

ORIENTATION OF MOLECULAR GROUPS IN CROSS SECTION OF POLYAMIDE-6 FIBER BY INFRARED ATTENUATED TOTAL REFLECTION DICHROISM STUDIES*

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ABSTRACT

The polymer fiber usually possess typical uniaxial orientation. The molecular chains are symmetrically distributed around fiber axis. In this work, the orientation of molecular groups in the cross section of polyamide-6 fiber has been measured by using IR ATR method. The results indicated that the polyamide-6 fiber mainly contains α -crystalline form. The direction of hydrogen bonds of amide groups is predominately parallel with the surface in the cross section of the fiber.

The polymer fiber usually possesses typical uniaxial orientation. The molecular chains are symmetrically distributed around fiber axis. But in the cross section of the fiber, the orientation of molecular groups can be tended parallel or perpendicular to the fiber surfaces. It is important to study the relationship between process and structure of the fibers. But it is difficult to measure this kind of orientation before. As well known, the three dimensional orientation of polymer film can be measured by using IR sample tilted method^[1-3]. But it is impossible to measure the orientation of molecular groups in cross section of the fibers. Flournoy et al. first proposed that the three dimensional orientation of polymer films can be measured by using infrared attenuated total reflection method^[4,5]. Hobbs et al. designed a new ATR attachment^[6], which allows a wide range of well-defined incidence angles to the crystal as well as increased sensitivity. Dechant measured that the orientation of the molecular chains along axial and radial direction on the surface of polyamide-6 fiber^[7]. The purpose of this work is to present a IR ATR method which can measure the orientation of molecular groups in the cross section of fibers.

PRINCIPLE

In the cross section of fiber, the ideal orientation of the molecular chains was shown in Figure 1. In Figure 1-a, the transition moments of the molecular groups are parallel to fiber surface. If using transmittance method, the electric vector of incidence polarized light is parallel to the transition moment of groups on the position A. But the electric vector is perpendicular to the transition moment in position B, so the measurement of this kind of orientation is impossible. In Fig. 1-b, the transition moments of molecular groups are perpendicular to the fiber surface, this measurement is also impossible.

If using ATR method, the only these parts of fiber, which contacted with the internal reflection plate, can absorb IR light, so orientation of molecular groups of these parts can be measured. Since the molecular chains are symmetrically distributed around the fiber axis, so the

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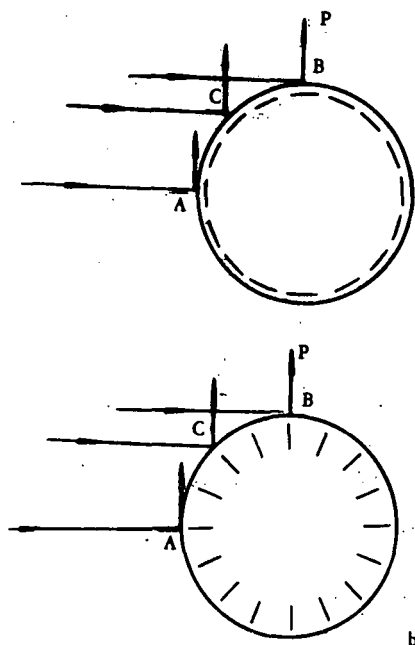


Fig. 1 Schematic of polarized light enters the ideal orientation fibers

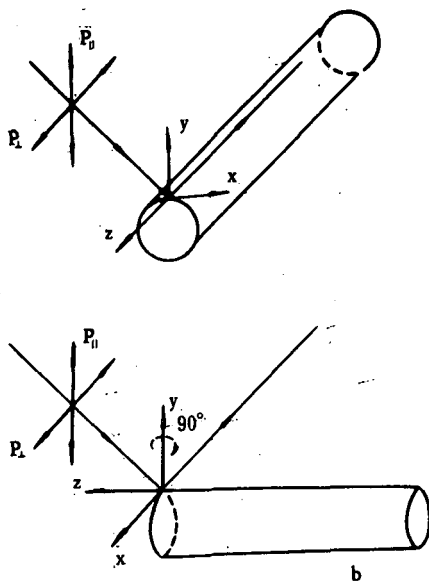


Fig. 2 Definition of three spatial axes and two polarizations for IR ATR dichroism studies on polymer fibers

measurement of orientation of molecular groups in cross section of fibers become possible.

Fig. 2. shows the definition of three spatial axes and two polarizations for IR ATR dichroism studies on polymer fibers. In entrance case of Figure 2-a, if using polarized light $P_{\perp}$, whose electric vector is perpendicular to the entrance plane of the polarized light, then the absorbance along z axis direction (fiber axis) can be measured; but if using polarized light $P_{\parallel}$, whose electric vector parallel to the entrance plane, then measured absorbance is the contribution along X axis (parallel to surface of fibers) and Y axis (perpendicular to surface of fibers) direction. In entrance case of Fig. 2-b, the fiber clockwise rotated 90° around the y axis, if using $P_{\perp}$, then absorbance along X axis direction can be measured; if using $P_{\parallel}$, then measured absorbance is the contribution along Y axis and Z axis direction. Since both the polymer fiber and the polarizer can be rotated by 90° , one can obtain four reflection spectra from which only three spatial absorbances need to be calculated according to the equations^[4,6]

$$A_{P_{\perp},z} = a A_z \quad (1)$$

$$A_{P_{\parallel},z} = b [\sin^2 \theta A_y + (\sin^2 \theta - n^2) A_x] \quad (2)$$

$$A_{P_{\perp},x} = a A_x \quad (3)$$

$$A_{P_{\parallel},x} = b [\sin^2 \theta A_y + (\sin^2 \theta - n^2) A_z] \quad (4)$$

in these equations:

$$a = \frac{4n^2 \cos \theta}{(\sin^2 \theta - n^2)^{\frac{1}{2}} (1 - n^2)}$$

$$b = \frac{4n^2 \cos \theta}{(\sin^2 \theta - n^2)^{\frac{1}{2}} (\sin^2 \theta - n^2 + \cos^2 \theta n^4)}$$

where θ is incidence angle, $n = n_s/n_c$, n_s and n_c are refractive indices of the sample and the reflective crystal, respectively.

For three dimensional orientational measurement, the polarizer needs to be rotated by 90° from the $P_\perp$ to the $P_\parallel$. The effective depth of penetration (d_e/λ_1) for the $P_\perp$ or the $P_\parallel$ light for isotropic materials is determined by equations (5) and (6), respectively.

$$\frac{d_e(P_\perp)}{\lambda_1} = \frac{n \cos \theta}{\pi(1 - n^2)(\sin^2 \theta - n^2)^{\frac{1}{2}}} \quad (5)$$

$$\frac{d_e(P_\parallel)}{\lambda_1} = \frac{n \cos \theta (2 \sin^2 \theta - n^2)}{\pi(1 - n^2)[(1 + n^2) \sin^2 \theta - n^2](\sin^2 \theta - n^2)^{\frac{1}{2}}} \quad (6)$$

where $n = n_s/n_c$, $\lambda_1 = \lambda/n_c$ and θ is the incidence angle.

If using KRS-5 internal reflection plate, its refractive index is 2.4, and the refractive index of polyamide-6 is about 1.5^[7]. From equations (5) and (6), the effective depths for the $P_\perp$ and $P_\parallel$ lights are shown in Table 1 for isotropic polyamide-6 at a given incidence angle.

Table 1 Effective penetration depth (d_e/λ_1) as a function of incidence angle and polarization for polyamide-6

θ , deg	$d_e(P_\perp)$	$d_e(P_\parallel)$
45	0.70	1.40
51.2	0.44	0.80

The effective depth for the $P_\parallel$ light is greater than for the $P_\perp$ light as shown in Table 1. This trend also be valid even for anisotropic materials. It would be desirable to compare A_x , A_y , and A_z values at a similar depth, since structure orientation may be a function of the surface depth. Fortunately, Table 1 shows that a 45° angle for the $P_\perp$ light provides similar depth to that of a 51.2° angle for the $P_\parallel$ light, so this combination of angle and polarization was chosen for the three dimensional orientation analyses in this study.

EXPERIMENTAL

The polyamide-6 fiber was kindly provided by synthesis laboratory of our institute. The diameter of the fiber is 0.2mm. The fiber was regularly wound onto a PMMA sheet, the size is 20×20 mm. So that, after the sample rotated by 90° and remounting, the effective optical contact area between the crystal and the wound fiber nearly keeps constant.

The Specac continuously variable incidence angle ATR devices and KRS-5 crystal internal reflection plate with 45° entrance and exit face angles was used. The polarized spectra were obtained with a Perkin-Elmer gold wire grid polarizer. ATR single-beam reflection spectra were collected with a Bruker IFS-113v fourier transform infrared spectrometer. The liquid nitrogen cooled broadband mercury-cadmium telluride detector was used. The spectral range is $4000\text{--}500\text{ cm}^{-1}$. Each spectrum was the average of 500 scans at resolution of 2 cm^{-1} .

For characterization at a given depth, four ATR spectra of the fiber were collected corresponding to $A_{P_\perp, x}$ and $A_{P_\perp, z}$ at a nominal 45° incidence angle and $A_{P_\parallel, x}$ and $A_{P_\parallel, z}$ at a

nominal 60° incidence angle to compare for a similar effective depth. Due to the beam refraction at the entrance face of the crystal, the actual effective angles of incidence were 45° and 51.2° , rather than the nominal 45° and 60° . The effective depth of the surface probed under these conditions was about $3\ \mu\text{m}$ at $1000\ \text{cm}^{-1}$. The depth range is calculated based on equations (5) and (6), which assume ideal contact between sample and the crystal and smoothness of both surfaces. Furthermore, the calculated depth is based on the refractive index for isotropic polymer, which introduces 5–10% error in the case of anisotropic fiber. Therefore, the depths given throughout this paper should be only regarded as approximate values.

RESULTS AND DISCUSSION

Figure 3 shows the four IR ATR spectra obtained from the surface of polyamide-6 fiber for the four possible combinations of sample and polarizer orientation. According to aforementioned measurement condition, the parameters for equations (1)–(4) can be written in the following form:

$$A_{P\perp,z} = 5.48 A_z \quad (\text{for } 45^\circ) \quad (7)$$

$$A_{P\parallel,z} = 4.62 A_y + 1.65 A_x \quad (\text{for } 51.2^\circ) \quad (8)$$

$$A_{P\perp,x} = 5.48 A_x \quad (\text{for } 45^\circ) \quad (9)$$

$$A_{P\parallel,x} = 4.62 A_y + 1.65 A_z \quad (\text{for } 51.2^\circ) \quad (10)$$

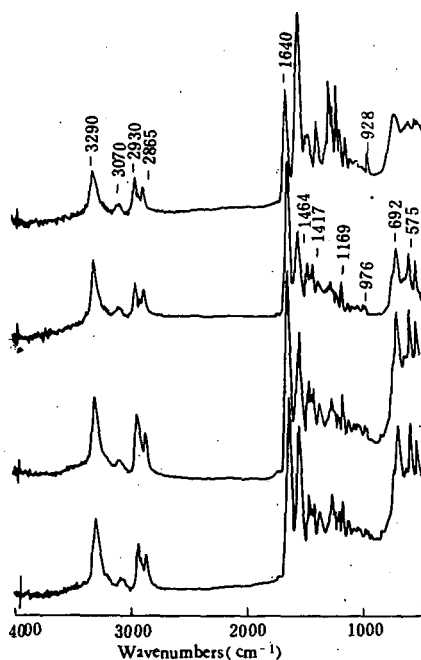


Fig. 3 The $A_{P\perp,z}$, $A_{P\perp,x}$, $A_{P\parallel,z}$, and $A_{P\parallel,x}$ spectra (from top to bottom) obtained from surface of polyamide-6 fiber as a function of sample rotation and polarizer rotation

According to the parameters for equations (7)–(10), the digital absorbance subtractions were done. The two A_y spectra were obtained from each of the $A_{P_{||,z}}$ and $A_{P_{||,x}}$ spectra, as shown in Fig. 4.

As well known, the polyamide-6 possesses two crystalline modifications, one is α -form, and another is γ -form, both have characteristic infrared bands^[8-10]. The characteristic bands for α -form are 3070, 1477, 1417, 1201, 959, 928, 692, and 575 cm^{-1} , and the characteristic bands for γ -form are 3096, 1463, 1439, 1169, 976, 914, 771, and 628 cm^{-1} . From the infrared spectra in Fig. 3, the crystalline structure of the polyamide-6 fiber mainly is α -form. But the presence of 1169 and 976 cm^{-1} bands in these spectra indicated that the γ -form modification also presents in the fiber.

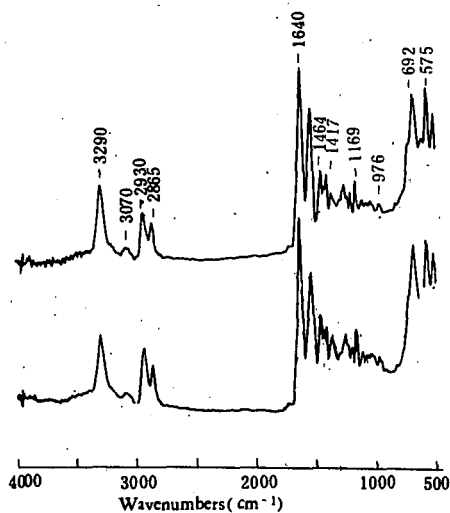


Fig. 4 The two A_y spectra obtained from $A_{P_{||,z}}$ and $A_{P_{||,x}}$ spectra by digital absorbance subtractions. (top: A_{yz} ; bottom: A_{yx})

From these four spectra, the A_x , A_z , and two A_y values of polyamide-6 bands have been calculated based on equations (7)–(10). The assignment, absorbance, and dichroism of main bands of polyamide-6 fiber have been listed in Table 2, where π shows the parallel bands ($A_z > \frac{A_x + A_y}{2}$), σ shows the perpendicular bands ($A_z < \frac{A_x + A_y}{2}$), $\parallel$ shows the bands which $A_x > A_y$, and $\perp$ shows the bands which $A_x < A_y$. In order to compare, the bands dichroism of the α -polyamide-6 film, which was measured by using microtomed sections method, is also listed in Table 2^[10].

Comparison of the two A_y values in Table 2 shows a general agreement between them. But the coefficients for equations (7)–(10) are based on the refractive index for isotropic polymer. For highly anisotropic polymer fiber, the coefficients change at most 10%, which affects the A_x , A_y , and A_z values. However, it does not affect the dichroic ratio⁽⁶⁾.

From Table 2, we can see that the dichroism of infrared bands of α -polyamide-6 fiber is similar to the dichroism of bands of α -polyamide-6 film. This results indicate that the direction of hydrogen bonds of amide groups is predominately parallel with the surface in cross section of the

Table 2 Three spatial absorbances and dichroism of some IR bands of polyamide-6 fiber

Band (cm^{-1})	Assign- ment	A_z	A_x	A_{yz}	A_{yx}	$\bar{A}_y$	Dichroism	Dichroism of film
3290	$\nu(\text{NH})$	0.0172	0.0268	0.0216	0.0208	0.0212	$\sigma \parallel$	$\sigma \parallel$
3070	$2x\delta(\text{NH})$	0.0024	0.0036	0.0030	0.0030	0.0030	$\sigma \parallel$	$\sigma \parallel$
2930	$\nu_{as}(\text{CH}_2)$	0.0104	0.0112	0.0128	0.0160	0.0144	$\sigma \parallel$	$\sigma \parallel$
2865	$\nu_s(\text{CH}_2)$	0.0056	0.0088	0.0068	0.0072	0.0070	$\sigma \parallel$	$\sigma \parallel$
1640	$\nu(\text{CO})$	0.0372	0.0630	0.0558	0.0530	0.0544	$\sigma \parallel$	$\sigma \parallel$
1477	$\delta(\text{CH}_2)$	0.0056	0.0060	0.0026	0.0030	0.0028	$\pi \parallel$	$\pi \parallel$
1464		0.0016	0.0110	0.0104	0.0092	0.0098	$\sigma \parallel$	$\sigma \parallel$
1438		0.0012	0.0024	0.0030	0.0036	0.0033	$\sigma \perp$	$\sigma \perp$
1417		0.0024	0.0096	0.0076	0.0068	0.0072	$\sigma \parallel$	$\sigma \parallel$
1169	$\iota(\text{CH}_2)$	0.0104	0.0112	0.0116	0.0126	0.0121	$\sigma \perp$	$\sigma \perp(\gamma)$
976	$\nu(\text{CC})$ or $r(\text{CH}_2)$	0.0012	0.0024	0.0028	0.0030	0.0029	$\sigma \perp$	$\sigma \perp(\gamma)$
959		0.0010	0.0030	0.0020	0.0018	0.0019	$\sigma \parallel$	$\sigma \parallel$
928		0.0086	0.0010	0.0004	0.0002	0.0003	$\pi \parallel$	$\pi \parallel$
833		0.0006	0.0014	0.0022	0.0020	0.0021	$\sigma \perp$	$\sigma \perp$
731	$r(\text{CH}_2)$	0.0010	0.0048	0.0066	0.0070	0.0068	$\sigma \perp$	$\sigma \perp$
692	$\gamma(\text{NH})$	0.0068	0.0152	0.0180	0.0180	0.0180	$\sigma \perp$	$\sigma \perp$
575	$\gamma(\text{CO})$	0.0028	0.0136	0.0188	0.0164	0.0176	$\sigma \perp$	

fiber. However, all hydrogen bonds in the film tend to be parallel to each other. But the hydrogen bonds in the fiber are symmetrically distributed along the circumference surface. Moreover, Arimoto^[10] also found that the direction of hydrogen bonds of amide groups is preferentially normal to the surface for γ -form polyamide-6 film. In this work, the A_x/A_y value of the 976 cm^{-1} band is slightly smaller than 1. Because the direction of transition moment of 976 cm^{-1} band is the same with that of N-H stretching mode^[10], so the result indicates that the direction of hydrogen bonds of amide groups for γ -form is preferentially normal to the surface in the cross section of fiber. Even if the orientation is very low, but the trend is similar to that for film.

CONCLUSION

1. In the cross section of polymer fiber, the orientation of molecular groups can be measured by using infrared attenuated total reflection methods. The probed depth is about few micron from the surface of fiber.

2. The polyamide-6 fiber, which was measured, mainly contains α -crystalline form. The direction of hydrogen bonds of amide groups is predominately parallel to the surface in the cross section of the fiber. Moreover, the hydrogen bonds direction of small amount γ -crystalline form, which is present in the fiber, is preferentially normal to the fiber surface.

Keywords:

Fiber; Infrared Dichroism; Orientation; Polyamide-6

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