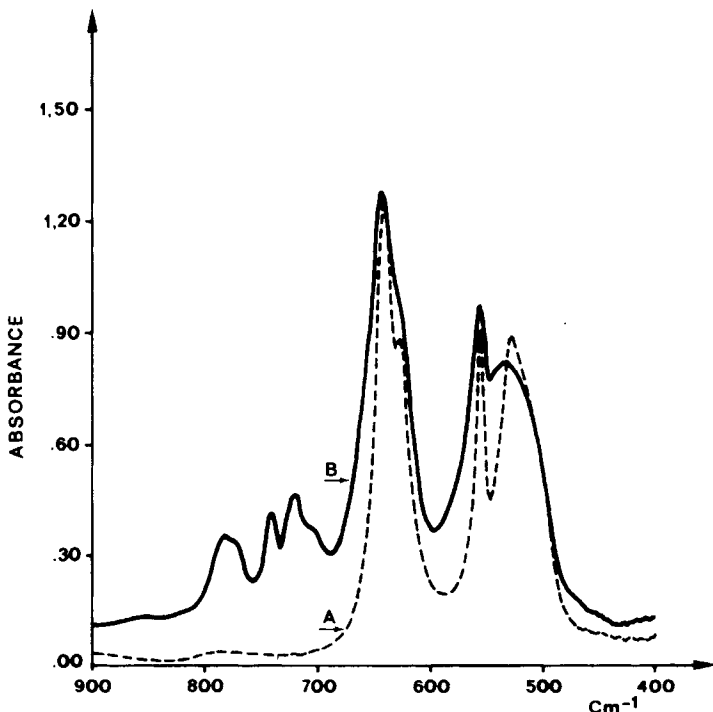


Fig. 9. Changes in the spectrum of a PTFE film (thickness $30\ \mu\text{m}$) quenched from 380°C (A) before and (B) after heat treatment.

CONCLUSION

In conclusion, the present study shows that IR spectroscopy represents a valuable technique of measurement of the orientation in PTFE. Absorption bands of different intensities can be used as required by the film thickness. In particular, several combination bands are well suited for measuring crystalline orientation because they do not overlap amorphous absorption bands.

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