A rheo-optical study of the stress-induced crystallization of Poly(Ethylene terephthalate).

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A RHEO-OPTICAL STUDY OF
THE STRESS-INDUCED CRYSTALLIZATION
OF POLY(ETHYLENE TEREPHTHALATE)

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by
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DEDICATION

To my mother,
who made many sacrifices
for the fulfillment of my education
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I wish to express my sincere appreciation to Dr. Richard S. Stein for his guidance, patience, and continual encouragement throughout the course of this research. I have benefited immensely from his vast knowledge and experience.

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ABSTRACT
A Rheo-Optical Study of
the Stress-Induced Crystallization
of Poly (ethylene terephthalate)
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The stress-induced crystallization of polyethylene terephthalate (PET) has been studied using simultaneous measurements of birefringence and stress during and after the deformation of thin films. Measurements were made at various strain rates and elongations at temperatures above the glass transition but below where noticeable isothermal crystallization occurs, insuring that all crystallinity observed was stress-induced.

The total birefringence is a consequence of contributions from both the crystalline and amorphous phases. The amorphous contribution may be calculated from the observed stress, while the crystalline contribution is proportional to the degree of crystallinity. Thus, crystallinity changes may be calculated from the simultaneous ob-
servations of stress and birefringence during the course of the crystallization.

Trends in the variation of volume fraction crystallinity with deformation conditions were observed. The crystallinity was observed to increase with increasing elongation ratio and strain rate. Lower temperatures resulted in higher crystallinity values.

Infrared dichroism studies were employed to determine the orientation function of the crystalline phase. It was observed that the orientation of the crystallites formed during the experiments was approximately the same for all the deformation conditions.

The kinetics of the stress-induced crystallization of PET were studied as a function of elongation ratio and temperature. Avrami analyses were performed on the crystallinity data calculated at the higher strain rates tested. It was found that the crystallization rate increased dramatically with elongation and appeared to decrease with increasing temperature. From the Avrami exponent it was determined that the crystal goes from a radial to more unidirectional growth with increasing elongation. Using a method of analysis by Ziabicki it was observed that the sensitivity of crystallization to orientation was a function of both the temperature and strain rate.
It appears that the stress-induced crystallization is affected by the elongation, strain rate, and temperature, as is the rate of crystallization and the superstructure obtained.
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CHAPTER I

INTRODUCTION

A. Crystallization

Many solid polymers show characteristics of both crystalline solids and highly viscous liquids. Physical investigations such as X-ray and electron diffraction show sharp features typical of ordered, crystalline material and diffuse features typical of liquids. These ordered and unordered regions are referred to as crystalline and amorphous, respectively. Most polymers are amorphous, although regular polymers may be semi-crystalline.

Several theories have been presented to describe the exact nature of polymer crystallinity. One of these theories is the fringed-micelle theory. In this theory the crystallites consist of parallel bundles of chain segments distributed at random in the unordered amorphous matrix. The polymer molecules pass through several crystalline regions with crystallites forming when segments from polymer chains are aligned together. The length of the crystallite is short in comparison to the polymer chain length. Each polymer can contribute ordered segments to several crystallites with the segments of chain between crystallites forming the amorphous matrix.
Another of these theories is the folded-chain lamellae theory. A lamella is a thin platelet of polymer single crystals grown from polymer solutions. Some of the polymer molecules fold back and forth on themselves to form chain folded lamellae while others will not. In this way a system of both crystalline and amorphous regions are formed. The individual lamellae are connected to each other through tie molecules which correspond to the segment of the polymer chain not involved in the folding process.

As the exact nature of polymer crystallinity is still quite controversial, it is usually practical to use a model of crystallinity which contains the features of both theories. Low to medium crystalline polymers fit well into the fringed-micelle theory, where the crystalline regions may be chain-folded lamellae, while highly crystalline polymers are not suitably treated by this theory.

Examination under the optical microscope of crystalline polymers shows a definite structure. The crystalline and amorphous regions are organized into supermolecular structures called spherulites. Rays emanate in all directions from the center of the spherulite and are called radial fibrils. They continue until they meet radial fibrils from a neighboring spherulite, thus forming a boundary. The rays consist of crystal lamellae growing outward from the nucleated center of the spherulite. The noncrys-
talline polymer is arranged around the growing crystals within the spherulite. These spherulites give a Maltese cross pattern under crossed Nicols, again indicating their essentially spherical symmetry.

The extent of crystallization is important as it plays a major role in the way polymers are used. This is a consequence of the large effect of crystallinity on the thermal, mechanical and other properties of polymers. The degree of crystallinity is a commonly used parameter. It is a ratio of the masses of material in the crystalline state and in the total material. There are numerous methods of measuring this parameter. First order thermodynamic properties such as the changes in enthalpy and volume are proportioned to the weight of the material. Many conventional methods such as calorimetry, nuclear magnetic spectroscopy, X-ray diffraction, dilatometry, density, infrared spectroscopy, small angle light scattering, and birefringence changes are used to study the crystallinity of polymeric materials.

It is known that the mechanical and optical properties of polymers are dependent on the structure of the crystalline and amorphous regions. The orientation of these regions as well as the degree of crystallinity and morphology are important factors which effect polymer properties. Crystallization can arise by two means, ther-
mally-induced and stress-induced crystallization. In the first, the amorphous polymer is held at temperatures between the melting point and glass transition temperature of the material, while in the second the polymer is sufficiently stretched to produce crystallization in a sample which would not otherwise crystallize at an appreciable rate at the same temperature.

Early studies on rubbers\(^1\) showed that crystallization in the stressed state caused increases in both the crystallization rate and melting temperatures as compared to crystallization in the unstressed state. This increase in melting temperature has been explained thermodynamically using the enthalpy and entropy of fusion\(^2-7\). The crystallization rate increase has been explained kinetically using the activation energy and critical free energy of nucleus formation\(^7-9\). Several studies \(^10-13\) have included experimental work which shows the influence of molecular orientation of amorphous polyethylene terephthalate on crystallization. It was found that the crystallization half-times for PET were greatly reduced when a pre-oriented amorphous sample was used in isothermal crystallization studies as compared to an initially isotropic sample.

The morphology of polymer crystallization is also affected by orientation of the amorphous material. Fibrillar structures seem to be particularly important in fiber form-
mation\(^{(14)}\), but this is only one of the variety of morphologies suggested by various authors\(^{(15-19)}\). Keller and Machin\(^{(15)}\) observed flattened spherulites at low orientations, while elongated spherulites parallel to the drawing direction were reported by Zubovitch\(^{(16)}\). Shish-kebab structures have also been proposed\(^{(17,18)}\). Wasiak\(^{(19)}\) concluded that the degree of initial orientation effected the orientation of the growing crystallites as well as the kinetics of the crystallization.

Factors other than orientation also affect the crystallization kinetics of polymers. Crystallization temperature is known to exert a great influence on the rate of crystallization. Studies by Turnbull and Fisher\(^{(20)}\) were concerned with the effects of supercooling and nucleation on crystallization. Molecular weight has been shown to affect not only the overall rate of crystallization but also the spherulitic growth rate in PET\(^{(21)}\). The influence of additives in the polymer on the kinetics and growth rates has also been studied\(^{(21)}\). Type of nucleation, either heterogeneous or homogeneous, and nucleus shape, influence the crystallization rate and have been studied theoretically\(^{(22,23)}\). Several review articles have been written on polymer crystallization. One by Sanchez\(^{(24)}\) deals with crystallization theories. The kinetics of PET crystallization has been presented by Van Antwerper\(^{(25)}\).
An important analysis commonly used to express the kinetics of crystallization is that developed by Avrami. His analysis describes crystal growth rates in a manner similar to the expanding circles produced when raindrops fall on the surface of a pond. This assumes constant growth from randomly distributed nuclei throughout the material. The general progress of isothermal crystallization can be expressed by:

\[
\left( \frac{\chi_C}{\chi_\infty} \right) = 1 - \exp (K_C t^n) \tag{1}
\]

where \( \chi \) is the degree of crystallinity, \( \chi_\infty \) is the ultimate crystallinity which can be obtained from extrapolation to long times, \( K_C \) is a rate constant containing nucleation and growth parameters, and \( n \) is the Avrami exponent whose value depends on the mechanism of nucleation and the form of crystal growth (it is often associated with the dimensionality of the process).

Equation (1) can be written in the form:

\[
\ln \{-\ln[1 - (\chi_C - \chi_\infty)]\} = \ln k_C + n \ln t \tag{2}
\]

This is a more useful form for kinetic studies of crystallization. Plots can be made of the left hand side versus \( \ln t \), where the slope has the value of \( n \) and the intercept has the value of \( \ln k_C \). In this manner information about
the form of crystal growth can be obtained. It is found that the Avrami equation can only be expected to fit over relatively early stages in the crystallization. Non-integral values of \( n \) have also been obtained which could be due to different nucleation processes or different forms of crystal growth simultaneously occurring. Other problems with this type of analysis are the assumptions of constant radial crystal growth and the induction time for crystallization.

The crystallization of polymers does have some general kinetic features. In isothermal crystallization the material first undergoes an induction period where the crystallization is very slow. Then the process accelerates to a maximum crystallization rate and finally slows down again as the final equilibrium state is approached. Temperature affects both the length of the induction period and the acceleration rate during crystallization. Polymers crystallize over a temperature range distinctive to the polymer. It usually extends from about 30° C above the glass transition temperature to about 10° C below the melting point. The typical temperature range for measurable crystallization of PET is approximately 110° C to 240° C\(^{(21)}\). It will be shown in this thesis that crystallization occurring below this temperature range, induced by stress, will also show some temperature dependence.
B. Stress-Induced Crystallization

Deformation of polymers, like polyethylene terephthalate (PET), often results in oriented crystallization. This deformation has been studied by several means, such as simple extension of the solid state\(^{28-35}\), shearing of the melt\(^{15,36-38}\), and stirring in solution\(^{39,40}\). It is known that crystallization and orientation under stress often enhances the physical properties of polymers. This is due to the degree of orientation which leads to changes of crystal morphology. Polymers are often deformed during processing procedures such as extrusion\(^{41,42}\), where heat and stress are applied, injection molding\(^{43}\), fiber spinning\(^{44}\), and blow molding\(^{45}\). Crystallization under stress is also known to occur in nearly all fiber making\(^{46}\).

As seen in a review article by Yeh\(^{47}\), stress-induced crystallization (SIC) has been studied by a number of researchers using methods such as electron microscopy, X-ray diffraction, IR dichroism and absorption, DSC, pulse propagation, and stress relaxation. It was found that SIC near the rubbery region tends to generate a fibrillar morphology in the absence of thermally-induced crystallization regardless of the applied strain as long as the polymer has reached the critical strain for SIC at a given temperature. Upon thermal treatment changes to a more lamellar morphol-
ogy can take place. It has also been found that SIC does not occur in the glassy state due to lack of atomic mobility for rearrangement into a three-dimensional lattice. However, an improvement in the atomic packing can be brought about by stretching in the glassy state.

Previous work in this laboratory has involved the deformation studies of various polymers such as cis- and trans-1,4-polybutadiene\(^{(34,48,49)}\), polyvinylcarbazole\(^{(50)}\), PE\(^{(51)}\), polyvinyl chloride\(^{(52)}\), and polyethylene terephthalate\(^{(55)}\), using methods of X-ray diffraction, small angle light scattering, optical microscopy, static and dynamic birefringence, and infrared spectroscopy.

Studies were performed by Misra\(^{(53)}\) on PET films both below and above the glass transition temperature using light scattering and optical microscopy techniques. On cold-drawn samples it was unexpectedly found that significant crystallinity developed in the necked portion of the film while no significant crystallinity appeared in the un-necked portion. Cold-drawing appeared to cause the formation of a rod-like, non-volume filling superstructure in the necked region which was oriented preferentially in the stretching direction.

The existence of this superstructure means that some mobility of the molecular chains took place during the necking to allow their formation. Three possible origins
of this mobility have been presented\(^{54}\). The first is that viscous dissipation related to the necking process caused local heating in the neck. Secondly, a lowering of the glass transition temperature by the stress-induced effect is possible. And the third is that exothermic effects due to the strain-induced crystallization of extended chain or fibrillar crystals caused local heating.

When PET was stretched above the glass transition temperature, it was observed that the crystallinity increased with increasing strain. Light scattering patterns indicated a rod-like superstructure aligned perpendicular to the stretching direction at low elongations, while at higher elongations it appeared that the rods changed into ellipsoidal spherulites elongated normal to stretching. Rhodes and Stein\(^{55}\) reported similar behavior for stretched polyethylene.

Several models have been proposed to explain the molecular orientation and structure of oriented polymers\(^{56-63}\). Depending on the amount of orientation, one can obtain samples that lead upon stretching to twisted lamellae\(^{64,65}\), chains parallel to the lamella\(^{66,67}\), oriented or bended lamella\(^{68}\) or a paracrystalline lattice split into mosaic blocks\(^{60,69-72}\). Biangardi and Zachman\(^{68,73}\) have found that the orientation cannot be characterized simply by the draw ratio unless temperature and
drawing ratio are kept constant. They have shown that the same birefringence values can be obtained for samples of draw ratio 4.4 and 2.2 if the temperature and drawing rate are varied. Therefore, it appears that orientation is dependent on a number of variables.

Thompson(46) has noted that PET crystallizes about a thousand times faster under high stress than under zero stress. He has also suggested that the stress could have a large effect on the nucleation process. In his studies of SIC he found that crystallization occurs at a given temperature when the strain rate is sufficient to produce a critical stress level in the polymer material.

Heffelfinger and Schmidt(58) studied uniaxial extensions of PET using X-ray diffraction, IR, and density measurements. They showed that uniaxial stretching extends the molecular chains in the direction of stretch such that some of the gauche isomers are transformed into trans isomers by covalent bond rotations. This trans isomer is the extended form and can occur in both the crystalline and amorphous phases in relation to the gauche isomer which occurs in only the amorphous phase of the polymer. They measured the sizes of the crystallites and amorphous regions in the stretched PET as a function of draw ratio and found that the crystallite length increased while the amorphous length decreased with increasing elongation.
Dumbleton (74) has also performed deformation studies on amorphous PET. He found that the amorphous orientation function rises linearly up to a point where crystallization can occur. Then upon further drawing the amorphous orientation function remains approximately constant since material which orients beyond this point will crystallize. He also found that the orientation of the crystalline regions was not much greater than that of the highly oriented amorphous regions from which they originated. McGraw (75) has found similar results using fluorescence polarization for studies of molecular orientation of PET.

In general, it is believed that the polymer molecules are extended and oriented along the direction of drawing in PET. The morphology of the polymer is known to be different for stress-induced and isothermal crystallization. The mechanical history of the sample influences the crystallization kinetics of polymers from the melt. This is seen where strained samples show smaller crystallization half-times than samples which are strain free. It is assumed that a larger number of nuclei are present in the strained samples and is referred to as "orientation-induced" or "stress-induced" nucleation (76). The crystals produced by the stress are also known to have higher melting temperatures than their isothermal counterparts. Several models have been offered in an attempt to explain these differ-
ences in crystallization as well as observations of other effects.

A thermodynamic model was proposed by Flory\(^{(2)}\) for the crystallization of polymers induced by stretching. Expressions were proposed which related the elongation with a rise in crystal melting temperature, and related the temperature and elongation to the degree of crystallinity and to the decrease in stress at crystallization equilibrium. It was believed that the nuclei were strain-induced with a fringed-micelle conformation and that the strain-induced crystallites had their greatest dimension in the stretching direction.

The degree of crystallinity, \(\chi\), was described by:

\[
(1-\chi) = \left\{ \left[ \frac{3}{2} - \phi(\lambda) \right]/\left[ \frac{3}{2} - \theta \right] \right\}^{1/2}
\]  

(3)

with

\[
\phi(\lambda) = (6/n)^{1/2} \lambda/n^{1/2} - [(\lambda^2/2) - (1/\lambda)]/n
\]  

(4)

and

\[
\theta = (h_f/R)[(1/T_m^o)-(1/T)]
\]  

(5)

where \(\lambda\) is the elongation of the polymer, \(n\) is the number of segments per molecular chain, \(h_f\) is the heat of fusion per polymer segment, and \(T_m^o\) is the incipient crystallization temperature for the undeformed polymer. These equations
are for values at the equilibrium crystallization state which is ordinarily not reached when crystallization occurs simultaneously with elongation.

Keller and Machin (15, 36) proposed a two-stage model for polymer crystallization under stress. First, a small number of crystals form which are highly oriented in the stress direction and act as nucleation points for further crystallization. This is followed by a second group of crystals which are of a more lamellar-type and at right angles to the nucleating lines. These lamellae grow in columns which lie parallel to the stress direction. It was felt that the stress level influenced the orientation of the growing lamellae and the number of nucleating lines. At low stress, twisted lamellae dominate forming parallel spherulitic discs. Higher stress produced more nucleating lines resulting in a more fibrillar texture and flat lamellae with their normals parallel to the stress-direction.

Kraus and Gruver (33) studied the kinetics of strain-induced crystallization of trans-polypentenamer as a function of strain and temperature. They found the crystallization rate to be sensitive to both variables as well as a function of the degree of under-cooling alone. They also found that the melting point of the crystals increased with
elongation. The isothermal, isometric crystallization rate was found by differentiating the Avrami equation with respect to time

\[ \dot{\chi}(\lambda) = n(k/\chi_e)^{1/n}(\chi_e - \chi)^{(1/n)\ln(\chi_e/(\chi_e - \chi))} \]  

(6)

where \( n \) is the Avrami exponent, \( k \) is the crystallization rate constant, \( \chi_e \) is the equilibrium crystallinity, and \( \chi \) is the measured crystallinity. If the strain rate is constant \((n, \chi_e \text{ and } k \text{ are functions of strain})\) then

\[ d\chi = R^{-1} \dot{\chi}(\varepsilon) d\varepsilon \]  

(7)

where \( \varepsilon \) is the strain on the sample. Using the Avrami analysis the rate constant increased while the Avrami exponent decreased with increasing elongation ratio. The decrease in exponent was interpreted as a transition from radial to unidirectional crystal growth with the increasing elongation.

Gaylord(77) has proposed a theoretical model for the SIC of polymeric networks which includes the free energy of fusion, crystal surface energy, and entropic changes. He assumes the free energy of crystallization is minimized by orientation of the crystallite in the stretching direction. The theory predicts that a perfectly oriented crystal occurs initially which changes to a one-fold crystal perpendicular to extension and then to a two-fold crystal with perfect orientation as extension increases. It also predicts a shish-kebab structure at higher elonga-
Alfonso et al. (78) studied the effects of molecular orientation on crystallization half-times for PET.

Using a Gaussian approximation for uniaxial deformation of polymer developed by Ziabicki (79), the effect of orientation on the crystallization rate was represented by

\[
\frac{1}{t_{1/2}(f_a)} = \frac{1}{t_{1/2}(0)} \exp \left( A f_a^2 + B f_a^3 + \ldots \right) \tag{8}
\]

which for small orientations leads to

\[
\frac{1}{t_{1/2}(T,f_a)} = \frac{1}{t^{*}_{1/2}} \exp \left( -\frac{4 \ln 2}{D^2} \frac{(T-T^*)^2}{D^2} \right) \exp \left( A f_a^2 \right) \tag{9}
\]

where \( t_{1/2} \) is the crystallization half-time, \( f_a \) is the orientation function of the amorphous phase, \( t^{*}_{1/2} \) is the minimum half-time corresponding to the maximum crystallization rate at the temperature \( T^* \), \( T \) is the temperature of the experiment, \( D \) is the half-width of the Gaussian curve, and \( A \) is a parameter describing the sensitivity of the crystallization rate towards the amorphous orientation function. They found that the crystallization half-times increased as a function of initial orientation of the polymer. Therefore, the orientation of the molecular chains in the amorphous phase plays an important part in the crystallization. It was also found that the magnitude of this orientation effect
was dependent on the temperature where the crystallization took place.

Ziabicki\textsuperscript{(14,79,80)} has contributed heavily to the theory of molecular orientation in polymer systems. He found that the kinetics of isothermal crystallization of oriented systems differed qualitatively from that of un-oriented systems. He showed that the growth and nucleation rates could be represented by tensor equations involving molecular displacements and that the crystallization rate could be expressed as a function of orientation. It was also stated that the orientation resulting from drawing was a function of deformation, strain rate, and relaxation time at constant temperatures. It also appears that orientation can occur in several stages of processing dependent on these different variables.

Orientation occurring during the drawing process was described by

\[
f(\varepsilon) = (1 - \frac{a_1}{\lambda} - f_0)(1 - f_\infty) \exp (-b_2^* \frac{\varepsilon}{\lambda})
\]

where \( f(\varepsilon) \) is the orientation factor as a function of deformation rate \( (q^*) \) and relaxation time \( (\tau) \), \( a_1^* \), and \( b_2^* \) are coefficients in the expansions of \( f_{st}(\lambda) \) and \( \lambda(\lambda) \), respectively, \( \lambda \) is the elongation, and \( f_0 \) and \( f_\infty \) are the orientations at zero and infinite relaxation times, re-
spectively. This shows that the orientation should increase with elongation and draw speed.

Jarecki and Ziabicki\(^{(5)}\) have studied the thermodynamics of crystal orientation in stressed polymers. They found that different mechanisms control the crystal shape. At low stress the orientation is controlled by the hydrodynamic potential while at high stress it is controlled by the strain energy.

Our studies will include several of these variables, elongation, strain rate, and temperature, in an attempt to quantify to some degree the basic propositions of some of these various models.

C. Birefringence

When a beam of light enters matter, it undergoes a velocity change and becomes refracted. The degree of refraction is defined as the refractive index, \(n\), by the equation

\[
n_m = \frac{\sin \theta_1}{\sin \theta_2} = \frac{\lambda_0}{\lambda_m}
\]

where \(\theta_1\) is the angle of incidence, \(\theta_2\) is the angle of refraction, \(\lambda_0\) is the wavelength of light in vacuum and \(\lambda_m\) is the wavelength of light in the material. For many materials, such as liquids, the index of refraction is in-
dependent of the orientation of the material with respect
to the direction of the incident light and are termed
isotropic. For other materials, such as oriented polymers,
the refractive index is dependent on the orientation of the
material with respect to the direction of the incident
light and are termed anisotropic.

Anisotropic materials may be either uniaxial or bi-
axial. In uniaxial materials, the refractive indices along
two of the three mutually perpendicular axes are equal to
each other and unequal to the third. In biaxial materials,
the refractive indices along all three axes are unequal.
The difference in refractive index along any two of these
axes is defined as the birefringence along the third axis.
The phenomena of birefringence is shown in Figure (1).

The difference between the wave paths along the two
areas in a uniaxial material is the retardation, \( R \), defined
by

\[
R = \frac{d}{\lambda_1} - \frac{d}{\lambda_2}
\]

(12)

where \( \lambda_1 \) and \( \lambda_2 \) are the wavelengths of light along the
stretching direction and perpendicular to the stretching
direction, respectively, and \( d \) is the thickness of the
sample. Retardation can be related to the birefringence
using equations (11) and (12) to give
\[ \Delta = n_1 - n_2 = \frac{\lambda}{d} \quad (13) \]

Birefringence can also be described in terms of the bond polarizabilities using methods developed by Kuhn and Grün \(^{(81)}\) and Treloar \(^{(82)}\). The principal indices of refraction can be related to the polarizability per unit volume using the Lorenz-Lorentz equation

\[ \frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi \varphi \quad (14) \]

where \( n \) is the refractive index of the sample and \( \varphi \) is the bond polarizability per unit volume. The change in refractive index corresponding to a small change in polarizability can be found by differentiation of equation (14) to give

\[ \frac{6n}{(n^2 + 2)^2} \quad \frac{dn}{d\varphi} = \frac{4}{3} \pi d\varphi \quad (15) \]

which can be rearranged to give

\[ dn = \frac{4\pi}{3} \frac{(n^2 + 2)^2}{6n} \quad d\varphi \quad (16) \]

When the refractive index difference is small, the birefringence can be calculated from the polarizability difference by
\[ \Delta = n_1 - n_2 = \frac{2\pi}{9} \left( \frac{n^2 + 2}{n} \right)^2 (P_1 - P_2) \]  

(17)

where \( \bar{n} \) is the mean value of the refractive index.

The polarizability can be evaluated using the statistical segment model for a polymer chain. The chain is assumed to be composed of \( N \) noninteracting elements per unit volume which are small with respect to the wavelength of light. The principal polarizabilities and orientations of these elements must be assumed to be known or postulated. If the material is uniaxial, the elements are uniaxial and are oriented with cylindrical symmetry about the Z-axis (stretch direction), the optical anisotropy can be shown to be

\[ P_1 - P_2 = N\int_0^{\pi} \left( \frac{3 \cos^2 \theta - 1}{2} \right) (b_1 - b_2) \rho(\theta)d\theta \]  

(18)

where \( b_1 \) and \( b_2 \) are the principal polarizabilities parallel and perpendicular, respectively, to the optic axis, and \( \rho(\theta)d\theta \) is the fraction of elements in the material oriented with their optic axis at an angle \( \theta \) to \( \theta + d\theta \) with the optic axis of the material. The principal polarizabilities can be determined using the bond polarizability values of Denbigh\(^{82}\) or Bunn\(^{83}\).

The total birefringence of a multicomponent system has been described by Stein\(^{85}\) and Wilkes\(^{86}\) by assuming
the birefringence to be the sum of the various components as given by

$$\Delta = \sum \phi_i \Delta_i + \Delta_f + \Delta_d$$  \hspace{1cm} (19)$$

where $\phi_i$ is the volume fraction and $\Delta_i$ is the birefringence of the $i$-th phase. $\Delta_d$ is the deformation birefringence due to localized polarizability changes caused by bond angle distortion. It is significant below the glass transition temperature where a deformation perpendicular to the molecular chains will pull the chains apart causing changes in the distances between the molecules. Below $T_g$ there is little orientation when a polymer is stretched and so the deformation birefringence is not negligible with respect to the other contributions to the total birefringence. However, above $T_g$ it is negligible due to the significant orientation of the molecular chains upon stretching. $\Delta_f$ is the form birefringence which is a result of the distortion of the field of the light wave at the interface between isotropic phases, such as the boundaries of the crystalline and amorphous regions or microvoids. Treatment of this effect has been presented by several authors $^{(87-90)}$ and it has been found to be on the order of a 5% contribution. At low degrees of crystallinity, it is negligible for most polymers.
The birefringence for a uniaxial polymer system can be described by the equation of Stein and Norris\(^{(91)}\).

\[
\Delta = \phi_c \Delta_c + (1 - \phi_c) \Delta_a + \Delta_f
\]  

(20)

where \(\phi_c\) is the volume fraction crystallinity, and \(\Delta_c\) and \(\Delta_a\) are the birefringence values per unit volume of the crystalline and amorphous phases, respectively.

The value for the crystalline birefringence may be given by

\[
\Delta_c = \frac{2}{9} \pi \frac{(n^2 + 2)^2}{n} (b_1 - b_2) c f_c
\]  

(21)

or

\[
\Delta_c = \Delta_c f_c
\]  

(22)

where \((b_1 - b_2) c\) is the anisotropy of the crystal, \(\Delta_c\) is the intrinsic birefringence of a perfectly oriented crystalline component, and \(f_c\) is the crystal orientation function defined by\(^{(92,93)}\)

\[
f_c = (3\cos^2 \theta_c - 1)/2
\]  

(23)

where \(\theta_c\) is the angle between the crystal optic axis and the stretching direction. The orientation function can be calculated using wide-angle X-ray diffraction procedures like that of Dumbleton and Bowles\(^{(94)}\) for polyethylene.
terminate. At appreciable elongations, it is often a good approximation to allow $f_c$ to equal one, the value for perfectly oriented crystals.

The crystalline intrinsic birefringence can be calculated using Denbigh's bond polarizabilities\(^{(83)}\). Several researchers\(^{(95-100)}\) have also reported values of intrinsic birefringence for PET and their values could also be used in equation (22).

The amorphous birefringence can be given by the equation

$$\Delta = \Delta_a f_a$$

where $\Delta$ is the intrinsic birefringence of the amorphous phase and $f_a$ is the orientation function of the amorphous phase. The amorphous orientation function can be determined using infrared dichroism\(^{(101)}\) or sonic modulus measurements\(^{(102)}\). The amorphous intrinsic birefringence can be determined using methods similar to those of Samuels\(^{(102)}\) and Onongi\(^{(103)}\).

This approach has been extended by Stein and Yau\(^{(104)}\) for the quantitative study of rubber crystallization. In this approach, the amorphous birefringence is related to the relaxation of stress accompanying crystallization by the equation \(^{(105)}\)
\[ \Delta_a = C \sigma \]  \hspace{1cm} (25)

where \( \sigma \) is the total stress on the system and \( C \) is the stress-optical coefficient defined by the Kuhn-Grünen theory \(^{(81)}\) and Treloar \(^{(106)}\) as

\[ C = \frac{\Delta}{\sigma} = \frac{2 \pi}{45 k t} \left( \frac{n^2 + 2}{n} \right)^2 (b_1 - b_2)_s \]  \hspace{1cm} (26)

where \( k \) is Boltzmann's constant, \( n \) is the average refractive index, and \((b_1 - b_2)_s\) is the anisotropy of the statistical segment. The application of equation (25) involves two assumptions: (1) the amorphous phase of the crystallized polymer is identical with that of the completely amorphous polymer, which neglects perturbations that could occur in the amorphous phase in the presence of crystals, and (2) the stress on the amorphous phase equals the total stress, which neglects a possible stress concentrating effect by the crystals. These assumptions are fair approximations at low degrees of crystallinity. At higher degrees of crystallinities, a better approximation is to introduce a stress concentration factor, \( \kappa \), in equation (25)

\[ \Delta_a = C \kappa \sigma \]  \hspace{1cm} (27)

where \( \kappa \) is defined by the Guth-Smallwood \(^{(107,108)}\) equation
or by Hashiyama and Stein\(^{(109)}\), assuming spherically shaped crystals,

\[
\kappa = \left[ 1 + 2.5 \phi_C + 14.1 \phi_C^2 \right]^{-1}
\]  

Substituting equations (22) and (25) into equation (20) and neglecting the form birefringence, one obtains

\[
\Delta = \phi_c \Delta_c f_c + (1-\phi_c) C_0
\]

which can be solved for degree of crystallinity to give

\[
\phi_c = \frac{(\Delta - C_0)}{(\Delta_c f_c - C_0)}
\]

By making simultaneous measurements of the birefringence and stress and calculating the intrinsic birefringence and orientation function of the crystalline phase from other methods, the amount of crystallinity present in a stretched polymer sample can be calculated.

Birefringence can be caused by a number of conditions as described by Houwinck\(^{(110)}\). They are:

1. Stress birefringence, which is caused by deformation of the density distribution in an isotropically dense substance. An example of this is the compression of
glass.

2. Intrinsic birefringence, which is fundamental to the asymmetric molecular arrangement in the crystal lattice. An example of this is the double refraction of quartz.

3. Orientation birefringence, which occurs when long chain molecules are elongated to become parallel and give different density distributions in different directions. An example of this is the stretching of polymers.

4. Form birefringence, which occurs when asymmetric particles are oriented in a medium of different refractive index. An example of this is oriented crystals in a polymer.

5. Streaming birefringence, which occurs when liquids containing highly asymmetric molecules are induced to flow. An example of this is high polymer solutions.

In this research, the first four classes of birefringence contribute to the observed birefringence of a stretched polyethylene terephthalate film.

D. Infrared Dichroism

Polyethylene terephthalate (PET) has been studied using infrared spectroscopy for a variety of informa-
Cobbs and Burton, and Miller and Willis have studied the changes in the IR Spectrum before and after crystallization of PET. Cobbs used the bands at 1340 and 972 cm$^{-1}$ to measure the rapid crystallinity during isothermal crystallization of PET, while Miller used the band at 898 cm$^{-1}$ to determine the amorphous content of the polymer. Mikake studied several bands in an attempt to determine the kinds of structural changes that caused the spectral changes observed during PET crystallization. Polarized infrared spectroscopy was utilized by Schmidt to separate the orientation and structural factors which compose a given absorption band of oriented amorphous PET. The dichroic ratios of uniaxially drawn PET films were measured by Koenig and Cornell to determine the orientation of the crystalline and amorphous regions. Boerio et al. studied deuterated derivatives of PET to complete the vibrational analysis of disordered PET. Fourier transform IR was used by D'Esposito and Koenig to study the component phases of semi-crystalline PET.

Infrared dichroism can be used to determine the orientation of the molecular chains in an oriented polymeric film. A direct method of measurement involves measuring the transmission of the infrared radiation polarized both parallel and perpendicular to the principal axis of orient-
tation of the material. The absorbance is defined by Beer's law as

$$A = \frac{1}{d} \ln \frac{I_o}{I_t}$$

(32)

where $d$ is the sample thickness, and $I_o$ and $I_t$ are the incident and transmitted intensities, respectively. For a non-isotropic material, the absorbance is independent of the polarization direction of the incident radiation. However, for a uniaxially oriented sample, there are two principal absorbances, $A_y$ and $A_z$, perpendicular and parallel to the stretching direction, respectively.

The dichroism of a material is defined as

$$D = \frac{A_z}{A_y}$$

(33)

For uniaxially oriented samples, Fraser\(^{117}\) has shown

$$\frac{D-1}{D+2} = \frac{3 \langle \cos^2 \theta_i \rangle - 1}{2} = f_n$$

(34)

where $\theta_i$ is the angle between the transition moment and dielectric field, and $f_n$ is the orientation function for the transition moment. $f_n$ can be defined for symmetri-
cally distributed transition moments as
\[ f_n = f \cdot f_\alpha \]  
(35)

where \( f \) is the orientation function of the molecular axis with respect to the principal absorption axis and \( f_\alpha \) is the orientation function of the transition moment with respect to the molecular axis.

Using equations (34) and (35), the orientation of the polymeric material can be determined if the angle, \( \alpha \), between the transition moment and the molecular axis is known. The absorption intensity is measured parallel (\( A_x \)) and perpendicular (\( A_y \)) to the orientation direction of the film and used to obtain the dichroic ratio by equation (33). The dichroic ratio can vary from zero if there is no absorption in the perpendicular direction to infinity if there is no absorption in the parallel direction. Usually, one expects a dichroic ratio of one for an unoriented sample and infinity for a perfectly oriented sample.

By measuring the infrared dichroism of a band known to be caused by crystallinity in a sample, the orientation function of the crystallities in the sample can be obtained. In polyethylene terephthalate, several crystalline bands are strong enough to be used by this method for orientation determination. One such band is the
972 cm\(^{-1}\) band assigned to the C-O stretching mode of the transethyleneglycol residue\(^{(113)}\). This band has also been used by Schmidt\(^{(114)}\) in his orientation studies where he determined that the 972 cm\(^{-1}\) band is a structure and orientation-sensitive band. He determined that for elongations up to 3.5 times the band was a function of axial structure and above 3.5 times was a function of both axial and uniplanar structures. His results are consistent with the X-ray studies of Heffelfinger and Burton\(^{(69)}\).

It appears that infrared dichroism is a valuable technique in determining the crystalline orientation function for semi-crystalline polymers as long as a band which is due only to the crystalline component is available. For PET, this seems to be a viable alternative to X-ray diffraction for low degrees of crystallinity.
CHAPTER II
EXPERIMENTAL

A. Sample Preparation and Characterization

Preliminary studies were carried out on melt pressed films of polyethylene terephthalate (PET). The PET was obtained in the form of pellets from the General Electric Company. The pellets were dried in a vacuum oven for a period of twenty-four hours at 120°C to remove any solvent or water. The pellets were then compression molded into thin films. Films were pressed on a Carver Laboratory Press at 280°C between sheets of teflon-coated aluminum foil. The sample was placed inside the boundaries of a five mil thick shim and the two pieces of foil placed teflon-side toward the sample. The sheets were placed in the preheated press at zero pressure for thirty seconds to melt the sample. Then, the pressure was applied to 12,000 psi and held there for ninety seconds. The sheets were then immediately quenched in an ice water bath. The teflon sheets were peeled away and the films stored in a desiccator over dririte.

It was found that these molded films were not entirely uniform in thickness and appeared to have some air
bubbles in them. Therefore, new thin film samples were obtained for the main study. Three mil thick films of PET were obtained through the courtesy of the 3M Corporation. These thin films were extruded films which showed negligible orientation when checked for birefringence with a Berek compensator prior to experimentation.

Wide angle X-ray diffraction patterns were obtained for the undrawn and drawn PET films and are shown in Figure (2). The sample-to-film distance was 5 cm for samples a and b and 3 cm for sample c. Exposure time was 12 hours for the unoriented sample, which consisted of stacked layers for a total thickness of 10 mm, and 48 hours for the oriented samples, which had a total thickness of 3 mm. A characteristic amorphous halo was obtained from the undrawn amorphous PET sample as shown in Figure (2a). From this, it is known that the initial samples are amorphous and unoriented before the deformation and any structure observed later is due only to the experimental conditions. The drawn PET films have diffraction patterns consisting of two diffuse lobes oriented in the equatorial direction, Figure (2b,c). The existence of semi-crystalline or crystalline material is thus indicated for the deformed sample. The crystals are interpreted to be very imperfect which causes the deflection lines to become broadened to the extent that they
are not recognizable. However, the orientation of the lobes implies that there is a preferred orientation of the crystals after deformation.

The initial PET film was characterized using intrinsic viscosity and gel permeation chromatography as:

Number average molecular weight, $\bar{M}_n = 1.97 \times 10^5$

Weight average molecular weight, $\bar{M}_w = 5.14 \times 10^5$

Viscosity average molecular weight, $\bar{M}_v = 2.66 \times 10^7$

Molecular weight dispersity, $(\bar{M}_w/\bar{M}_n) = 2.59$.

The three mil thick films of PET were cut into thin strips with an initial length-to-width ratio of 5:1. The strips were then heated and stretched as described below.

B. Sample Heating and Deformation

Sample strips of PET were studied on a Table Model Instron equipped with a constant temperature chamber and an optical system, similar to that described by Keedy et al. (118). See Figure (3). The temperature control system consisted of an aluminum heating chamber with embedded heating elements, a Fenwal regulator, and a thermocouple temperature read-out as described by Su (50). The strain rate and elongation of the sample were controlled using the crosshead speed and gauge length dials,
respectively, on the Instron.

The PET sample strip was placed between the two clamps in the Instron at a temperature near the preset temperature and adjusted so there was no initial strain on the strip. After the temperature reached equilibrium, the strip was stretched at a constant strain rate to the desired elongation ratio. Strain rates tested were in the range \(3.38 \times 10^{-3}/\text{sec}\) to \(1.694/\text{sec}\). Elongations were in the range 1.16 to 5.0.

Simultaneous to the stretching process, as well as after completion of the stretching, the output of force was recorded continuously through the Instron load cell onto the recorder. The stress was then evaluated, assuming an affine deformation, using the equation

\[
\sigma = \frac{f}{A}
\]

(36)

where \(\sigma\) is the stress on the sample strip, \(f\) is the measured force value, and \(A\) is the cross-sectional area of the sample.

The PET strips were stretched at temperatures which ranged from \(75^\circ\text{C}\) to \(100^\circ\text{C}\). These temperatures were above the glass transition temperature for PET of \(69^\circ\text{C}(121,122)\) but below the temperature range where isothermal crystallization occurs significantly, \(110^\circ\text{C}\) to \(240^\circ\text{C}(21)\).
By conducting the stretching experiments within this temperature range, no isothermal crystallization should take place (111,112) and thus any crystallization observed should be strain induced.

C. Birefringence Measurements

Birefringence measurements were made both directly, using a Babinet compensator with a mercury lamp source, and indirectly, using a photomultiplier tube with a laser light source. The Babinet compensator was employed for the experimental runs of low strain rate and low elongation ratio where the birefringence changes were smaller and slower. At higher elongation ratios and faster strain rates, the light transmission method was utilized since birefringence changes were very quick and large. In either method, the same experimental arrangement exists (see Figure (4)) which consists of, in this order:
1. a light source, 2. a polarizer placed 45° to the stretching direction of the sample, 3. the sample, 4. an analyzer placed 90° to the polarizer, and 5. the Babinet compensator or photomultiplier tube.

The Babinet compensator (see Figure (5)) contains a wedge of birefringent material such as quartz which can be adjusted so that the retardation of the sample can be
determined (119). A non-monochromatic light source results in one black fringe and several tinted fringes being seen through the compensator eyepiece. This black fringe is brought to a reference cross-wire with no sample in the light path. When a sample is introduced into the path of the light beam, the black fringe shifts if the sample is birefringent. The black fringe is brought back to the central cross-wire by the compensating effect of the wedge. The shift of the wedge is measured with a scale on the compensator and the birefringence determined using the retardation measured and the equation

$$\Delta = \frac{\lambda_m}{d} R$$

(37)

where $\Delta$ is the birefringence, $\lambda_m$ is the wavelength of light, $R$ is the retardation as measured by the shift of the black fringe, and $d$ is the sample thickness.

The light transmission technique involves measuring the light intensity after it has passed through the polarizer, sample, and analyzer and relating this to the retardation. The transmitted intensity is detected by a photomultiplier tube and recorded on an oscilloscope or chart recorder. (Fig. 4b) A typical transmission is seen in Figure (6). Through crossed polaroids, light transmission ($T$) is related to retardation ($R$) through the equation (119, 120)

$$T = \left(\frac{I_t}{I_o}\right) = \sin^2\left(\frac{R}{2}\right) \sin^2(2\theta) \exp(-\pi d)$$

(38)
where $I_t$ and $I_o$ are the transmitted and incident intensity, $\theta$ is the angle between the optic axis of the sample and the polarization direction (usually $45^\circ$), $\tau$ is the turbidity of the sample and $d$ is the sample thickness. The retardation obtained is then used in equation (37) for the determination of birefringence. In our experiments, the retardation was measured before deformation with the Babinet compensator. Then the number of interference fringes were determined by the light transmission output to obtain the order of the retardation. A final Babinet measurement after relaxation was completed and combined with the transmission output of order to obtain the actual retardation of the deformed film.

Other methods can also be used to measure birefringence such as refractometry$^{(123)}$ and interference microscopy$^{(124)}$. These methods are not well suited to our experiment, however, and will not be discussed here.

D. Infrared Measurements

Measurements were taken from 600 to 1200 cm$^{-1}$ using a Perkin-Elmer Model 180 infrared spectrophotometer. Preliminary scans were made of the initial amorphous film and a film crystallized at $180^\circ$C for 48 hours. Bands attributed to the crystalline regions by several authors$^{(111,112)}$
were observed to be more defined in the crystallized sample. Scans were taken with no polarization, with polarization parallel to the stretching direction, and with polarization perpendicular to the stretching direction. Samples used had been subjected to various combinations of elongation ratio, strain rate, and temperature. Determination of the orientation effects of these variables on the stress-induced crystallization of PET was thus obtained.
CHAPTER III
RESULTS AND INTERPRETATION

A. Stress Optical Coefficient Determination

In a normal relaxation process, where normal is an amorphous, non-crystalline polymeric material, the birefringence and stress relaxation behave in the same manner. They both decrease at the same rate which keeps the stress optical coefficient constant during the progress of relaxation. This suggests that the stress decay due to the rearrangement of molecular configuration in a deformed state held at constant length is always accompanied by a decrease in birefringence for a simple relaxation process.

This type of stress and birefringence behavior was observed with very low elongation ratios at very slow strain rates. Figures (7 & 8) show measurements of stress and birefringence typical of conditions necessary for the determination of the stress optical coefficient. It can be seen that during the stretching process, both the birefringence and the stress increase simultaneously to a maximum, achieved at the termination of stretching. Upon the completion of stretching, both the stress and the
birefringence are observed to decrease at the same rate. This is typical of amorphous polymer films.

Elongation of an amorphous polymer to a relatively small degree results in several types of deformation. First, there is rotation of the molecular segments from gauche to trans configurations leading to elongated chains. Then the bonds between the primary structural units are stretched elastically with accompanying valance angle deformation. These processes are reversible upon the termination of stretching where relaxation occurs to relieve stresses. The relaxation also occurs by a number of processes. First, the stresses due to the bent and stretched covalent bonds are relieved by small amounts of atomic and molecular motions. Then, the rotations about the covalent bonds occur which requires motion of larger parts of the molecule. These processes occur as the molecules move to retain the lowest energy state of a randomly coiled molecule.

Since birefringence is a measure of the orientation of a material, it will change accordingly with the movement of the molecular chains. During the elongation, when the chains are undergoing bond stretching and rotation, the orientation will correspondingly increase as the chains move toward a higher state of entropy. Therefore,
the movement of the amorphous chains induces the birefringence changes observed.

Observations of the change in birefringence with time during the stretching process suggest the increasing orientation of the molecular chains with the increase of elongation ratio. It is also observed that the maximum birefringence value for a constant strain rate and elongation is greater for the experiments performed at lower temperatures. Therefore, at temperatures closer to the glass transition, the molecular chains are more highly oriented than they would be under similar conditions at a higher temperature. This means that, at temperatures approaching the glass transition, chain mobility for relaxation is impeded.

Impedence of chain mobility would also lead to the necessity of more force for polymer deformation. This can be observed in Figures (7 & 8). It is seen that the maximum stress value for a constant strain rate and elongation is greater for the experiments performed at lower a temperature. At the higher temperature, the short range motions of the molecular chain segments occur faster requiring less force, which is observed in our experiments.

Measurements such as these where the stress and birefringence decrease at the same rate were used in the calculation of the stress optical coefficient. This was
done as the samples remained amorphous, both during and after the stretching process as observed by the birefrin-
gence decreases after termination of stretching. The stress optical coefficient for the amorphous polymer was calculated using the equation

\[ C = \frac{\Delta a}{\sigma a} \]  

(39)
as defined earlier. Values used in further calculations were those determined when the system had reached an equil-
ibrium state for relaxation. The stress optical coeffi-
cients obtained are plotted as a function of temperature in Figure (9). It is seen that the values increase slightly with temperature. This is opposite of the pre-
dicted reciprocal relation between the stress optical coefficient and temperature for rubbers\(^{(119)}\). However, it is explainable in terms of internal energy and polar-
izability considerations.

Kuhn and Grün\(^{(81,125)}\) have described the stress op-
tical coefficient, as shown earlier, by the equation

\[ C = \frac{\Delta}{\sigma} = \frac{2\pi}{45} \frac{(n^2 + 2)^2}{\bar{n}kT} (\bar{b}_|| - \bar{b}_\perp) \]  

(40)
This can be rearranged to the form

\[ (\bar{b}_|| - \bar{b}_\perp) = \frac{45\bar{n}kT\Delta}{2\pi(n^2 + 2)2\sigma} \]  

(41)
In this manner, it can be seen that the difference of the polarizabilities of the statistical segment are dependent on the temperature of the system. Therefore, all other
factors remaining the same, the quantity $(b_{\|} - b_{\perp})$ would increase with increasing temperature. If this increase did occur to a large enough extent, it may account for an increase in the stress optical coefficient not otherwise expected.

Another possible explanation concerns the contributions of the entropic energy and internal energy to the total stress on the system (126). The total stress can be written as

$$\sigma = \left( \frac{\partial E}{\partial \varepsilon} \right) - T \left( \frac{\partial S}{\partial \varepsilon} \right)$$

where $E$ is the energy, $\varepsilon$ is the strain, and $S$ is the entropy on the system. In this manner, the stress can be thought to consist of both internal energy and entropic energy contributions.

$$\sigma = (\sigma)_E + (\sigma)_S$$

where $(\sigma)_E$ is the stress due to internal energy and $(\sigma)_S$ is the stress due to the entropic energy. These terms can be applied to the stress optical coefficient by

$$C = \frac{\Delta}{\sigma} = \Delta \left( \frac{1}{\sigma_E + (\sigma)_S} \right)$$

It is known that the internal energy term decreases with temperature over a short temperature range near $T_g$ while the entropic energy term increases more slowly with temperature. Therefore, if $\sigma_E$ undergoes a large decrease
the first term in equation (44) will increase rapidly while the second term decreases more gradually. This would cause an overall increase in the stress optical coefficient as observed in our experiments. Our measurements are performed at temperatures near enough the glass transition for this internal energy contribution to the stress to have such an effect. It is believed this could be the reason for our unexpected increase in stress optical coefficient with temperature.

B. Orientation Function Determination

Preliminary measurements using X-ray diffraction and the (105) plane reflection method of Dumbleton and Bowles (94) to determine the orientation function of the crystalline phase proved ineffective. The low degree of crystallinity and extreme thinness of the sample films (0.001 to 0.003 in.) made the length of time necessary for a usable diffraction pattern to be obtained (48 hours) unreasonable. It was therefore decided to use the infrared dichroism method for determination of the crystalline orientation function.

The dichroic ratio of the infrared bands at 875 and 973 cm\(^{-1}\) were analyzed for determination of the orientation function of the crystalline phase. These bands
are known to arise from the crystalline phase and have been shown to be orientation sensitive as well. The 875 cm\(^{-1}\) band arises from the transition moment normal to the benzene ring and is characteristic of axial orientation according to the study of PET by Schmidt\(^{(114)}\). He also found that the 973 cm\(^{-1}\) band is a function of the axial orientation. Figure (10) shows the spectra of oriented PET with the radiation polarized parallel and perpendicular to the stretching direction of the film from 600 to 1200 cm\(^{-1}\).

The crystal structure of PET as reported by Daubeny and Bunn\(^{(133)}\) was used to determine the orientation of the transition moment with respect to the molecular axis. It was determined that the unit cell contains one monomer unit and is triclinic with \(a = 4.56 \text{ Å}\), \(b = 4.94 \text{ Å}\), \(c = 10.75 \text{ Å}\), \(\alpha = 98.5^\circ\), \(\beta = 118^\circ\), and \(\gamma = 112^\circ\). The molecular chain is in an extended form and is nearly planar. The value of the transition moment with respect to the molecular axis was used in equation (35) along with the orientation of the transition moment, calculated from the dichroic ratio in equation (34), to determine the crystalline orientation function. Values for the dichroic ratio and crystal orientation function are presented in Table 1 for various combinations of elongation ratio, strain rate, and temperature.
TABLE 1

CRYSTALLINE ORIENTATION FUNCTION
CALCULATED FROM INFRARED DICHROISM

<table>
<thead>
<tr>
<th>Elongation Ratio</th>
<th>Strain Rate (°C)</th>
<th>Temperature (°C)</th>
<th>Dichroic Ratio</th>
<th>Orientation Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.338</td>
<td>80</td>
<td>0.62</td>
<td>0.63</td>
</tr>
<tr>
<td>2.6</td>
<td>0.338</td>
<td>80</td>
<td>0.66</td>
<td>0.68</td>
</tr>
<tr>
<td>3.4</td>
<td>0.338</td>
<td>80</td>
<td>0.70</td>
<td>0.76</td>
</tr>
<tr>
<td>4.2</td>
<td>0.338</td>
<td>80</td>
<td>0.73</td>
<td>0.82</td>
</tr>
<tr>
<td>6.0</td>
<td>0.338</td>
<td>80</td>
<td>0.87</td>
<td>0.90</td>
</tr>
<tr>
<td>2.6</td>
<td>1.694</td>
<td>90</td>
<td>0.67</td>
<td>0.69</td>
</tr>
<tr>
<td>4.2</td>
<td>1.694</td>
<td>90</td>
<td>0.75</td>
<td>0.83</td>
</tr>
<tr>
<td>4.2</td>
<td>1.694</td>
<td>100</td>
<td>0.78</td>
<td>0.86</td>
</tr>
<tr>
<td>4.2</td>
<td>0.017</td>
<td>90</td>
<td>0.76</td>
<td>0.85</td>
</tr>
</tbody>
</table>
It can be seen that the dichroic ratio, and hence the orientation function, remains relatively constant with changes in strain rate and temperature while it increases with increasing elongation. These values will be used in the Stein-Norris equation for the determination of crystallinity.

C. Variable Elongation Ratio

As described previously, the normal relaxation process is accompanied by simultaneous decreases of stress and birefringence. These decreases indicate that the polymer is retaining its amorphous character. Consequently, the increase in birefringence with time at higher extension is believed to arise from the growth of crystallites which have preferred molecular orientation with respect to the stretching direction. It will be shown in this section that there is increasing crystallization taking place as the elongation ratio is increased.

Figure (11) shows the typical behavior of birefringence at the end of stretching as a function of elongation for a polyethylene terephthalate film. The birefringence is seen to increase with increasing elongation ratio. The amount of increase varies depending on the conditions of strain rate and temperature. This increase in birefrin-
gence indicates the increase in orientation of the molecular chains with increasing elongation. It will be observed later that this increase in orientation leads to an increase in the crystallization of these films under stress.

The general behavior of birefringence as a function of time after elongation for various elongation ratios is illustrated in Figure (14). It is observed that, for a constant strain rate and temperature, the birefringence tends to decrease for the lower elongations, remain relatively constant for the middle elongations, and increase slightly for the higher elongations. These changes in birefringence with time are significant with relation to the orientation and overall structural changes in the polymer film.

At the lower elongations, the molecular chains will orient during the stretching process with the accompanying increase in birefringence. After the completion of stretching, the molecular chains start to relax even though the overall sample is held at constant elongation. Relaxation which takes place is due to the amorphous chains in the system moving to relieve the stress built up during stretching. If totally amorphous, the orientation, and hence the birefringence, would decrease to zero during the
relaxation process. Since the birefringence does not decrease to the zero value in these samples, there must be chains present which are not amorphous and therefore not undergoing relaxation. Some crystallization due to stress is suspected for these non-relaxing chains.

The molecular chains also orient during stretching at the middle elongation ratios. However, more orientation takes place as the chains are deformed to a greater extent and undergo more bond rotations and stretching. After the completion of stretching, no change in orientation appears to take place according to the constant birefringence measurements observed with time after elongation. One possible explanation is that the growth of crystals can prevent relaxation of the amorphous chains by behaving similarly to crosslinks. The difference between crosslinks and crystals is that there is no stress decrease when crosslinks are present. Since we observe a simultaneous stress decrease during stretching, it is believed that crystals are present holding the amorphous chains taut. Another explanation could be that the number of crystallites has increased to a degree where the crystalline contribution to the birefringence outweighs the amorphous contribution. Then, the orientation decrease
due to the relaxation of the amorphous chains would be concealed by the crystalline orientation in the observed birefringence measurement.

At the higher elongations, the molecular chains which have oriented during the stretching process are deformed to an even greater extent. The increase in birefringence after elongation implies that the chains are undergoing further orientation in addition to that which took place during stretching. Since no further elongation is taking place, to cause this extra orientation, a possible explanation is that crystallization is taking place which is additional to that incurred during stretching. This could be due to the increase of nucleation rate with amorphous orientation causing the formation of more crystallites (nuclei) in the oriented film. There is also the possibility of crystallization taking place in the nuclei formed during deformation. Past studies\(^{(50)}\) have stated that a rise of the birefringence in the deformed state is due to stress-induced crystallization with the crystallites produced lying parallel to the stretching direction. This is in agreement with predictions here and with later crystallization calculations.
Figure (12) shows the typical behavior of stress at the end of stretching as a function of elongation for PET. The stress is seen to increase with increasing elongation ratio which is typical of polymeric materials. It is also noted that, at the higher elongations, there is a drastic increase in the stress. This could correspond to the point where the chains are approaching their limiting extensions between crystallites and entanglements acting as crosslinks. The onset of strain-induced crystallization could also be occurring causing a rise in the elastic stress as it ties together a number of the chains exerting a crosslinking effect.\(^{127,128}\)

The general behavior of stress as a function of time after elongation for various elongation ratios is illustrated in Figure (15). It is observed that, for a constant strain rate and temperature, the stress is higher and decreases at a greater rate for the higher elongations. These stress changes, when compared to the birefringence results for the same experimental conditions, give significant information concerning the crystallization which occurs upon deformation of the PET films.

At the lower elongations, the stress rise during elongation is relatively small. The decrease after the completion of stretching is also small with a slight in-
crease in the rate of stress relaxation. However, the rate of decrease for the stress is greater than the corresponding birefringence rate decrease. This combination indicates that the polymer film is not entirely amorphous, since in the totally amorphous films, the birefringence and stress decreased at the same rate after stretching. It will be shown later that this difference in decrease between stress and birefringence is indicative of stress-induced crystallization.

The stress is observed to be higher for the films deformed to larger elongations. There is a larger overall decrease in the stress during relaxation and a correspondingly greater increase in the rate of stress relaxation. The stress is also seen to decrease to a value higher than that at the lower elongations. This stress decay behavior, when compared to the corresponding birefringence behavior, is easily interpretable if it is assumed that crystallization has taken place during the orientation at higher stress. Molecular chain mobility is inhibited when the chains have formed crystallites. Once incorporated into a crystal, the chains do not undergo the necessary relaxation for a stress decrease. This would account for the fact that the stress does not decrease to the initial zero value before deformation took place. The
greater rate of stress decay for these higher elongations could be due to the smaller amount of amorphous chains which could relax and the extent to which relaxation could now take place. The amorphous chains are stretched further at this deformation and relaxation to a higher entropy state occurs with a correspondingly greater decrease in stress since these chains now will relax, both by small amounts of molecular motion to relieve stretched covalent bonds and larger molecular motion to relieve covalent bond rotations brought about by the elongation process.

The drastic difference between the birefringence and stress for these higher elongations (birefringence increasing and stress decreasing) leads to the conclusion that some crystallization due to stress on the sample has occurred. That this is in fact happening will be seen in the next set of curves.

Crystallinity was calculated from these simultaneous stress and birefringence values using the modified Stein-Norris equation described earlier. Figure (13) shows the typical behavior of this crystallinity at its equilibrium value, after stretching and relaxation, as a function of elongation for PET. The value of crystallinity is seen to increase with increasing elongation ratio. The rate
of increase is seen to vary with strain rate which will be discussed later.

The general behavior of percent crystallinity as a function of time after elongation is illustrated in Figure (16). It is observed that, for a constant strain rate and temperature, the crystallinity is greater for the higher elongation ratios. At the lower elongations, the crystallinity is seen to increase only slightly, almost remaining relatively constant, at values scarcely greater than zero. At the middle elongations, the percent crystallinity increases slowly, while at the higher elongations, the crystallinity increases rapidly initially and then increases more slowly to a relatively constant value (this is seen more clearly in later graphs).

Comparisons of the stress and birefringence curves taken simultaneously for each elongation lead to the conclusions shown in the curves for percent crystallinity. At the lower elongations, the birefringence was observed to decrease with time after elongation. This decrease was also observed with the stress after elongation. However, the rate of stress decay was greater than the rate of birefringence decline. This combination leads to the suggestion that some crystallite formation has taken place during the elongation of the polymer film.
This is borne out in the crystallinity plots. For these low elongations, the PET films have crystallized but only to a small degree. Since the crystallinity remains relatively constant with time after the termination of stretching, it can be assumed that all the crystallization took place during the deformation process. This means that some crystallization occurred as the chains were undergoing elongation, due to bond rotations. As the chains become extended, the free energy of the amorphous phase increases from a level less than the free energy of the crystalline phase to a level greater than that of the crystalline level. The change in free energy going from the amorphous to crystalline phases is then favorably increased, making crystallization possible. It is not clear what would be the exact morphology resulting from this process. A rod-like crystallite or micellar formation would be the most likely structures.

At the middle elongations, the birefringence was observed to remain relatively constant while the stress decreased moderately rapidly. Once again, this implies that the molecular chains are not remaining totally amorphous and that some formation of crystals is taking place. That this is true can be seen in the plot of crystallinity vs. time for these elongations. It can be seen that the
percent crystallinity increases with time at a relatively slow rate. It seems that as the molecular chains relax, some will find themselves lined up next to a formed crystallite with which, due to the decrease in energy upon crystallization, they will combine to form a larger structure. Another possibility is in the method of crystallinity calculation itself, where the amount of crystallinity present is calculated by the difference of birefringence and stress. Perhaps the initial stress after elongation is high enough that when placed in the modified Stein-Norris equation, it overpowers the birefringence measurement and thus decreases the crystallinity value from the true amount of crystallinity. When the amorphous chains relax to relieve stress, the actual amount of crystallization which occurred during deformation is actually observed by our calculations. The method used in this study cannot readily distinguish between these two possibilities.

Higher elongations were seen to lead to a slight increase in the birefringence and a large decrease in stress with time after the termination of elongation. In the crystallization curve, it can be observed that the crystallinity increases with time after elongation to a rather great extent and rapid rate. This further crystallization during the relaxation process could again be
due to the formation of new nuclei by the rise in amorphous free energy or to the further crystallization of nuclei formed during the deformation. The vast increase of rate and extent is due to the greater orientation at these higher elongation ratios and hence their greater effect on the kinetics and thermodynamics of the crystallization process.

The typical behaviors for the birefringence, stress, and percent crystallinity as functions of time after elongation shown thus far can be seen to be similar for the various combinations of constant strain rate and temperature in Figures (17-49). There is some variation as to what differentiates a higher or lower elongation due to the temperature and strain rate effects, but the specifics of these effects will be discussed later in this section. It can generally be seen that the faster strain rates have trend values for birefringences, stresses, and crystallinities which are higher overall than the slower strain rate described previously. For the elongations at the highest rates of 1.694/sec, it is seen that even the lower elongations undergo birefringence, stress, and crystallinity changes quite similar to those for the higher elongations. It will be seen later that all three variable factors must be taken into account when determining crystallization effects induced by stress.
D. Variable Strain Rate

It will be shown in this section that there are distinct changes in the birefringence, stress, and percent crystallinity as the strain rate is varied while maintaining constant the parameters of elongation ratio and temperature.

Figure (50) shows the typical behavior of birefringence at the end of stretching as a function of strain rate for a polyethylene terephthalate film. The birefringence is seen to increase, indicating an increase in orientation with increasing strain rate. The amount of increase varies depending on the conditions of elongation and temperature. The birefringence undergoes a great increase initially, but levels out to an equilibrium value at a moderate strain rate. This leveling out shows that the effect of strain rate on orientation is relatively constant for all but the lowest rates. Therefore, in actual processing procedures, using very high strain rates, the orientation would be little effected by relatively small changes in rate.

The general behavior of birefringence as a function of time after elongation for various strain rates is illustrated in Figure (53). It is observed that for a constant elongation ratio and temperature, the birefringence
tends to decrease at the lower strain rates to a much greater degree than at the higher strain rates where the birefringence appears to remain relatively constant with time after elongation. These changes of birefringence with time are again significant with relation to the orientation which is occurring in the polymer film.

At the lower strain rates, the molecular chains are oriented during deformation but to a lesser extent than at the higher rates. At extremely low rates, the relaxation time for the molecular chains is small in relation to the time for total elongation. The chains can undergo some relaxation during the process and so their total orientation is correspondingly low. Relaxation of these chains accelerates after the termination of stretching which results in a decrease in the orientation and hence the birefringence as observed here. A totally amorphous film would decrease in birefringence back to the initial value of zero after the end of deformation. Since this is not observed, there must be some molecular chains which are not relaxing back to their randomly coiled state and some crystallization due to the elongation is suspected.

At the higher strain rates, the birefringence is also observed to decrease slightly with time after elon-
gation. However, this decrease becomes less and less noticeable upon increasing the strain rate. The molecular chains again orient during the elongation of the film, but to a greater extent than at the lower strain rates as can be seen by the relative birefringence values in this figure. At the faster strain rates, the time for chain relaxation movement around covalent bonds becomes longer in relation to the time for total elongation to occur, leading to higher orientation during stretching. The small decrease in the birefringence during relaxation is again due to the formation of crystallites which prevent the relaxation of the amorphous chains.

Figure (51) shows the typical behavior of stress at the end of stretching as a function of strain rate for PET. As expected, the stress is observed to increase with increasing strain rate, but appears to level off at higher strain rates. This implies that dramatic effects on the stress by the strain rate occur only at the lowest rates. Therefore, small changes in the rate for industrial processing conditions will not make great changes in the stress at these conditions.

The general behavior of stress as a function of time after elongation for various strain rates is illustrated in Figure (54). It can be seen that the stress is higher
at the faster strain rates and also appears to decrease at a greater rate than the slower strain rates, all at a constant elongation ratio and temperature. Significant information concerning the crystallization which occurs upon deformation of these films is obtained when these stress changes are compared to the birefringence results for the same experimental conditions.

At the lower strain rates, the stress rise during elongation is relatively small. After deformation, the stress decreases, but to a small degree and at a relatively slow rate. The stress is also observed to decrease to a non-zero value at the end of relaxation, where totally amorphous systems decay to zero stress. This non-zero value plus the difference in decay rates between the stress and birefringence is indicative of a small amount of stress-induced crystallization as will be shown later.

The stress is observed to be somewhat greater for the films deformed at faster strain rates. There is also a larger decrease in the stress during the relaxation and a correspondingly greater increase in the rate of stress decay in these samples. This rate of stress decay appears to be greater at times shortly after the termination of deformation and becomes less with increasing time after
elongation. At times long after elongation, the stress decay rate is about the same for all strain rates.

It can also be seen that the rate of stress decay for these faster strain rates is much greater than the changes in birefringence during the relaxation process. Crystallization due to stress upon elongation would be one cause of such a drastic difference in decay rates. That this is in fact happening will be seen in the next set of curves.

Figure (52) shows the typical behavior of crystallinity, calculated from the stress and birefringence, at its equilibrium value, after stretching and relaxation as a function of strain rate for PET. The value of crystallinity is seen to increase with increasing strain rate. There is also a variation of this increase with conditions of elongation and temperature. The crystallinity increases at a rapid rate for small strain rates and then appears to level off as the strain rate increases further. This implies that the strain rate exerts less of an influence on crystallinity variation as the rate increases from zero. At strain rates used for industrial processing, which are much greater than those investigated in this study, a small variation in the rate would have a negligible effect on the overall structure and crystallinity.
The general behavior of percent crystallinity as a function of time after elongation is illustrated in Figure (55) for various strain rates and constant elongation and temperature. It is observed at these conditions that the amount of crystallinity present is greater for the faster strain rates. At the lowest strain rate, the crystallinity is seen to remain approximately constant after deformation. This would imply that all crystallinity takes place during the deformation process at the lower strain rates. Comparison of the birefringence and stress curves for this strain rate shows that the rates of decay of both are approximately the same, but that their final equilibrium values are higher than the initial values before elongation. This shows that the material after elongation and relaxation is not entirely amorphous as the similar decay rates suggest, but have some crystallites present as shown in the crystallinity curve.

At the higher strain rates, the crystallinity increases with time after elongation. It appears to increase rapidly at first and then quickly levels out to an equilibrium level. It would appear that fast crystallization takes place directly after the cessation of stretching which slows down with increasing time after
elongation. The chains which are still amorphous after elongation may find themselves oriented in the direction of the formed crystallites which can then act as nuclei for further crystallization by these oriented amorphous chains. It is possible that this crystallization could take place before the oriented molecular chains had time to relax into a more randomly coiled and unoriented state. New crystallites could also form from these oriented chains before relaxation.

The typical behaviors for the birefringence, stress, relaxation, and percent crystallinity as functions of time after elongation shown thus far in this section are seen to be similar for the various combinations of constant elongation ratio and temperature in Figures (56-79). The variation of conditions of temperature and elongation alter the rates which can be considered to fall under fast or slow strain rate behavior. It can be seen that the faster strain rates in any set of curves generally have trend values for birefringence, stress, and crystallinity which are higher overall than the slower strain rates. It was seen in a previous section that the higher elongation ratios also tend to increase these values and it will be shown in the next section that temperature also adds an effect to the measured quantities. It is seen that at the higher elongations, even the slower strain
rates undergo birefringence, stress, and crystallinity changes quite similar to those for the faster strain rates. However, the effect of strain rate does not appear to be as great of an influence on the crystallization induced by stress as the elongation ratio over the same temperature range.

E. Variable Temperature

Temperature was the third variable studied in these experiments. Figure (80) shows the typical behavior of birefringence at the end of stretching as a function of temperature while maintaining constant the elongation ratio and strain rate for PET. It can be seen that the birefringence decreases with increasing temperature. The rate of decrease is dependent on the strain rate and elongation ratio of the experiment. The large decrease shows that the orientation of the material is very dependent on the temperature at which deformation occurs.

The general behavior of birefringence as a function of time after elongation for various temperatures is shown in Figure (73). At constant elongation and strain rate, it is observed that the birefringence remained relatively constant after deformation at the lower temperature, while it increased slightly for the higher temperatures. It would appear that no further orientation is occurring at
these lower temperatures while further orientation or crystallization occurs at the higher temperatures. The magnitude of the birefringence is also noted to be greater at the lower temperatures. During the deformation process, more relaxation of the molecular chains could be taking place due to increased chain mobility at the higher temperatures. This would result in the lower degree of orientation observed in these experiments. Treloar has observed similar effects for natural rubber\(^{119}\). Since the birefringence changes are directly related to the stress on the molecular chains, the same arguments which will be presented next for the stress effect can also be applied to these birefringence observations.

Figure (81) shows the variation of equilibrium stress after relaxation as a function of temperature for several combinations of strain rate and elongation ratio. The stress is observed to decrease with increasing temperature. Thermodynamically, it is known that the restoring force, \(f\), exerted by the rubber after deformation consists of both energy and entropy contributions.

\[
f = \left( \frac{\partial E}{\partial L} \right)_T - T \left( \frac{\partial S}{\partial L} \right)_T
\] (45)
where the first term corresponds to the change in internal energy and the second to the change in entropy with extension. Substituting the Maxwell's relation
\[
\left( \frac{\partial S}{\partial L} \right)_T = \left( \frac{\partial f}{\partial T} \right)_L
\] (46)
into equation (45) and rearranging for the force change with temperature gives
\[
\left( \frac{\partial f}{\partial T} \right)_L = \frac{1}{T}[f - \left( \frac{\partial E}{\partial L} \right)_T]
\] (47)
This equation shows that for the slope of the force vs. temperature curve to be negative, the change in internal energy with elongation must be greater than the force. This has been shown to be true for low elongations of natural rubber\(^{(129,130)}\). They found that the internal energy term changes with the same order of magnitude as the entropy term at low elongations, while at high elongations, it accounts for less than one-sixth the total change in free energy. The entropy term is observed to change sign at the extension corresponding to the thermoelastic inversion point.

The thermoelastic inversion phenomenon has been interpreted\(^{(130)}\) in terms of volume expansion upon the heating of rubber. The expansion will increase the length at constant stress, which is the same as decreasing the
stress at constant length. At low elongations, the reduction of stress due to internal energy by thermal expansion exceeds the increase of entropic stress expected from the kinetic theory of elasticity. When these two effects balance exactly, it is called the thermoelastic inversion point.

The observation that stress decreases with increasing temperature for PET implies that the elongation ratios studied are all below the thermoelastic inversion point. This means that the change in force due to the internal energy changes is greater than that due to the entropy changes in PET during relaxation. This also substantiates the conclusions drawn about the stress-optical coefficient increases with temperature.

The behavior of stress with time after elongation is shown for various temperatures in Figure (84). The observation that the higher temperatures give overall lower stress values was accounted for previously. The stress decrease with time after elongation is seen to be greater than the decrease in the birefringence for the same experimental conditions. This difference signifies that crystallization may be occurring at these conditions.

The calculated crystallinity is shown in Figure (82) as a function of temperature at conditions of constant elongation ratio and strain rate. It is observed that
generally the percent crystallinity decreases sharply with increasing temperature between $T_g$ and normal isothermal crystallization temperatures for PET. Differences in the decrease with temperature appear to depend on the strain rate and elongation ratio, as described earlier.

Typical crystallinity, calculated from the simultaneous stress and birefringence, as a function of time after elongation, appears in Figure (85) for various temperatures. It is observed that at these conditions of strain rate and elongation, the crystallinity increases with time after elongation for all cases. The magnitude of the crystallinity is greater for the lower temperatures, but the crystallinity does not appear to increase as much with time as it does for the higher temperatures. Increasing crystallinity with time is again indicative of either the formation of new nuclei from the oriented molecular chains or further growth occurring on the crystallites formed during deformation.

The behaviors of the birefringence, stress, and percent crystallinity as functions of time after elongation shown thus far are similar for the various combinations of elongation ratio and strain rate as shown in Figures (86-108). The absolute degree of change of the
birefringence and stress are seen to vary with conditions, as do the equilibrium crystallinity values.

It has been shown in these last three sections that all three of the variables tested (elongation ratio, strain rate, and temperature) have marked effects on the final crystallinity attained after the deformation of PET. How these results conform to the theories presented earlier will be demonstrated in the following sections.
A. Avrami Analysis

As discussed in the introduction, the Avrami equation is often used to study crystallization kinetics and to distinguish the different nucleation processes and crystal growth patterns. Avrami-type analyses were performed on several of the experiments done at the higher strain rates.

Figures (109-113) show plots of \( \ln\{-\ln[1-(\chi_C/\chi_\infty)]\} \) vs. \( \ln t \) for various elongation ratios at constant strain rate and temperature. The usual deviations in the late stages of transformation in Avrami plots for polymers\(^{(6)}\) are observed in our experiments. Therefore, the slopes and intercepts were determined by least squares analysis over the initial time range before these deviations occurred, approximately \( \ln t = 0.25-2.0 \). The values obtained for the values of \( n \) and \( k_C \) determined at various temperatures, elongation ratios, and strain rates are listed in Table 2.

The crystallization rate constants as a function of elongation ratio are shown in Figures (114 & 115). It is observed that the rate constant increases dramatically
### TABLE 2

**CRYSTALLIZATION RATE CONSTANTS AND AVRAMI EXPONENTS**

<table>
<thead>
<tr>
<th>Strain rate (/sec)</th>
<th>Temperature (°C)</th>
<th>Elongation rate</th>
<th>ln $k_c$</th>
<th>$k_c$ (×10²)</th>
<th>n</th>
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</thead>
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<tr>
<td>0.678</td>
<td>75</td>
<td>1.8</td>
<td>-3.95</td>
<td>1.93</td>
<td>1.42</td>
</tr>
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<td></td>
<td></td>
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<td>-3.17</td>
<td>4.20</td>
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<tr>
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<td>1.74</td>
<td>1.28</td>
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<td>1.36</td>
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<tr>
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<td>-3.46</td>
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<td>1.25</td>
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<tr>
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<td>1.694</td>
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<td>-4.43</td>
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<td>-2.58</td>
<td>7.58</td>
<td>1.17</td>
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</tbody>
</table>
with the elongation ratio. This increase shows the great enhancement to crystallization when an amorphous sample is oriented. The rate is greater at the lower temperatures and does not increase linearly with elongation ratio. One revealing result of this is the sensitivity of the crystallization rate to both elongation and temperature. This is in agreement with the results of Kim and Mandelkern\(^{(31)}\) for natural rubber who found a marked dependence of the crystallization rate on both elongation and the degree of undercooling. The undercooling is greater with increasing elongation due to the melting point elevation which is known to occur with strain\(^{(2)}\).

From Table 2, the Avrami exponent, \(n\), is seen to decrease with increasing elongation. Since \(n\) is related to the mode of crystal growth, this implies that the crystal undergoes a transition from a radial plate-like growth to a more uni-directional growth with increasing elongation. This same result has been found by others\(^{(31,33)}\).

The non-linearity of these rates vs. elongation curves can be attributed to the fact that the stress is decreasing with time after elongation. The crystallization rate is known to be dependent on the amorphous orientation\(^{(79)}\), and this orientation is dependent on the relaxation of the molecular chains. A more accurate analysis would take the relaxation into account. By substituting
the Ziabicki equation for the crystallization rate into the Avrami equation, an equation is obtained which accounts for this stress relaxation.

\[
\{\ln[-\ln(1- \frac{\chi c}{\chi_\infty})] - A \left( \frac{C_0}{\chi a} \right)^N\} = \ln k + n \ln t \tag{48}
\]

After the Ziabicki parameters of \(N\) and \(A\) are evaluated, this equation will be tested to determine its usefulness.

B. Ziabicki Analysis

Ziabicki\(^{(79)}\) has modified the Avrami equation to include the crystallization of oriented systems. His theory, as shown earlier, takes into account the amorphous orientation prior to the onset of crystallization, equation \((8)\). A modification of this equation can be used to determine the sensitivity of the crystallization rate on the amorphous orientation. The modified Avrami equation

\[
k = k_0 \exp (A f_a^N) \tag{49}
\]

is used where \(k\) is the crystallization rate constant at the oriented conditions, \(k_0\) is the rate constant for the unoriented material, \(A\) is the orientation function, and \(N\) is the exponent which describes the amorphous orientation dependence.
Equation (49) can be rewritten in the form

$$\ln[\ln (k/k_0)] = \ln A + N \ln f_a$$

(50)

By plotting the left hand side of equation (50) vs. $\ln f_a$, the slope will give the value of $n$ and the intercept will be the value of $\ln A$. In this manner, the dependence of the crystallization on the amorphous orientation can be determined.

Plots of $\ln [\ln (k/k_0)]$ vs. $\ln f_a$ are shown in Figures (116 & 117). The amorphous orientation was determined at times just prior to the onset of crystallization using the relation

$$C_0 = f_a^{\Delta_a}$$

(51)

where $C$ is calculated as described previously, the stress is that measured just prior to the crystallization, and $\Delta_a^0 = 0.275$, as defined by Dumbleton$^{(94)}$. It can be seen that the rate of crystallization increases dramatically with the amorphous orientation. This implies that crystallization is enhanced by the deformation of PET films.

The values of the slope and intercept for each curve were determined using the least squares method and are listed in Table 3. It is noted that the values of $N$ decrease slightly with increasing temperature at each strain rate shown. $N$ values are larger at the larger strain rates. The values of $N$ in all cases appear to be close
<table>
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<tr>
<th>$\dot{\varepsilon}$</th>
<th>$f_a$</th>
<th>$\ln f_a$</th>
<th>$\ln k$</th>
<th>$\ln[\ln \frac{k}{k_0}]$</th>
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</tr>
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<td>-4.59</td>
<td>-1.54</td>
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<td>-3.02</td>
<td>-3.82</td>
<td>-0.02</td>
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<td>0.091</td>
<td>-2.40</td>
<td>-2.58</td>
<td>0.80</td>
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</table>
to one which implies that a linear function of orientation is applicable.

The values for the parameter, A, are observed to decrease as a function of temperature and to increase with strain rate. This behavior is opposite that presented by Alfonso et. al\(^{78}\) who found that A increased with temperature. Their A values were also an order of magnitude greater than those reported here. Those differences may be due to a slight difference in calculation. In this study, the crystallization rate was analyzed where in the Alfonso study, the crystallization half-times were used. Other authors\(^{14,132}\) have determined differing values for A, which suggests more work needs to be done on this type of analysis.

The values of A obtained in this analysis were used in equation (48) to determine the influence of stress relaxation on the crystallization parameters. It was observed that the rate vs. elongation curves were more linear upon inclusion of the stress term in the analysis, but were still somewhat non-linear. The same values for the Avrami exponent and crystallization rate constant were obtained from both equation (2) and equation (48).
CHAPTER V

CONCLUSION

Stress-induced crystallization was found to occur in polyethylene terephthalate from the deformation applied in our studies. All three variables, elongation, strain rate, and temperature affected the percent crystallinity. Increasing elongation was found to increase the orientation and hence birefringence, as well as the stress measured. The increase in orientation led to greater values of crystallinity.

Strain rate effects were seen to be of a lesser magnitude. The orientation, birefringence, and stress increased with increasing strain rate, which again led to increased crystallinity for a given elongation ratio and temperature.

Decreases in the orientation and stress were observed with increasing temperature. Greater relaxation at the higher temperatures resulted in the lower crystallinity values obtained.

The infrared dichroism studies showed that the crystalline orientation function remained relatively constant for the conditions employed in our studies. The value was also the same for a sample film elongated and
then isothermally crystallized in the deformed state.

An Avrami analysis on the stress-induced crystallization provided information about the crystallization rate and growth mechanism. It was observed that the crystallization rate increased dramatically with increasing elongation ratio. Higher values of crystallization rate were obtained at the lower temperatures, other conditions remaining the same. The growth of the crystal appeared to undergo a transition from radial, plate-like growth to a more uni-directional growth as the elongation ratio was increased.

The sensitivity of crystallization to orientation, as defined by Ziabicki, increased with strain rate and temperature. From this analysis, it appeared that either several nucleation processes or crystal forms were present during the stress-induced crystallization of PET.

The method of simultaneous measurements of birefringence and stress during the deformation and the subsequent relaxation of PET proved to be useful for determining the crystallization produced under the variable conditions of elongation, strain rate, and temperature.
CHAPTER VI
SUGGESTIONS FOR FUTURE WORK

Future studies on the stress-induced crystallization of polymers could be extended to other polymers used commercially for fibers or films, such as other polyesters, polyamides, nylons, and acrylics. Strain rates and elongation ratios could be chosen to more closely simulate actual processing conditions. Polymer blends and the effect of blending or copolymerization on stress-induced crystallization could be studied if the effects on the individual components were known.

It is apparent that both the melting point and glass transition temperature change with the stress-induced crystallization of polymers. A quantitative study of the change in \( T_g \) and \( T_m \) with the conditions of elongation and strain rate would be useful since, in this study, it appeared that the glass transition rose appreciably at the high elongations, thus changing the drawing process to one of cold-drawing. A rise in \( T_g \) would appreciably affect the stress measurements, while the lowering of \( T_m \) affects crystallinity by a lowering of the supercooling.
The molecular weight of a polymer can also affect the stress-induced crystallization. A systematic study could be made utilizing various well-defined molecular weight fractions of a polymer. Each fraction could be tested under similar conditions to determine the role of both the low and high molecular weights in the overall process.

In this work, the crystallization was determined using birefringence and stress measurements. However, no information about the exact size and shape of the crystallites formed during deformation is available from this technique. Low angle light scattering studies could be performed during the deformation process, similar to the light transmission measurements, to observe the superstructure during the stress-induced crystallization. In this manner, any changes in the crystals during relaxation would be determined and could be compared to the Avrami analysis of growth type presented in this study.
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52. T. Kokubo, unpublished research.


120. R. S. Stein, Rubber Chemistry and Technology, 49 (3), 458 (1976).


123. E. Leitz Inc., General Catalogue, Rockleigh, N.J.


Figure 1

\[ n_1 = \frac{\lambda_0}{\lambda_1} \]

\[ n_2 = \frac{\lambda_0}{\lambda_2} \]
Elongation Ratio = 2.6
Strain Rate = 0.068 1/sec
Temperature = 90°C
Elongation Time = 60 sec
Scale = 5 seconds/division

Figure 6
Figure 9

STRESS-OPTICAL COEFFICIENT ($\times 10^8$)

TEMPERATURE (°C)
Figure 10
Figure 11
Figure 12

```
<table>
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<tr>
<th>STRESS (x 10^-1 kg/cm^2)</th>
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<table>
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<th>ELONGATION RATIO</th>
</tr>
</thead>
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</tr>
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</table>

\[
\frac{\dot{\varepsilon}}{0.678} \frac{T}{95}
\]

0.678 90

Figure 12
Figure 13
\( \varepsilon = 0.017 \quad \text{1/sec} \)
\( T = 90^\circ \text{C} \)

Figure 14
\[ \dot{\epsilon} = 0.017 \quad \text{1/sec} \]
\[ T = 90^\circ\text{C} \]

**Figure 15**
\[ \dot{\varepsilon} = 0.017 \quad \text{1/sec} \]
\[ T = 90^\circ \text{C} \]

\[ \lambda \]

\[ \frac{t_e}{480} \]

\[ \frac{2.6}{240} \]

\[ \frac{2.2}{180} \]

\[ \frac{1.8}{120} \]

\[ \frac{1.4}{60} \]

PERCENT CRYSTALLINITY

TIME AFTER ELONGATION (sec)

Figure 16
Figure 17

\[ \dot{\varepsilon} = 0.034 \quad \text{1/sec} \]
\[ T = 90^\circ C \]

\[ \lambda \]
\[ \frac{\lambda}{3.4} \]
\[ \frac{\dot{t}_e}{180} \]

Birefringence \( (\times 10^3) \)

Time after elongation (sec)


Figure 18

\[
\dot{\varepsilon} = 0.034 \\
T = 90^\circ C
\]

\[
\frac{t_e}{180} = \frac{\lambda}{3.4} \\
\lambda = 3.0, 2.6, 2.1, 1.1
\]

Stress (\( \times 10^{-1} \) kg/cm²) vs. Time After Elongation (sec)
Figure 19
Figure 20

\[
\dot{\varepsilon} = 0.170 \quad 1/\text{sec} \\
T = 90^\circ \text{C}
\]
Figure 21

\[ \varepsilon = 0.170 \text{ 1/sec} \]

\[ T = 90^\circ\text{C} \]

\[
\begin{array}{c|c|c}
\lambda & t_e & \\
3.4 & 36 & \\
2.6 & 24 & \\
1.8 & 12 & \\
\end{array}
\]
Figure 22

\[ \dot{\varepsilon} = 0.170 \quad \text{1/sec} \]

\[ T = 90^\circ \text{C} \]

\[ \frac{\lambda}{3.4} \quad \frac{t_e}{36} \]

TIME AFTER ELONGATION (sec)

PERCENT CRYSTALLINITY
\[ \dot{\varepsilon} = 0.338 \quad \text{l/sec} \]

\[ T = 80^\circ\text{C} \]

Figure 23
Figure 24
Figure 25

\[ \dot{\varepsilon} = 0.338 \text{ I/sec} \]

\[ T = 80^\circ C \]

<table>
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<th>( \lambda )</th>
<th>( t_e )</th>
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<tr>
<td>2.6</td>
<td>12</td>
</tr>
<tr>
<td>1.8</td>
<td>6</td>
</tr>
</tbody>
</table>

\[ \text{PERCENT CRYSSTALLINITY} \]

\[ \text{TIME AFTER ELONGATION (sec)} \]
Figure 26

\[ \dot{\varepsilon} = 0.338 \text{ 1/sec} \]

\[ T = 90^\circ C \]
Figure 27

\[
\dot{\epsilon} = 0.338 \quad \text{l/sec} \\
T = 90^\circ \text{C}
\]
$\dot{\varepsilon} = 0.338 \ \text{1/sec}$

$T = 90^\circ C$

$\frac{\lambda}{3.4} \ \frac{t_e}{18}$

Figure 28
\[ \dot{\varepsilon} = 0.338 \text{ l/sec} \]

\[ T = 95^\circ C \]

Figure 29
\( \dot{\varepsilon} = 0.338 \) \( \text{1/sec} \)

\( T = 95^\circ \text{C} \)

Figure 30
Figure 31

\( \dot{\varepsilon} = 0.338 \) 1/sec
T = 95°C

\[ \frac{\lambda}{4.2} \quad \frac{t_e}{24} \]

\[
\begin{array}{c|c|c}
\varepsilon & 5.0 & 30 \\
& 3.4 & 18 \\
& 2.6 & 12 \\
& 1.8 & 6 \\
\end{array}
\]
Figure 32
Figure 33

\[ \dot{\varepsilon} = 0.678 \quad 1/\text{sec} \]

\[ T = 85^\circ \text{C} \]
Figure 34
Figure 35

Birefringence (x 10^3)

\[ \lambda = 5.0 \quad t_e = 15 \]

\[ \dot{\varepsilon} = 0.678 \quad \text{l/sec} \]

\[ T = 95^\circ C \]
$\varepsilon = 0.678 \quad 1/\text{sec}$

$T = 95^\circ \text{C}$

Figure 36
Figure 37
\[ \epsilon = 0.678 \quad \text{l/sec} \]
\[ T = 100^\circ \text{C} \]

Figure 38
\[ \dot{\varepsilon} = 0.678 \quad \text{1/sec} \]

\[ T = 100^\circ\text{C} \]

Figure 39
Figure 40
Figure 41

Birefringence (x 10^3) vs. Time After Elongation (sec)

- λ = 5.0
- t_e = 6

\( \dot{\varepsilon} = 1.694 \) 1/sec

T = 90°C
\[ \dot{\varepsilon} = 1.694 \quad \text{l/sec} \]
\[ T = 90^\circ \text{C} \]
\[ \varepsilon = 1.694 \text{ 1/sec} \]
\[ T = 90^\circ \text{C} \]

\[ \frac{\lambda}{5.0} \quad \frac{t_e}{6} \]

Figure 43
Figure 44

\[ \frac{\lambda}{5.0} \quad \frac{t_e}{6} \]

\[ \dot{\varepsilon} = 1.694 \text{ 1/sec} \]

\[ T = 95^\circ \text{C} \]
\[ \dot{\varepsilon} = 1.694 \text{ 1/sec} \]
\[ T = 95^\circ\text{C} \]

Figure 45
Figure 46

\[ \dot{\varepsilon} = 1.694 \ \text{1/sec} \]

\[ T = 95^\circ \text{C} \]
Figure 47

Birefringence ($\times 10^3$)

Time after elongation (sec)

$\dot{\varepsilon} = 1.694$ l/sec

$T = 100^\circ C$
Figure 48

\[ \dot{\varepsilon} = 1.694 \text{ 1/sec} \]

\[ T = 100^\circ C \]
\( \dot{\varepsilon} = 1.694 \text{ 1/sec} \)
\( T = 100^\circ C \)

Figure 49
Figure 50
Figure 52
\[ \lambda = 2.6 \]
\[ T = 100^\circ C \]

Figure 54
Figure 55

\[ \lambda = 2.6 \]

\[ \frac{t_e}{T} = 100^\circ C \]

Time After Elongation (sec)

Percent Crystallinity

10^1

10^2

10^3

0.678

0.338

0.170

0.034

12

24

120

12

10

8

6

4

2

0
$\lambda = 1.8$
$T = 85^\circ C$

**Figure 56**
\[ \lambda = 1.8 \]
\[ T = 85°C \]

**Figure 57**

**Stress (x 10^1 kg/cm^2) vs. Time After Elongation (sec)**

<table>
<thead>
<tr>
<th>( \dot{\varepsilon} )</th>
<th>( t_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>1.2</td>
</tr>
<tr>
<td>0.34</td>
<td>6</td>
</tr>
<tr>
<td>0.03</td>
<td>60</td>
</tr>
<tr>
<td>0.01</td>
<td>300</td>
</tr>
</tbody>
</table>
Figure 59

$\lambda = 1.8$

$T = 90^\circ C$
Figure 60

\( \lambda = 1.8 \)

\( T = 90^\circ C \)
Figure 61

\[ \lambda = 1.8 \]

\[ T = 90^\circ C \]

Percent Crystallinity vs. Time After Elongation (sec)
\( \lambda = 2.6 \)
\( T = 90^\circ C \)

\[
\frac{\dot{\varepsilon}}{0.68} \quad \frac{t_e}{6}
\]

**Figure 62**
Figure 63

\[ \lambda = 2.6 \]

\[ T = 90^\circ C \]
Figure 64

\[ \lambda = 2.6, \quad T = 90^\circ C \]

- Time after elongation (sec)
- Percent crystallinity
\( \lambda = 2.6 \)

\( T = 95^\circ C \)

\[ \frac{\dot{\varepsilon}}{t_e} = \frac{1.69}{2.4} \]

\[ \begin{array}{cccc}
10^0 & 10^1 & 10^2 & 10^3 \\
0.68 & 0.34 & 0.17 & 0.07 \\
6 & 12 & 24 & 60 \\
\end{array} \]

\[ \begin{array}{cccc}
10^0 & 10^1 & 10^2 & 10^3 \\
0.03 & 0.03 & 0.03 & 0.03 \\
120 & 120 & 120 & 120 \\
\end{array} \]

Figure 65
\[ \lambda = 2.6 \]
\[ T = 95^\circ C \]
\[ \lambda = 2.6 \]
\[ T = 95^\circ C \]
Figure 68

\( \lambda = 3.4 \)

\( T = 85^\circ C \)
Figure 69

\( \lambda = 3.4 \)

\( T = 85^\circ C \)
Figure 70

\[ \lambda = 3.4 \]
\[ T = 85^\circ C \]

\[ \dot{\varepsilon} \quad t_e \]
\begin{align*}
1.69 & \quad 3.6 \\
0.68 & \quad 9 \\
0.34 & \quad 18 \\
0.17 & \quad 36 \\
0.03 & \quad 180 \\
0.02 & \quad 360
\end{align*}
\( \lambda = 3.4 \)
\( T = 90^\circ \text{C} \)

Figure 71
\[ \lambda = 3.4 \]
\[ T = 90^\circ C \]

Figure 72
\( \lambda = 3.4 \)
\( T = 90^\circ C \)

\[ \dot{\varepsilon} \quad t_e \]

\[
\begin{array}{c|c|c}
\dot{\varepsilon} & t_e \\
1.69 & 3.6 \\
0.68 & 9 \\
0.17 & 36 \\
-0.07 & 90 \\
-0.02 & 360 \\
\end{array}
\]

Figure 73
Figure 74

\[ \lambda = 5.0 \]
\[ T = 85^\circ C \]
Figure 75

\[ \lambda = 5.0 \]
\[ T = 85^\circ C \]
\[ \lambda = 5.0 \]
\[ T = 85^\circ C \]

Figure 76
Figure 77
\( \lambda = 5.0 \)
\( T = 95^\circ C \)

Figure 78
\[ \lambda = 5.0 \]
\[ T = 95^\circ C \]

Figure 79
Figure 30

Birefringence ($\times 10^3$)

Temperature (°C)

$\frac{\lambda}{5.0}$

$\frac{\dot{e}}{0.68}$

2.6

0.03
Figure 81
Figure 82

PERCENT CRYSTALLINITY

TEMPERATURE (°C)

\[
\begin{array}{cc}
\lambda & \dot{\varepsilon} \\
5.0 & 1.69 \\
5.0 & 0.68 \\
1.8 & 1.69
\end{array}
\]
Figure 83

\[ \lambda = 2.6 \]
\[ \dot{\varepsilon} = 0.34 \text{ 1/sec} \]
\[ t_e = 12 \text{ sec} \]
\[ \lambda = 2.6 \]
\[ \dot{\varepsilon} = 0.34 \quad \text{1/sec} \]
\[ t_e = 12 \text{ sec} \]

Figure 84
Figure 85

\[ \lambda = 2.6 \]

\[ \dot{\varepsilon} = 0.34 \text{ 1/sec} \]

\[ t_e = 12 \text{ sec} \]
Figure 86

\( \lambda = 1.16 \)
\( \dot{\varepsilon} = 0.003 \ \text{1/sec} \)
\( t_{\text{elong}} = 120 \ \text{sec} \)

Birefringence (\( \times 10^4 \)) vs. Time after Elongation (sec) for different temperatures:
- 80°C
- 85°C
- 90°C
- 100°C
$\lambda = 1.16$
$\dot{\varepsilon} = 0.003$ $1/\text{sec}$
$t_{\text{elong}} = 120 \text{ sec}$

Figure 87
Figure 88

\[ \lambda = 1.8 \]

\[ \dot{\varepsilon} = 0.34 \quad \text{1/sec} \]

\[ t_e = 6 \quad \text{sec} \]
Figure 89

\[ \lambda = 1.8 \]
\[ \dot{\varepsilon} = 0.34 \text{ 1/sec} \]
\[ t_e = 6 \text{ sec} \]
Figure 90

\[ \lambda = 1.8 \]
\[ \dot{\varepsilon} = 0.34 \text{ m/s} \]
\[ t_e = 6 \text{ sec} \]
Figure 91

\[
\begin{align*}
\lambda &= 1.8 \\
\dot{\varepsilon} &= 1.69 \quad 1/\text{sec} \\
\dot{t}_e &= 1.2 \text{ sec}
\end{align*}
\]
\[ \lambda = 1.8 \]
\[ \dot{\varepsilon} = 1.69 \text{ 1/sec} \]
\[ t_e = 1.2 \text{ sec} \]
Figure 93
Figure 94

$\lambda = 3.4$

$\dot{\varepsilon} = 0.338 \text{ l/sec}$

$t_e = 18 \text{ sec}$
Figure 95

\[ \lambda = 3.4 \]
\[ \dot{\varepsilon} = 0.338 \text{ \, \, \, 1/sec} \]
\[ t_e = 18 \text{ \, sec} \]
Figure 96
\( \lambda = 3.4 \)
\( \dot{\varepsilon} = 0.678 \text{ 1/sec} \)
\( t_e = 9 \text{ sec} \)

Figure 97
\( \lambda = 3.4 \)
\( \dot{\varepsilon} = 0.678 \text{ l/sec} \)
\( t_e = 9 \text{ sec} \)
\[ \lambda = 3.4 \]
\[ \dot{\varepsilon} = 0.678 \text{ 1/sec} \]
\[ t_e = 9 \text{ sec} \]

Figure 99
Figure 100
\( \lambda = 3.4 \)
\( \dot{\varepsilon} = 1.694 \text{ 1/sec} \)
\( t_e = 3.6 \text{ sec} \)
\( \lambda = 3.4 \)
\( \dot{\varepsilon} = 1.694 \ \text{l/sec} \)
\( t_e = 3.6 \ \text{sec} \)

Figure 102
Figure 103

\[
\lambda = 5.0 \\
\dot{\varepsilon} = 0.678 \text{ 1/sec} \\
\tau = 15 \text{ sec}
\]
Figure 104

\[ \lambda = 5.0 \]
\[ \dot{\varepsilon} = 0.678 \quad \text{l/sec} \]
\[ t_e = 15 \text{ sec} \]
$\lambda = 5.0 \quad \dot{\varepsilon} = 1.694 \quad \frac{1}{\text{sec}}$

$t_e = 6 \text{ sec}$

Figure 106

BIREFRINGENCE ($\times 10^3$) vs. TIME AFTER ELONGATION (sec)
Figure 107

\[ \lambda = 5.0 \]
\[ \dot{\varepsilon} = 1.694 \text{ } \text{1/sec} \]
\[ t_e = 6 \text{ sec} \]
Figure 108

PERCENT CRYSTALLINITY

TIME AFTER ELONGATION (sec)

\[ \lambda = 5.0 \]

\[ \dot{\varepsilon} = 1.694 \text{ l/sec} \]

\[ t_e = 6 \text{ sec} \]
\[ \dot{\varepsilon} = 0.678 \quad \text{1/sec} \]

\[ T = 75^\circ \text{C} \]

Figure 109
\[ \dot{\varepsilon} = 0.678 \quad 1/\text{sec} \]

\[ T = 85^\circ\text{C} \]

\[ \{ [(\infty X/\partial X) - 1]_\mu_1 - \} \_\mu_1 \]
Figure III

\[ \dot{\varepsilon} = 0.678 \text{ sec}^{-1} \]

\[ T = 95^\circ C \]

\[ \lambda = \frac{5.0}{4.2} \]

\[ \times \hspace{1cm} \Delta \hspace{1cm} \bullet \hspace{1cm} \square \]

\[ \left\{ \left[ \left( \frac{X}{\dot{X}} \right) - 1 \right] u_1 - 1 \right\} u_1 \]
\[ \dot{\varepsilon} = 1.694 \text{ 1/sec} \]

\[ T = 90^\circ \text{C} \]

\[ \lambda \]

\[ 2.6 \]

\[ 1.8 \]

\[ 3.4 \]

\[ 5.0 \]

Figure 112
$\dot{\varepsilon} = 1.694 \text{ l/sec}$

$T = 100^\circ C$

$\lambda$

$\frac{5.0}{3.4}$

$2.6$

$1.8$

$\ln t$

$\left\{ \left[ \left( \frac{\infty x}{x} \right) - 1 \right] \ln 1 \right\} \ln 1$
\[ \dot{\varepsilon} = 0.678 \text{ \text{1/sec}} \]

Figure 114
Figure 115

\[ \dot{\varepsilon} = 1.694 \text{ l/sec} \]

\[ k_c \times 10^2 \]

\( \text{ELONGATION RATIO} \)

90°C

100°C

Figure 115
Figure 116
Figure 117

\[
\ln \left[ \ln \left( \frac{k}{k_0} \right) \right] = \ln f_a
\]

\[\dot{\varepsilon} = 1.694 \ \text{1/sec}\]

- 90°C
- 100°C