

A New Method for Fiber Comparison Using Polarized Infrared Microspectroscopy*

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ABSTRACT: Polarized infrared (IR) microspectrometry was used to measure the changes in infrared absorption resulting from the molecular orientation of single textile fibers. Dichroic ratios were determined from single experimental fibers subjected to incremental elongation from an unstretched to a stretched condition. Similar measurements were made on commercial fibers of the same polymer with known draw ratios. These infrared spectroscopic measurements provided a direct means for comparing fibers drawn under production conditions with single fibers stretched in controlled experiments. The dichroic ratio data are indicative of the molecular orientation that occurs when fibers are drawn in the manufacturing process. Dichroic ratio data of commercial fibers can be used to monitor textile fiber quality and to compare fiber evidence in forensic investigations.

KEYWORDS: forensic science criminalistics, fiber, polyester, infrared microscopy, polarized infrared spectroscopy, dichroism, Fourier transform infrared microspectroscopy, textile, single-fiber analysis

Modern Fourier transform infrared (FT-IR) microspectroscopic technology allows reducing the target size of the specimen to a single fiber and determining its molecular chemical composition. Moreover, surface analysis is accomplished readily on a micro scale using an attenuated total reflectance (ATR) microscope objective (1). With this micro ATR procedure, spin finishes or treatments applied to fibers for end use can be detected. In forensic science each additional bit of information is potentially useful when comparing fiber evidence. Because of compositional variations that are prevalent in acrylic fibers, infrared microspectroscopy (IMS) has been used to separate acrylic fibers into several subclasses (2–4). Polarized IMS provides a new dimension for forensic fiber comparisons.

When the infrared absorption band intensity of a single fiber varies because the orientation of the direction of polarization changes, dichroic activity is present. This is a direct result of the orientation of the fiber's macromolecules. An absorbance band,

that exhibits dichroic activity, can be quantified by determining its dichroic ratio (5–7). The dichroic ratio at each wavelength or wave number is calculated by dividing the band intensity measured when the electronic field is aligned parallel to the fiber axis by the absorbance measured when the electronic field is aligned perpendicular to the fiber axis. Dichroic ratios provide evidence of the fiber treatment during the manufacturing process. These manufacturing processes produce fibers with the desired functional characteristics by controlling the crystallinity and molecular orientation (8–15). In particular, the draw ratio or simply the wind-up speed influences the dichroic ratio (16–19). Tungol and co-workers (20) at the FBI showed that groups of individual fibers taken from two different manufacturers could be distinguished by their infrared dichroic measurements. Those distinctions were based on the dichroism of a single wavelength measurement.

In this work, a systematic study of single fibers was made involving a number of infrared absorption bands recorded in the transmission mode. Unstretched acrylic, nylon, and polyester fibers were obtained directly from manufacturers by special dispensation. The dichroism that results from elongation was studied systematically beginning with undrawn test fibers. Additionally, several commercial fibers with known stretching histories were examined. This was done to assess the potential of polarized infrared to differentiate fibers by their molecular orientation resulting from processing conditions. The ability to measure dichroic ratios on single fibers under controlled conditions can lead to a better understanding of how fiber orientation occurs during manufacturing and provides a means for forensic fiber comparisons (21).

Experimental

Instrumentation

An IR μ s[®] model FT-IR microspectrometer (Spectra-Tech, Shelton, CT) was used. This integrated infrared spectrometer/infrared microscope provides optical efficiency as well as programmable operation and control. This microscope was equipped with a Schwartzchild first surface mirror lens. The IR μ s[®] was equipped with a microprocessor-controlled motorized stage and an infrared polarizer that could be rotated to the proper orientation. The zinc selenide, 600 lines/mm, wire-grid infrared polarizer was positioned in the interferometer between the beam-splitter and the sample in the optical path of the microscope.

The specimen was viewed with the instrument acting as a light microscope. The portion in the field of view defined for infrared spectral analysis was positioned at the cross hairs in the optical view (22,23). During spectral measurement, infrared radiation was directed along the same optical transmission path and the sample area was defined by image plane masks before the objective and

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after the condenser. Image plane masks restricted spectroscopic analysis to a chosen portion of the specimen. Typically, apertures of 12 by 48 μm were used. Similar dimensions were used for the bottom aperture to avoid incidental spectral contamination.

A single-fiber stretching device suitable for use on the microscope stage was designed for the project and fabricated in the KSU Physics Department machine shop. The stretching device consisted of a brass plate with an open rectangular hole (0.5 in. long, 0.25 wide) milled in the center. The open area was covered by a fixed and sliding moveable glass jaw that moved between glass guides over the smooth brass surface. The sliding member was controlled by the rotation of a screw. The brass plate was drilled, tapped, and equipped with three leveling screws for use on the microscope stage. This stretching device produced a measurable amount of fiber elongation. The fiber was fastened to the stationary and moving ends of the stretching device and stretched by controlled rotation of a screw. Actual dimensions between points scribed on the fiber with ink were determined using an ocular with 0.1 mm scale divisions to measure the dimensions before and after stretching.

Fiber Samples

The fiber samples included unstretched acrylic homopolymer, polyethylene terephthalate (PET), and nylon 6. The prestretched fibers evaluated were polyester with three different draw ratios, 2.72, 3.19 and 3.98. Undrawn polyacrylonitrile was obtained courtesy of MANN Industries. The acrylic single-fiber infrared dichroism stretching experiment served as a model for relating the observed spectroscopic response specifically to the orientation of the nitrile groups with respect to the fiber axis. This model was selected because classical infrared dichroic studies had previously elucidated these cause and effect relationships. The theoretical relationships between infrared dichroism and molecular orientation of the nitrile bands were described by Fraser (24,25).

The undrawn and drawn Dacron 54 PET fibers furnished by the DuPont Company are listed in Table 1. Undrawn fibers of two different sizes (3 and 6 denier) were used for the stretching experiments. Fifteen denier undrawn nylon 6 fibers were used for similar stretching purposes.

The polarized spectroscopic data obtained from polyester fibers prestretched by the manufacturers using three different draw ratios were used to study the relationship between the extent of molecular orientation optically revealed and known manufacturing process conditions.

Procedure for Obtaining Polarized Spectral Data of Single Fibers

The protocol used for obtaining dichroic spectra was comprised of several steps, mounting the fiber, aligning the fiber to the polarized infrared beam, selecting the area for analysis and recording the polarized infrared spectrum. After an unsupported fiber was

placed on the stage, the sample-defining aperture was set appropriately for the particular fiber (typically an aperture of 12 by 48 μm was used). The ViewThru™ feature of the IR μs ® allowed projection of the aperture image onto the image of the entire microscope field. The superimposed projected image on the video monitor facilitated the precise positioning of the specimen by moving the microprocessor-controlled motorized stage. Viewing was done with the bottom aperture out of the beam path. When the spectrum was recorded, a similar size of bottom aperture was used. The sample and background spectra were collected with the polarization vector in both a parallel and perpendicular position relative to the fiber axis. The operational parameters for the background spectra were identical to those used in recording polarized spectra of the single fibers. The programmable stage allows sample positions to be stored and the fiber repositioned with a precision of 1 μm . Data were collected, scans were coadded, the interferogram was transformed, and the single-beam spectrum was referenced to the polarized background stored in the computer. Similarly, with the polarizer rotated to the opposite position, a second single-beam spectrum was obtained and displayed as a transmission or absorbance spectrum with reference to the appropriate background. Spectra were collected for each fiber at both polarizations to allow calculations of dichroic ratios for absorption bands exhibiting dichroism.

Single Fiber Procedure for Dichroic Ratio/Stretching

The undrawn test fiber was placed in the stretching device and infrared transmission spectra were obtained at both polarizations prior to elongation. A $\times 15$ objective was used with a 12 by 48 μm sample area defined with dual masks. The spectral resolution used in all experiments was 4 cm^{-1} in the 4000 cm^{-1} to 600 cm^{-1} spectral region. Spectra were obtained with 256 scans coadded. The procedure was repeated at several successively increased elongation until the fiber was as much as 267% of its original length. Three replicate spectra were taken for each polarization at each elongation condition or draw ratio. Dichroic response curves were produced by plotting the average dichroic ratio for the bands of interest versus elongation of the fiber.

Fibers with various diameters were used in single fiber elongation experiments. Preliminary experiments were performed using 3 denier (approximately 10 μm diameter) fiber (26,27). To produce the larger elongations commonly used in the textile industry, the procedure was repeated on thicker fibers (6 denier and approximately 19 μm diameter). Since absorbance band values greater than 1.0 are generally regarded as unreliable for quantitative analysis, thick fibers limit the number of bands that can be used for dichroic ratio measurements.

Using this procedure, single undrawn acrylic, polyester and nylon fibers were examined by polarized infrared microspectroscopy to observe their dichroic ratio generated by stretching. This procedure was also used to measure dichroic ratios of the drawn commercial PET fibers. For polyester fibers, frequencies with a maximum change in dichroic response upon elongation were identified from preliminary stretching experiments.

The empirical relationships between the elongation and dichroic ratios produced for several different wavelengths were defined by this study. Dichroic ratios at several wavelengths provided multiple points of comparison for the further distinction between single fibers with different histories.

Results

A single acrylic fiber was drawn to test the relationship of single-fiber dichroic spectral data to the theory proposed by Fraser (24).

TABLE 1—DuPont polyester fibers from which polarized infrared spectra were obtained.

Code	Conditions
0101	undrawn—3 denier
0102	undrawn—6 denier
0103	2.72 draw ratio
0104	3.19 draw ratio
0105	3.98 draw ratio

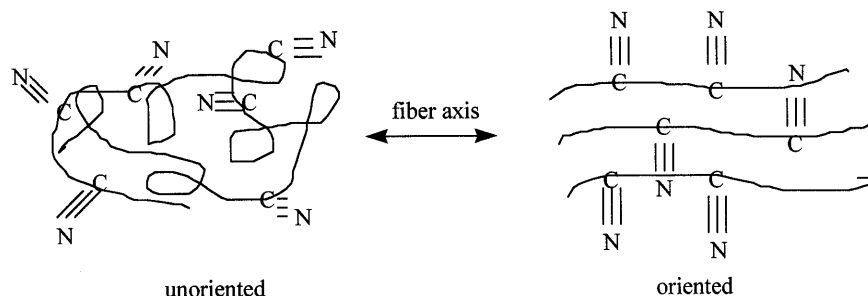


FIG. 1—Structure of the polyacrylonitrile shows the nitrile groups oriented 90° to the fiber axis. The left structure shows the fiber before being stretched and the right structure shows the result after stretching.

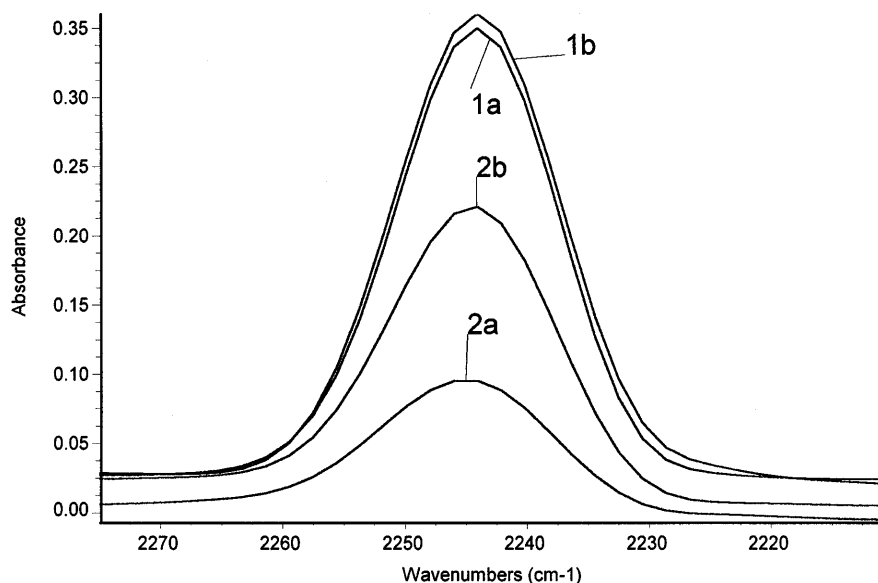


FIG. 2—Polarized infrared absorption spectra acrylic fiber showing the orientation of the nitrile functional group at 2244 cm^{-1} . Top: perpendicular (1b) and parallel (1a) polarized infrared spectra of a single unstretched fiber. Bottom: perpendicular (2b) and parallel (2a) polarized infrared spectra of a stretched fiber.

According to Fraser's equations, the percentage of the nitrile groups being orientated perpendicular to the fiber axis can be calculated from infrared dichroic ratio data. Fraser's equation relating the dichroic ratio to the orientation of the nitrile group with respect to the C—C backbone of the macromolecules along the fiber axis is shown below (where R = dichroic ratio function, f = perfect orientation, $(1 - f)$ = perfectly random orientation, and α = angle between transition moment direction and molecular axis):

$$R(\alpha, f) = [f \cos 2\alpha + 1/3 (1 - f)] / [1/2 f \sin 2\alpha + 1/3 (1 - f)] \quad (24)$$

The percentage of the nitrile groups oriented as a function of stretching a single acrylic fiber is shown in Table 2. The orientation of the nitrile groups was determined by measuring the dichroic ratio of the nitrile band at 2245 cm^{-1} . As the fiber was stretched, a larger fraction of the nitrile groups became oriented 90° to the fiber axis (Fig. 1). This resulted in the absorbance value for the

TABLE 2—Dichroic ratios and the percentage of the nitrile groups oriented 90° to the fiber axis.

Elongation Ratio	Dichroic Ratio	% Oriented 90° to Fiber Axis
1.00	0.96	2.7%
1.20	0.78	15.8%
1.40	0.66	25.6%
1.60	0.32	58.6%

perpendicular polarization at 2245 cm^{-1} being larger than that for parallel polarization. The dichroic ratio value is less than 1.0 for this orientation of the nitrile functional group. Figure 2 shows that the dichroic ratio for the nitrile band changed from 0.96 to 0.32 when the unstretched acrylic fiber was stretched from 0 to 160%. As the stretching increased, the percentage of the nitrile groups oriented 90° to the fiber chain axis increased. The elongation ratio was defined as the length of the fiber after being stretched divided by the original length of the fiber. Applications of this classical relationship to single-fiber infrared microspectroscopic data supported the expectation of meaningful single-fiber polarization results with other polymers.

Stretched single nylon fibers clearly exhibited dichroism for the bands at 3082 cm^{-1} and 997 cm^{-1} . Because of the fiber thickness (15 denier, $\sim 40\text{ }\mu\text{m}$ diameters), measuring the dichroic ratio of most strongly absorbing bands was impossible. The results of stretched single nylon fibers are not shown here because of the over-absorbing bands of the thick undrawn fiber. Near-infrared microspectroscopy is being investigated for the dichroic spectral analysis of thick fibers.

Similar studies were made on polyester fibers. Systematic single-fiber stretching experiments with polarized FT-IR microspectroscopy were undertaken on the microscope stage with 3 denier and 6 denier undrawn polyester fibers obtained from the DuPont Co. In these room temperature experiments, the maximum elongations obtained were 200% with the 3 denier fiber and 267% with the 6 denier fiber. In both cases, changes of dichroic ratios were observed. From observations of the spectra at maximum and zero elongation, the wavelengths were identified where maximum

change occurred. The undrawn fibers were found to have only a small amount of preferred orientation.

Preliminary comparison of dichroic ratios of single polyester fibers identified absorption bands that showed the greatest response to orientation (27). These are listed in Table 3 in order of their decreasing response to a fixed elongation.

The dichroic ratio of the 973 cm^{-1} band (C—O stretch of the *trans* ethylene glycol unit), shown in Fig. 3, increased by a factor of 2.03 when the unstretched 3 denier fiber was stretched to 183% of its original length. Further stretching to 200% elongation at room temperature resulted in a reduction in the dichroic ratio of this band. Before the polyester was stretched, the C—O groups in the ethylene glycol unit were oriented randomly. After stretching, this functional group rotated to the *trans* form and became oriented parallel to the fiber axis.

The 876 cm^{-1} band (phenyl C—H out-of-plane vibration) showed a different dichroism. This dichroic ratio decreased by a factor of 1.69, indicating that a larger fraction of the phenyl C—H band was oriented perpendicular to the fiber axis.

When an unoriented polyester fiber was stretched rapidly on the microscope stage, a "neck" was observed between the stretched and unstretched portions of the fiber. Figure 4 shows the "necking down" of a polyester fiber after it was stretched rapidly. As stretching was continued, the drawn section increased in length at the expense of the undrawn portion of the sample. Figure 5 shows spectra at both polarizations at the unstretched, neck, and stretched portions of a polyester fiber at 973 cm^{-1} . The average dichroic ratios were 1.04 at the unstretched portion, 1.32 at the neck portion, and 1.68 at the stretched portion. This shows the changes between different portions within a single polyester fiber.

In order to produce a larger range of elongation and fiber diameters more representative of commercial polyester fibers, the experiments were repeated on 6 denier undrawn polyester fibers. Dichroic responses for eight bands of interest at different elongations are shown in Table 4. The values listed are the means of three independent determinations on replicate fibers. The relationships between

TABLE 3—Infrared bands of PET in descending order of relative change in their dichroic ratios with stretching to a fixed elongation (140%) from an unstretched condition.

Frequency cm^{-1}	Assignment	Dichroic Ratio Stretched/Initial*	Orientation Factor†
973	C—O stretch of <i>trans</i> ethylene glycol	1.94	+1.94
876	phenyl C—H band (out-of-plane)	0.54	-1.85
1579	phenyl C—C stretch	1.36	+1.36
1376	CH ₂ wagging	0.73	-1.32
1505	phenyl C—C stretch (in-plane)	1.27	+1.27
1960	1,4- substituted phenyl overtone	0.86	-1.16
1455	CH ₂ bending	1.13	+1.13
3435	C=O stretch overtone	0.89	+1.13

* Dichroic ratio stretched/dichroic ratio initial.

† Fractional changes of the dichroic ratios compared to unstretched as 1.00.

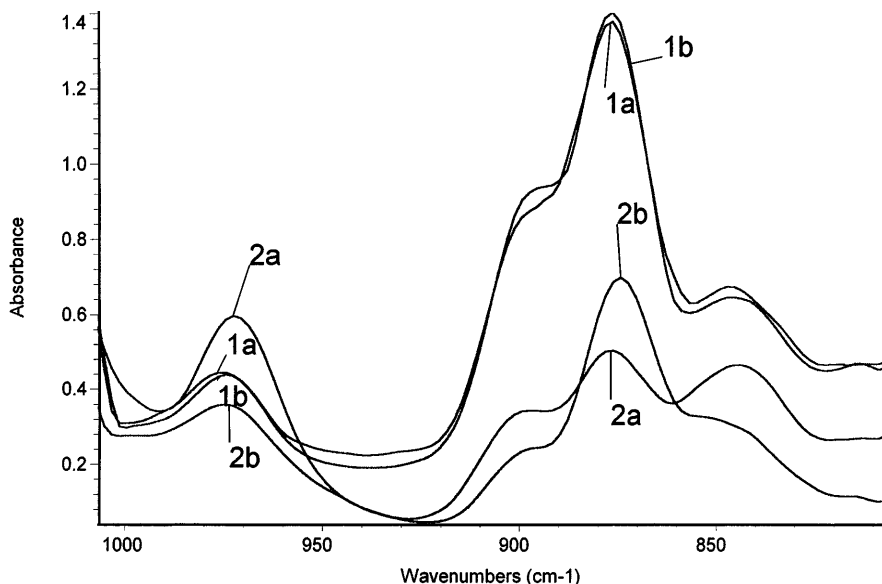
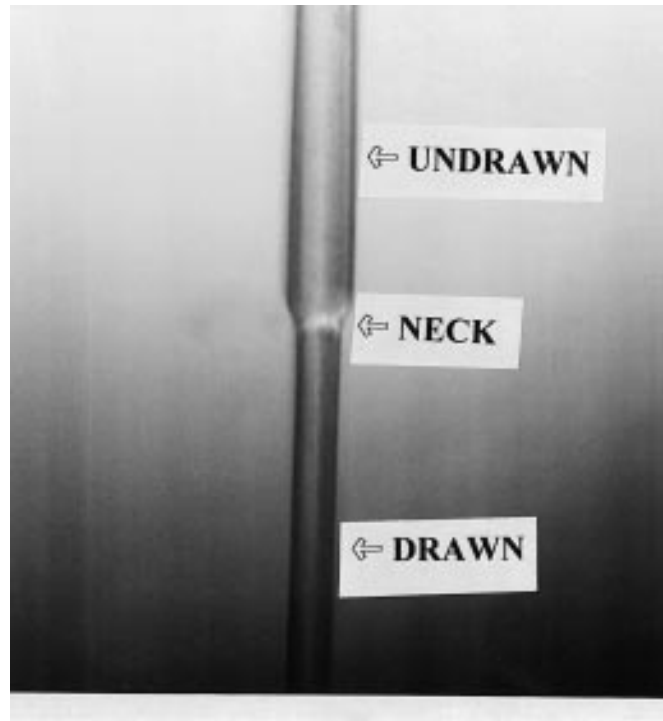


FIG. 3—Polarized FT-IR spectra of unstretched and stretched 3 denier polyester fiber showing that the dichroic ratio increased at 973 cm^{-1} and decreased at 876 cm^{-1} . 1a = unstretched parallel polarization, 1b = unstretched perpendicular polarization, 2a = stretched parallel polarization, 2b = stretched perpendicular polarization.



STRETCHED POLYESTER FIBER

FIG. 4—Necking of a polyester fiber after rapidly stretching position 1 (stretched), 2 (neck), and 3 (unstretched) points at which corresponding spectra shown in Fig. 4 were recorded.

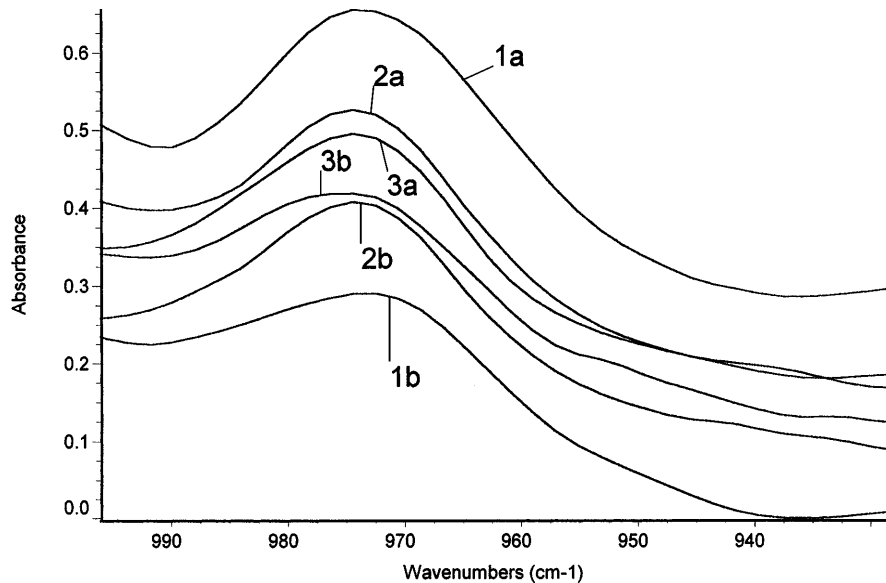


FIG. 5—Polyester polarized spectra at 973 cm^{-1} . 1a = parallel polarized spectrum of the stretched portion, 1b = perpendicular polarized spectrum of the stretched portion, 2a = parallel polarized spectrum of the neck portion, 2b = perpendicular polarized spectrum of the neck portion, 3a = parallel polarized spectrum of the unstretched portion, 3b = perpendicular polarized spectrum of the unstretched portion.

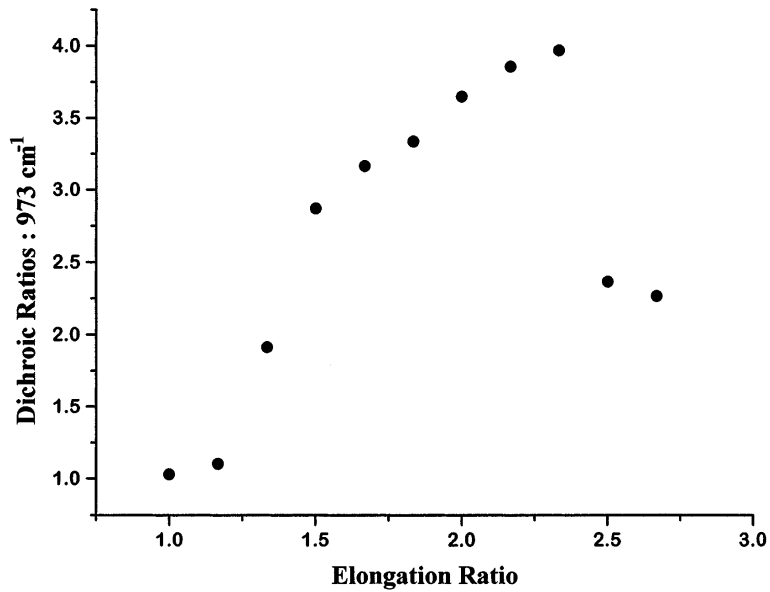


FIG. 6—Dichroic ratio of the C—O stretch vibration band of trans ethylene glycol at 973 cm^{-1} vs. elongation ratio for a drawn, 6 denier, polyester fiber showing the increase in dichroic ratio as the elongation was increased.

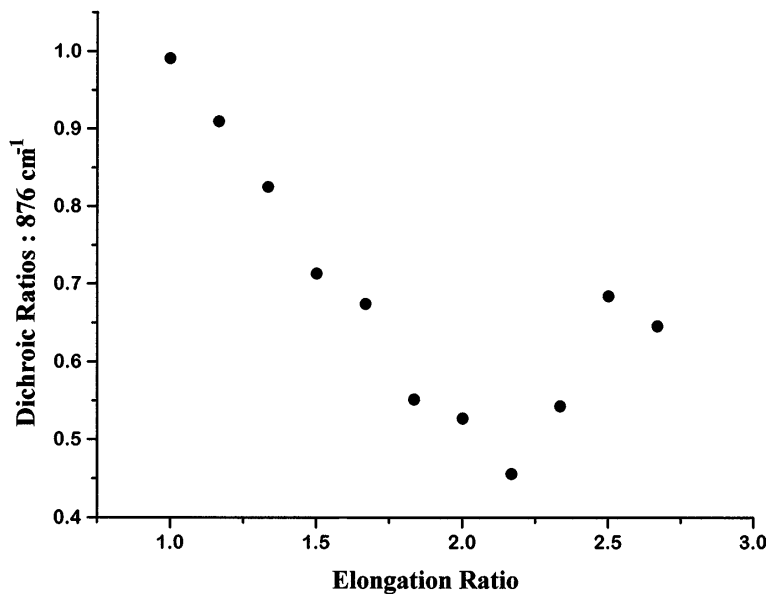


FIG. 7—Dichroic ratio of the phenyl C—H band at 876 cm^{-1} vs. elongation ratio for a drawn, 6 denier, polyester fiber showing the decrease in dichroic ratio with increased elongation.

dichroic ratios and elongation observed for bands at 973 cm^{-1} and 876 cm^{-1} (Figs. 6 and 7) were similar to those observed for the 3 denier fiber. Note that as the elongation was increased at the 876 cm^{-1} band, the dichroic ratio was decreased. At the elongation ratio of 2.17, the dichroic ratio of the 876 cm^{-1} band reached the lowest value. The opposite situation was found for the 973 cm^{-1} band; at the elongation ratio of 3.96, the dichroic ratio had the highest value. Figures 6 and 7 show the dichroic ratio responses to stretching plots for the bands at 973 cm^{-1} and 876 cm^{-1} , respectively. The plots of the dichroic ratios were based upon baseline corrected peak height versus elongation ratio.

Examination of the data showed several interesting features. For the dichroic ratio versus elongation data of the 976 cm^{-1} band (Fig. 6), two linear ranges were observed between 1.17 to 1.51

and 1.51 to 2.17. These changes in dichroic ratio are consistent with changes in the orientation of the amorphous and crystalline phases. When the elongation exceeded 2.34, the value of the dichroic ratio dropped dramatically. This decrease in dichroic ratio was unexpected and suggests that at the high elongation at room temperature, crystal morphology may have been transformed from lamellae to extended chain forms. Note from Table 4 and in Figs. 6 and 7 that a limit to the stretching was reached beyond which continued stretching produced a break in the trend of dichroic ratios.

The infrared dichroism may be explained by consideration of the orientation of PET molecules (shown in Fig. 8) as the fibers are elongated. When the PET molecules are randomly dispersed, no dichroism is observed. After the fiber is stretched, the PET

molecules become preferentially aligned in a configuration where a greater fraction of the long —C—C— chain is parallel to the fiber axis. As predicated by Fraser's theory, the —C—O—C— stretching vibration of *trans* ethylene glycol (973 cm^{-1}) will produce a stronger absorption when the polarized radiation electric field is aligned parallel to the polymer chain axis. A weak absorption is predicted for this band when the polarized radiation electric field is aligned perpendicular to the PET polymer chain axis. Similar arguments predict, for the out-of-plane phenyl C—H vibrational bands (876 cm^{-1}), the stronger absorption would be observed when the electric field is aligned perpendicular to the polymer chain and weaker absorption when the field is aligned parallel to the polymer chain. If during the elongation of the PET fibers, the molecules become aligned parallel to the fiber axis, then the observed dichroic ratios are consistent with this model.

Three commercial polyester fibers having known draw ratios were examined. Table 5 shows the dichroic ratios of eight bands of interest at the three different draw ratios. The dichroic ratios reported are the means of three independent measurements on replicate fibers. As expected, the higher the draw ratio, the higher the resultant molecular orientation. Figure 9 shows the dichroic

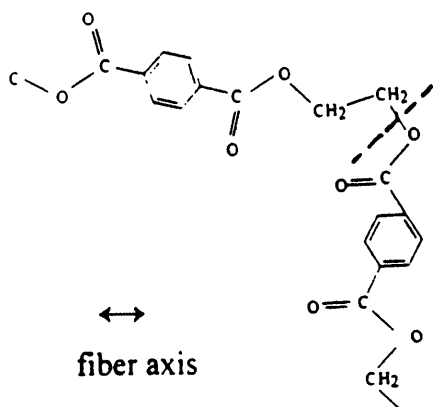


FIG. 8—Diagram of chemical structure showing part of an extended molecular chain of a polyester (PET) fiber.

differences at 973 cm^{-1} and 876 cm^{-1} for two commercial fibers with two different draw ratios. Because of the parallels observed between data obtained from the commercial and laboratory undrawn and drawn fibers, the draw ratio used in the manufacturing of an unknown fiber could be inferred from determination of its dichroic ratio.

TABLE 4—Dichroic ratio results of a stretched single polyester (6 denier) fiber.

Elongation Ratio	Wave Number, cm^{-1}							
	876	973	1376	1455	1505	1579	1960	3435
1.00	0.99	1.02	1.03	0.90	1.00	0.99	1.00	1.02
1.17	0.91	1.10	0.90	0.91	1.02	1.01	1.01	0.98
1.34	0.82	1.91	0.66	1.08	1.40	1.63	1.17	0.85
1.51	0.71	2.87	0.66	1.14	1.35	1.44	1.19	0.84
1.67	0.67	3.17	0.52	1.05	1.28	1.43	1.14	0.79
1.84	0.55	3.33	0.56	1.01	1.29	1.48	1.24	0.85
2.00	0.52	3.64	0.71	1.04	1.44	1.55	1.15	0.78
2.17	0.45	3.85	0.68	1.04	1.36	1.45	1.08	0.74
2.34	0.54	3.96	0.60	1.14	1.44	1.69	1.22	0.86
2.50	0.68	2.36	0.61	1.03	1.41	1.56	1.05	0.74
2.67	0.64	2.26	0.68	1.04	1.50	1.64	0.99	0.76

TABLE 5—From three commercial polyester fibers produced at different draw ratios, dichroic ratio calculated from eight different wave numbers.

Frequency, cm^{-1}	Dichroic Ratio		
	Draw Ratio = 2.72	Draw Ratio = 3.19	Draw Ratio = 3.98
876	0.49	0.43	0.40
973	1.31	1.64	1.75
1376	0.75	0.64	0.56
1455	1.04	1.06	1.14
1505	1.30	1.49	1.57
1579	1.36	1.49	1.58
1960	1.04	0.96	1.18
3435	0.64	0.63	0.58

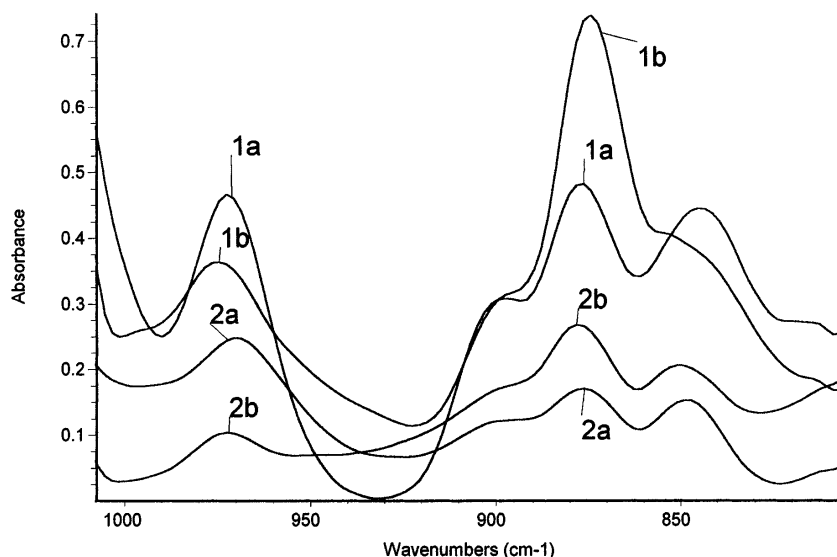


FIG. 9—Polarized spectra at 973 cm^{-1} and 876 cm^{-1} for polyester. The upper two spectra have a draw ratio of 3.19 (1a = parallel, 1b = perpendicular) and the lower two spectra have a draw ratio of 2.72 (2a = parallel, 2b = perpendicular). The dichroic ratio increased 25.2% at 973 cm^{-1} and decreased 12.5% at 876 cm^{-1} .

During the commercial fiber manufacturing process, drawing is carried out at the elevated temperatures, and much higher draw ratios are produced than could be achieved by stretching undrawn fibers at room temperature. Although the draw ratios for the commercial fibers were much greater than those from the controlled laboratory experiments, the dichroic ratio values shown in Table 5 are comparable with those in Table 4. Although the processes for the commercial and laboratory drawing were different, the degree of molecular orientations were similar.

Summary

A method for the measurement of infrared dichroic ratios was developed and tested to advance forensic fiber comparisons. The direction and magnitude of the dichroic ratio response of a single fiber to stretching were revealed in this study by controlled systematic experimentation. A miniature device suitable for stretching single fibers was designed and fabricated to allow measuring the elongation and infrared dichroism of a single fiber on the microspectrometer stage.

The model chosen for preliminary single-fiber stretching experiments was acrylic (polyacrylonitrile) fibers. This was used to test the response of single fiber dichroic ratio data to the theory advanced by Fraser. Single-fiber measurements on the acrylic fibers were consistent with the predicted orientation of nitrile groups resulting from fiber stretching.

Polarized infrared microspectroscopic data were collected for 3 and 6 denier polyester fibers when stretched under laboratory conditions. Starting with undrawn fibers, the progression of changes in the dichroic ratio was followed for each of eight absorption bands during elongation. The dichroic ratios for the individual bands were functions of the elongation ratios. The 973 cm^{-1} band showed the greatest increase with elongation, and the 876 cm^{-1} band showed the greatest decrease. These changes were consistent with the orientation of the long chain axis of the polyester molecules being aligned parallel to the fiber axis.

Commercial polyester fibers at three different known draw ratios were used to obtain dichroic ratios at the same eight frequencies. These commercial fibers produced comparable dichroic ratio data.

This work includes original experiments that allowed dichroic ratios to be determined with the infrared microspectrometer at progressive stages of elongation of a single fiber at multiple frequencies. The results from this study and experience in using polarized FT-IR microspectroscopic techniques will allow investigation of the potential classification of fibers having the same chemical composition by using multidimensional dichroic ratio profiles.

References

1. Reffner JA, Martoglio PA. Uniting microscopy and spectroscopy. In: Humecki HJ, editor. Practical guide to infrared microspectroscopy. New York: Marcel Dekker, Inc., 1995;41–86.
2. Grievol MC. The role of fibers in forensic science examinations. *J Forensic Sci* 1983;28(4):877–87.
3. Grievol MC, Cabiness LR. The recognition and identification of modified acrylic fibers. *Forensic Sci Int* 1985;29:129–46.
4. Tungol MW, Bartick EG, Montaser A. Forensic analysis of acrylic copolymer fibers by infrared microscopy. *Appl Spectrosc* 1993;47(10):1655–8.
5. Chase DB. Dichroic infrared spectroscopy with a microscope. In: Messerschmidt RG and Harthcock MA, editors. Infrared microspectroscopy: theory and applications. New York: Marcel Dekker, Inc., 1988;93–102.
6. Griffiths PR, de Haseth JA. Fourier transform infrared spectroscopy. New York: John Wiley and Sons, Inc., 1986.
7. Hill SL, Krishnan K. Some applications of polarized FT-IR microsampling technique. In: Messerschmidt RG and Harthcock MA, editors. Infrared microspectroscopy: theory and applications. New York: Marcel Dekker, Inc., 1988;115–28.
8. Church SP, Khan N. Infrared dichroism of liquid crystalline terephthalate and biphenyldicarboxylate polyesters. *Polymer Bulletin* 1993;30:559–66.
9. Church S. Polarized infrared microspectroscopy of fibers and crystals. *Spectra-Tech Scan Time* 1992;2:1–4.
10. Kaito A, Kyotani M, Nakayama K. Orientation distribution of liquid-crystalline polyester sheets studied by polarized infrared spectroscopy. *J Polym Sci: Part B: Polym Phys* 1993;31:1099–108.
11. Daniels WW, Kitson RE. Infrared spectroscopy of polyethylene terephthalate. *J Polym Sci* 1958;34:161–70.
12. Brasch JW, Lustger A. Applications of polarized infrared microspectroscopy on polymers. In: Messerschmidt RG and Harthcock MA, editors. Infrared microspectroscopy: theory and applications. New York: Marcel Dekker, Inc., 1988;103–114.
13. Cao B, Mar K. Determination of the principal direction of molecular orientation in FT-IR measurement using two polarizer. *Appl Spectrosc* 1993;47(12):2135–9.
14. Lifgren EA, Abrin SA. Polarized internal reflectance spectroscopic studies of oriented poly(ethylene terephthalate). *J Appl Polym Sci* 1994;51:1251–67.
15. Carton A, Carlsson DJ, Wiles DM. Infrared spectroscopy of polyethylene terephthalate fibers: uses and limitation. *Textile Res J* 1981;52:28–34.
16. Fujimoto K, Iohara K, Ohwaki S, Murase Y. Superstructure in ultrahigh speed spun fibers of poly(ethylene terephthalate). *J Appl Polym Sci* 1991;42:1509–17.
17. Cater RO III, Carduner KR, Paputa Peck MC, Motry DH. The infrared analysis of polyethylene terephthalate fibers and their strength as related to sample preparation and particle size. *Appl Spectrosc* 1989;43(5):791–4.
18. Statton WO, Koenig JL, Hannon. Characterization of chain folding in poly(ethylene terephthalate) fibers. *J Appl Phys* 1970;41:4290–95.
19. Yazdaniyan M, Ward IM, Brody H. An infrared study of the structure of oriented poly(ethylene terephthalate) fibers. *Polymer* 1985;1779–90.
20. Tungol MW, Bartick EG, Montaser A. Forensic examination of synthetic textile fibers by microscopic infrared spectrometry. In: Humecki HJ, editor. Practical guide to infrared microspectroscopy. New York: Marcel Dekker, Inc., 1995;245–86.
21. Cho L. Single fiber analysis by FT-IR microspectroscopy [Ph.D. dissertation]. Manhattan, KS: Kansas State University, 1997.
22. Wetzel DL. Microbeam molecular spectroscopy of biological materials. In: Charalambous G, editor. Food flavors: generation, analysis and process influence. Amsterdam: Elsevier Science, 1995; 2039–108.
23. Wetzel DL. Microbeam molecular analysis. *Microscopy and Analysis* 1996;(5) 17–19.
24. Fraser RDB. *J Chem Phys* 1953;21:1511–5.
25. Fraser RDB. Interpretation of infrared dichroism in fibrous proteins— 2μ region. *J Chem Phys* 1956;24(1):89–95.
26. Cho L, Wetzel DL. Polarized microbeam FT-IR analysis of single fibers. In: Bailey GW, Corbett JM, Dimlich RVW, Michael JR, Zaluzec NJ, editors. Proceedings of microscopy and microanalysis; August 11–15 1996; Minneapolis, MN. San Francisco, CA: San Francisco Press, Inc., 1996;206–7.
27. Wetzel DL, Cho L. Single fiber characterization by polarization FT-IR microspectroscopy. *Mikrochim Acta* 1997;14(Suppl):349–51.

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