Determination of Optical Properties, Dispersion, and Structural Parameters of Poly(ethylene terephthalate) Fibers Using Automatic Variable Wavelength Interferometry Technique

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ABSTRACT: Automatic variable wavelength interferometry (VAWI) is used in combination with a Pluta double refracting polarizing interference microscope for measuring the spectral dispersion parameters of the refractive indices of poly(ethylene terephthalate) (PET) highly oriented yarn fibers (1000 denier/250 filaments). The resulting data are utilized to calculate the spectral dispersion and structural parameters such as Cauchy's constants, the dispersion energy, the oscillation energy, the density, the mean polarizability of the monomer unit, the number of monomer units per unit volume, the dielectric constant, the electric susceptibility, the optical orientation function, and the electric polarizability constant. Microinterferograms are given for illustration. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1737–1742, 2003

Key words: dispersions; refractive index; structure–property relations; automatic variable wavelength interferometry technique

INTRODUCTION

The refractive indices of fibers and their birefringence are generally accepted as good indicators of molecular orientation, structural homogeneity, polarizability, and other physical properties that describe the functional behavior of natural and manufactured fibers. The investigation of dielectric properties is one of the most conventional and sensitive methods of studying the polymer structure.[1]

Microinterferometry has been recognized as a useful tool for the investigation of natural, synthetic, and optical fibers.[2–8] A detailed survey of the investigators, methods, and techniques of microinterferometry applied to fibrous materials is given by Barakat and Hamza.[9]

The main task of any kind of interferometry is to correctly determine the interference order in the image of the object under study. This task was simplified by using an interferometric method reported by Pluta,[10] referred to as variable wavelength interferometry (VAWI). Pluta[11] used his VAWI method to measure the spectral dispersion for the birefringence and/or the refractive indices of textile fibers. Recently, the two beam interference Pluta microscope[12,13] has been

modified to be suitable for automatic measurements and studies of optical and textile fibers.[14]

Hamza et al.[7,15,16] used this method to determine the spectral dispersion curves of polypropylene and highly oriented fibers. Sokkar and El-Bakary[17] also used this method to determine the refractive index profile of highly oriented fibers.

In the present work, the automatic VAWI technique is used to measure the spectral dispersion parameters of the refractive indices of poly(ethylene terephthalate) (PET) fibers. The resulting data are utilized to calculate the spectral dispersion and some structural parameters of the polymer material such as Cauchy's constants, the dispersion energy, the oscillation energy, the density, the mean polarizability of the monomer unit, the dielectric constant, the electric susceptibility, the optical orientation function, and the electric polarizability constant of PET fibers.

THEORETICAL

Dispersion properties of fiber material using automatic VAWI technique

The VAWI[10] method uses highly monochromatic light of a continuously variable wavelength. This method is commonly used in combination with the double refracting polarizing interference microscope (Pluta microscope[12,13]) for measuring the initial interference order (m_1) of the interference pattern produced by a fiber, which is found via the following equation[10]:

$$m_1 = q_s \frac{b_s}{b_1 - b_s} \qquad (1)$$

where b_s is the interfringe spacing corresponding to the wavelength λ_s and b_1 is due to the wavelength λ_1. The subscript S denotes the coincidence number, and q_s is the increment of the initial interference order. Using eq. (1), the initial interference order can be determined from which the refractive indices and birefringence can be calculated using the following equations:

$$\delta_s^{\parallel} = (n_{\parallel s} - n_s)t = (m_1^{\parallel} + q_s)\lambda_s^{\parallel} \qquad (2)$$

$$\delta_s^{\perp} = (n_{\perp s} - n_s)t = (m_1^{\perp} + q_s)\lambda_s^{\perp} \qquad (3)$$

where $\delta_S^{\parallel}$ and $\delta_S^{\perp}$, $m_1^{\parallel}$ and $m_1^{\perp}$, and $\lambda_S^{\parallel}$ and $\lambda_S^{\perp}$ are the optical path differences, the initial interference orders, and the wavelengths for light vibrating parallel ($\parallel$) and perpendicular ($\perp$) to the fiber axis, respectively. Using the above equations, the spectral dispersion parameters of the refractive indices ($n_{\parallel}$ and $n_{\perp}$) can be obtained. The birefringence is given by the following equation:

$$\Delta n = n_{\parallel} - n_{\perp} \qquad (4)$$

Cauchy's dispersion relation

The variation of the refractive index of the fiber material with the wavelength can be written from Cauchy's dispersion relation[18]:

$$n(\lambda) = A + \frac{B}{\lambda^2} \qquad (5)$$

where $n(\lambda)$ is the refractive index at a given λ and A and B are Cauchy's constants, which depend on the fiber material.

Dispersion and oscillation energy

The dispersion energy and oscillation energy are given by the following equation[19]:

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} + \frac{E^2}{E_d E_o} \qquad (6)$$

where E_o is the average energy gap or oscillation energy, E is the photon energy, n is the refractive index of the fiber material, and E_d is the dispersion energy. The dispersion energy is called the electronic oscillator strength, which is a measure of the strength of the interband optical transition. It is related to the charge distribution within each unit cell and to chemical bonding. It plays an important role in determining the behavior of refractive indices and properly normalizes

the interaction potential describing these optical effects. This is due to the relationship between the electronic optical properties of the material and its chemical bond.[20] Equation (6) can be used for light vibrating parallel and perpendicular to the fiber axes.

Mean polarizability of monomer unit

The polarizability of a monomer unit like the polarizability of a simple organic molecule usually differs in different directions. Because the refractive index of a polymer depends upon the total polarizability of the molecules, this leads to the Lorentz–Lorenz by the following equations[21]:

$$\frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2} = \frac{N_{(1)}\alpha^{\parallel}}{3\psi} \qquad (7)$$

An analogous formula can be used for $n_{\perp}$, where $n_{\parallel}$ and $n_{\perp}$ are the mean refractive indices of the fiber for light vibrating parallel and perpendicular to the fiber axis, respectively; $\alpha^{\parallel}$ and $\alpha^{\perp}$ are the corresponding polarizabilities of the monomer unit; and ψ is the permittivity of free space. For a bulk polymer of density ρ and monomer unit molecular weight M, the number of monomer units per unit volume, which also equals the number of carriers of the dipole moment, is given by the following equation[22]:

$$N_{(1)} = \frac{N_A \rho}{M} \qquad (8)$$

where N_A is Avogadro's number, the PET M value is 192,[22] and de Vries et al.[23] gives ρ for PET fiber in the following form:

$$\rho = K \frac{(n_{iso}^2 - 1)}{(n_{iso}^2 + 2)} \qquad (9)$$

where $n_{iso} = (n_{\parallel} + 2n_{\perp})/3$ is the isotropic refractive index[24] and $K = 4.047$ for PET fiber.[23]

Dielectric constant and electric susceptibility

The following relation[25] gives the dielectric constant d:

$$d^{\parallel} = n_{\parallel}^2 \qquad (10)$$

With an analogous formula, $n_{\perp}$ can be given. The electric susceptibility η is related to the d value by the following equation[25]:

$$\eta = \frac{d - 1}{4\pi} \qquad (11)$$

The index of refraction n_{iso} is given by the square root of the direct current (dc) dielectric constant (d_{dc}) by the following equation[25]:

$$n_{iso} = \sqrt{d_{dc}} \quad \text{or} \quad d_{dc} = n_{iso}^2 \qquad (12)$$

Plotting $\{1/(n_{iso}^2 - 1)\}$ versus $(1/\lambda^2)$, a linear relationship is obtained from which the d_{dc} value can be calculated.[26,27]

Optical orientation function and electric polarizability constant

The optical orientation function can be calculated using the classical relation[28]

$$\langle P_2(\theta) \rangle = \frac{\Delta n}{\Delta n_{max}} = f_\Delta \qquad (13)$$

which is the same function named by Hermans.[29] The Δn_{max} value of PET fibers has been previously determined, which equals 0.24 according to de Vries[22] for a perfectly (or fully) oriented fiber, and Δn is the measured mean birefringence. Hermans' optical orientation function (f_θ) has been corrected by de Vries[22] to be in the range of $0 < \Delta n < 0.8$, as determined by

$$f_\theta = (1 + a)f_\Delta - af_\Delta^2 \qquad (14)$$

where the constant a is given by the following equation:

$$a = \frac{2n_\parallel^2 n_\perp^2}{n_v^3(n_\parallel + n_\perp)} - 1 \qquad (15)$$

in which n_v is the virtual refractive index as defined by the following equation[22]:

$$n_v = \sqrt{1 + \frac{3[n_\parallel^2 - 1][n_\perp^2 - 1]}{[n_\perp^2 - 1] + 2[n_\parallel^2 - 1]}} \qquad (16)$$

Cunningham et al.[30] derived a relation between the optical orientation function $\langle P_2(\theta) \rangle$ and the polarizability, which is given by

$$\frac{\Phi^\parallel - \Phi^\perp}{\Phi^\parallel + 2\Phi^\perp} = \left[\frac{\Delta \alpha}{3\alpha_o}\right] \langle P_2(\theta) \rangle \qquad (17)$$

where

$$\Phi^\parallel = \frac{n_\parallel^2 - 1}{n_\parallel^2 + 2}, \quad \Phi^\perp = \frac{n_\perp^2 - 1}{n_\perp^2 + 2}$$

are the polarizabilities per unit volume when using monochromatic light vibrating parallel and perpendicular to the fiber axis, respectively. The quantity $[\Delta \alpha / 3\alpha_0]$ is a structure constant for a given polymer that depends on the molecular orientation function.

EXPERIMENTAL

Automatic VAWI technique

An automatic computer-aided microinterferometer[14] is used. This technique is specially designed to measure and study the spectral dispersion of the refractive indices of fibrous material using the VAWI technique. The main part of the automatic optical system is the Biolar PI microinterferometer.[12,13] It is fitted with a halogen lamp (12 V/100 W) as a highly monochromatic light source, a wedge interference filter, a stepper motor controller, a PC computer with frame-grabber, a CCD camera, and an image display monitor. The intensity of the interference field and the contrast of the fringes are optimized by adjusting the width of the condenser slit. The measurements using this technique are controlled using an image analysis software program.

Automatic measurement of fiber thickness and refractive indices using VAWI technique

The test sample of PET fibers is placed on the microscope stage and the microinterferometer is adjusted in subtractive position[14] for measuring the thickness of the fiber. The average thickness of the test sample is 21.8 μm.

The microinterferometer is adjusted in crossed position[14] for obtaining the duplicated images, one for the parallel direction and the other for the normal direction of the vibrating light, to measure the refractive indices of the PET fiber at different wavelengths. Figure 1(a,b) shows the printed microinterferograms taken from the image screen of duplicated images for the refractive indices of PET fiber using the automatic VAWI technique. The upper image shows the parallel direction of light vibration and the lower image shows the perpendicular one.

Figure 2 gives the refractive indices ($n_\parallel$ and $n_\perp$) as a function of $1/\lambda^2$ in the wavelength range from 400 to 620 nm. Constants A and B of the Cauchy's dispersion formula are calculated. The results are given in Table I.

From the spectral dispersion of the refractive indices $n(\lambda)$, the E_d and E_o values for the PET fiber are determined using eq. (6). Figure 3 shows the plot of $(n^2 - 1)^{-1}$ versus the square of photon energy (E^2). The results of the calculations of E_d and E_o are given in Table I.

The density of PET fiber is calculated using eq. (9) at a 590-nm wavelength and it is found to be 1.358 g/cm^3. The value of the density is used to determine the number of monomer units per unit volume ($N_{(1)}$) at the same wavelength using eq. (8), and it is found to
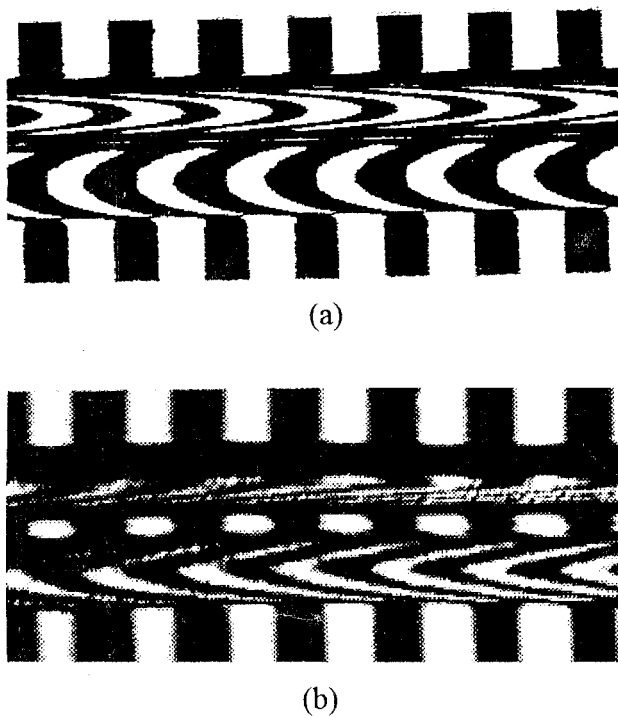
(a)

(b)

Figure 1 The printed microinterferograms of the duplicated images of PET fibers for the refractive indices in the cases of light vibrating (a) parallel and (b) perpendicular to the fiber axis using the automatic VAWI technique.

be 4.255×10^{21} monomer units/cm^3. Also, the polarizabilities of the monomer units per unit volume ($\alpha_{\parallel}$ and $\alpha_{\perp}$) are calculated for the same wavelength using eq. (7). The results are given in Table I.

The dielectric constants for light vibrating parallel ($d^{\parallel}$) and perpendicular ($d^{\perp}$) to the fiber axis and the electric susceptibilities ($\eta^{\parallel}$ and $\eta^{\perp}$) are calculated using eqs. (10) and (11), respectively, at a 590-nm wavelength. The results are given in Table I. Figure 4 gives the relation between $(n_{\mathrm{iso}}^2 - 1)^{-1}$ and $1/\lambda^2$, from which the d_{dc} value is calculated. We found it to be 2.458.

The experimental values of the $n_{\parallel}$ and $n_{\perp}$ and the birefringence (Δn) at a 590-nm wavelength are used for calculating the polarizabilities ($\phi_{\parallel}$, $\phi_{\perp}$) and the $\langle P_2(\theta) \rangle$ according to eqs. (17) and (13), respectively. The $\langle P_2(\theta) \rangle$ value is 0.841 and the $[\Delta\alpha/3\alpha_0]$ value is 0.111 for PET fiber material. The value of the electric polarizability constant depends on the molecular structure.

RESULTS AND DISCUSSION

The interaction between light and matter leads to the refraction effects, which are essentially forced vibrations of electrons with a natural wavelength (λ_o) by an oscillatory electric field of wavelength λ. The refractive index varies with the variation of the wavelength of the incident light beam because of these interactions. The relationships between the structural parameters (such as the optical orientation function, density,
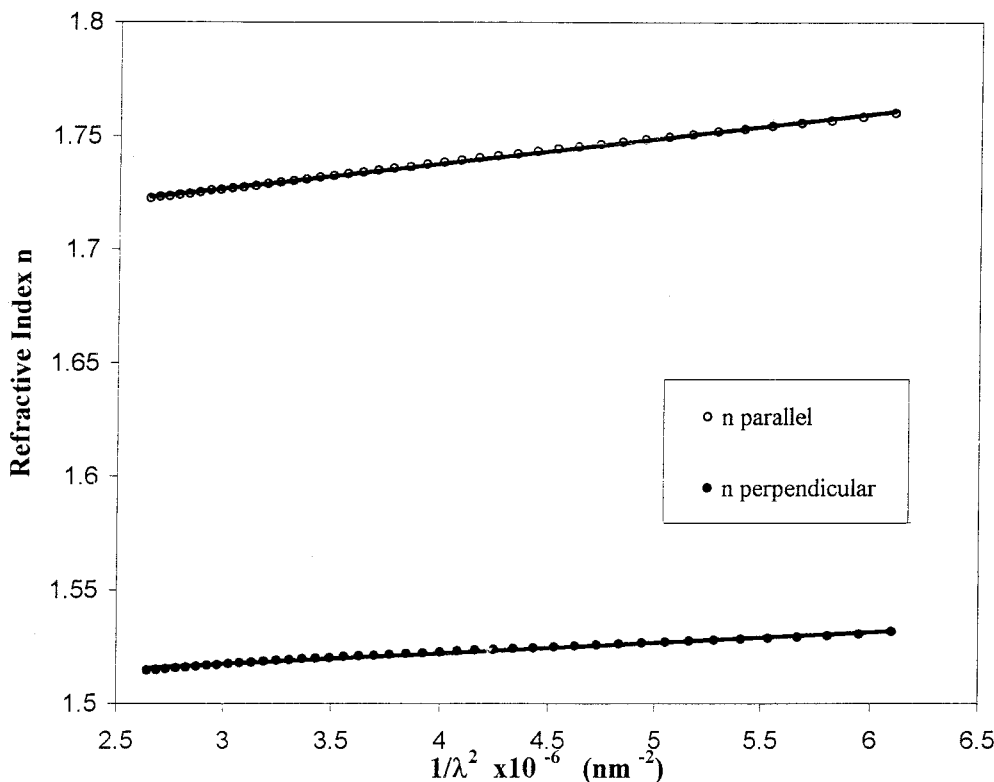

Figure 2 The refractive indices ($n_{\parallel}$ and $n_{\perp}$) as a function of $1/\lambda^2$ to verify Cauchy's dispersion relation for PET fiber.

TABLE I
Calculated Spectral Dispersion and Structural Parameters for PET Fiber at 590-nm Wavelength
Using VAWI Technique

Direction of vibrating light	Constants						
	A	B ($\times 10^3$ nm^2)	E_d (eV)	E_o (eV)	α ($\times 10^{-33}$)	d	η
Parallel	1.694	11	17.69	9.416	2.476	2.976	0.157
Perpendicular	1.503	4.7	15.28	12.11	1.884	2.299	0.103

and other physical structural parameters) and the refractive index is a qualitative relation because these structure parameters are intrinsic properties of the material.

CONCLUSION

The transmitted light VAWI technique is suitable for microinterferometry of polymers or other synthetic fibers. These techniques enable the spectral dispersions $[n_\parallel(\lambda), n_\perp(\lambda)]$ to be quickly determined. The accuracy of the measurement of the refractive index is about 0.1%. In addition, it is 0.5 nm for the wavelength λ using this technique.[9] Moreover, this method should be particularly useful and important for the structural investigation of a given test fiber.

The following conclusions may be drawn from the measurements carried out in the present work using the automatic VAWI technique for PET fibers:

1. The constants that relate the molecular arrangement of PET to the wavelength of the incident light beam can be found from the plot of $n(\lambda)$ versus $1/\lambda^2$.
2. The plot of $(n^2 - 1)^{-1}$ as a function of the E^2 enables us to determine the E_o and E_d values according to eq. (6).
3. The number of monomer units per unit volume is calculated and found to be 4.255×10^{21} monomer units/cm^3.
4. The d_{dc} value is calculated from the plot of $(n_{iso}^2 - 1)^{-1}$ and λ^{-2}, and it is found to be 2.458.
5. The calculated value of the $[\Delta\alpha/3\alpha_0]$ (0.111) depends on the molecular structure of the PET fiber material.

Finally, the above experimental results and calculations confirm the dispersion of selected structural parameters of PET fibers. These results are useful for
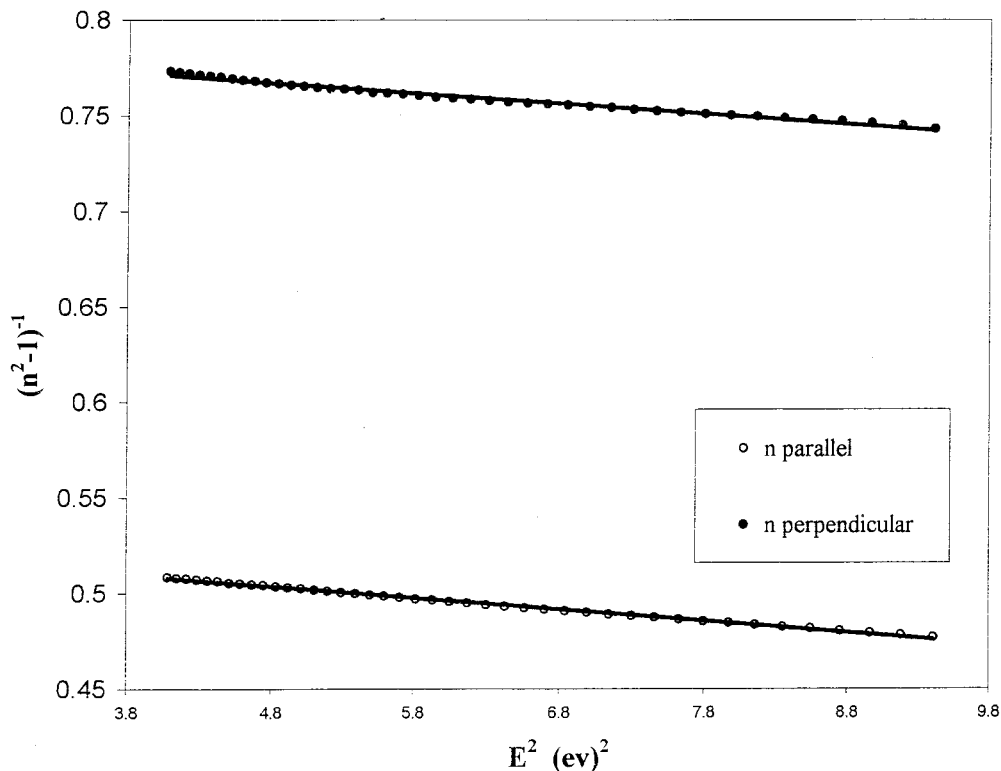

Figure 3 The plot of $(n_{iso}^2 - 1)^{-1}$ versus the square of the photon energy (E^2) of PET fiber.
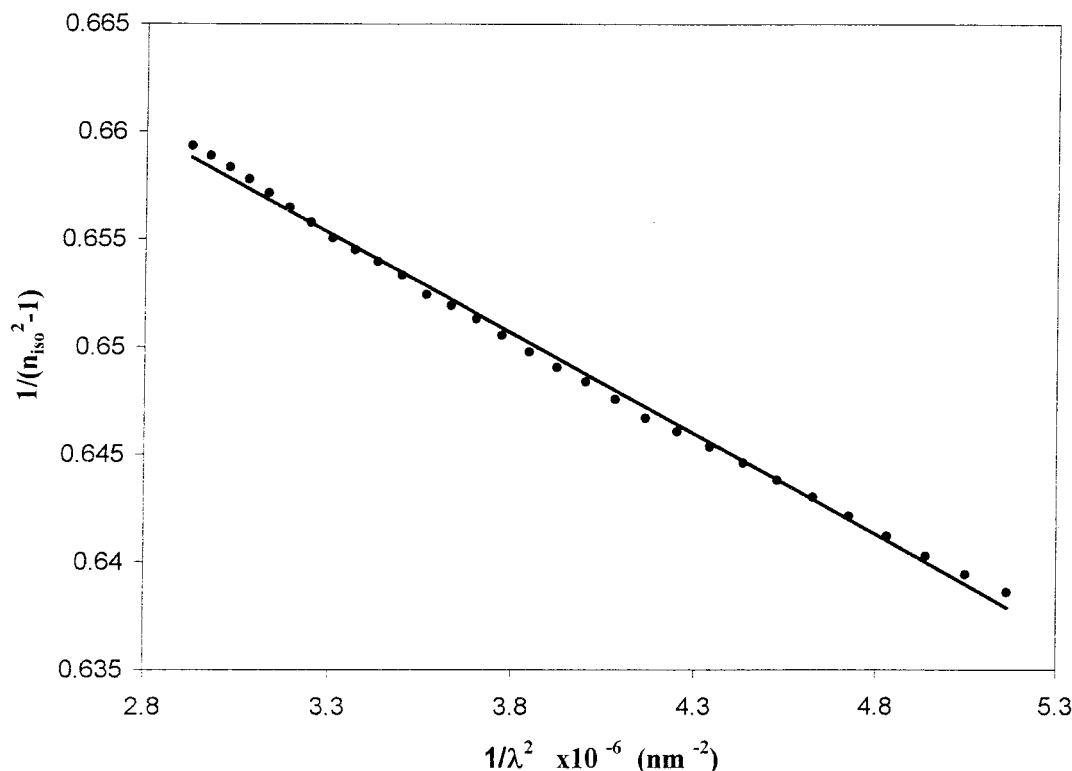
Figure 4 The relation between $(n_{iso}^2 - 1)^{-1}$ and $1/\lambda^2$ from which the dc dielectric constant (d_{dc}) is calculated.

industry and human's end use. The VAWI technique is a more suitable and promising technique for the accurate determination of the optical and structural parameters of PET fibers.

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