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A New Fiber-Sampling Technique for Infrared Spectroscopy as Applied to Nylon 6 and Poly(ethylene Terephthalate)

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Synopsis

A number of techniques have been used in the past for obtaining the infrared spectra of fine fibers. A new technique has been developed which overcomes many of the problems of previous methods. The present technique involves winding a single filament between two salt windows which are separated by a spacer which is the same or slightly greater in thickness than the fibers. This results in a layer of adjacent parallel fibers. Good-quality polarized infrared spectra were obtained on oriented poly(ethylene terephthalate) and oriented nylon 6 fibers with the new technique. The data demonstrate the high level of "A" conformation orientation present in highly drawn nylon 6 fibers and the existance of chain folds in drawn poly(ethylene terephthalate) fibers. The structural changes which occur during the shrinkage of nylon 6 fibers are also demonstrated.

INTRODUCTION

There are a number of techniques which are presently in use for obtaining the infrared spectra of fibers. However, there are problems associated with all of the current methods. In Table I is listed a comparison of some of the more common techniques with their major disadvantages.

TABLE I
Comparison of Techniques for Obtaining the Infrared Spectrum of Fibers

Technique	Disadvantages
Chopping or grinding and dispersing in a matrix such as KBr or nujol	Fiber morphology may change and orientation information is lost
Dissolving fibers in a solvent	Orientation information is lost
Aligning fibers crudely (with fiber overlap and air spaces between fibers)	Quantitative data are difficult to obtain
Use of an infrared microscope or beam condenser	Quantitative data are difficult to obtain owing to low energy and geometry of the optics

The technique described in this paper overcomes many of the problems listed in Table I and has been used effectively for obtaining quantitative polarized infrared data on fibers in our laboratories.

EXPERIMENTAL

The technique is based on the idea of carefully aligning single fibers adjacent and parallel to one another.

It was found that reeling about 100 ft of a single strand of 1-mil fiber between a pair of flat salt plates held apart at the center by a spacer slightly greater in thickness than the fiber was readily feasible. With a rectangular spacer, the fibers align themselves parallel to the sides and in continuous contact, forming an ideal specimen for study with polarized light.

In Figure 1 is shown a diagram of the "bobbin" as used in our laboratory. In order to analyze a yarn sample, a single strand of fiber was first separated from the bundle comprising the yarn. For a 1-mil strand; the total length was approximately 100 ft. Although it is desirable to work with a single length, two or three pieces could also be successfully used. A good specimen could be obtained as long as the second and third windings were begun at the opposite side of the window where the defects were not in the light beam. The uniformity of the windings can be seen in the photograph in Figure 2.

In order to remove a single strand from the yarn, the strand had to be reeled (not wound in the conventional sense) onto a cylinder such as a test tube to avoid twisting. This was also necessary when reeling from the test tube onto the specimen holder (bobbin). The protruding end of the bolt was used as a handle to rotate the entire cell assembly when reeling the fiber on it.

The size of the window shown in Figure 1 was made large enough ($\sim 3/16 \times 3/4$ in.) to allow unobstructed passage of the incident beam. Samples could

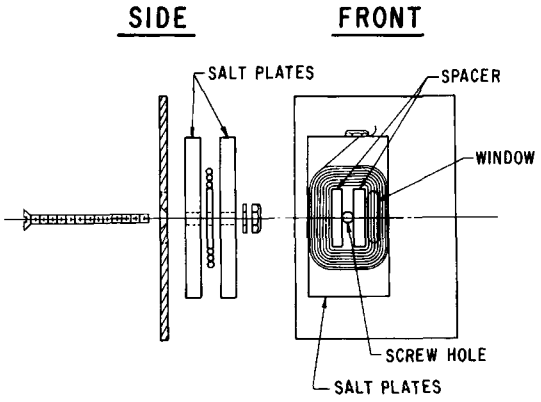

Fig. 1. Diagram of bobbin used for infrared analysis of fiber samples.

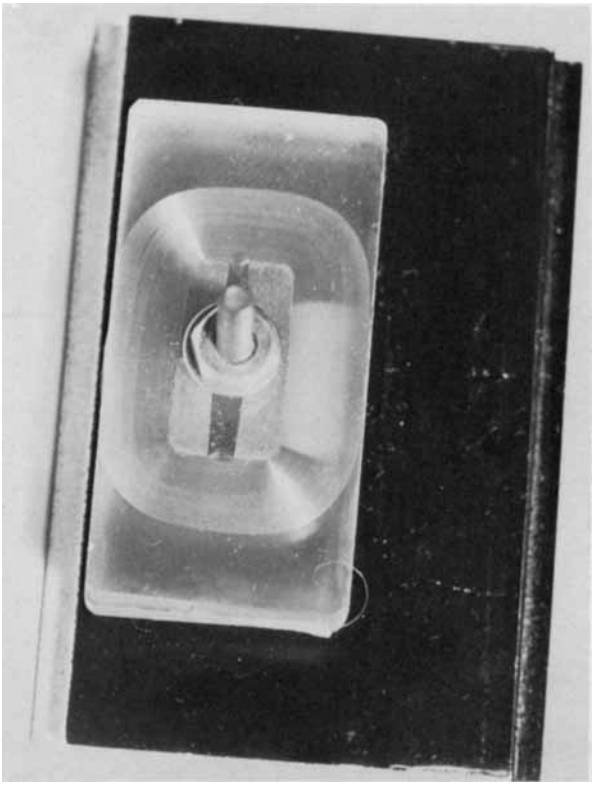

Fig. 2. Photograph of a bobbin-mounted sample of a 25-micron-diameter drawn fiber of nylon 6.

be reeled on and off the bobbin as the need arose, providing that the fiber diameter was compatible with the spacer.

In order to make quantitative measurements, it is critical to know the light path through the sample. Since the cross section of the fiber is circular, an average distance of $\pi d/4$, where d is the diameter of the fiber, may be used. This is an approximation since the true light path is affected by refraction and scattering of the infrared light beam.

The quality of the IR spectra obtained is shown in Figures 3 and 4. The spectra are of poly(ethylene terephthalate) (PET) and nylon 6 fibers, respectively, with polarized light parallel ($\parallel$) and perpendicular ($\perp$) to fiber draw direction. Lack of light leakage between fibers is evidenced by the zero transmittance areas which bottom out equivalent to an opaque material.

RESULTS AND DISCUSSION

The highly dichroic nature of the fibers is evident by the differences between the parallel and perpendicular scans. In Figure 3, the very weak

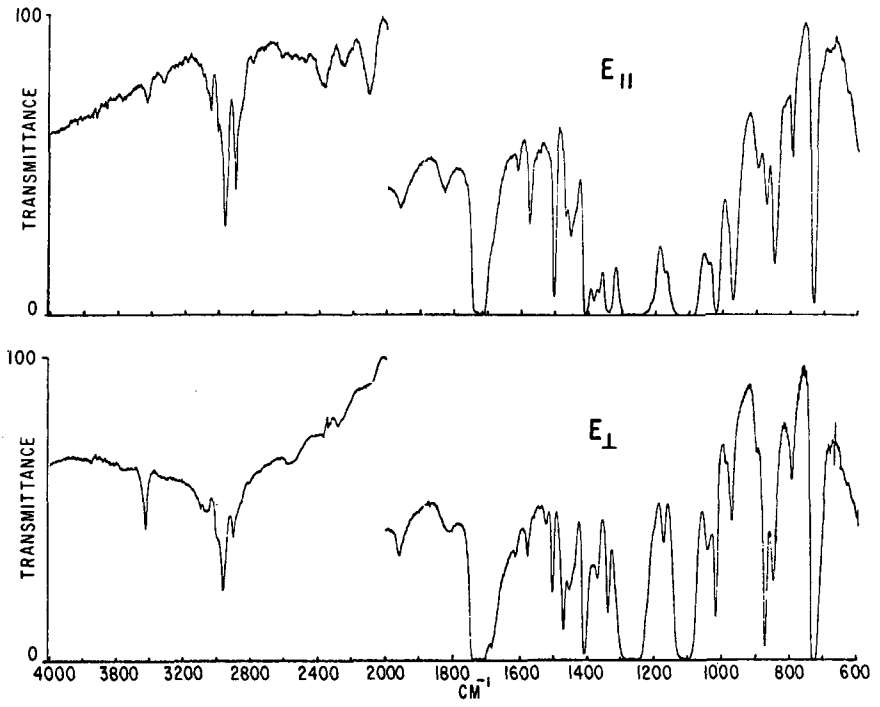

Fig. 3. Perpendicular ($E_\perp$) and parallel ($E_\parallel$) polarized infrared spectra of a highly drawn [drawn 6:1 and subsequently relaxed (20%), fiber diameter approximately 25 microns] poly(ethylene terephthalate) fiber obtained by the bobbin mounting technique.

but evident band at 988 cm^{-1} is indicative of the folded chains[1] in the relaxed PET sample. This band was previously noted[2] in both highly drawn and highly drawn–20% relaxed PET samples. However, these spectra[2] were obtained by crudely aligning fibers and would not lend themselves to good quantitative measurements. The spectra such as those in Figure 3 have been used for quantitative estimates of chain folding as well as for other structural features of oriented PET fibers.

In Figure 4 (nylon 6), the presence of the 930 cm^{-1} band in the parallel spectrum and its absence in the perpendicular spectrum indicates that the "A" conformation (extended zigzag conformation) has reached high levels of orientation at the 4:1 draw ratio level.[3] Likewise, the high intensity of the 830 cm^{-1} band in the perpendicular spectrum relative to the parallel spectrum is also consistent with the "A" conformation being highly oriented with the molecular chain direction in the direction of the fiber axis.[3]

Table II gives quantitative data obtained on nylon 6 by the new "bobbin" wound fiber technique.

The orientation function

$$\frac{A_y - A_x}{A_y + 2A_x} \times 100$$

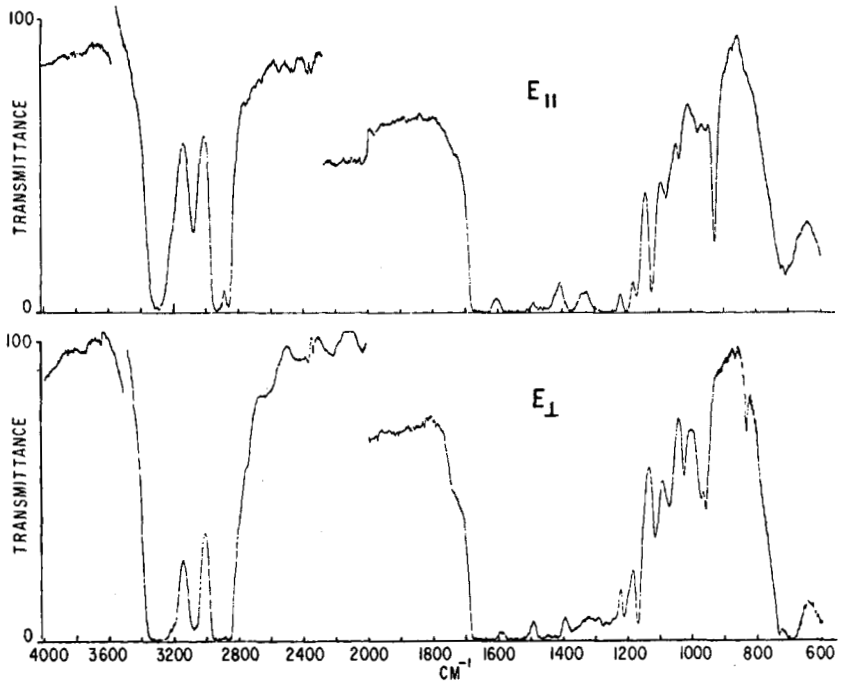

Fig. 4. Perpendicular ($E_{\perp}$) and parallel ($E_{||}$) polarized infrared spectra of a drawn nylon 6 fiber (drawn 4:1, fiber diameter approximately 25 microns) obtained by the bobbin mounting technique.

where A_y and A_x represent absorbance of the 1120 cm^{-1} band with parallel and perpendicular light, respectively, was used to described the orientation of the "B" or twisted conformation.[4]

The "A" conformation orientation was described by the function

$$\frac{A_x - A_y}{A_x + A_y} \times 100$$

where A_x and A_y represent the absorbance with perpendicular and parallel light, respectively, for the 835 cm^{-1} band of nylon 6.

TABLE II
Data Obtained by Infrared Analysis of Nylon 6 Fibers

Fiber draw ratio	3:1	4:1	5.4:1	3:1[a]	4:1[a]	5.4:1[a]
%"B" orientation	47	47	52	47	48	53
%"A" orientation	88	89	84	76	74	77
%"A" conformation	45	51	54	55	65	72

[a] After boiling in H_2O for 1 hr.

Estimates of the amount of the "A" conformation could also be obtained from the fiber spectra by utilization of the expression

$$\%\text{"A"} = \frac{A_{930\ \text{cm}^{-1}}}{A_{C930\ \text{cm}^{-1}}} \times 100$$

where $A_{930\ \text{cm}^{-1}}$ is the absorptivity of the 930 cm^{-1} band in the fiber, and $A_{C930\ \text{cm}^{-1}}$ is the theoretical absorptivity value for a 100% alpha-crystalline (100% "A" conformation) material. The $A_{C930\ \text{cm}^{-1}}$ value was obtained by extrapolation of an absorptivity-versus-alpha-crystallinity plot where the latter values were determined by x-ray analysis. A value of $A_{C930\ \text{cm}^{-1}} = 78\ \text{OD/g/cm}^2$ was found in this manner.

The data in Table II are not reported to represent an in-depth study of the molecular fiber structure, but rather as an illustration of the type of information that may be obtained with the new technique.

The "B" or twisted conformation of nylon 6 (based on the 1120 cm^{-1} band[4]), which to a large part represents the amorphous phase, shows a slight increase in orientation upon drawing from 3:1 to 5.35:1. The "A" conformation is highly oriented at 3:1 and does not change much upon drawing to 5.35:1. "A" conformation content, however, does increase as the draw ratio increases.

This same set of samples was boiled in water for 1 hr to determine what changes in structure or orientation might occur. Shrinkage was allowed to occur during this treatment. The infrared data on these samples indicate that a decrease in the "A" orientation has occurred while an increase in "A' content resulted from the boiling water treatment. Orientation of the "B" conformation did not change although its content must have decreased due to the increase in "A".

These data indicate the utility of the infrared fiber technique and suggest that it can be applied to many types of fiber structure problems.

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