# Opto-Thermal Properties Of Fibers: XVII. Structure Characterization Of Cold Drawn Boiled Viscose Fibers 

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#### Abstract

A two-beam interferometric method is used to study the change of optical parameters of cold drawn boiled viscose fibers at different times. A stress-strain device conjugated to the Pluta polarizing interference microscope is used to investigate the dynamical behavior of opto-mechanical properties at room temperature. Some structural parameters such as the number of molecules per unit volume, the virtual and isotropic refractive indices, the optical orientation factor and angle, the strain and the stress optical coefficients are evaluated. Some mechanical parameters such as, Young's modules, elastic shear modules and the compressibility are calculated over different strain values. Also the number of network chain per unit volume $N_{c}$, work per unit volume $W$, average work per chains $W^{\prime}$, reduction in entropy $\Delta S$, and the optical configuration parameter $\Delta \alpha$ are determined. Also calculation of the constants of Moony-Rivilin equation are given. A systematic study over different wavelengths range extending from 405 to 590 nm was carried out to obtain the dielectric constant at infinity. The obtained results clarify that new reorientations occurred due to cold drawing at different conditions. Empirical formula is suggested to correlate the change in $\Delta n, f(\theta), W, W^{\prime}, A, \theta$, and $N_{c}$ with different draw ratio, and its constants were determined. Microinterferograms and curves are given for illustrations. © 1999 John Wiley \& Sons, Inc. J Appl Polym Sci 72: 1185-1201, 1999


Key words: interferometry; viscose fibers; birefringence; optical configuration; orientation

## INTRODUCTION

Optical anisotropy produced in fibers by stretching gives valuable information for characterization of these fibers on the molecular level. An analysis of the relation between the birefringences and the draw ratios of some synthetic fibers has appeared in extensive publications. The orientation can be produced by either hot stretching of a molten polymer followed by rapidly cooling of the melt, by cold drawing, or by cold rolling.

[^0]Cold drawing manifests itself as a necking of the polymer during stretching. Cold drawing after the yield point means that there must be a strain hardening process; otherwise, the material would break without drawing at the reduced cross section where necking took place. The strain hardening generally results from molecular orientation, which increases the modules and tensile strength. The draw ratios are functions of temperature, orientation, and other variables. On further stretching of the cold drawn polymer, the stress generally rapidly increases and failure soon occurs. Oriented polymers have birefringence: the refractive indices along the orientation and at right angle to it are different. When this
difference $(\Delta n)$ is larger, the segments are oriented more in the direction of force action. ${ }^{1-9}$

In the present work a modified microstrain device designed ${ }^{10}$ earlier and modified ${ }^{11}$ was used in conjunction with a double-beam interference microscope to study the optical and mechanical parameters produced in viscose fibers (viscose rayon filament, Misr Co. of Artificial Silk, Egypt) under different conditions. The variations of refractive indices and birefringence by different stresses were studied. The resulting data were utilized to calculate the strain optical coefficient, stress optical coefficient, optical orientation function, orientation angle, Poisson's ratio, and the virtual refractive index. Also determined were the constants of Moony-Rivlin equation, $\left(\Delta \alpha / 3 \alpha_{0}\right)$ the electric polarizability polymer structure constant, and other optical and mechanical parameters.

## Theoretical Consideration

The totally duplicated image of the examined fibers by the double-beam interference Pluta microscope was used to measure the mean refractive indices of the fibers. Measuring the area under the fringe shift $F$, the difference between the refractive indices of the fiber and that of immersion liquid was used to overcome the irregularity of fibers. The following expression ${ }^{9,12}$ was used to determine the refractive indices of the fiber which has irregular cross section and deformed during the drawing process.

$$
\begin{equation*}
n^{\|}=n_{L}+\left(F^{\|} D / A\right)(\lambda / h) \tag{1}
\end{equation*}
$$

with an analogous formula for $n^{\perp} . n_{L}$ is the liquid refractive index, $h$ the interfringe spacing, $D$ the draw ratio, $A$ the cross section area of undrawn sample, $A / D$ the cross section area of drawn sample, $F^{\|}$the area under fringe shift, and $\lambda$ the wavelength of the source used. $n^{\|}$and $n^{\perp}$ are the refractive indices of the fiber with light vibrating along and across the axis of the fiber. Equation 1 can be applied, fairly, to interferograms of viscose fibers that undergo a successive deformation during the drawing process. ${ }^{9}$ In addition to measuring both $n^{\|}$and $n^{\perp}$, the microscope can be adjusted for measuring birefringence directly using the following equation:

$$
\begin{equation*}
\Delta n=F \frac{D}{A} \frac{\lambda}{h} \tag{2}
\end{equation*}
$$

## Mechanical Properties

The applied stress can be obtained, using the general equation

$$
\begin{equation*}
\sigma=\frac{m g}{A} \tag{3}
\end{equation*}
$$

Young's modules was calculated from the following equation:

$$
\begin{equation*}
E=\sigma / \varepsilon \tag{4}
\end{equation*}
$$

where $\varepsilon$ is the strain $=D-1$. The strain optical coefficient is given from the following equation ${ }^{8}$ :

$$
\begin{equation*}
C_{\varepsilon}=\frac{d(\Delta n)}{d \varepsilon} \tag{5}
\end{equation*}
$$

where the change in birefringence is $d(\Delta n)$ and the corresponding change in strain is $d \varepsilon$. Poisson's ratio $\mu$ given from the following equation:

$$
\begin{equation*}
d r / r=-\mu d L / L \tag{6}
\end{equation*}
$$

where $d r$ is the change in radius ( $r$ ) and $d L$ is the change in fiber length $(L)$. The elastic shear module $G$ is given using the following equation ${ }^{14}$.

$$
\begin{equation*}
G=\frac{E}{2(1+\mu)} \tag{7}
\end{equation*}
$$

where $E$ is Young's modules. The compressibility ${ }^{13}$ is given by


Plate 1 The resultant cross section of irregular viscose fiber.

Table I Values of Draw Ratio, Strain, Stress, Young's Modulus, Strain Optical Coefficient, Stress Optical Coefficient, Poisson's Ratio, Elastic Shear Modulus, and Compressibility

| D | $\varepsilon$ | $\begin{gathered} \sigma \\ \times 10^{10} \\ (\mathrm{~Pa}) \end{gathered}$ | $\begin{gathered} E \\ \times 10^{10} \\ (\mathrm{~Pa}) \end{gathered}$ | $\begin{array}{r} C_{\varepsilon} \\ \times 10^{-3} \end{array}$ | $\begin{gathered} C_{S} \\ \times 10^{-10} \\ (\mathrm{~Pa})^{-1} \end{gathered}$ | $\mu$ | $\begin{gathered} G \\ \times 10^{10} \\ (\mathrm{~Pa}) \end{gathered}$ | $\begin{gathered} \chi \\ \times 10^{-10} \\ (\mathrm{~Pa})^{-1} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Unboiled Sample |  |  |  |  |  |  |  |  |
| 1.00 | 0 | - | - | - | - | - | - | - |
| 1.04 | 0.04 | 3.54 | 88.5 | 25 | 1.27 | 0.48 | 29.89 | 1.35 |
| 1.08 | 0.08 | 5.67 | 70.87 | 17 | 0.917 | 0.46 | 24.27 | 3.38 |
| 1.16 | 0.16 | 7.81 | 48.81 | 8 | 0.755 | 0.43 | 17.06 | 8.60 |
| 1.20 | 0.2 | 9.46 | 47.30 | 15 | 0.687 | 0.41 | 16.77 | 11.41 |
| Sample Boiled for 15 min |  |  |  |  |  |  |  |  |
| 1.00 | 0 | - | - | - | - | - | - | - |
| 1.04 | 0.04 | 2.73 | 68.25 | 17 | 1.72 | 0.48 | 23.05 | 1.76 |
| 1.08 | 0.08 | 3.54 | 44.25 | 20 | 1.55 | 0.46 | 15.15 | 5.42 |
| 1.16 | 0.16 | 4.56 | 28.5 | 8 | 1.36 | 0.43 | 9.96 | 14.70 |
| 1.20 | 0.2 | 5.52 | 27.6 | 10 | 1.19 | 0.41 | 9.78 | 19.56 |
| Sample Boiled for 30 min |  |  |  |  |  |  |  |  |
| 1.00 | 0 | - | - | - | - | - | - | - |
| 1.04 | 0.04 | 2.73 | 68.25 | 20 | 1.86 | 0.48 | 23.05 | 1.76 |
| 1.08 | 0.08 | 4.25 | 53.12 | 27 | 1.46 | 0.46 | 18.19 | 4.52 |
| 1.16 | 0.16 | 7.62 | 47.62 | 10 | 0.918 | 0.43 | 16.65 | 8.82 |
| 1.20 | 0.2 | 9.08 | 45.4 | 7 | 0.804 | 0.41 | 16.10 | 11.89 |
| Sample Boiled for 60 min |  |  |  |  |  |  |  |  |
| 1.00 | 0 | - | - | - | - | - | - | - |
| 1.04 | 0.04 | 3.54 | 88.5 | 20 | 1.49 | 0.48 | 29.89 | 1.35 |
| 1.08 | 0.08 | 5.67 | 70.87 | 25 | 1.11 | 0.46 | 24.27 | 3.38 |
| 1.16 | 0.16 | 6.38 | 39.87 | 5 | 1.05 | 0.43 | 13.94 | 10.53 |
| 1.20 | 0.2 | 7.56 | 37.80 | 10 | 0.94 | 0.41 | 13.40 | 14.28 |

$$
\begin{equation*}
\chi=\frac{3(1-2 \mu)}{E} \tag{8}
\end{equation*}
$$

For uniaxial tensile stress, the birefringence and the retractive stress are related by the equation ${ }^{14}$

$$
\begin{equation*}
\left(n^{\|}-n^{\perp}\right)=C_{S} \sigma \tag{9}
\end{equation*}
$$

The constant $C_{s}$ is called the stress-optical coefficient. Its value is dependent on the chemical structure of the polymer, and it decreases as the draw ratio is increased.

## Application of Continuum Theories of Rubber Elasticity

The rubber elasticity experiments were performed to determine the number-average molec-
ular weight between network junctions. ${ }^{15}$ Rubberlike force-extension curves were obtained for all filaments boiled and unboiled. Treatment of stress-strain relationship for deformable materials was carried out without the assumption of any specific molecular model. Arising from this one widely employed equation (Mooney-Rivlin) ${ }^{16}$

$$
\begin{equation*}
\sigma /\left(D-D^{-2}\right)=2 c_{1}+2 c_{2} D^{-1} \tag{10}
\end{equation*}
$$

plots of $\left[\sigma /\left(D-D^{-2}\right)\right]$ and $1 / D$ are found to be linear, especially at low elongation. The intercept on the $D^{-1}=0$ axis yields $2 C_{1}$, and the slope yields $2 C_{2}$. The second term was attributed to energy dissipation resulting from chain interactions during deformation, and in conformity with


Figure 1 (a)-(d) The relationships among the draw ratio $D$ and $E, G, \chi$, and $C_{S}$ for the unboiled sample and samples boiled for 15,30 , and 60 min , respectively.
this view $C_{2}$ becomes zero when the elastomer is swollen by solvents. ${ }^{16}$

Because the stress is related to the elongation by

$$
\begin{equation*}
\sigma=N_{c} K T\left(D-D^{-2}\right) \tag{11}
\end{equation*}
$$

where $\sigma$ is the stress, $K$ is the Boltzman's constant, $T$ is the absolute temperature, and $N_{c}$ is the number of network chains per unit volume given from the following equation:

$$
\begin{equation*}
N_{c}=\frac{\sigma}{3 K T}\left[\varepsilon+\frac{1}{3} \frac{\varepsilon^{3}}{1+\varepsilon}\right]^{-1} \tag{12}
\end{equation*}
$$

Also the elongation leads to a reduction in the entropy $\Delta S$ by the following equation:

$$
\begin{equation*}
\Delta S=-\frac{1}{2} K N_{c}\left[(1+\varepsilon)^{2}+\frac{2}{(1+\varepsilon)}-3\right] \tag{13}
\end{equation*}
$$

The average work per chain for a collection of chains will depend on the distribution of chainend distances and is obtained by the following equation ${ }^{17}$ :

$$
\begin{equation*}
W^{\prime}=\frac{3 K T}{2}\left[\frac{1}{3}\left(D^{2}-D^{-1}\right)+\left(D^{-1}-1\right)\right] \tag{14}
\end{equation*}
$$



Figure 2 The relationships among $\left[\sigma /\left(D-D^{-2}\right)\right]$ and $D^{-1}$ for unboiled sample.

For a collection of chains containing $N_{c}$ chains per unit volume, the work per unit volume $W$ is given by

$$
\begin{equation*}
W=\frac{N_{c} K T}{2}\left[\left(D^{2}-D^{-1}\right)+3\left(D^{-1}-1\right)\right] \tag{15}
\end{equation*}
$$

The storable, elastic energy of the network is only a function of the strain invariant. It can be represented by the following equations for uniaxial elongation:
$W^{\prime \prime}=C_{1}\left(D^{2}+(2 / D)-3\right)+C_{2}\left(D^{-2}+2 D^{-3}\right)$
and

$$
\begin{equation*}
\sigma=\frac{d W}{d D}=C_{1}\left(2 D-2 D^{-2}\right)+C_{2}\left(2-2 D^{-3}\right) \tag{17}
\end{equation*}
$$

or

$$
\begin{equation*}
\sigma=2\left(C_{1}+\left(C_{2} / D\right)\right)\left(D-D^{-2}\right) \tag{18}
\end{equation*}
$$

Equation (18) is the well-known Mooney-Rivlin equation. A plot of the reduced stress $\sigma / 2$ ( $D$ $-D^{-2}$ ) as a function of reciprocal elongation $D^{-1}$ gives straight line whose slope is $C_{2}$ and whose intercept with the ordinate is $C_{1}$. In practice the constants $C_{1}$ proved to be a useful measure of the crosslink density.

## Stress-Optical Coefficient

The value of the stress-optical coefficient $C_{S}$ is dependent on the chemical structure of the polymer. Also the value of this coefficient depends solely on the mean refractive index and the optical anisotropy of the random link as seen from the following equation ${ }^{18}$ :

$$
\begin{equation*}
\frac{\Delta n}{\sigma}=C_{S}=\frac{2 \pi}{45 K T} \frac{\left(\bar{n}^{2}+2\right)^{2}}{\bar{n}}\left(b_{1}-b_{2}\right) \tag{19}
\end{equation*}
$$

where $\bar{n}$ is the average refractive index and $b_{1}$ and $b_{2}$ are the polarizabilities along and across the axes of such units.

From the above equation it can be seen that birefringence in elastomers is proportional to the applied stress.

## Calculation of the Optical Configuration Parameter

The optical configuration parameter $\Delta \alpha$ is related to the stress-optical coefficient $C_{S}$ by the following equation ${ }^{18}$ :

$$
\begin{equation*}
\Delta \alpha=\frac{\left(45 K T C_{S} / 2 \pi\right) \bar{n}}{\left(\bar{n}^{2}+2\right)^{2}} \tag{20}
\end{equation*}
$$

where $\Delta \alpha=b_{1}-b_{2}$ from eq. (19) and $n$ is the refractive index of the network. Values of $\Delta \alpha$ at different values of $n$ and $C_{S}$ are summarized in the tables.

The values obtained for $n^{\|}$and $n^{\perp}$ were utilized in calculating the following optical parameters: the polarizabilities per unit volume $P^{\|}$and $P^{\perp}$, the isotropic polarizability $P_{0}$, the isotropic refractive index $n_{\text {iso }}$. Other optical parameters are given later on, where

$$
\begin{equation*}
P^{\|}=\frac{3}{4 \pi} \frac{\left(n^{\|^{2}}-1\right)}{\left(n^{\left.\|^{2}+2\right)}\right.} \tag{21}
\end{equation*}
$$

Table II Constants $C_{1}$ and $C_{2}$ of Mooney-Rivlin Equation

| Type of Sample | $C_{1} \times 10^{7}$ | $C_{2} \times 10^{7}$ |
| :--- | :---: | :---: |
| Unboiled | -31.67 | 48.63 |
| Boiled for 15 min | -35.79 | 48.73 |
| Boiled for 30 min | -7.89 | 19.93 |
| Boiled for 60 min | -47.62 | 65.49 |

Table III Values of Number of Network Chain per Unit Volume $N_{c}$, Work per Unit Volume W, Average Work per Chains $W^{\prime}$, Reduction in Entropy $\Delta S$, Polarizabilities along and across the Axes of Unit Chain $b_{1}-b_{2}$, and the Optical Configuration Parameter $\Delta \alpha$

| D | $N_{c} \times 10^{30}$ | $\underset{(\mathrm{J})}{ } \times 10^{6}$ | $W^{W^{\prime}} \times 10^{-23}$ | $\begin{gathered} \Delta S \times 10^{7} \\ \left(\mathrm{JK}^{-1}\right) \end{gathered}$ | $\begin{gathered} \left(b_{1}-b_{2}\right) \\ \times 10^{-25} \\ \left(\mathrm{~cm}^{3}\right) \\ \hline \end{gathered}$ | $\begin{gathered} \Delta \alpha \\ \times 10^{-25} \\ \left(\mathrm{~cm}^{3}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Unboiled Sample |  |  |  |  |  |  |
| 1.00 | - | - | - | - | - | - |
| 1.04 | 71.66 | . 88 | 1.234 | -2.3 | 2.99 | 2.99 |
| 1.08 | 57.31 | 2.12 | 3.703 | -7.2 | 2.19 | 2.19 |
| 1.16 | 39.26 | 5.33 | 13.57 | -18.8 | 1.80 | 1.80 |
| 1.20 | 37.9 | 7.95 | 20.98 | -27.7 | 1.64 | 1.64 |
| Sample Boiled for 15 min |  |  |  |  |  |  |
| 1.00 | - | - | - | - | - | - |
| 1.04 | 55.27 | 0.68 | 1.234 | -1.78 | 4.05 | 4.05 |
| 1.08 | 35.78 | 1.32 | 3.703 | -4.49 | 3.70 | 3.70 |
| 1.16 | 22.92 | 3.11 | 13.57 | -11.02 | 3.25 | 3.25 |
| 1.20 | 22.11 | 4.64 | 20.98 | -16.18 | 2.84 | 2.84 |
| Sample Boiled for 30 min |  |  |  |  |  |  |
| 1.00 | - | - | - | - | - | - |
| 1.04 | 55.27 | 0.68 | 1.234 | -1.78 | 4.38 | 4.38 |
| 1.08 | 42.95 | 1.59 | 3.703 | -5.39 | 3.44 | 3.44 |
| 1.16 | 38.30 | 5.2 | 13.57 | -18.43 | 2.19 | 2.19 |
| 1.20 | 36.38 | 7.63 | 20.98 | -26.62 | 1.92 | 1.92 |
| Sample Boiled for 60 min |  |  |  |  |  |  |
| 1.00 | - | - | - | - | - | - |
| 1.04 | 71.66 | 0.68 | 1.234 | -2.3 | 3.51 | 3.51 |
| 1.08 | 57.31 | 1.59 | 3.703 | -7.2 | 2.62 | 2.62 |
| 1.16 | 32.07 | 4.35 | 13.57 | -15.43 | 2.51 | 2.51 |
| 1.20 | 30.28 | 6.35 | 20.98 | -22.15 | 2.24 | 2.24 |

The $n$ values were also used to calculate an analogous equation for $P^{\perp}$. The isotropic polarizability is given by

$$
\begin{equation*}
P_{0}=\frac{1}{3}\left(P^{\|}+2 P^{\perp}\right) \tag{22}
\end{equation*}
$$

whereas the isotropic refractive index $n_{\text {iso }}$ is given from the following equation:

$$
\begin{equation*}
n_{\text {iso }}=\frac{1}{3}\left(n^{\|}+2 n^{\perp}\right) \tag{23}
\end{equation*}
$$

Also, de Vries ${ }^{19}$ defined the invariant refractive index, which he calls the "virtual refractive index," $n_{v}$ by

$$
\begin{equation*}
n_{v}=\sqrt{1+\frac{3\left[n_{\|}^{2}-1\right]\left[n_{\perp}^{2}-1\right]}{\left[n_{\perp}^{2}-1\right]+2\left[n_{\|}^{2}-1\right]}} \tag{24}
\end{equation*}
$$

where the virtual refractive index $n_{v}$ replaces the isotropic refractive index equation.

The optical orientation function $f_{\Delta}$ was measured from the following equation ${ }^{20}$ :

$$
\begin{equation*}
f_{\Delta}=\frac{\Delta n_{a}}{\Delta n_{\max }} \tag{25}
\end{equation*}
$$

where ( $\Delta n_{\text {max }}$ ) is the maximum birefringence of a fully oriented fiber. Its value was previously ${ }^{20}$ determined to be 0.055 .


Figure 3 (a)-(d) The relationships among $\Delta S$ and draw ratio for all samples.

Ward ${ }^{21,22}$ studied the average value of the optical orientation function from the following equation:

$$
\begin{equation*}
\left\langle P_{2}(\theta)\right\rangle=\frac{\Delta n_{a}}{\Delta n_{\max }} \tag{26}
\end{equation*}
$$

$\left\langle P_{2}(\theta)\right\rangle$ is related to the polarizabilities $\Phi^{\| \|}$and $\Phi^{\perp}$ by the relation ${ }^{23}$


Figure 4 The relationships among the number of network chain per unit volume and the draw ratio for all samples.


Figure 5 (a)-(d) The relationships among work per unit volume and the draw ratio for all samples.

$$
\begin{equation*}
\frac{\Phi^{\|}-\Phi^{\perp}}{\Phi^{\|}+2 \Phi^{\perp}}=\left\langle P_{2}(\theta)\right\rangle P_{2}\left(\theta_{m}\right) \tag{27}
\end{equation*}
$$

where $P_{2}\left(\theta_{m}\right)$ is constant. The values of $\Phi^{\|}$and $\Phi^{\perp}$ are determined from the following equation due to Stein and Wilkes ${ }^{24}$ :

$$
\begin{equation*}
\Phi^{\|}=\frac{n_{\|}^{2}-1}{n_{\|}^{2}+2} \tag{28}
\end{equation*}
$$



Figure 6 The relationships among the average work per chain and the draw ratio.


Plate 2 (a)-(h) Some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position.

The above equation (15) can be written in the form

$$
\begin{equation*}
\frac{\Phi^{\|}-\Phi^{\perp}}{\Phi^{\|}+2 \Phi^{\perp}}=\left[\frac{\Delta \alpha}{3 \alpha_{0}}\right]\left\langle P_{2}(\theta)\right\rangle \tag{29}
\end{equation*}
$$

where $\left(\Delta \alpha / 3 \alpha_{0}\right)$ as a quantity depends on the molecular structure and can be obtained from the relation between $P_{2}(\theta)$ and $\left[\left(\Phi^{\|}-\Phi^{\perp}\right) /\left(\Phi^{\|}\right.\right.$ $\left.\left.+2 \Phi^{\perp}\right)\right]$, which gives a straight line.

The function $f_{\theta}$ is developed in a new approach to the continuum theory of birefringence of oriented polymer ${ }^{25}$ where

$$
\begin{equation*}
f_{\theta}=\frac{n_{1}^{2} n_{2}^{2}}{n_{\|}^{2}+n_{\perp}^{2}} \frac{n_{\|}+n_{\perp}}{n_{1}+n_{2}}\left(\frac{\Delta n}{\Delta n_{\max }}\right) \tag{30}
\end{equation*}
$$

$n_{1}$ and $n_{2}$ were previously determined ${ }^{25}$ to be 1.590 and 1.535 , respectively. Equation (30) is slightly different from the original expression in eq. (26), used by Hermans and Platzek ${ }^{19}$ and Kratky, ${ }^{26}$ which can be given by

$$
\begin{equation*}
f_{\theta}=(1+a) f_{\Delta}-a f_{\Delta}^{2} \tag{31}
\end{equation*}
$$

where

$$
\begin{equation*}
a=\frac{2 n_{1}^{2} n_{2}^{2}}{n_{v}^{3}\left(n_{1}+n_{2}\right)}-1 \tag{32}
\end{equation*}
$$

and where $n_{v} \cong n_{\text {iso }}$. The value of a constant $\alpha$ is found to be 0.63 , and the angle $\theta$ is determined from

Table IV Values of Cross-Sectional Area, Refractive Indices $\boldsymbol{n}^{\|}$, $\boldsymbol{n}^{\perp}$, Birefringence, Isotropic Refractive Index $\boldsymbol{n}_{\text {iso }}$, Virtual Refractive Index $\boldsymbol{n}_{v}$, and Polarizabilities $\boldsymbol{P}^{\|}, \boldsymbol{P}^{\perp}$

| D | $A\left(\mathrm{~mm}^{2}\right)$ | $n^{\prime \prime}$ | $n^{\perp}$ | $\Delta n$ | $n_{\text {iso }}$ | $n_{v}$ | $P^{\\|}$ | $P^{\perp}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Unboiled Sample |  |  |  |  |  |  |  |  |
| 1.00 | 1.165 | 1.5315 | 1.5280 | . 0035 | 1.5292 | 1.5292 | . 0739 | . 0735 |
| 1.04 | 1.12 | 1.5320 | 1.5275 | . 0045 | 1.5290 | 1.5290 | . 0740 | . 0735 |
| 1.08 | 1.079 | 1.5323 | 1.5271 | . 0052 | 1.5288 | 1.5288 | . 0740 | . 0734 |
| 1.16 | 1.004 | 1.5327 | 1.5268 | . 0059 | 1.5288 | 1.5288 | . 0741 | . 0734 |
| 1.20 | 0.971 | 1.5331 | 1.5266 | . 0065 | 1.5288 | 1.5287 | . 0741 | . 0733 |
| Sample Boiled for 15 min |  |  |  |  |  |  |  |  |
| 1.00 | 1.165 | 1.5318 | 1.5278 | . 0040 | 1.5291 | 1.5291 | . 0740 | . 0735 |
| 1.04 | 1.12 | 1.5322 | 1.5275 | . 0047 | 1.5291 | 1.5291 | . 0740 | . 0735 |
| 1.08 | 1.079 | 1.5325 | 1.5270 | . 0055 | 1.5288 | 1.5288 | . 0740 | . 0734 |
| 1.16 | 1.004 | 1.5328 | 1.5266 | . 0062 | 1.5287 | 1.5286 | . 0741 | . 0733 |
| 1.20 | 0.971 | 1.5331 | 1.5265 | . 0066 | 1.5287 | 1.5287 | . 0741 | . 0733 |
| Sample Boiled for 30 min |  |  |  |  |  |  |  |  |
| 1.00 | 1.165 | 1.5321 | 1.5278 | . 0043 | 1.5292 | 1.5292 | . 0740 | . 0735 |
| 1.04 | 1.12 | 1.5325 | 1.5274 | . 0051 | 1.5291 | 1.5291 | 0.740 | . 0734 |
| 1.08 | 1.079 | 1.5332 | 1.5270 | . 0062 | 1.5291 | 1.5290 | . 0741 | . 0734 |
| 1.16 | 1.004 | 1.5336 | 1.5266 | . 0070 | 1.5289 | 1.5289 | . 0742 | . 0733 |
| 1.20 | 0.971 | 1.5338 | 1.5265 | . 0073 | 1.5289 | 1.5289 | . 0742 | . 0733 |
| Sample Boiled for 60 min |  |  |  |  |  |  |  |  |
| 1.00 | 1.165 | 1.5322 | 1.5277 | 0.0045 | 1.5292 | 1.5292 | . 0740 | . 0735 |
| 1.04 | 1.12 | 1.5326 | 1.5273 | 0.0053 | 1.5291 | 1.5291 | . 0740 | . 0734 |
| 1.08 | 1.079 | 1.5332 | 1.5269 | 0.0063 | 1.5290 | 1.5290 | . 0741 | . 0734 |
| 1.16 | 1.004 | 1.5334 | 1.5267 | 0.0067 | 1.5289 | 1.5289 | . 0741 | . 0734 |
| 1.20 | 0.971 | 1.5335 | 1.5264 | 0.0071 | 1.5288 | 1.5287 | . 0742 | . 0733 |

$$
\begin{equation*}
f_{\theta}=1-\frac{3}{2} \sin ^{2} \theta \tag{33}
\end{equation*}
$$

For a random link, the orientation function $P_{2}$ $(\theta)$ as previously calculated ${ }^{27}$ is given by

$$
\begin{equation*}
P_{2}(\theta)=\left(D^{2}-D^{-1}\right) / 5 N_{1} \tag{34}
\end{equation*}
$$

where $N_{1}$ is defined as the number of random links between the network junction points (the entanglements).

Roe and Krighaum ${ }^{28}$ derived an expression for the distribution function of segments at an angle $\theta$ with respect to the draw ratios.

$$
\begin{equation*}
\omega(\cos \theta)=\frac{1}{2}+\frac{1}{4 N_{1}}\left(3 \cos ^{2} \theta-1\right)\left(D^{2}-D^{-1}\right) \tag{35}
\end{equation*}
$$

Before orientation, the segments will be randomly oriented at an angle $\theta$ with respect to the
draw direction. After drawing the segments will be constrained at an angle $\beta$ given by

$$
\begin{equation*}
\tan \beta=D^{-3 / 2} \tan \theta \tag{36}
\end{equation*}
$$

## Determination of the Number of Molecules Per Unit Volume

The difference of the two main refractive indices $\Delta n$ of the sample is linked with the difference in the mean polarizabilities of the macromolecule for the same directions [ $\Delta P=\left(P^{\|}-P^{\perp}\right)$ ] by the relation ${ }^{29}$

$$
\begin{equation*}
\Delta n=\frac{2 \pi N}{\bar{n}}\left[\frac{(\bar{n})^{2}+2}{3}\right]^{2}\left(P^{\|}-P^{\perp}\right) \tag{37}
\end{equation*}
$$

where $N$ is the number of molecules per unit volume and $\bar{n}$ is the mean refractive index of the sample


Figure 7 The relationships among $n^{\|}$and $n^{\perp}$ and draw ratio for unboiled sample.

$$
\bar{n}=\left(\frac{n^{\|}+n^{\perp}}{2}\right)
$$

To find the polarizabilities of the macromolecule in the laboratory system, we used the measured values of the refractive indices in LorentzLorenz's eq. (21).

## Experimental Procedure

A microstrain device was described before and used in conjunction with a two-beam polarizing interference Pluta microscope. It was modified to measure stress as well as strain ${ }^{11,12,30,31}$ and was used to measure both the refractive indices for the two principal vibration directions and the birefringence values as a function of stress, strain, and draw ratio of viscose fibers. The viscose fibers are manufactured by Misr Rayon Co. The untreated sample has $T_{g}$ of $45.9^{\circ} \mathrm{C}$ and its crystallinity index is 0.22 .

## RESULTS

The stress-strain device attached to a double refracting polarizing interference Pluta microscope was used to measure both the refractive indices for the two principal vibration directions (along $n{ }^{\|}$ and across $n^{\perp}$ ) and the birefringence $\Delta n$ values
as a function of stress, strain, and draw ratio of viscose fibers.

## Measurement of Transverse Sectional Area

Plate 1 shows the cross section of the viscose fibers seen by high power optical microscope. According to this plate the cross-sectional view shows irregular shape. The cross-sectional area $A$ is found to be $1.165 \times 10^{-3} \mathrm{~mm}^{2}$. The crosssectional areas of the drawn samples are given in Table IV.

## Mechanical Properties

The stress-strain device is then used with the undrawn fiber to get different draw ratios. Table I shows the obtained experimental values of different draw ratios, strain, stresses, Young's modules, strain optical coefficient $C_{\varepsilon}$, stress optical coefficient $C_{S}$, Poisson's ratio $\mu$, the elastic shear modules $G$, the compressibility $\chi$ for an unboiled sample and samples boiled for 15,30 , and 60 min . The value of $C_{S}$ is dependent on the chemical structure of the polymer, and it decreases as the draw ratio is increased.

Figure 1(a)-(d) shows the relationship between the draw ratio $D$ and $E ; G, \chi$, and $C_{S}$ for the unboiled sample; and samples boiled for 15,30 , and 60 min , respectively.


Figure 8 (a)-(d) Shows the relationships among the birefringence $\Delta n$ and draw ratio for all samples.

Table V Values of the Constants $A^{\|}, A^{\perp}, B^{\|}, B^{\perp}$ of Cauchy's Dispersion Equation and the Dielectric at Infinity

| Type of Sample | $A^{\\|}$ | $A^{\perp}$ | $B^{\\|} \times 10^{2}$ | $B^{\perp} \times 10^{2}$ | $\varepsilon_{\infty}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Unboiled | 1.492 | 1.489 | 119 | 112 | 2.302 |
| Boiled for 15 min | 1.497 | 1.493 | 113 | 108 | 2.288 |
| Boiled for 30 min | 1.497 | 1.495 | 113 | 105 | 2.305 |
| Boiled for 60 min | 1.501 | 1.492 | 108 | 113 | 2.303 |

The relationship between stress and draw ratio is given from Mooney-Rivlin eq. (16). Figure 2 shows the relationship between $[\sigma /(D$ $\left.-D^{-2}\right)$ ] and $D^{-1}$ for an unboiled sample that shows a linear relationship. The other samples showed the same behavior. The constants $C_{1}$
and $C_{2}$ were determined for the unboiled sample and samples boiled for 15,30 , and 60 min ; the obtained values are given in Table II. The constant $C_{2}$ was attributed to energy dissipation resulting from chain interactions during deformation and in conformity with this view, $C_{2}$


Plate 3 (a)-(h) Some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position of the different samples at different wavelengths.


Figure 9 The relationships among [ $\left.1 /\left(n_{\text {iso }}^{2}-1\right)\right]$ and $1 / \lambda^{2}$.
becomes zero when the elastomer is swollen by solvents. ${ }^{23}$

The obtained values of the above mechanical parameters given in Table I were utilized for calculating the number of network chains per unit volume $N_{c}$, the work per unit volume $W$, and the average work per chain $W^{\prime}$ using eqs. (12), (15), and (14), respectively. The obtained results of $N_{c}$, $W$, and $W^{\prime}$ are given in Table III for the unboiled sample and samples boiled for 15,30 , and 60 min , respectively. In addition, the reduction in entropy $\Delta S$, the difference in polarizabilities along and across the axes of chain units ( $b_{1}-b_{2}$ ), and the optical configuration parameter $\Delta \alpha$ were calculated from eqs. (13), (19), and (20), respectively. The obtained values of $\Delta S,\left(b_{1}-b_{2}\right)$, and $\Delta \alpha$ are given also in Table III for the unboiled sample and samples boiled for 15,30 , and 60 min , respectively. From Table III one can observe that the values of the parameter $\left(b_{1}-b_{2}\right)$ and that of the optical configuration parameter $\Delta \alpha$ are the same. This means that the difference in polarizabilities along and across the axes of chain units $\left(b_{1}-b_{2}\right)$ is equal to the optical configuration parameter $\Delta \alpha$.

Figure 3(a)-(d) shows the relationship between $\Delta S$ and the draw ratio, whereas Figure 4(a)-(d) shows the relationship between the number of network chains per unit volume and the draw ratio for all samples. Figure 5(a)-(d) shows the relationship between the work per unit volume and the draw ratio. Figure 6 shows the relation-
ship between the average work per chain and the draw ratio.

## Double-Beam Interferometry

Viscose fiber was examined before and after applying stress by the double-beam interference microscope. Monochromatic light of wavelength $\lambda$ $=546 \mathrm{~nm}$ for green light was used. The microscope was adjusted first to show the totally duplicated image of the examined fiber, where the two fringe shifts for light vibrating parallel and perpendicular to the fiber axis are shown. Plate 2(a)(h) shows some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position. Plane-polarized light of $\lambda=546 \mathrm{~nm}$ was used for vibrating along and across the fiber axis, and liquid of refractive index was $n_{L}=1.528$ at $21.5^{\circ} \mathrm{C}$. At different

Table VI Values of $\Delta n, P_{2}(\theta)$, and the Constant ( $\Delta \alpha / 3 \alpha_{0}$ )

| D | $\Delta n$ | $\begin{gathered} \left(\Phi^{\\|}-\Phi^{\perp} / \Phi^{\\|}+2 \Phi^{\perp}\right) \\ \times 10^{-4} \end{gathered}$ | $\begin{aligned} & P_{2} \\ & (\theta) \end{aligned}$ | $\left(\Delta \alpha / 3 \alpha_{0}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| Unboiled Sample |  |  |  |  |
| 1.00 | . 0035 | 18 | . 0636 | . 028 |
| 1.04 | . 0045 | 24 | . 0818 | . 029 |
| 1.08 | . 0052 | 27 | . 0945 | . 028 |
| 1.16 | . 0059 | 31 | . 1073 | . 029 |
| 1.20 | . 0065 | 34 | . 1182 | . 029 |
| Sample Boiled for 15 min |  |  |  |  |
| 1.00 | . 0040 | 21 | . 0727 | . 029 |
| 1.04 | . 0047 | 25 | . 0855 | . 029 |
| 1.08 | . 0055 | 29 | . 1000 | . 029 |
| 1.16 | . 0062 | 33 | . 1127 | . 029 |
| 1.20 | . 0066 | 35 | . 1200 | . 029 |
| Sample Boiled for 30 min |  |  |  |  |
| 1.00 | . 0043 | 23 | . 0782 | . 029 |
| 1.04 | . 0051 | 27 | . 0927 | . 029 |
| 1.08 | . 0062 | 33 | . 1127 | . 029 |
| 1.16 | . 0070 | 37 | . 1273 | . 029 |
| 1.20 | . 0073 | 38 | . 1327 | . 029 |
| Sample Boiled for 60 min |  |  |  |  |
| 1.00 | 0.0045 | 24 | . 0818 | . 029 |
| 1.04 | 0.0053 | 28 | . 0964 | . 029 |
| 1.08 | 0.0063 | 33 | . 1145 | . 029 |
| 1.16 | 0.0067 | 35 | . 1218 | . 029 |
| 1.20 | 0.0071 | 37 | . 1291 | . 029 |

Table VII Values of $f_{\Delta}, f_{\theta}, \theta, \theta^{\prime}$, the Ratio $f_{\theta} / f_{\Delta}$, and the Constant $a$

| D | $f_{\Delta}$ | $f_{\theta}$ | $\theta^{\circ}$ | $\theta^{\circ}$ | $f_{\theta} / f_{\Delta}$ | $\left(f_{\theta}-f_{\Delta}\right) / f_{\theta}$ | $a$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Unboiled Sample |  |  |  |  |  |  |  |
| 1.00 | . 0636 | . 0678 | 51.8 | 51.0 | 1.065 | . 0610 | . 636 |
| 1.04 | . 0818 | . 0871 | 51.1 | 50.9 | 1.065 | . 0610 | . 637 |
| 1.08 | . 0945 | . 1007 | 50.6 | 50.4 | 1.065 | . 0611 | . 637 |
| 1.16 | . 1073 | . 1142 | 50.1 | 49.8 | 1.065 | . 0610 | . 637 |
| 1.20 | . 1182 | . 1258 | 49.7 | 49.4 | 1.064 | . 0608 | . 638 |
| Sample Boiled for 15 min |  |  |  |  |  |  |  |
| 1.00 | . 0727 | . 0774 | 51.5 | 51.3 | 1.065 | . 0609 | . 636 |
| 1.04 | . 0855 | . 0910 | 50.9 | 50.7 | 1.064 | . 0608 | . 636 |
| 1.08 | . 1000 | . 1065 | 50.4 | 50.2 | 1.065 | . 0610 | . 637 |
| 1.16 | . 1127 | . 1201 | 50.0 | 49.6 | 1.065 | . 0611 | . 638 |
| 1.20 | . 1200 | . 1278 | 49.6 | 49.3 | 1.065 | . 0609 | . 638 |
| Sample Boiled for 30 min |  |  |  |  |  |  |  |
| 1.00 | . 0782 | . 0832 | 51.2 | 51.1 | 1.064 | . 0606 | . 636 |
| 1.04 | . 0927 | . 0987 | 50.7 | 50.5 | 1.064 | . 0606 | . 636 |
| 1.08 | . 1127 | . 1200 | 49.9 | 49.6 | 1.064 | . 0604 | . 636 |
| 1.16 | . 1273 | . 1354 | 49.3 | 49.1 | 1.064 | . 0604 | . 638 |
| 1.20 | . 1327 | . 1412 | 49.2 | 48.8 | 1.064 | . 0603 | . 637 |
| Sample Boiled for 60 min |  |  |  |  |  |  |  |
| 1.00 | . 0818 | . 0871 | 51.1 | 50.9 | 1.064 | . 0606 | . 636 |
| 1.04 | . 0964 | . 1026 | 50.5 | 50.3 | 1.064 | . 0606 | . 636 |
| 1.08 | . 1145 | . 1219 | 49.8 | 49.6 | 1.064 | . 0604 | . 636 |
| 1.16 | . 1218 | . 1297 | 49.6 | 49.3 | 1.064 | . 0604 | . 637 |
| 1.20 | . 1291 | . 1374 | 49.3 | 49.0 | 1.064 | . 0606 | . 638 |

draw ratios, $n^{\|}, n^{\perp}$, and $\Delta n$ were calculated for the unboiled sample and for samples boiled for 15 , 30 , and 60 min . The results of $n^{11}, n^{\perp}$, and $\Delta n$ are given in Table IV. Figure 7 shows the relationship between $n^{\|}$and $n^{\perp}$ and the draw ratio for unboiled sample. The other samples showed the same behavior.

Figure 8(a)-(d) shows the relationship between $\Delta n$ and draw ratio. The refractive index $n^{\|}$and the birefringence $\Delta n$ increase with increasing the draw ratios, whereas the refractive index $n^{\perp}$ decreases with increasing the draw ratios for all samples. The corresponding polarizabilities per unit volume ( $P^{\|}$, and $P^{\perp}$ ), the isotropic refractive index, and the virtual refractive index are calculated for all samples from eqs. (21), (23), and (24), respectively. The resultant data are given in Table IV.

The application of Cauchy's dispersion equation

$$
\begin{equation*}
n_{\lambda}^{\|}=A^{\|}+B^{\| /} / \lambda^{2} \tag{38}
\end{equation*}
$$

with an analogous equation for $n^{\perp}$ gives its constants $A$ and $B$ by plotting the relation between $n^{\|}$ and $n^{\perp}$ with $1 / \lambda^{2}$. The constants $A$ and $B$ for the different samples are given in Table V. Plate 3(a)(h) shows some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position of the different samples at different wavelengths. By plotting the relation between $\left[1 /\left(n_{\text {iso }}^{2}-1\right)\right]$ and $1 / \lambda^{2}$ (Fig. 9), the dielectric constant at infinity $\varepsilon_{\infty}$ is calculated, where $n^{2}=\varepsilon_{\infty}$. The values of $\varepsilon_{\infty}$ for the different samples are given in Table V.

In addition to the above optical properties, the optical orientation function $P_{2}(\theta)$ is calculated from eq. (26) for all samples. The values of ( $\Delta \alpha /$ $3 \alpha_{0}$ ) are calculated at different draw ratios for all samples and the results are given in Table VI, where it is constant for a given polymer due to its dependence on the molecular structure.

Also, the values of $f_{\theta}$ are determined due to the new approach; $f_{\theta}$ and the optical orientation angle $\theta$ (the angle between the fiber axis, the axis of the polymer units), are measured from eqs. (30) and (33), respectively, for all samples and given also in Table VII. The relationships among the draw ratio and both the optical orientation function $f_{\theta}$ and angle $\theta$ for all samples are given in Figures 10 (a)-(d) and 11 (a)-(d).

From the resulting values of the optical orientation function $\left\langle P_{2}(\theta)\right\rangle$ given by Ward and the values of angle $\theta$, the number of random links $N_{1}$ between entanglements were calculated from eq. (34). In addition to $N_{1}$, the distribution function of segments $\omega(\cos \theta)$ at an angle $\theta$ is determined with respect to the draw ratio from eq. (35). The angle $\beta$, where the segment is constrained after drawing, and the number $N$ of molecules per unit volume were determined from eqs. (36) and (37), respectively. The values of $N_{1}, \omega(\cos \theta), \beta$ and $N$ for all samples are given in Table VIII. The relationship between $N_{1}$ and the draw ratio is drawn in Fig. 12(a)-(d). An empirical formula is sug-


Figure 10 (a)-(d) The relationships among the optical orientation function $f(\theta)$ and draw ratio for all samples.


Figure 11 (a)-(d) The relationships among the orientation angle $\theta$ and draw ratio for all samples.
gested to evaluate the relationship between draw ratio and $\Delta n, f(\theta), W, W^{\prime}, A$, and $N_{c}$, as follows:

$$
\begin{equation*}
\ln \left[\Delta n W W^{\prime} f(\theta) / A N_{c}\right]=X D+Y \tag{39}
\end{equation*}
$$

where $X$ and $Y$ are constants characterizing the proportionality in eq. (23). The values of $X$ and $Y$ were determined to be 51.25 and -167.75 , respectively (see Fig. 13).

## DISCUSSION

Deformation due to drawing processes is the predominant means of producing new physical structures of polymeric fibers, which are so important commercially and are of much industrial interest. Developing the properties of polymers and fibers is done by various treatments-mechanical, chemical, thermal, and others. By means of the drawing process, the development of the properties is due to change in the molecular arrangement and, hence, the creation of a new structure that tends to change polymeric properties is expected. The drawing process produces an orientation in gaining greater insight at a microstructure level when investigating mechanical properties. In addition, the thermal process may change the crystalline and amorphous parts in a rayon viscose fibers, where the crystallized areas give high modules of rigidity, elasticity, and ultimate ten-

Table VIII Values of $\omega(\cos \theta)$, tan $\beta$, the Angle $\beta$, the Number of Network Junction Points $N_{1}$, and the Number of Molecules per Unit Volume $N$

| D | $\begin{gathered} \omega \\ (\cos \theta) \end{gathered}$ | $\tan \beta$ | $\beta^{\circ}$ | $N_{1}$ | $N$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Unboiled Sample |  |  |  |  |  |
| 1.00 | 0.500 | 1.234 | 51.0 | 0.000 | 1.000 |
| 1.04 | 0.519 | 1.156 | 49.1 | 0.295 | 1.000 |
| 1.08 | 0.526 | 1.075 | 47.1 | 0.520 | 1.000 |
| 1.16 | 0.533 | 0.946 | 43.4 | 0.904 | 1.000 |
| 1.20 | 0.540 | 0.886 | 41.5 | 1.032 | 1.000 |
| Sample Boiled for 15 min |  |  |  |  |  |
| 1.00 | 0.500 | 1.248 | 51.3 | 0.000 | 1.000 |
| 1.04 | 0.522 | 1.148 | 48.9 | 0.283 | 1.000 |
| 1.08 | 0.529 | 1.066 | 46.8 | 0.492 | 1.000 |
| 1.16 | 0.536 | 0.950 | 43.6 | 0.861 | 1.000 |
| 1.20 | 0.541 | 0.880 | 41.5 | 1.016 | 1.000 |
| Sample Boiled for 30 min |  |  |  |  |  |
| 1.00 | 0.500 | 1.239 | 51.1 | 0.000 | 1.000 |
| 1.04 | 0.525 | 1.140 | 48.7 | 0.260 | 1.000 |
| 1.08 | 0.536 | 1.045 | 46.3 | 0.436 | 1.000 |
| 1.16 | 0.545 | 0.923 | 42.7 | 0.762 | 1.000 |
| 1.20 | 0.550 | 0.868 | 40.9 | 0.920 | 1.000 |
| Sample Boiled for 60 min |  |  |  |  |  |
| 1.00 | 0.500 | 1.230 | 50.9 | 0.000 | 1.000 |
| 1.04 | 0.527 | 1.132 | 48.5 | 0.251 | 1.000 |
| 1.08 | 0.537 | 1.045 | 46.3 | 0.429 | 1.000 |
| 1.16 | 0.542 | 0.939 | 43.2 | 0.796 | 1.000 |
| 1.20 | 0.547 | 0.874 | 41.2 | 0.945 | 1.000 |

sile strength to viscose fibers. The amorphous areas give the fibers the flexibility, recovery, elongation, and swelling. The force-extension data for the filaments could be interpreted in two ways: by a simple statistical theory owing to Flory ${ }^{32,33}$ and via a modified Mooney-Rivlin analysis. ${ }^{16}$ The accuracy of both methods depends on how accurately the shear modulus $G$ can be calculated from tensile experiment.

The measured values of the mechanical properties achieved by using the modified stressstrain device are an indication to the above facts. The measured values of Young's modules tend to decrease by drawing processes. This observation is in similar agreement with observations given by other physical processes published before. ${ }^{34}$

The constant $C_{2}$ of the Mooney-Rivlin equation was attributed to energy dissipation resulting from chain interactions during deformation; in conformity with this view, $C_{2}$ becomes zero when the elastomer is swollen by solvents. ${ }^{16}$

Significant variations in the characteristic properties of viscose fibers, such as birefringence, orientation function and angle, the number of molecules per unit volume, and the distribution function of segments is due to the reorientation of molecules by drawing processes. Also, the boiling process changes the structural behavior because of accumulation of some structural phenomenon that may be summarized as follows: disorientation, recrystallization by nucleation, recrystallization by growth, shrinkage, and crystal decomposition.

## CONCLUSION

From the above measurements and calculations of the various optical and mechanical parameters and their changes with the applied stresses and boiling times, the following conclusions are drawn. (1) The mechanical properties, Young's modules, elastic shear modules, and the compressibility change with applied stress as well as thermal conditions. (2) Poisson's ratios decrease with the applied stresses and are not affected by the boiling times. (3) Both stress and strain optical coefficients change with both the draw ratios and the boiling times. (4) The work per unit volume $W$ increases with draw ratios and also changes because of boiling times. (5) The average work per chain $W^{\prime}$ increases with draw ratios but is independent of the boiling times. (6) The entropy $\Delta S$ of fibers decreases with the applied stresses and boiling times. (7) Increasing the draw ratios increased the optical configuration parameter $\Delta \alpha$. (8) As the draw ratios as well as the boiling times increase, the refractive indices $n^{\|}$and the birefringence $\Delta n$ increase. (9) The electric polarizability constant is unaffected by both the draw ratios and boiling times and equals 0.029 , where it depends on the molecular structure. (10) The orientation factor and orientation angle are affected by both the drawing process and boiling time. The orientation angle decreases with both, whereas the orientation factor increases. (11) The number of net-


Figure 12 (a)-(d) The relationships among the number of network junction points $N_{1}$ and draw ratio for all samples.


Figure 13 The relationships among $\ln \left[\Delta n W W^{\prime} f\right.$ ( $\theta$ )/A $N_{c}$ )] and draw ratio.
work junction points $N_{1}$ increases with the drawing effect and decreases with the boiling times effect, whereas the distribution function of segments at an angle $\theta$ slightly increases with increasing the draw ratios. (12) Finally, the above experimental results and calculations confirm that the drawing and boiling of viscose fibers, in conjunction with the application of double-beam interference microscope, do change mechanical, optical, and structural parameters of these fibers.

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