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I am submitting herewith a thesis written by Delroy A. Carey, entitled "Development of Orientation in Polystyrene under Isothermal and Non-Isothermal Conditions". I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

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DEVELOPMENT OF ORIENTATION IN POLYSTYRENE UNDER
ISOTHERMAL AND NON-ISOTHERMAL CONDITIONS

A Thesis
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ABSTRACT

Highly oriented polystyrene was prepared by pulling fiber-like samples in the rubbery state and quenching them rapidly to the glassy state. A primary objective of the work was to produce samples of high orientation (frozen-in stress) and to measure the resulting mechanical properties. A second objective was to theoretically analyze the rheological behavior during the elongational flow above the glass transition temperature (T_g). Isothermal and non-isothermal temperatures histories were imposed before quenching.

Under isothermal conditions it was found that one can maximize orientation by using temperatures about 10°C above the equilibrium T_g . Under non-isothermal conditions (cooling at linear rates of $2.5 - 4.5^{\circ}\text{C}/\text{sec.}$) it was possible to induce somewhat higher orientations, although it was not possible to take the very highest stress levels into the glassy state because of rapid relaxation.

The birefringence (orientation) in the quenched sample correlated quite well with the tensile stress developed in the rubbery state. The mechanical properties in the glassy state in turn correlated quite well with the birefringence, independent of how the stress was developed (isothermally or non-isothermally). The only significant effect of non-isothermal histories was to allow one to produce somewhat higher stresses before failure in the rubbery state.

Non-isothermal viscoelastic theory for flow above T_g is already available in the literature. Using that theory one finds that the predicted stresses are lower than the experimental ones. At moderate cooling rates ($2.5^{\circ}\text{C}/\text{sec.}$) introduction of a cooling rate-dependent T_g brought the curves into good agreement; but at higher cooling rates ($4.5^{\circ}\text{C}/\text{sec.}$) this modification alone was not adequate to resolve the difference.

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CHAPTER I

INTRODUCTION

Polymer processing operations usually involve moving and shaping a polymeric material in the molten state and then cooling it to the solid state. The deformation in the melt state serves not only to create the desired shape but also to orient the molecules in the direction of flow. Upon quenching a certain degree of orientation is frozen-in, which has a significant effect on the final properties of the material. This will be reviewed later.

Since most polymer processing operations are non-isothermal — in the sense that the polymer is deformed and shaped in the melt state and then cooled to a solid form — the subject of non-isothermal rheology has received considerable attention at the University of Tennessee. The main idea of the theory is that a generalized time-temperature superposition can describe the rheological response, except under conditions of rapid cooling near the glass transition temperature (T_g). Under these conditions one probably needs to consider a molecular mechanism associated with the glassy state.

It was the objective of the first part of the work to find usable deformations and thermal paths for preparing highly oriented polystyrene fibers. Prior workers have suggested that high orientations are obtainable somewhat above

T_g , but systematic data to determine the optimum conditions are not available. It was the purpose of the present work to do such systematic studies, with temperature level, cooling rate and elongation rate as the variables to be considered. Both zero cooling rate (isothermal) and finite cooling rate (non-isothermal) histories were considered. Finally the mechanical and optical properties of the oriented samples were measured.

The second part of the research dealt with the non-isothermal viscoelastic theory developed during previous research (29). It has been successfully used in predicting stress during simple elongational flow as long as the temperature was well above the glass transition temperature (T_g). However, at temperatures approaching the glass transition temperature, particularly at high cooling rates, some systematic deviations between theoretical and experimental stresses occur. Prior workers here at the University of Tennessee proposed that these differences are due to the effect of cooling rate on T_g . The second objective of the present work was to continue these theoretical analysis of non-isothermal response near T_g .

CHAPTER II

BACKGROUND

A. ISOTHERMAL AND NON-ISOTHERMAL RHEOLOGY ABOVE
THE GLASS TRANSITION TEMPERATURE

1. Constitutive Equations

The relationships which have come to be known as "constitutive equations" relate stress in a viscoelastic material to the deformation history to which the material has been subjected. In experiments in which the temperature is held constant (isothermal) during the deformation, the constitutive theory is well-developed. This theory can be summarized by considering an equation of the following form (4,7,18,10)

$$\sigma_{ij} = -p \delta_{ij} + \int_{-\infty}^t [m_1(t-t') c_{ij}^{-1} - m_2(t-t') c_{ij}] dt' \quad (\text{II-1})$$

where σ_{ij} is the stress, p is the isotropic pressure, $m_1(t-t')$ and $m_2(t-t')$ are deformation independent memory functions, c_{ij}^{-1} and c_{ij} are Finger and Cauchy strain tensors, respectively. Equation (II-1) is valid for either small or large strains, but in the form shown above leads to a constant viscosity. Therefore, it is restricted to small deformation rates. The memory functions (for example m_1) may be expressed in terms of a discrete or continuous

relaxation spectra as follows

$$m_1 = \sum_n \frac{G_n}{\tau_n} \exp(t' - t)/\tau_n = \int_{-\infty}^{\infty} \frac{H(\tau)}{\tau} \exp(t' - t)/\tau \, d \ln \tau \quad (\text{II-2})$$

where G_n (or $H(\tau)$) are the elastic moduli (or spectrum) and τ_n (or τ) are the relaxation times. Equation (II-1) has been shown to work reasonably well in stress relaxation, (29), steady shear (11), and elongation flows (13,14,30,62).

The temperature dependence of the constants in Equation (II-2) can be dealt with by using the time-temperature superposition principle first developed by Leaderman (27). This principle allows normalization of experiments done at different rates (or times) and temperatures by using a shift factor a_T (60).

$$\frac{\tau(t)}{\tau_0} = \frac{a_T(T)}{a_T(T_0)} \quad (\text{II-3})$$

Where T is some arbitrary temperature, T_0 is the reference temperature and a_T is the time-temperature shift factor. It is often correlated with the so-called Williams, Landel and Ferry (WLF) equation (16):

$$\log a_T(T) = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \quad (\text{II-4})$$

where C_1 and C_2 are constants.

A generalized superposition concept, one for dealing with temperature-varying (non-isothermal) histories, was first considered by Morland and Lee (36), who qualitatively explained the expansion of cylindrical samples. Bernstein, Kearsley and Zapas (4,5) later introduced a general functional form for dealing with temperature shifts, which can result in a slowing down or speeding up of the relaxation processes as the temperature changes.

A more general one was proposed by Abbott and White (1) in which the shift factor in Equation (II-4) was utilized. Matsui and Bogue (29), after carrying out systematic experimental studies, proposed a specific integral form. This form also incorporates Equation (II-1) as a special case. Their theory can be stated in the following integral form:

$$\sigma_{ij} = -p \delta_{ij} + \sum_n G_n^0(t) \frac{T(t)}{T_0} \int_{-\infty}^t \exp \left[-\frac{\int_{t'}^t \frac{dt''}{\tau_n(t'')}}{Z_n(t')} \right] c_{ij}^{-1}(t, t') dt' \quad (\text{II-5})$$

A shift of the reference modulus G_n^0 from T_0 to some arbitrary temperature $T(t)$ is shown above, although this small correction is normally omitted in actual calculations. The important effect of temperature is accounted for in the time constants (τ_n), which taken the form

$$\tau_n(\cdot) = a_T T(\cdot) \tau_n^0 \quad (\text{II-6})$$

with τ_n^0 designating the time constants at the reference temperature.

For most actual experiments a non-linear form of Equation (II-6) is needed. Matsui and Bogue (29) suggested non-linear time constants (τ_n^*) defined by

$$\tau_n^* = \frac{\tau_n^0 a_T}{1 + b II_d^{\frac{1}{2}} \tau_n^0 a_T(T(\cdot))} \quad (II-7)$$

where II_d is the second invariant of the deformation rate and b is an empirical dimensionless parameter. Matsui and Bogue (29) showed that Equation (II-5) works well for simple stress relaxation in polystyrene, when a step change of temperature is made. They also applied Equation (II-5) to melting spinning using data of Dees and Spruiell (15) for high density polyethylene. More recently Matsumoto and Bogue (31) applied Equation (II-5) to polystyrene, pulled at constant elongation rate. They found that Equation (II-5) works well except near T_g and at fast cooling rates. Under these conditions they found that it was also necessary to consider the effect of cooling rate on T_g . This will be discussed in the next section.

2. Cooling Rate-Dependent T_g

As the temperature of a polymer melt is lowered, a point is reached where the material undergoes a drastic change in rheological properties. This temperature, associated with a virtual cessation of molecular motion on the

local scale, is known as the glass transition temperature (T_g).

The treatment of non-isothermal effects involves the shift factor a_T , which in turn is related to T_g . From early work of Fox and Flory (17) it is known that there is an effect of cooling rate on T_g . In particular, they reported an increase in T_g of about 5 to 10°C when the time scale is decreased from 24 hours to 5 minutes. They indicated that the value of T_g strongly depends on the observed time. Kovacs (25) stated that a volume-temperature plot varies when the time scale of the experiment is increased. Thienel and Menges (52) stated that the glass transition temperature for polystyrene shifts about 20°C higher when changing from a low to a high cooling rate. Ferry (16) and Rusch (47) also reported a similar effect of cooling rate on T_g .

Recently Matsumoto and Bogue (31) have shown that one needs a rate-dependent T_g in order to correlate pulling data in the rubbery regime if the cooling rates are high. In their analysis they define a shift a_T^0 for isothermal deformation (cooling rate = 0) by a WLF (16) type of equation as follows

$$\log a_T^0 = \log \frac{\tau^0}{\tau_g^0} = \frac{-C_1(T-T_g^0)}{C_2 + T-T_g^0} \quad (\text{II-8})$$

where C_1 and C_2 are constants T_g^0 is the glass transition

temperature at zero cooling rate, and τ_g^0 is the relaxation time corresponding to T_g^0 . Replacing the superscript (o) with the superscript (R) for the corresponding quantities for a finite cooling rate results in the following equation

$$\log a_T = \log \frac{\tau^R}{\tau_g^R} = \frac{-C_1(T - T_g^R)}{C_2 + T - T_g^R} \quad (\text{II-9})$$

where T_g^R depends on the cooling rate while τ_g^R does not depend on glass transition temperature. Combining Equation (II-8) and (II-9) results in the following equation:

$$\log \frac{a_T^R}{a_T^0} = \log \frac{\tau^R}{\tau^0} = \frac{C_1 C_2 (T_g^R - T_g^0)}{(C_2 + T - T_g^0) (C_2 + T - T_g^R)} \quad (\text{II-10})$$

Using the shift factor of Equation (II-10) they were able to obtain good agreement between experimental and theoretical values. In fact, they have shown that a change in T_g of 10°C significantly increases the shift factor when a cooling rate-dependent T_g is used.

Wust (63), whose work was motivated by the above experiments, studied the effect of cooling rate on the glass transition temperature. He placed a fiber of polystyrene in an air chamber at an elevated temperature ($\approx 140^\circ\text{C}$) with both ends of the fiber constrained and imposed various linear

cooling rates. From these experiments he was able to determine the apparent T_g (cooling rate-dependent T_g). Figure (1) gives an example of the force temperature curves from which the apparent T_g was defined. As a result of a series of such experiments, it was found that a cooling rate of $\pm 1.0^\circ\text{C}/\text{sec.}$ can elevate T_g as much as 10°C (see Figure (2)). At higher cooling rates there is considerable scatter but it is still possible to estimate the magnitude of the change in T_g .

3. Flow Induced Orientation

The theories of rheology in the rubbery state reflect the basic idea that during deformation the molecules tend to line up (orient) in the direction of flow. This lining up gives rises to stresses, as previously discussed, and also to anisotropic optical properties (birefringence) — that is, to a difference in the principal refractive indices parallel $n_{\parallel}$ and perpendicular $n_{\perp}$ to the stretch direction. This birefringence can be characterized by means of the following rheo-optical law, first stated by Brewster (8)

$$\Delta n_{IJ} = C(\sigma_I - \sigma_J) \quad (\text{II-11})$$

where C is the stress-optical coefficient, σ_I and σ_J are the principal stress, and Δn_{IJ} is the difference in the principal refractive indices.

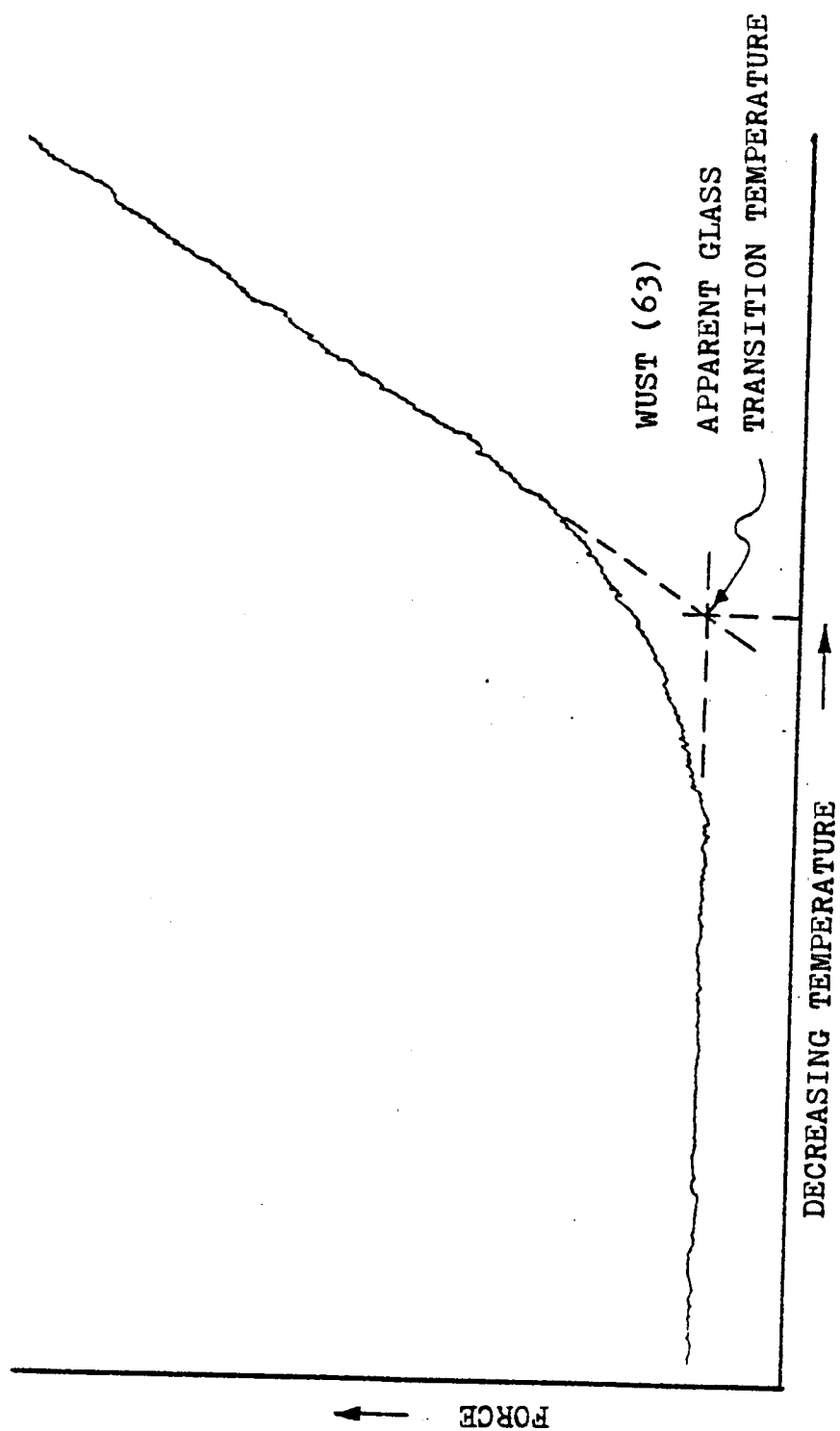


Figure 1. Typical force-temperature plot while cooling a constrained sample from above its glass transition temperature.

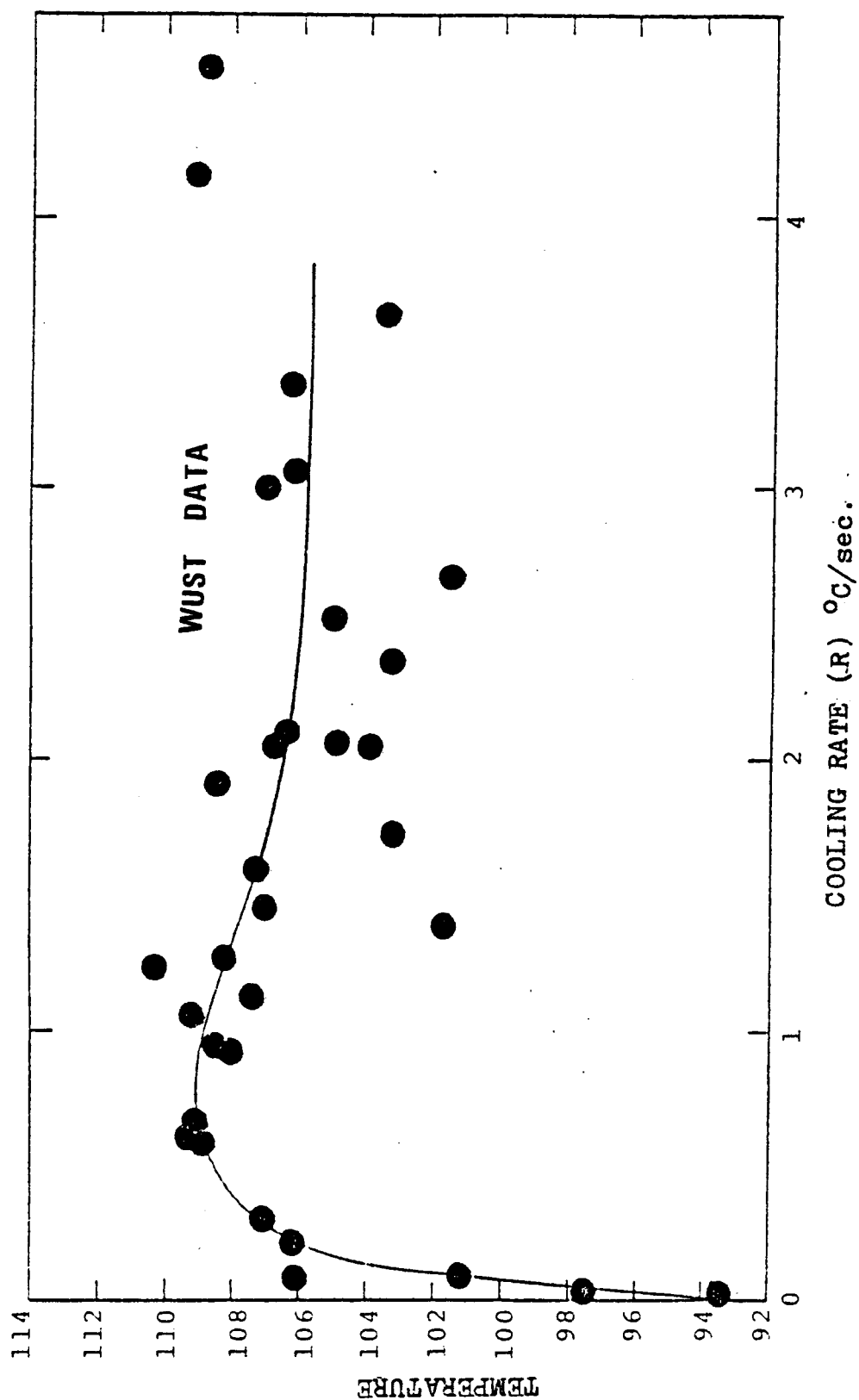


Figure 2. Apparent glass transition temperature versus cooling rate as measured from force-temperature curves.

This law states that the stress and optical ellipsoids are co-axial and that the birefringence is proportional to the corresponding principal stresses. Brewster (8) applied Equation (II-11) to inorganic glasses; it was then applied to the stress analysis of solids by Maxwell (33). Stress-induced birefringence in amorphous polymers was first studied by Kuhn and Grun (26) and Treloar (54,55) in conjunction the molecular theory of rubber elasticity. Later it was generalized by Stein and Tobolsky (49) and Lodge (28) to include polymer melts. For polymeric materials the stress optical coefficient takes the following form (26,28,54)

$$C = \frac{2\pi}{45KT} \left(\frac{\bar{n}^2 + 2}{\bar{n}} \right)^2 (\alpha_1 - \alpha_2) \quad (\text{II-12})$$

where T is the absolute temperature, $\bar{n}$ is the average refractive index of the material, K is the Boltzmann's constant and α_1 and α_2 are the principal polarizabilities of the statistical segment.

Equation (II-11) is a very general one and holds over a wide range of experimental conditions for many materials. Read (46) and Stein and coworkers (50) have shown that Equation (II-11) holds in the case of dynamic experiments in polystyrene solution. Philippoff and coworkers (40,41,42,43) have performed extensive work with polyisobutylene and also

silicones solutions which showed the general applicability of Equation (II-11) even when the shear stress and normal stress are highly nonlinear with respect to shear rate.

More recently at the University of Tennessee Oda, White and Clark (39) have also experimentally shown the generality of Equation (II-11) in uniaxial extension and in shear flow for various polymers. They made measurements both on-line (at melt temperatures) and on quenched samples (at room temperature), in the latter case relating the frozen-in birefringence to the stress in the melt. In related work on polystyrene, Matsumoto and Bogue (30) have provided detailed on-line verification of the rheo-optical law under both isothermal and non-isothermal conditions. Oda, White and Clark (39) and also Matsumoto and Bogue (30) noted that there appear to be deviations from linearity at high stress levels. However, for certain other polymers, exposed to non-isothermal quenching histories, the birefringence-stress-temperature relationships are quite complicated. Recent work by Boateng (6) on poly(methyl methacrylate) shows that the stress-birefringence relationship for melt spun samples is different from that of isothermal oven drawn samples. Andrew and Hammack (2) explain that the lack of temperature dependence in the case of polystyrene is due to the rigid phenyl ring, which appears to be unaffected by temperature changes below T_g ; while in poly(methyl methacrylate) one has a non-rigid ester group which

still has some mobility below T_g .

While detailed information about the orientation of the crystalline portions of crystallizable polymers can be obtained by x-ray diffraction methods (37,45), only certain average information is obtainable in the case of amorphous polymers. For birefringence measurements the relevant orientation parameter is that defined by Hermans (20), which is of the following form

$$f = \frac{\overline{\alpha_{\parallel}} - \alpha_{\perp}}{\alpha_1 - \alpha_2} \quad (\text{II-13})$$

where f is the Hermans' orientation factor, which is a measurement of the average orientation (second moment) of the polymer chain relative to the axis of the fiber and $\alpha_{\parallel}, \alpha_{\perp}$ are respectively, the polarizabilities that are parallel and perpendicular to the axis (see Equation (II-12)). The overbar denotes an average over all of the molecules.

A rough but sometimes useful measurement of orientation in fabricated polymers involves shrinkage measurements. That is, a solid is heated above T_g (or T_m) and the resulting change in dimensions interpreted as an elastic recovery, which is related to the molecular orientation in the fiber or film. This procedure has been used in studying orientation in synthetic fibers (64) and has been applied to injection molded parts by Menges and Wubken (34,35).

B. THE RELATIONSHIP OF ORIENTATION TO MECHANICAL PROPERTIES

An important variable in regard to mechanical properties of polymeric materials is molecular orientation. If a sample is deformed in the rubbery state (usually just above T_g), a high degree of orientation can be created and frozen-in during subsequent quenching, resulting in an improvement in the mechanical properties. Results of this kind will now be discussed. The properties of oriented polymers have been reviewed by Ward (59) and Nielsen (37), especially in the case of crystalline polymers. There have also been extensive studies done at the University of Tennessee in connection with the development of structure in melt by Spruiell and White (48), White, Dharod and Clark (62) and White et al. (36). They reported that filaments spun at a high stress (high orientation) have a high modulus, high tensile strength and low elongation-to-break. While the enhancement of mechanical properties by orientation is a widely used technology in the case of crystalline polymers, much less work has been done on the improvement of properties for amorphous polymers.

Most of the work done on oriented amorphous polymers shows that the mechanical properties are quite different from the isotropic materials. Nielsen and Buchdahl (38) have reported a correlation between orientation and mechanical properties. In particular, they found that both the

dynamic modulus and the Young's modulus increased with increasing orientation. Similarly, Thomas and Cleereman (53), ✓ Kanetsuna (23), Jones (21), and others (21,3,11) have also reported improvement in Young's modulus and tensile strength with increase in orientation.

Any general description of mechanical properties in the solid state involves measurement of the elastic compliance tensor S_{ijkl} or the elastic modulus tensor G_{ijkl} defined by

$$\tilde{\epsilon}_{ij} = S_{ijkl} \sigma_{kl} \quad (\text{II-14})$$

or

$$\sigma_{ij} = G_{ijkl} \tilde{\epsilon}_{kl} \quad (\text{II-15})$$

where σ_{ij} is the stress tensor and $\tilde{\epsilon}_{ij}$ is the infinitesimal strain tensor. Certain physical symmetries reduce the 81 compliance components or elastic moduli to a small number. Most oriented fibers or films can be considered to be transversely isotropic, which reduces the number of independent compliances (or moduli) to five (59). Using the abbreviated notation of Ward (56) these are designated S_{11} , S_{12} , S_{13} , S_{33} and S_{44} . The various compliance or moduli are diagrammatically illustrated in Figure (3).

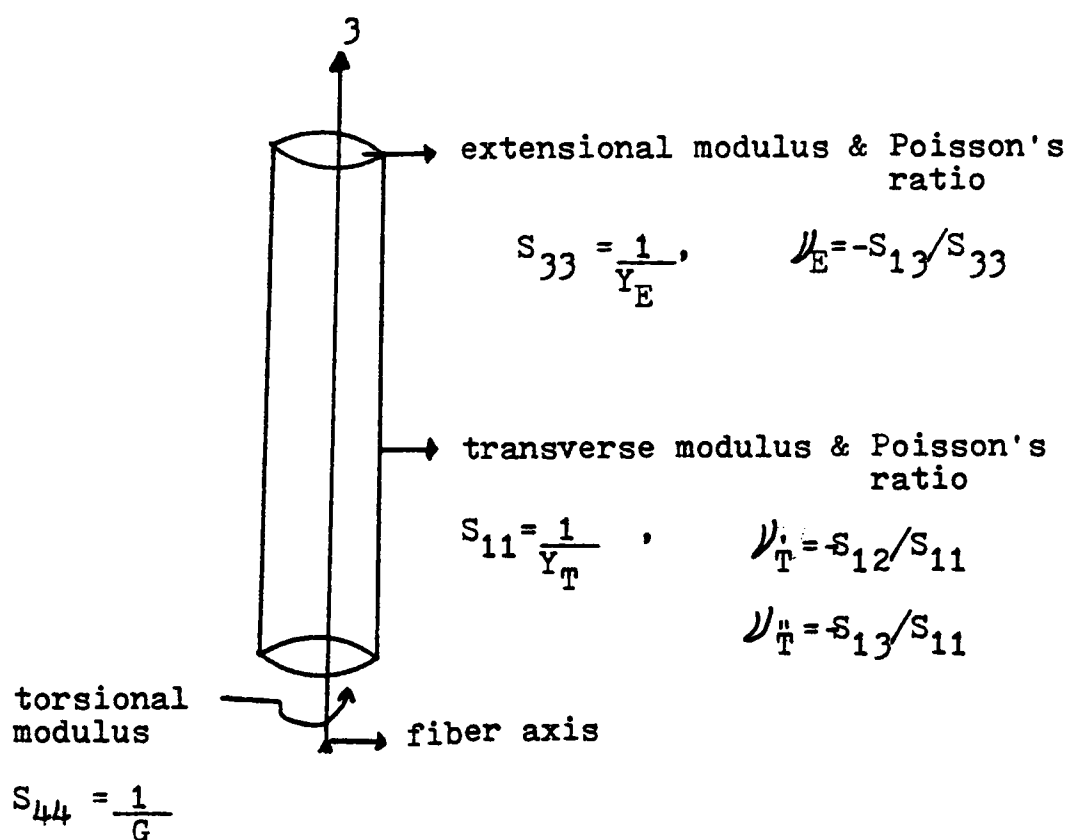


Figure 3. Illustration of compliance constants.

Their relationships to the better known moduli and Poisson's ratios are as follows:

1. S_{33} is the reciprocal of Young's modulus.
2. S_{13} and S_{33} are related to the Poisson's ratio ν_E , associated with the longitudinal extension such that $\nu_E = -S_{13}/S_{33}$.
3. S_{11} , S_{12} , and S_{13} , are related to the transverse modulus Y_T and the corresponding Poisson ratios ν_T' and ν_T'' for application of load in the plane perpendicular to the fiber axis.

For example, $S_{11} = \frac{1}{Y_T}$, $\nu_T' = -S_{12}/S_{11}$ and $\nu_T'' = -S_{13}/S_{11}$.

4. S_{44} is the reciprocal of the torsional modulus G .

In the case of films, three of the five independent parameters can be determined from simple tensile measurements on a strip cut from various angles to the direction of stretch; the remaining two can be determined from shear moduli measurements. Measurements of these anisotropic constants for oriented films of polyethylene have been made by Raumann and Saunders (45). Ward and co-workers have made measurement on a few other crystalline polymers (57,58,59). Henning (19), Cheatham and co-workers (9), and others (22,21,12,3) have made some of these measurements on uniaxial stretched amorphous polymers. It is a general observation that the moduli are enhanced and are made anisotropic by increasing the orientation. In the case of crystalline

polymers, where all five compliances are available, it seems to be generally true that the ratio of torsional compliance to the tensile compliance increases from a value of three as the material become increasingly oriented (45).

CHAPTER III

EXPERIMENTAL

A. MATERIAL

The material investigated was a typical commercial polystyrene (Shell TC-3-30) furnished by the Shell Chemical Company. This material has a broad molecular weight distribution with a number average molecular weight, $M_n=61.2 \times 10^3$, weight average molecular weight, $M_w=283 \times 10^3$ and $M_w/M_n=4.62$. It has been extensively studied in earlier work (29,30,44,63). The polystyrene was extruded from an Instron Capillary Rheometer using either a 0.02" or 0.03" die to form cylindrical rods. The 0.02" die was used for extruding samples for the non-isothermal investigations while the 0.03" die was used for isothermal investigations. These samples were stress relieved by placing them overnight in an oven at 130°C. The final diameter of the rods used in the non-isothermal experiments were about 500 - 600 μ . The rods for isothermal investigation ranged between 800 and 900 μ in diameter.

B. EQUIPMENT

The basic experimental apparatus is that reported by Matsui and Bogue (29) and later modified by Matsumoto and Bogue (30,31) (Figure (4) and (5)). It consists of two "clam shell" chambers each containing nichrome wires. The "clam shell" chambers surrounds the sample, which is held at

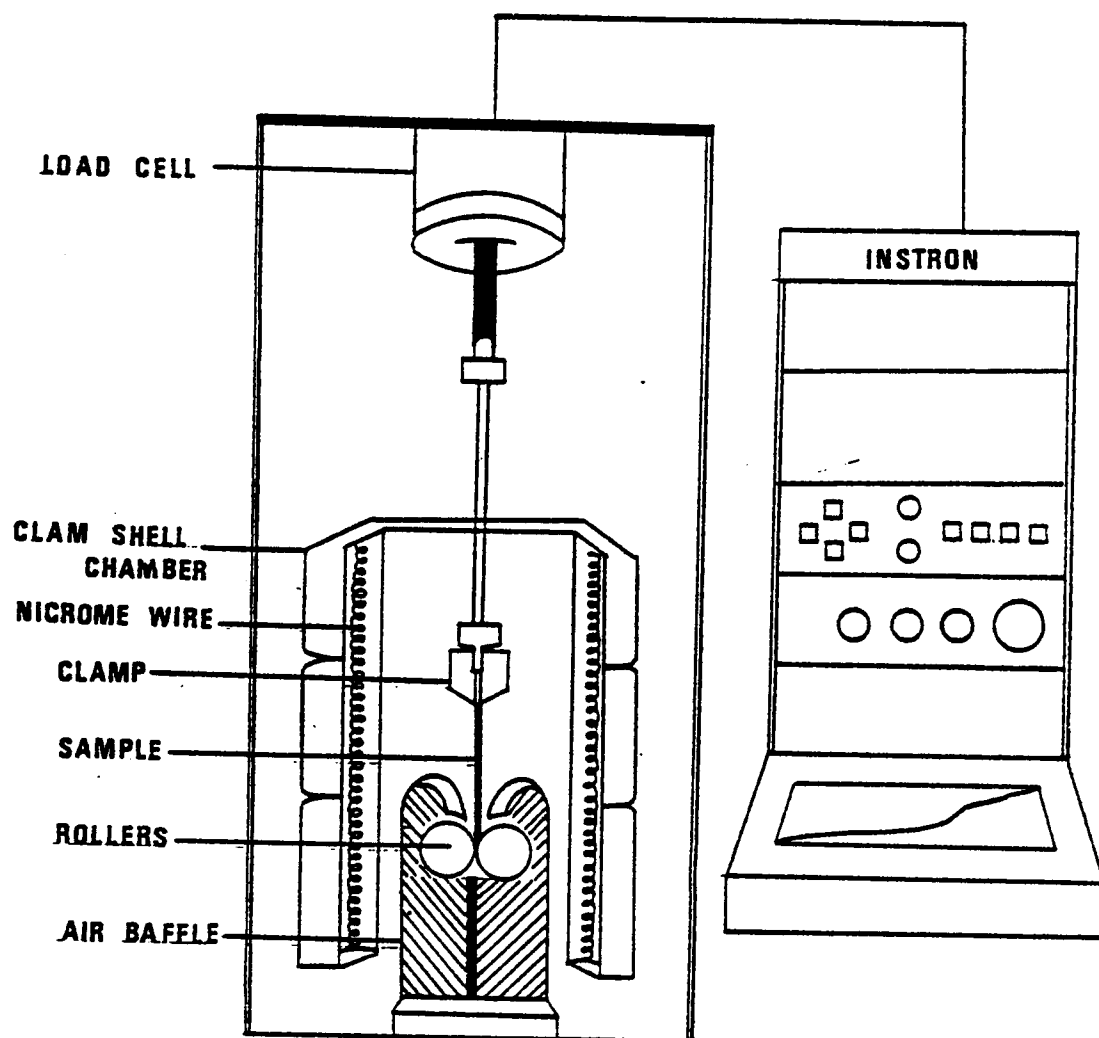


Figure 4. Schematic diagram of experimental set-up (front view).

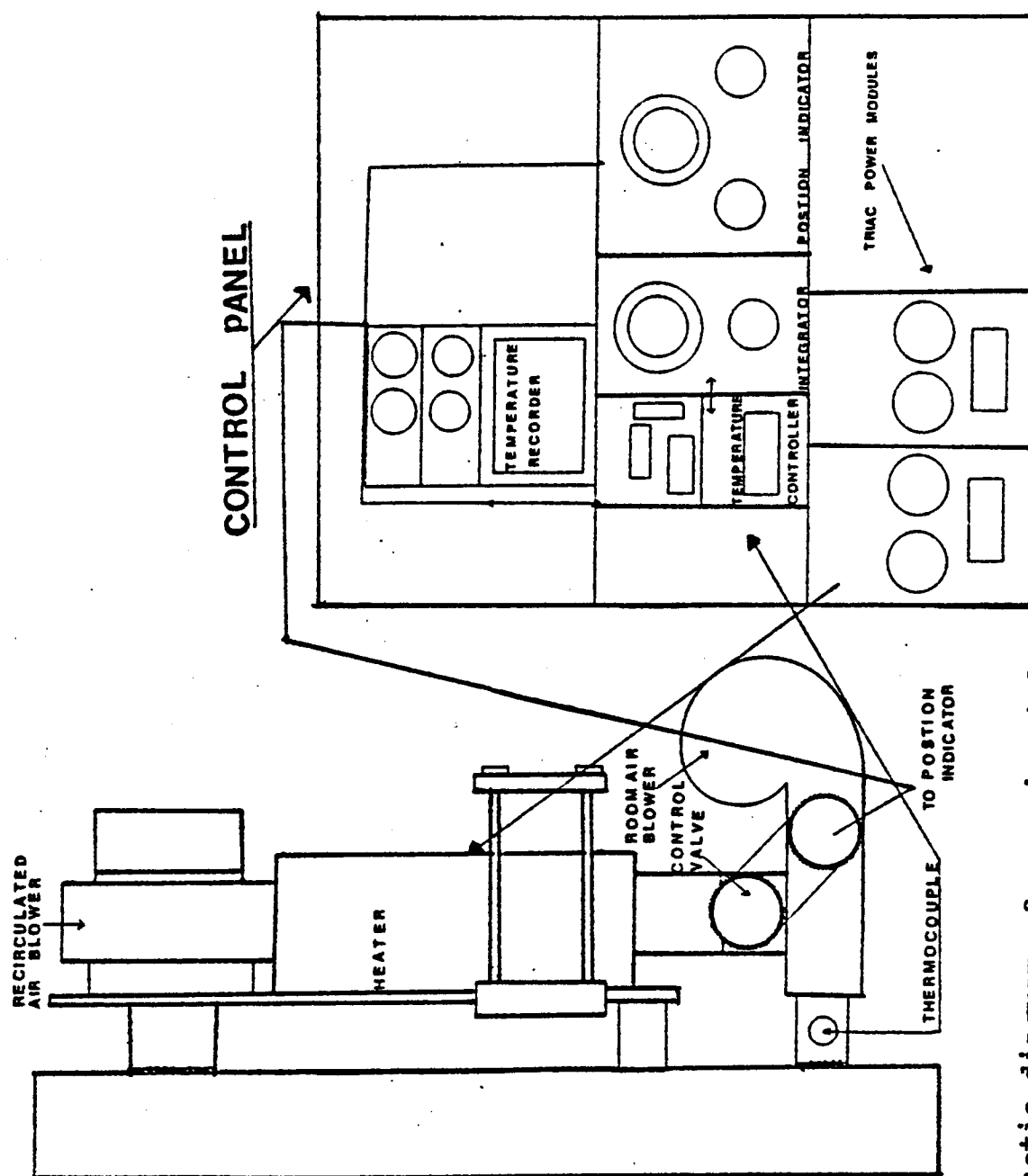


Figure 4. Schematic diagram of experimental set-up (side view, showing also details of control panel)

one end with a clamp that is attached to an Instron load cell. The other end of the sample was squeezed between two rollers or attached to another clamp. Heat to the unit is provided by an external system, which circulates varying mixtures of hot and room temperature air. The mixture of air entering the chambers is controlled by an Electromax III temperature controller by means of a butterfly valve. The nichrome wires in the heating unit provide radiant heat that helps to smooth out any axial temperature gradients.

For providing linear cooling or heating rates an integrator is incorporated in the thermocouple system. This instrument is capable of cooling or heating linearly from $0.005^{\circ}\text{C}/\text{sec}$ to $4.5^{\circ}\text{C}/\text{sec}$. The upper temperature limit of the unit is about 160°C .

The optical system used for making the birefringence measurements at room temperature was an orthoplan polarized microscope with crossed polarizers and a Leitz-type compensator. A Mechanical Spectrometer (manufactured by Rheometrics Inc.) was used for making torsional measurements at room temperature.

C. PROCEDURE

In each set of experiments the Instron Tensile Tester was calibrated using the instructions provided by the manufacturer. The heating unit previously described was put in place. The sample was clamped in the unit, then closed

and allowed to equilibrate at the desired temperature. A small force, of the order of 0.2 to 0.4 grams, was put on the sample to eliminate any slack. When this force was released the experiment was begun. The fiber was stretched either isothermally (temperature constant during the experiment) or non-isothermally (temperature changing linearly with time while stretching). While stretching the fiber the force build-up was measured using an Instron load cell (2000 g. cell). At the end of each experiment the fiber quenched by separating the "clam shell heaters" and allowing room air to surround the fiber. Because of some experimental difficulties most isothermal investigations were carried out at a constant crosshead speed; and non-isothermal at a constant elongation rate. That is, during isothermal investigations, sample slippage occurred at the lower temperatures ($<112^{\circ}\text{C}$) when placed in the constant elongational rate (roller) apparatus. This slippage did not occur, however, in the case of the non-isothermal experiments probably due to a time lag in cooling down the rollers which are of high mass compared to the sample. Therefore the roller apparatus was used in the non-isothermal runs, but was not used in most isothermal runs.

The quenched sample was removed from the unit and its birefringence measured. The birefringence was measured using a polarizing microscope and a 10 order Leitz compensator. The compensator was used to determine the phase

difference (retardation) between two mutually perpendicular plane polarized light waves emerging from the sample. The retardation is proportional to the birefringence of the sample. The experimental procedure suggested by the manufacturer of the compensator was followed in determining the retardation. The birefringence was calculated from the following relationship

$$\Delta n = \frac{\Gamma}{d} \quad (\text{III-1})$$

where Γ is the retardation and d is the diameter of the fiber.

The torsional moduli of oriented and unoriented polystyrene fibers were determined at room temperature using the Rheometrics Mechanical Spectrometer. Figure (6) shows the torsional test fixtures that were attached to the Mechanical Spectrometer. The bottom fixture was held stationary, while the top fixture was rotated at the desired speed (0.278 - 0.334 rad./sec.). The diameter of the fibers range from 350 to 500 microns. The time and torque required to twist to a certain angle was measured. The twist angle is related to the modulus of elasticity in shear by the following relationship

$$\phi = \frac{TL}{GJ} \quad (\text{III-2})$$

where ϕ is the twist angle in radians, T is the torque,

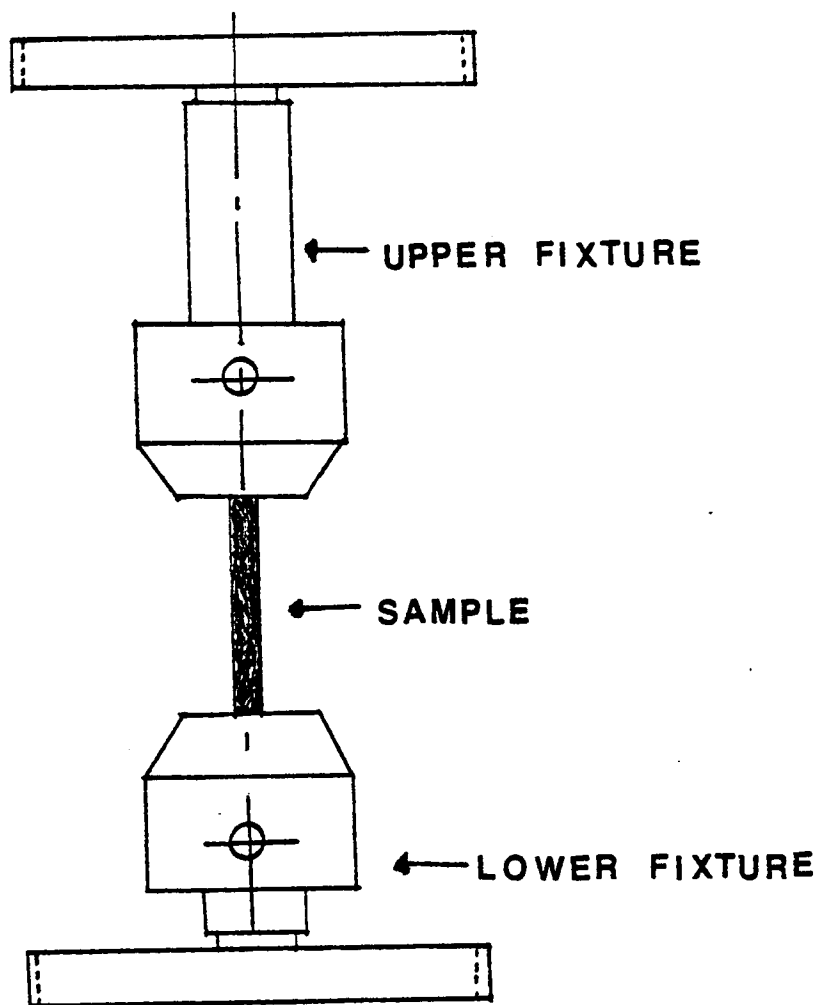


Figure 6. Torsional fixtures used in measuring the torsional modulus.

L is the length of the fiber (usually about 0.5 cm), and
 J is the moment of an inertia of the fiber. The torsional
modulus was calculated using the above relationship.

CHAPTER IV

PREPARATION AND PROPERTIES OF ORIENTED SAMPLES

A. STRESS (ORIENTATION) DEVELOPMENT ABOVE
THE GLASS TRANSITION TEMPERATURE

1. Isothermal

This section and the next will deal with the development of orientation in the rubbery state under isothermal and non-isothermal conditions. In general, oriented fibers were made by pulling them at elevated temperatures, the deformation process terminated before failure, and the sample quenched rapidly to room temperature. The breaking stress during the preparation of the sample (that is, above T_g) was determined for each fiber as a function of the particular pulling rate and temperature.

Figure (7) presents a plot of these rubbery state breaking stresses at various pulling rates and temperatures. If the temperature is kept constant during the deformation and the elongation rate is allowed to increase, then the rupture stress increases up to a critical stress level. Beyond this elongation rate, the breaking stress decreases. Also at low and relatively high elongation rates the rupture stress level increases with decreasing temperatures. Behavior of this sort is expected, since a lower temperature tends to be equivalent to a higher elongation rate.

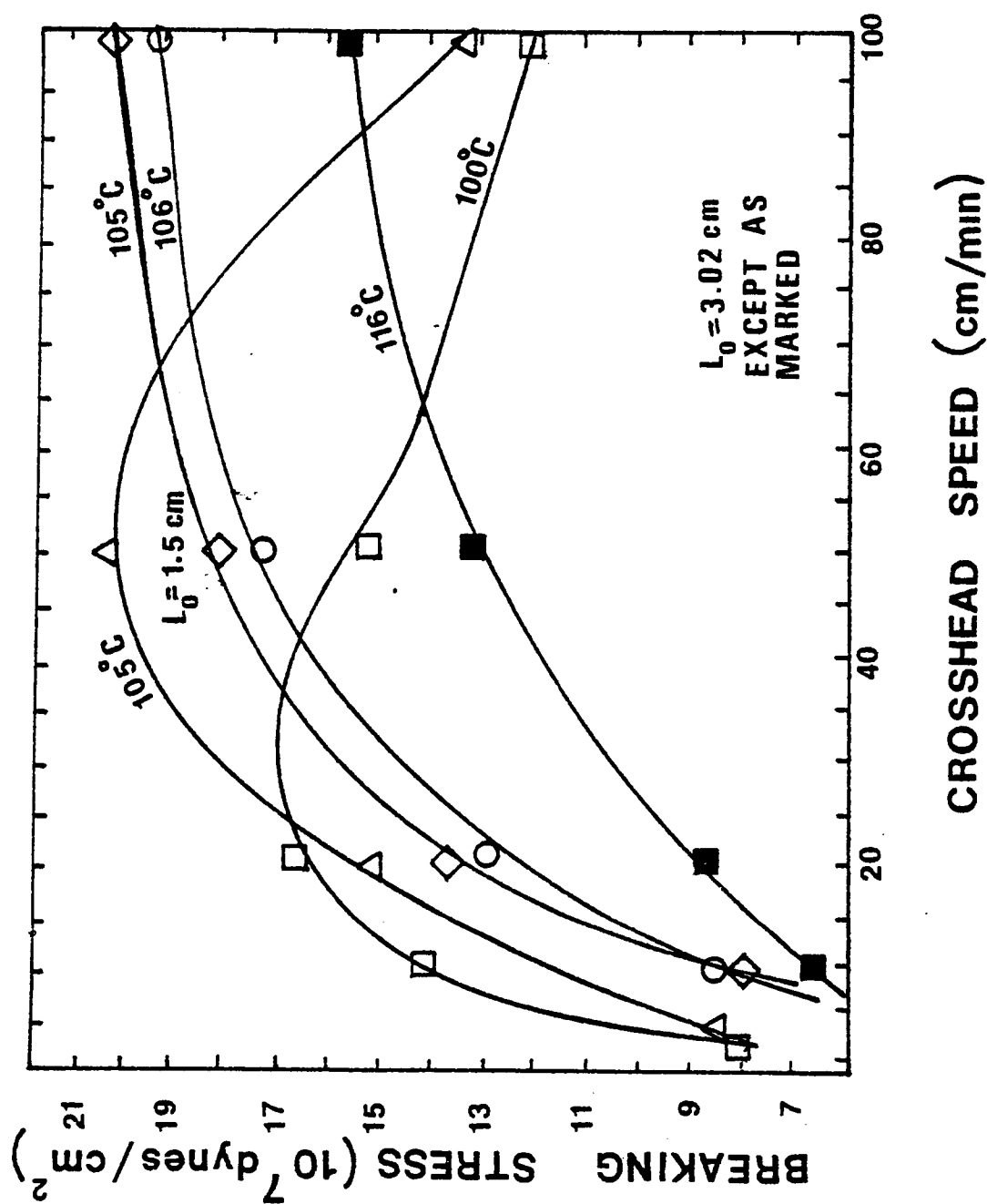


Figure 7. Breaking stress of polystyrene as a function of crosshead speed.

The optimum isothermal temperature for making highly oriented samples was found to be about 105°C . Below this temperature the fiber does not extend very much, that is, it behaves like a brittle glassy solid and a great deal of orientation cannot be achieved. At high temperatures (for example, 116°C) the fiber behaves in a more fluid-like manner with a great deal more extension, but a rapid relaxation prevents the development of the stress (orientation) levels obtainable at lower temperature. The optimum between those two mechanisms was found to be about 105°C .

2. Non-Isothermal

The objective of this set of experiments was to try to improve the stress (orientation) level by using non-isothermal (cooling) conditions. Figure (8) shows the temperature strategy which was used. Initial experiments were carried out in which the fiber was cooled while pulling. In the vicinity of 105°C there was evidence of crazing (solid-like behavior); therefore it was determined that the deformation process should be stopped slightly above 105°C .

Figure (9) presents non-isothermal data obtained at various cooling and elongation rates and starting temperatures. These experiments were done under conditions of constant elongation rate, while most isothermal runs were done under conditions of constant crosshead speed. The reason for this has been explained in Chapter III. The

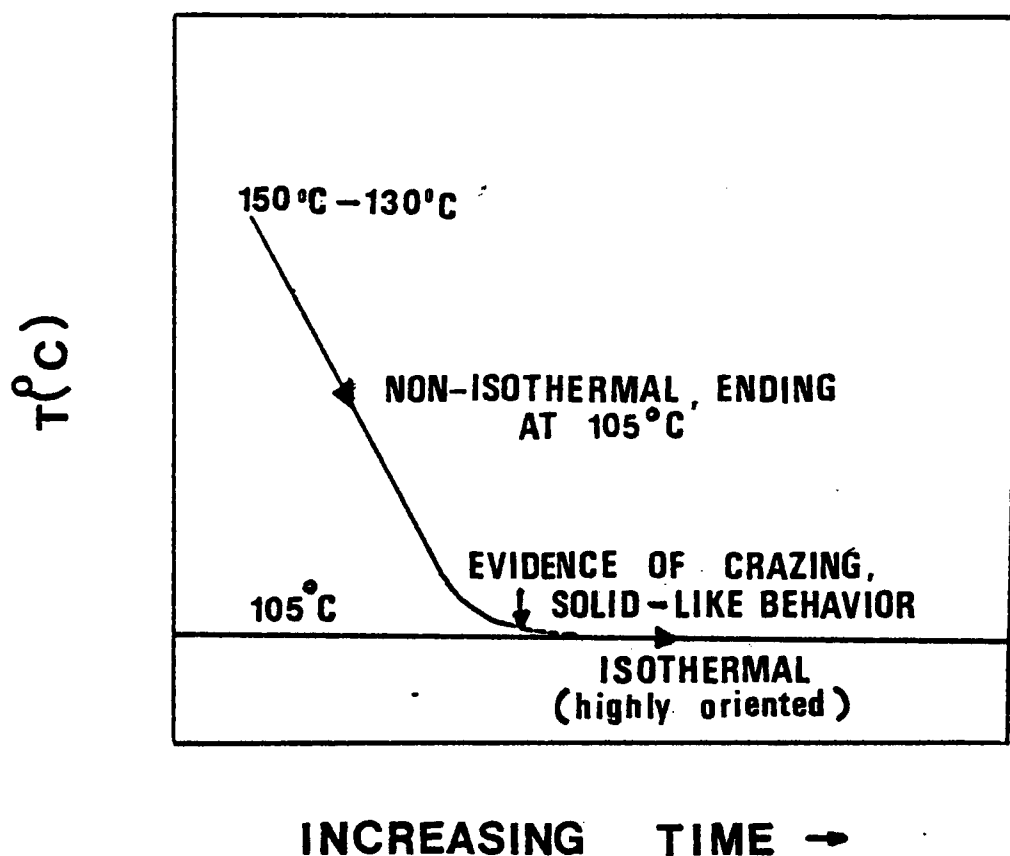


Figure 8. Sketch of temperature strategies used during non-isothermal runs.

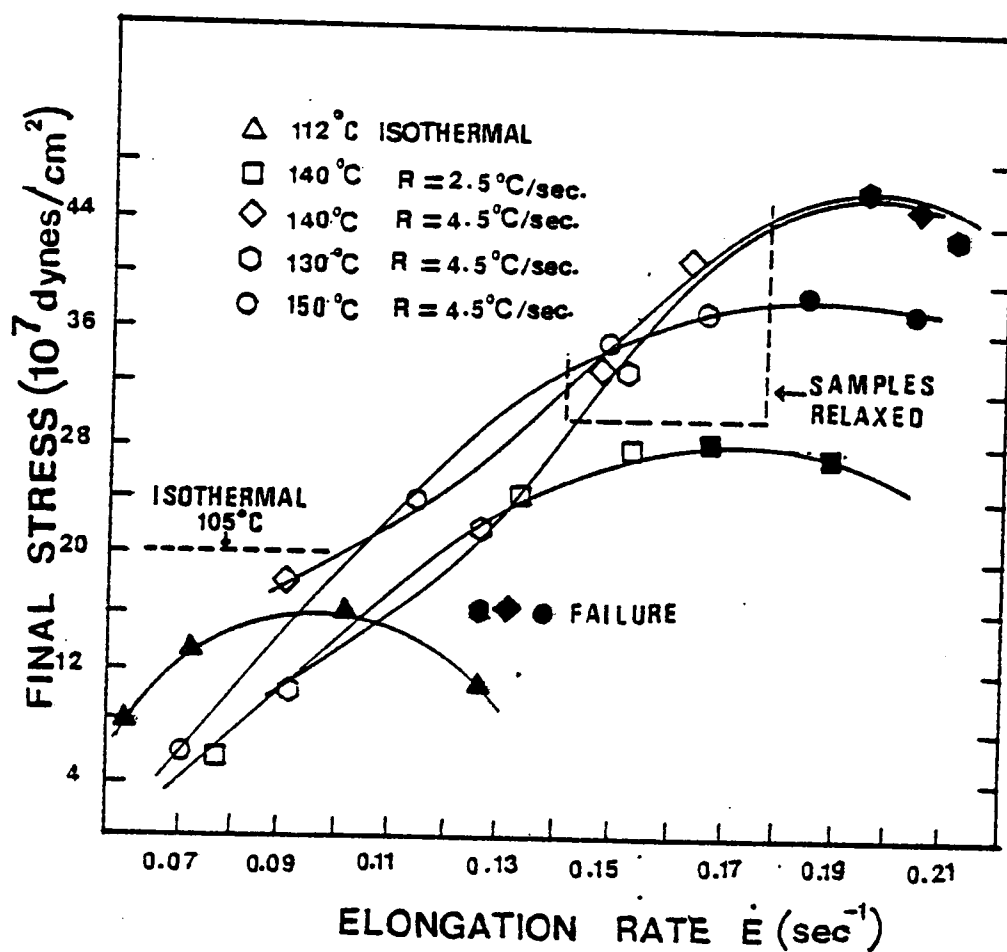


Figure 9. Final stress of polystyrene as a function of elongation rate.

solid symbols show the failure stress levels. Data inside the dotted lines show samples that could not be removed from the oven under the indicated stress levels. At those particular pulling and cooling rates the stress relaxed very quickly. The rate of relaxation was so fast that even when a special quenching device (consisting of cold CO₂ jets) was used, significant relaxation occurred before the glassy state was achieved. Because of this rapid relaxation process, it is believed that the stress within the dotted region has a glassy-like component in addition to a rubbery-like component. It appears impossible to freeze-in this glassy-like stress. Disregarding those samples, it is still possible to introduce somewhat higher stress levels under non-isothermal conditions.

One wonders what is different in the non-isothermal runs that permits increasing the stress levels compared with the isothermal runs. The stress level is finally limited by a cohesive failure mechanism involving the breakage of the rubbery network. This mechanism is perhaps initiated at a micro level (involving the "void regime") because one would suppose that macro defects are healed by flow. The good reproducibility of the breaking stresses, usually within ten percent, strongly suggests that macro defects in the samples are not responsible for the initiation of failure. If such an argument is valid, then higher temperatures would allow greater molecular mobility and the "massaging out" of micro

irregularities. But competing with this mechanism is the adverse effect of temperature in the development of orientation—that is, high temperatures cause rapid relaxation. Somehow, then the high temperature is perhaps needed for "massaging-out" defects, while the lower temperature is needed for creating high orientations. The best balance between these competing mechanism occurs under non-isothermal conditions.

B. OPTICAL AND MECHANICAL PROPERTIES OF QUENCHED SAMPLES

This section will present data concerning frozen-in orientation (birefringence) as a function of the tensile stresses which were induced in the rubbery state. The mechanical properties of these oriented samples will then be discussed. Forces induced in the fibers above T_g were measured and later converted to tensile stresses by measuring the final diameter and calculating the cross-sectional area. The orientation (birefringence) levels on the quenched samples were measured using a polarizing microscope. Figure (10) presents a plot of birefringence levels as a function of tensile stress. All data, both the isothermal and non-isothermal runs, are superposed on one curve. The curve appears linear at low and moderate stress levels, but a slight non-linearity is observed at high stress levels. Under non-isothermal conditions somewhat higher birefringence (stress) levels are obtainable. Some explanation for this

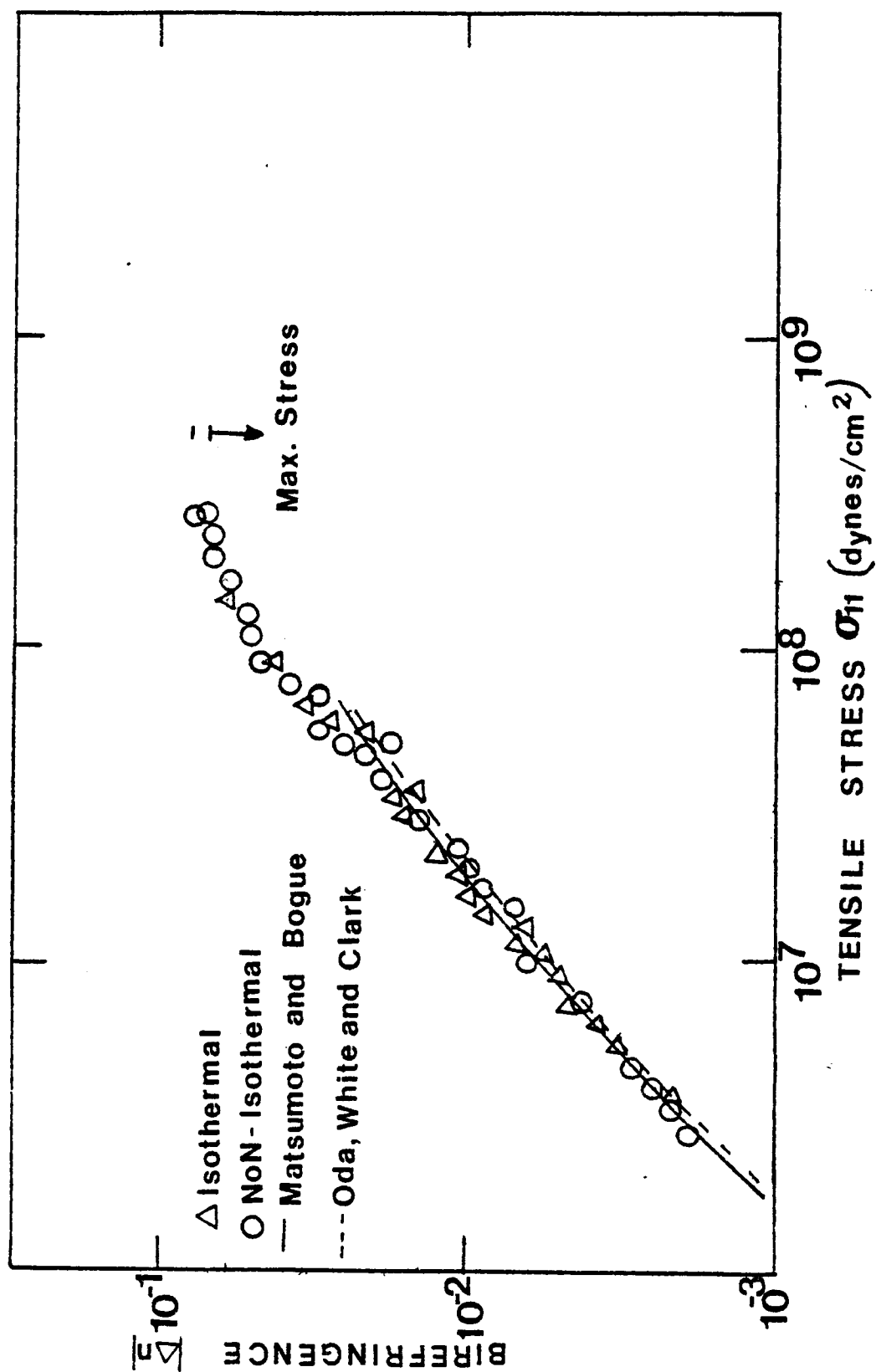


Figure 10. Summary of stress-birefringence data.

has been given in the previous section. The data in Figure (10) were compared with those of Matsumoto and Bogue (30) and also Oda, White and Clark (39) they agreed with only moderate scatter.

The tensile properties of these optically characterized fibers were then determined using an Instron tensile tester. The tests were carried out at room temperature at a crosshead speed of 2 cm./min and a fiber gauge length of 2 cms. Figure (11) shows typical stress-strain curves for fiber with varying degrees of orientation. In general, as the orientation (birefringence) increases one has a higher modulus, yield strength and tensile strength (breaking stress). A distinct yield point is observed with a slight degree of orientation; this is associated with a neck which travels throughout the fiber and results in an enormous increase in the elongation-to-break. This large elongation-to-break gradually decreases as the birefringence continues to increase, since the material deformed homogeneously above a certain birefringence level ($\Delta n > 30 \times 10^{-3}$).

Figures (12), (13), (14) and (15) show the Young's modulus, yield strength, tensile strength and percent elongation-to-break plotted against birefringence. These plots contain samples oriented under isothermal and non-isothermal conditions. These experimental data are compared with melt spun samples of Kanetsuna (23) who used commercial polystyrene Styron 679. Young's modulus is a difficult property to measure

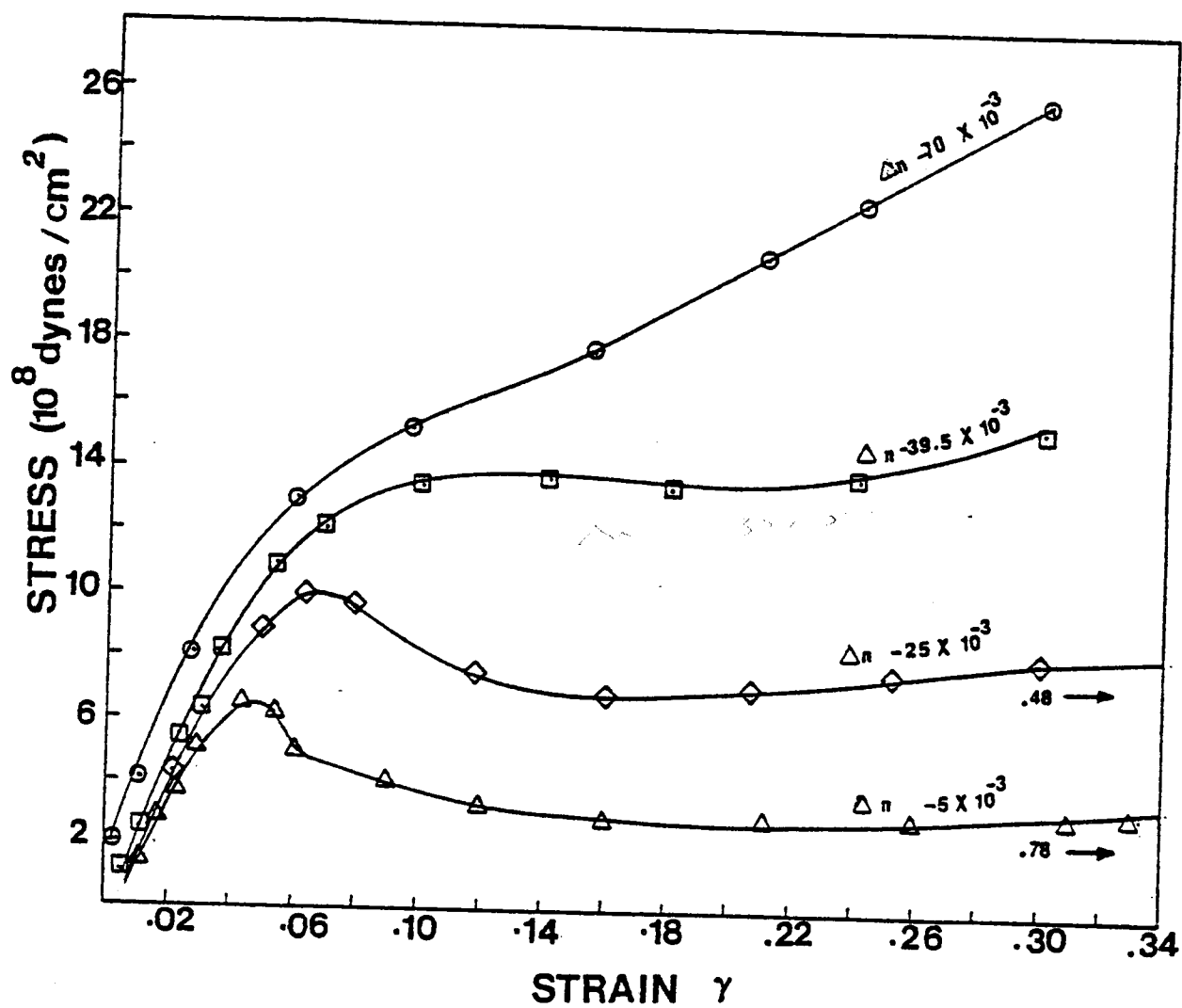


Figure 11. Typical tensile curves for polystyrene.

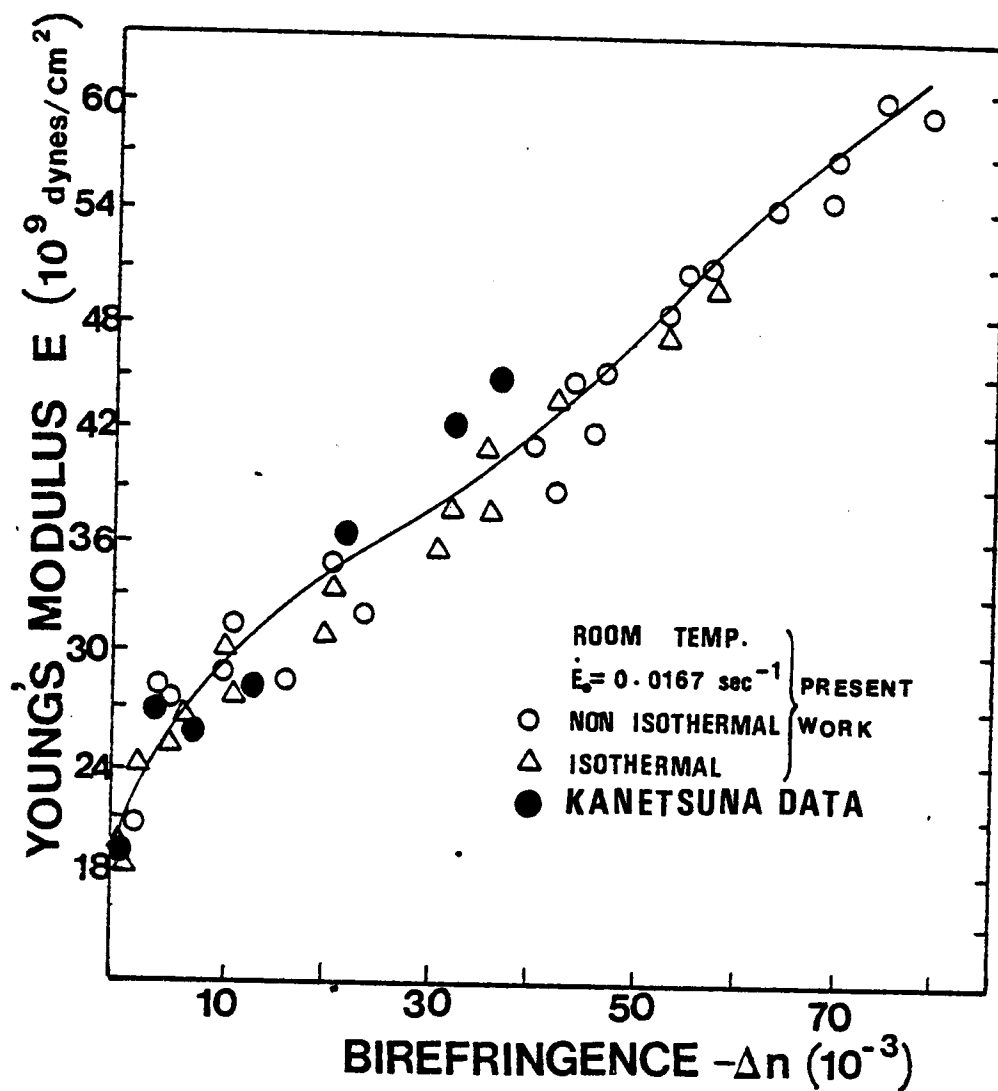


Figure 12. Young's modulus of polystyrene as a function of birefringence.

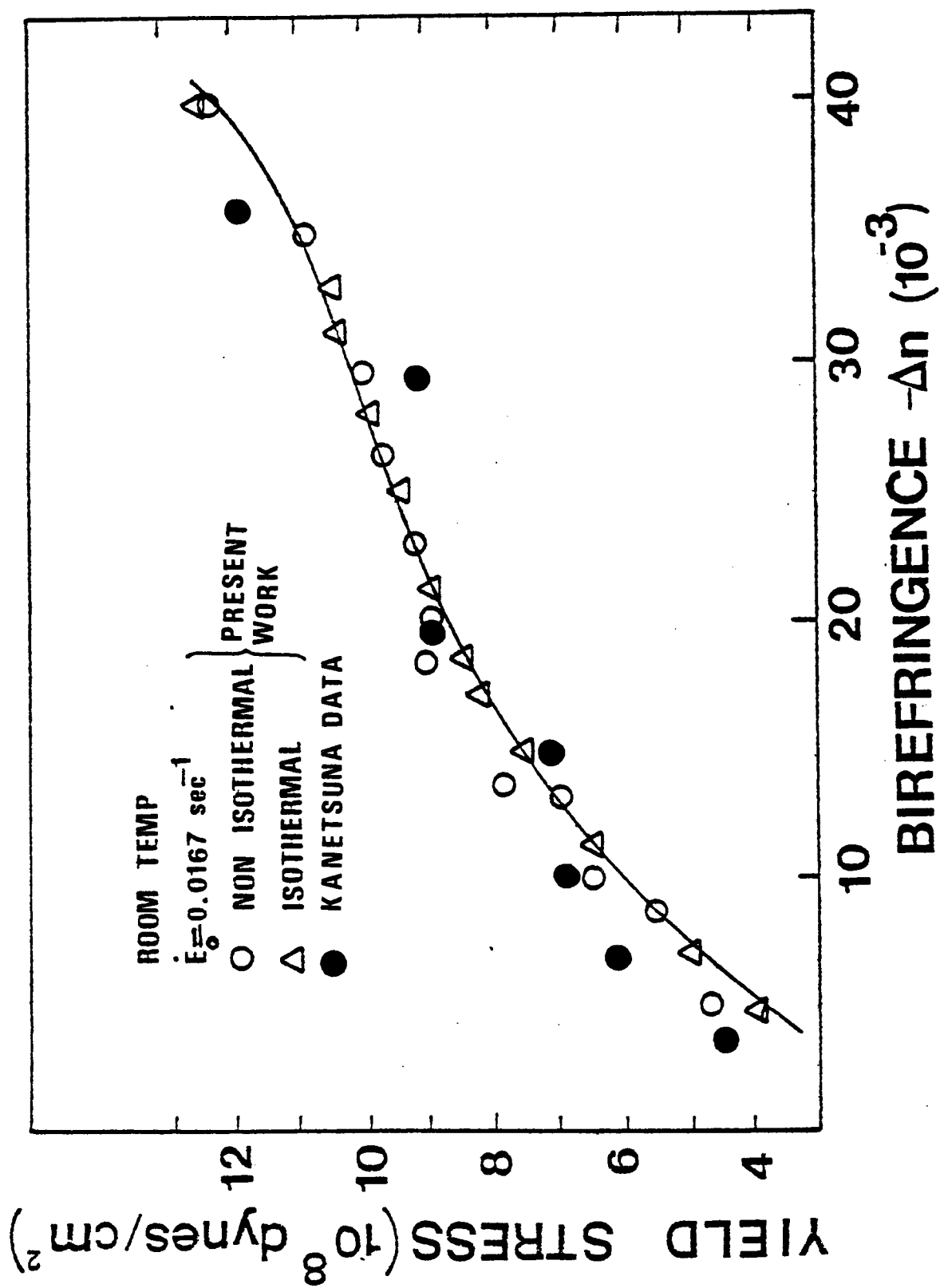


Figure 13. Yield stress of polystyrene as a function of birefringence.

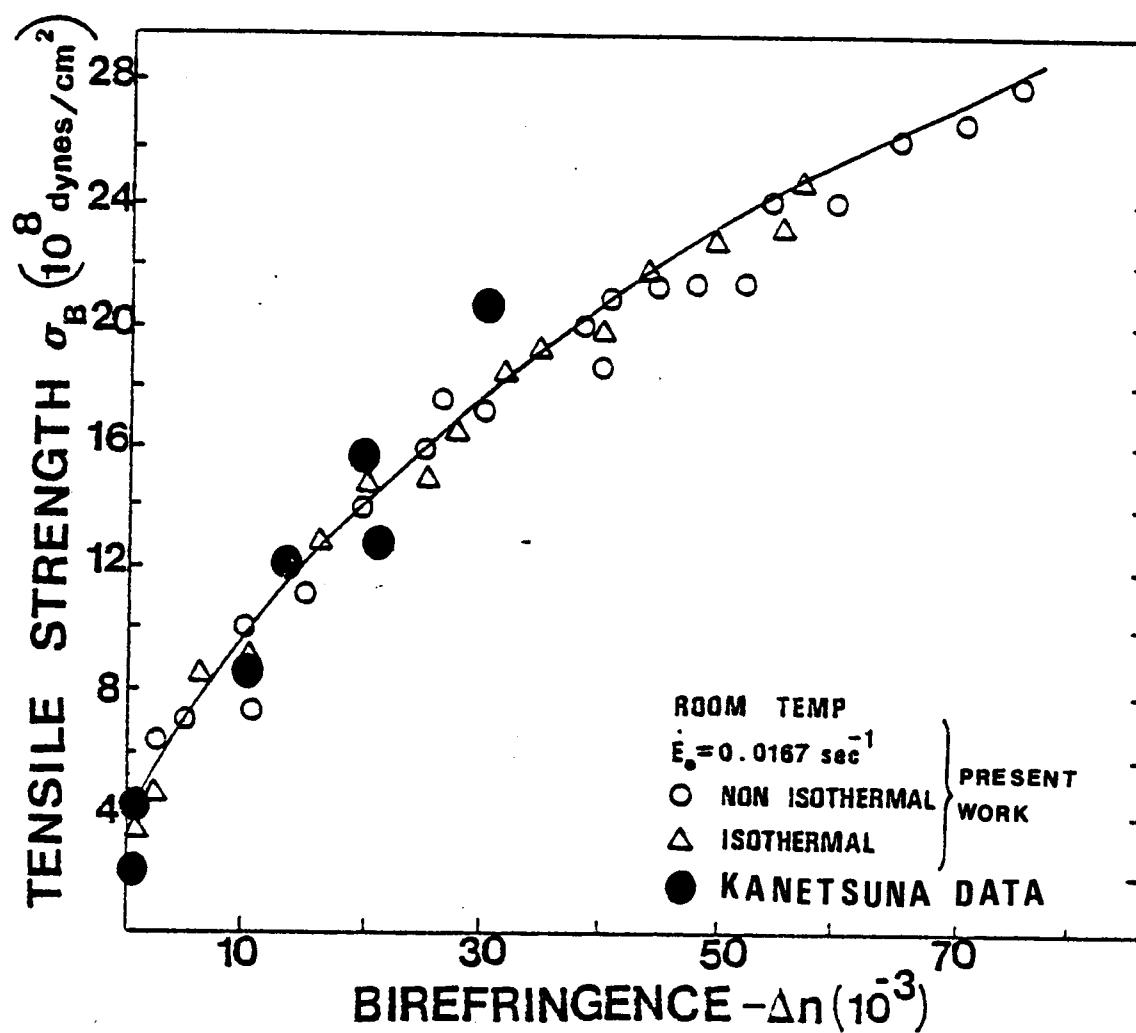


Figure 14. Tensile strength of polystyrene as a function of birefringence.

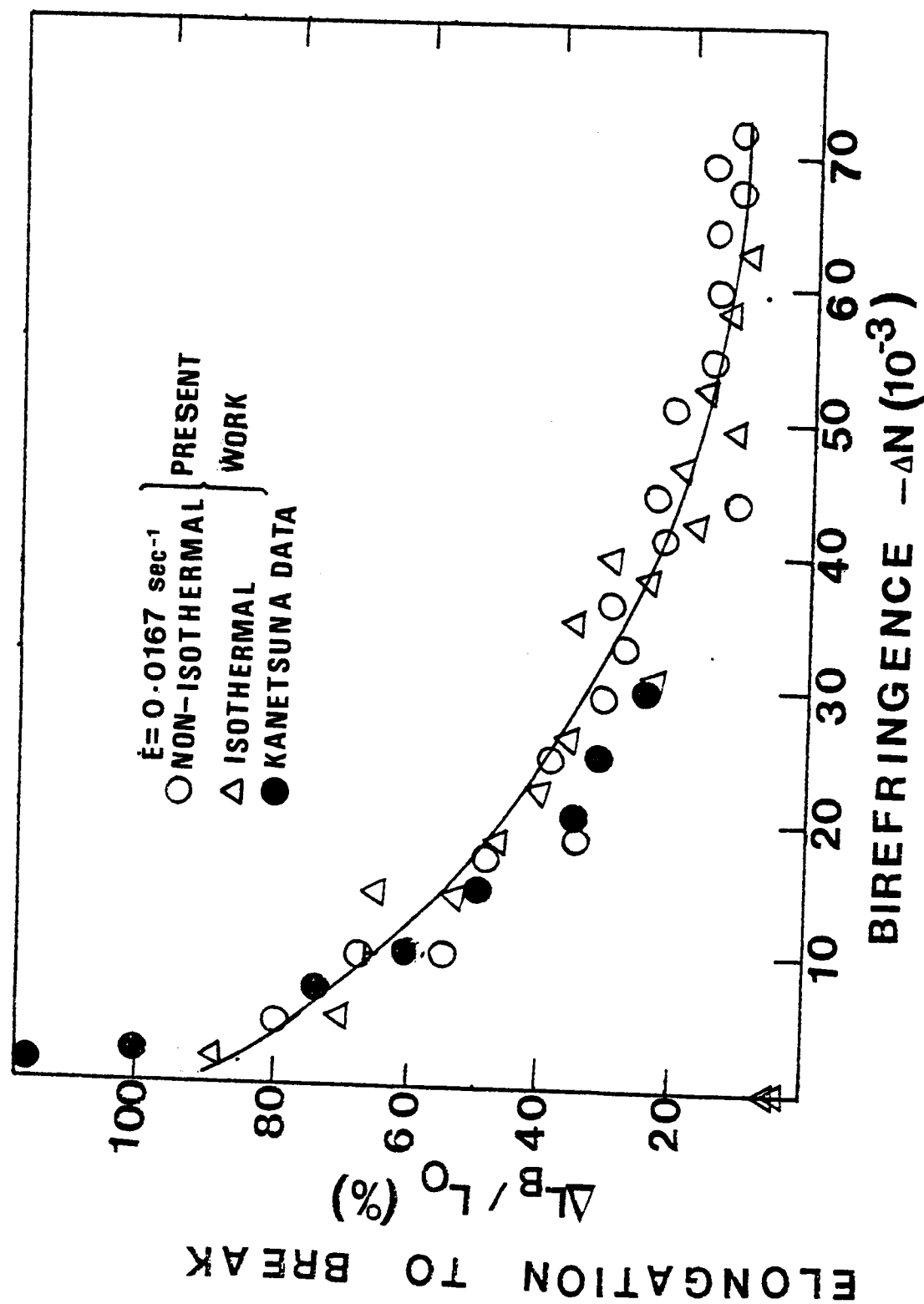


Figure 15. Elongation-to-break of polystyrene as a function of birefringence.

accurately because of "slack" at the onset of the experiment and therefore the data in Figure (12) scatter to a certain extent. However, a general trend toward increased tensile modulus can be observed with increasing birefringence. A similar trend is also observed in the behavior of the tensile strength (Figure (14)) and yield strength (Figure (13)). The yield strength increases with birefringence until the yield point become undetectable (for example, at a birefringence level $> -40 \times 10^{-3}$). The elongation-to-break (Figure (15)) decreases with increasing birefringence. This relationship hold only above a certain birefringence level (23,24).

✓ The torsional modulus was measured using the Mechanical Spectrometer (see Chapter III). Figure (16) contains a plot of Young's modulus and the torsional modulus of un-oriented and oriented fibers. The torsional modulus appears to be approximately $1/3$ the Young's modulus. It has been reported by Tanabe and Kanetsuna (24) that the density of polystyrene increase with increasing orientation. Form accompanying WAXS measurements this seems to be associated with a tendency for the phenyl rings to orient perpendicular to the chain direction and to "slide together" with rings from adjacent molecules. Apparently, this increased contacting (packing) of the molecules increased the modulus but not in a directionally dependent manner. The remaining three elastic moduli have not been measured and some anisotropic might be

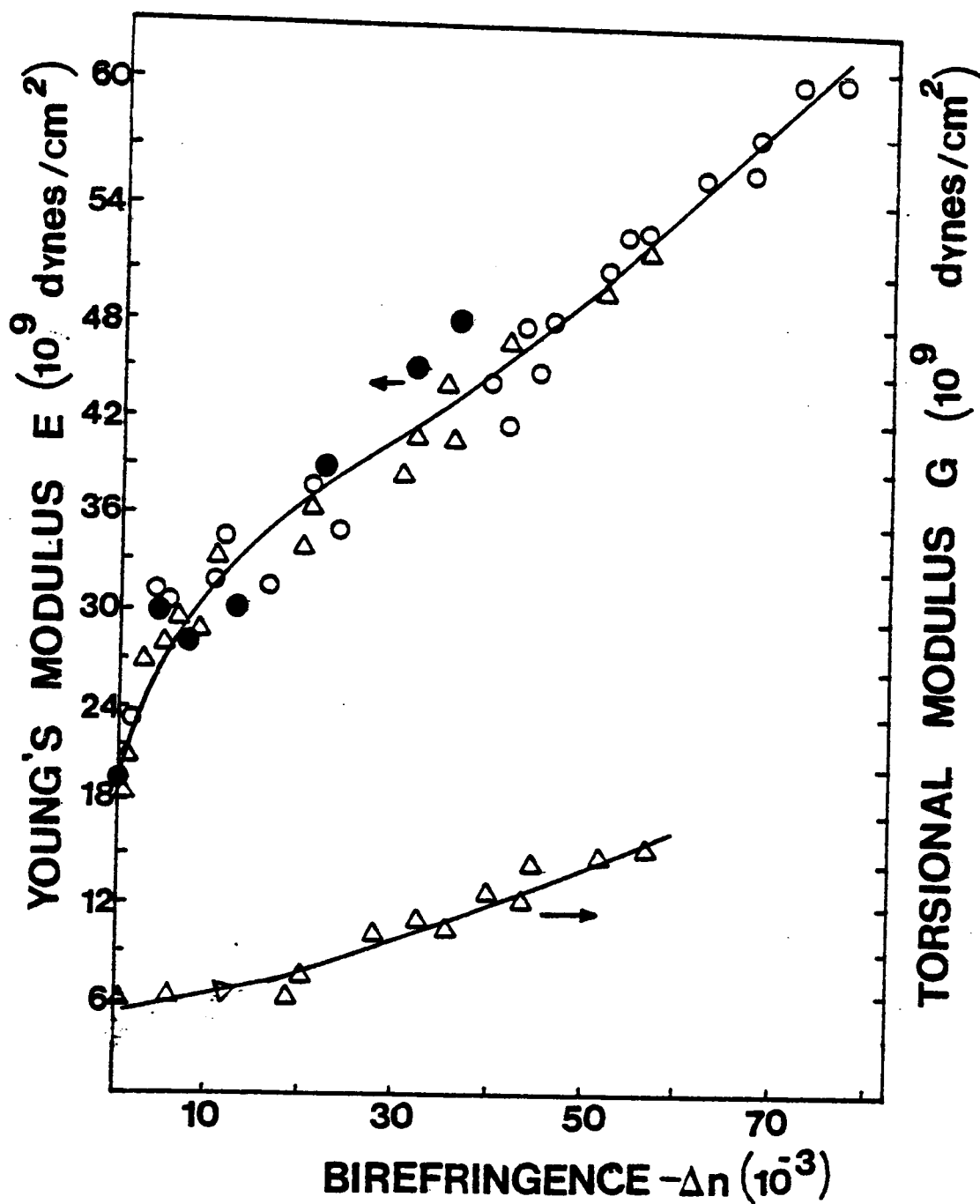


Figure 16. Young's modulus and torsional modulus of polystyrene as a function of birefringence.

seen there. Henning (19) (using polyvinyl chloride) and Cheatham and Dietz (9) (using polystyrene) reported that the torsional modulus remains relatively constant while the Young's modulus increases somewhat with orientation.

The mechanical properties of the fibers prepared under isothermal and non-isothermal conditions correlate remarkably well with the orientation (birefringence) frozen-in during the quenching. Also data from another investigator (Kanetsuna (23)) are in good agreement. This series of results seems to indicate that the mechanical properties strongly depend on the orientation and perhaps independent of how one develops the stress (orientation) in the rubbery state.

In order to understand the cooling process itself, as distinct from the orientation process, a series of experiments were carried out in which the sample was taken to an elevated temperature (150°C) and cooled without stretching. With the sample constrained, various linear cooling rates were applied to cool them to the glassy state without stretching them; of course some small contractual stress occurs due to cooling. The tensile properties of these fibers were measured at room temperature. Figure (17) presents a plot of Young's modulus and tensile strength; Figure (18) presents the elongation-to-break data plotted against cooling rate. There is a slight increase in the Young's modulus as the cooling rate increases. Similar behavior was found in tensile strength and elongation-to-break.

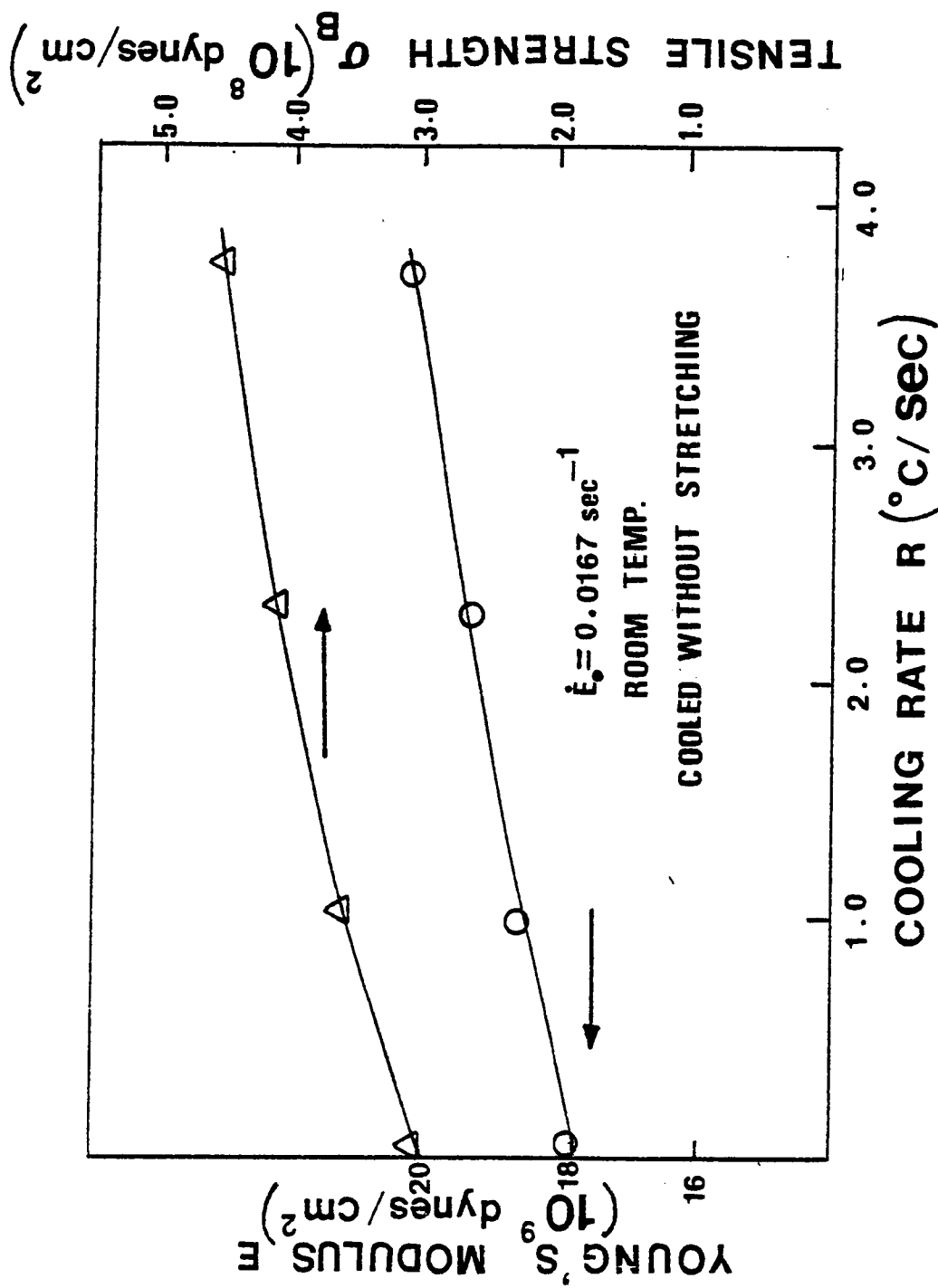


Figure 17. Young's modulus and tensile strength as a function of cooling rate. ⁴⁵

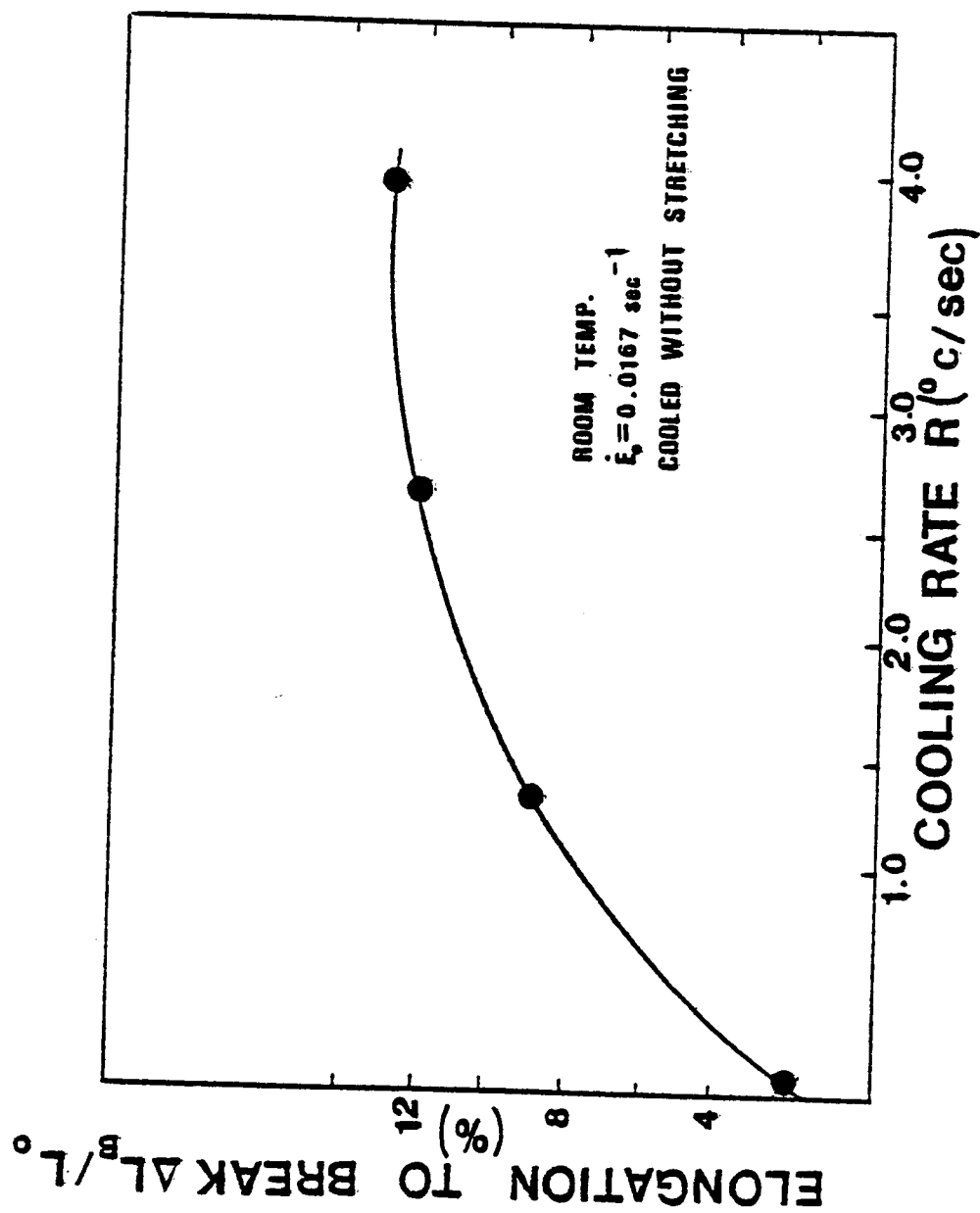


Figure 18. Elongation-to-break as a function of cooling rate.

However, comparing the modulus, elongation-to-break and tensile strength values with those for oriented samples (Figure (12), (15), and (14)) it was concluded that cooling has only slight effect on the mechanical properties. Also one notes that mechanical properties of isothermal (constant temperature while stretching) and non-isothermal (cooled while stretching) are quite similar if the orientation level is the same.

CHAPTER V

THEORETICAL ANALYSIS OF STRESS DEVELOPMENT ABOVE
THE GLASS TRANSITION TEMPERATURE

In elongation flows a steady state is achieved if the elongation rate is low enough $\left(\dot{E} < \frac{1}{2\tau_0}\right)$; for this case the elongational stress approaches a steady value. However, if the elongation rate is high $\left(\dot{E} > \frac{1}{2\tau_0}\right)$ a steady state cannot be achieved and the elongational stress grows in unbounded manner until failure occurs. Physically at high elongation rates the molecules cannot relax fast enough to accommodate the strain being imposed and the stress builds up until failure occurs. These two types of stress developments have been demonstrated experimentally and theoretically under isothermal conditions (62,30,31). In this section similar studies under non-isothermal conditions will be presented.

The non-isothermal theory due to Matsui and Bogue (29) (Equation II-5) will be used to describe the stress development in elongation flow at a constant elongational rate. When dealing with elongation flow, one is only concerned with the rheological tensile stress (σ_{11}). Thus, Equation (II-5) needs only to be written out for tensile stress. The Finger tensor for a flow at constant elongation rate is given by

$$c_{ij}^{-1} = \begin{vmatrix} \exp(2\dot{E}s) & 0 & 0 \\ 0 & \exp(-\dot{E}s) & 0 \\ 0 & 0 & \exp(-\dot{E}s) \end{vmatrix} \quad \begin{matrix} \\ (t' > 0) \\ (V-1) \end{matrix}$$

$$c_{ij}^{-1} = \begin{vmatrix} \exp(2Et) & 0 & 0 \\ 0 & \exp(-Et) & 0 \\ 0 & 0 & \exp(-Et) \end{vmatrix} \quad (t' \leq 0) \quad (V-2)$$

where $s = t - t'$, t' denotes any past time, t is the present time. The second invariant of the deformation rate tensor is calculated by

$$\Pi_d^{\frac{1}{2}} = \sqrt{3} \dot{E} \quad (V-3)$$

Substituting Equation (V-1), (V-2) and (V-3) into Equation (II-5) and (II-7); the tensile stress (σ_{11}), can be obtained by considering the boundary condition $\sigma_{22} = 0$ as follows

$$\sigma_{11} = G\dot{E} \int_0^t \exp \left[- \int_{t'}^t \frac{dt''}{T(t'')} \right] \left(2 \exp [AE(t-t')] + \exp [-BE(t-t')] \right) dt' \quad (V-4)$$

where $A = 2 - \sqrt{3} b$, $B = 1 + \sqrt{3} b$, and b is an empirical dimensionless parameter. However, for the present work b was set equal to zero. The temperature changes during the deformation are describable by the following equation

$$T(t) = T_i - RT \quad (V-5)$$

where T_i and R denote the initial temperature and cooling rate respectively. The shift factor of relaxation time taken from Takaki's work (51) was approximated by a generalized

shift factor (see Figure (19)) of the following form

$$\log a_T^{o,*} = \frac{-C_1 C_2 (T - T^*)}{(C_2 + T^* - T_g^o)(C_2 + T - T_g^o)} \quad (V-6)$$

where T is the actual temperature, $(^o)$ denotes zero cooling rate (equilibrium conditions) and $(*)$ denotes the reference temperature. The equilibrium T_g^o was taken from previous work by Wust (see Chapter II) C_1 and C_2 are constants. In order to fit Takaki's data, C_1 and C_2 were 15.5 and 45.5°C respectively. These are slightly different from the so-called "universal constants" (16). Equation (V-6) incorporates the well-known WLF equation as a special case. That is, at $T^* = T_g^o$ Equation (V-6) reduces to the familiar WLF equation

$$\log a_T^{o,o} = \frac{-C_1 (T - T_g^o)}{C_2 + T - T_g^o} \quad (V-7)$$

In the present analysis Equation (V-6) was approximated by the following simplified form

$$\ln a_T^{o,*} [T(t)] = -\alpha_{o,*} (T(t) - T^*) \quad (V-8)$$

The required $\alpha_{o,*}$ depends on the initial temperature. Table I shows a list of values used and other experimental parameters

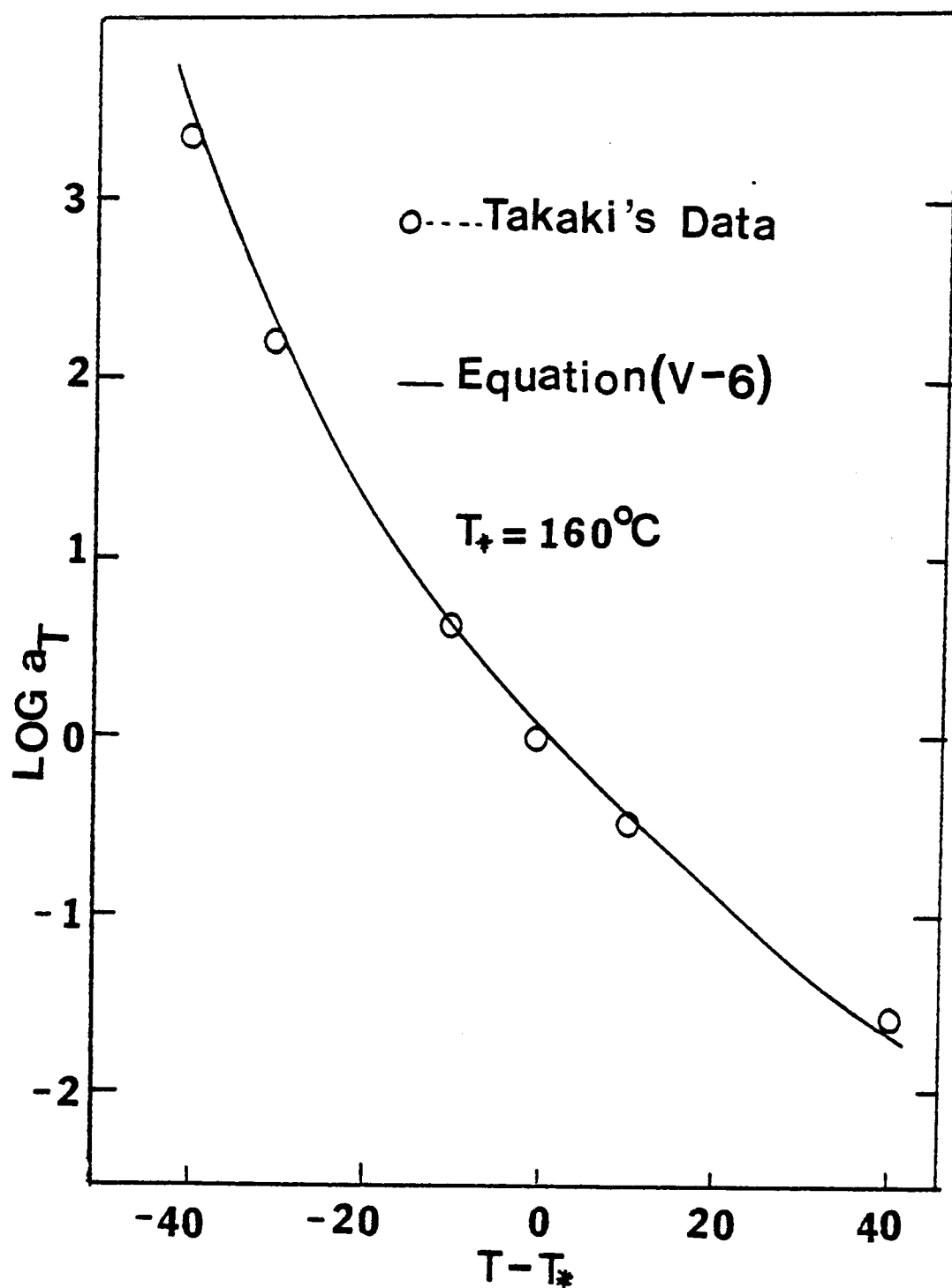


Figure 19. Comparison of a generalized shift factor with a particular form used in earlier work.

(see Appendix A) Figure (20) shows an example of how $\alpha_{o,*}$ was determined. Returning to Equation (V-4), one can then write the inside integral as

$$\begin{aligned} \int_{t'}^t \frac{dt''}{T(t'')} &= \frac{1}{T_*} \int_{t'}^t \exp[\alpha_{o,*}(T_i - Rt'' - T_*)] dt'' \\ &= \frac{\exp(-\alpha_{o,*}Rt) - \exp[-\alpha_{o,*}R(t-s)]}{\alpha_{o,*}RT_*} \end{aligned} \quad (V-9)$$

where T_* is taken to be the same as T_i . The tensile stress (σ_{11}) may be rearranged to

$$\begin{aligned} \sigma_{11} = \sum G \dot{E} \int_0^t \exp \left[\frac{\exp(-\alpha_{o,*}Rt) - \exp[-\alpha_{o,*}R(t-s)]}{\alpha_{o,*}RT_*} \right] \\ [2 \exp(A\dot{E}s) + \exp(-B\dot{E}s)] ds \end{aligned} \quad (V-10)$$

In order to carry out the analysis, certain material parameters, such as moduli and relaxation times, must be known in advance. The polymer used in this analysis was a typical commercial polystyrene (Shell TC3-30), which was described in Chapter III. In previous work by Matsui (29), a set of six moduli and relaxation times were determined in order to fit steady shear and dynamic data of Takaki (51). These

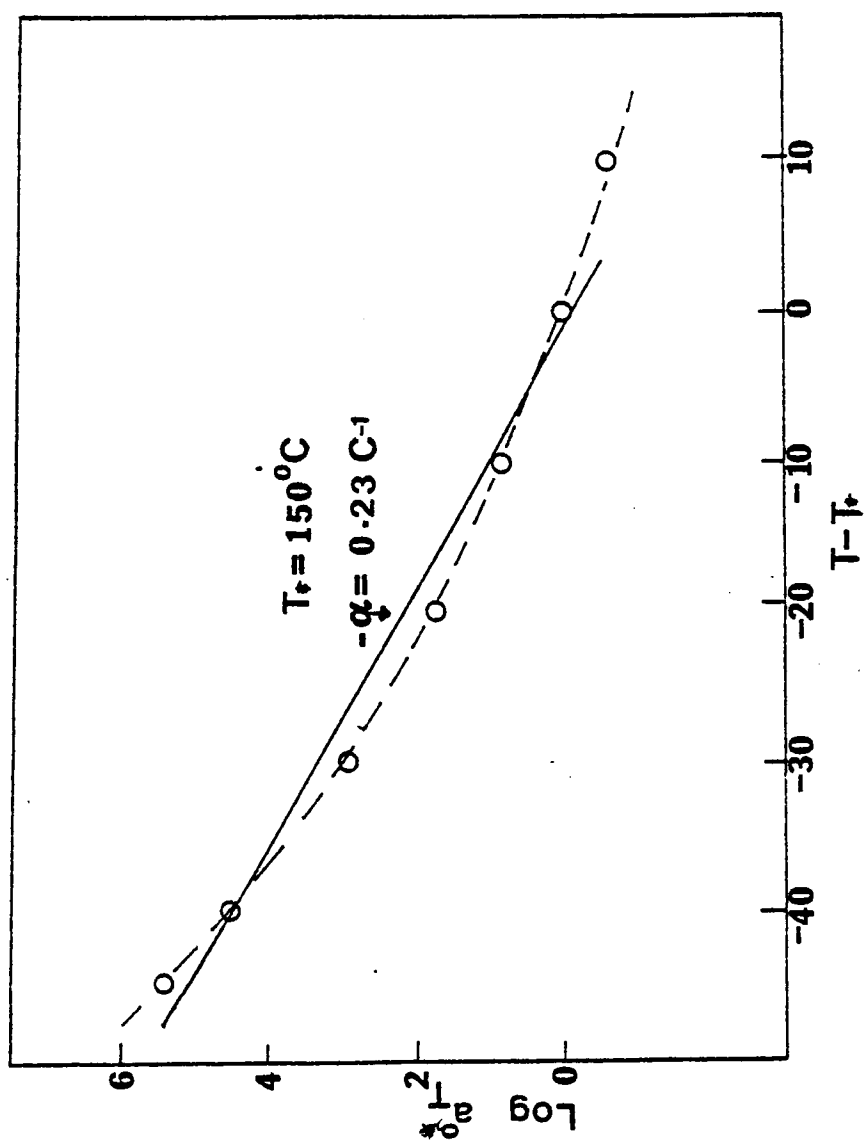


Figure 20. Temperature dependence of the shift factor at a reference temperature of 150°C.

values at 137°C are summarized below

$G_1 = 8.0 \times 10^6$ dynes/cm ²	$\tau_1 = 0.01$ sec.
$G_2 = 1.0 \times 10^6$	$\tau_2 = 0.1$
$G_3 = 6.0 \times 10^5$	$\tau_3 = 1.0$
$G_4 = 8.0 \times 10^5$	$\tau_4 = 10.0$
$G_5 = 4.0 \times 10^5$	$\tau_5 = 100.0$
$G_6 = 1.6 \times 10^5$	$\tau_6 = 1000.0$

Equation (II-3) was used to correctly shift relaxation time constants to the desired initial temperature, but the correction for the moduli were omitted.

Figure (21) presents non-isothermal experimental data of stress development as a function of time at various cooling rates and initial temperatures. A comparison with the theory is made in Figure (22). The theoretical curves shown there are predicted by using Equation (V-10). There are noticeable deviations between theory and experiment results; in particular, the stresses during the experiment developed much faster than the theory predicts. This behavior has also been reported by Matsumoto and Bogue (31). They believed that rapid immobilization of molecules occurred at high cooling rates (in the range of 1-5°C/sec.). In their work they suggested and used a cooling rate-dependent T_g in the analysis. This appears reasonable since it is well-known that there is an effect of cooling rate on the

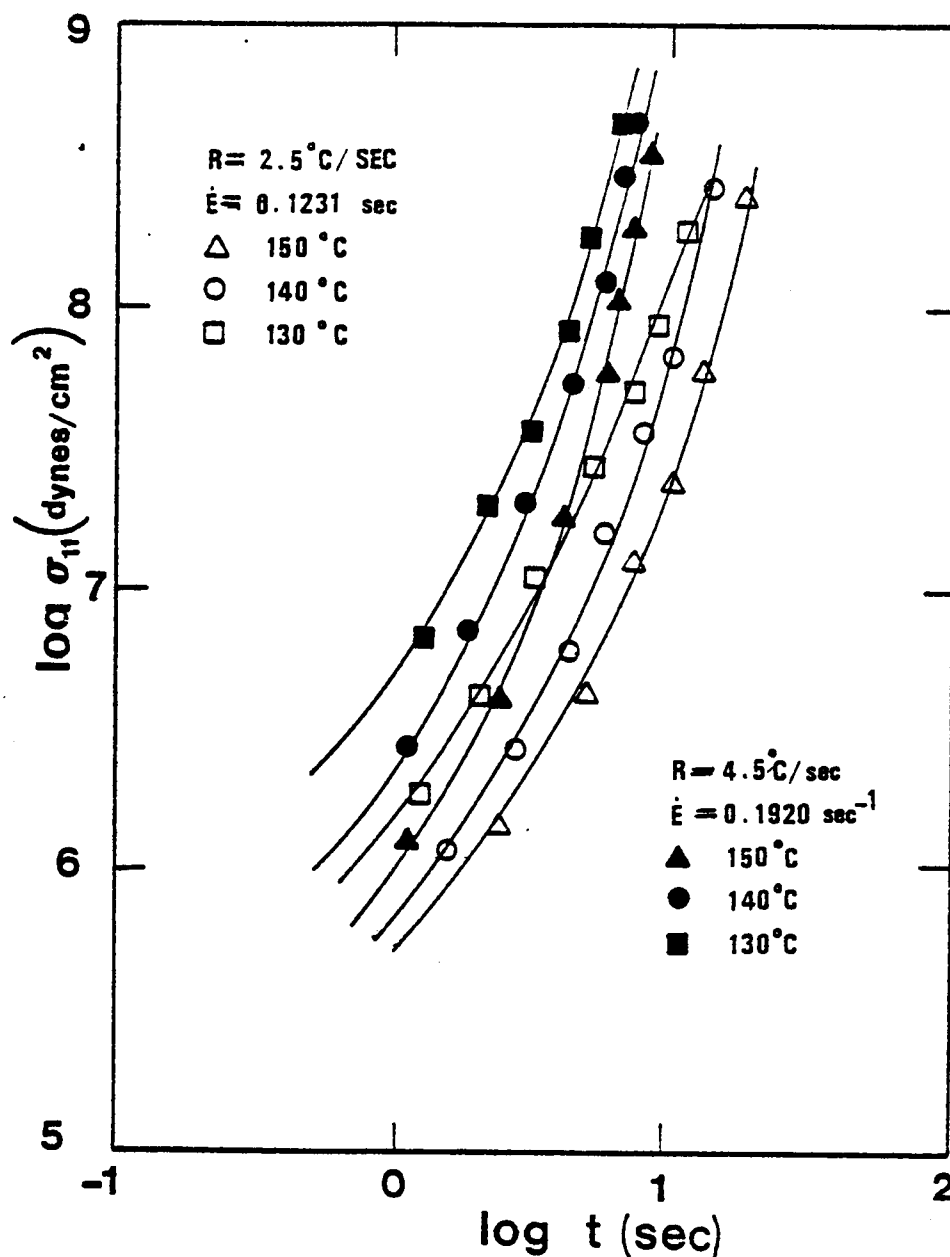


Figure 21. Stress development of polystyrene as a function of time during various non-isothermal runs.

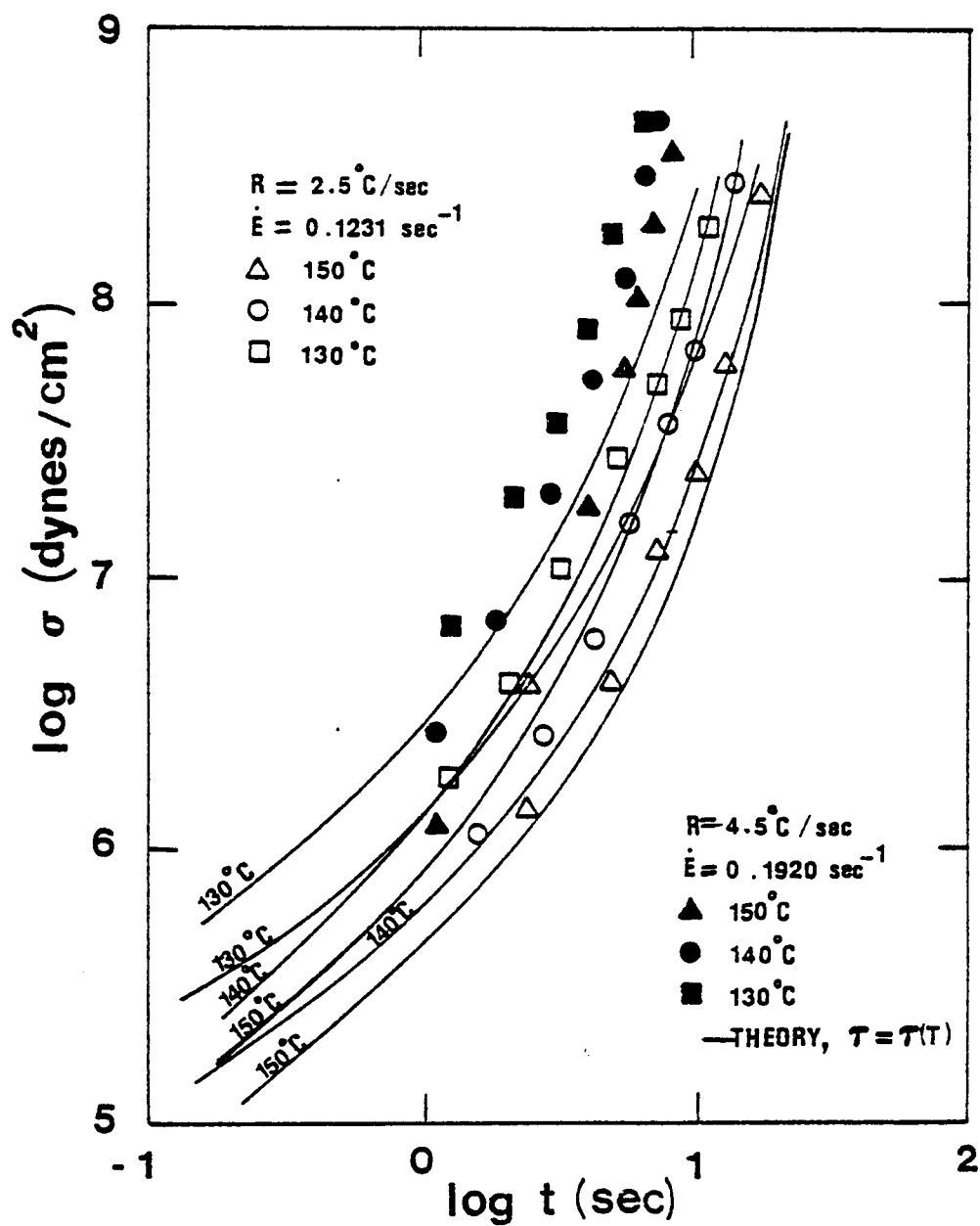


Figure 22. Comparison of predicted and experimental tensile stresses for non-isothermal tensile pulling.

glass transition temperature (63). That is, higher rates lead to higher values of T_g . Therefore, it seemed logical to also rework the analysis using a cooling rate-dependent T_g . To consider a rate-dependent T_g , Equation (V-6) was redefined in the following form

$$\log a_T^{R,*} = \frac{-C_1 C_2 (T - T_*)}{(C_2 + T_* - T_g^R) (C_2 + T - T_g^R)} \quad (V-11)$$

where replacing the superscript (o) with the superscript (R) denotes a cooling rate dependency. The cooling rate-dependent glass transition temperature (T_g) was also taken from previous work done by Wust (see Chapter II). Equation (V-11) was also approximate to a simplified form

$$\ln a_T^{R,*} [T(t)] = -\alpha_{R,*} (T(t) - T_*) \quad (V-12)$$

Figure (23) shows an example of the shift factor change when a cooling rate dependent T_g was considered (for comparison see Figure (20)). Equation (V-12) was used in Equation (V-10) to calculate a revised prediction of the stress build-up. The result using both Equation (V-8) and (V-12) were compared in Figure (24) and (25). The dotted line represents the original theory and the solid line represents the modified theory. In Figure (24) the theoretical line of the

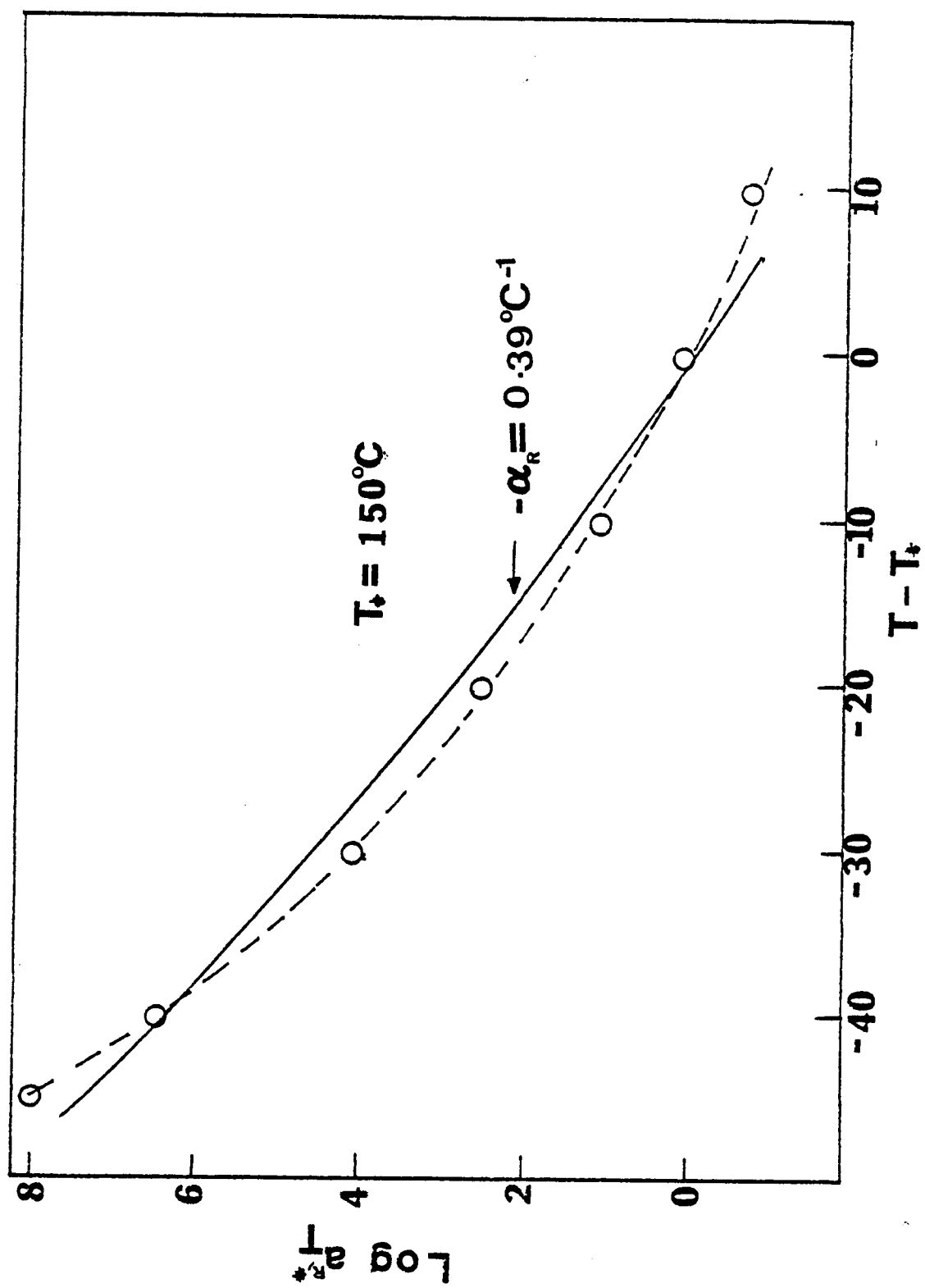


Figure 23. An example of the change in the shift factor when a cooling-rate-dependent T_g is used. ⁵⁸

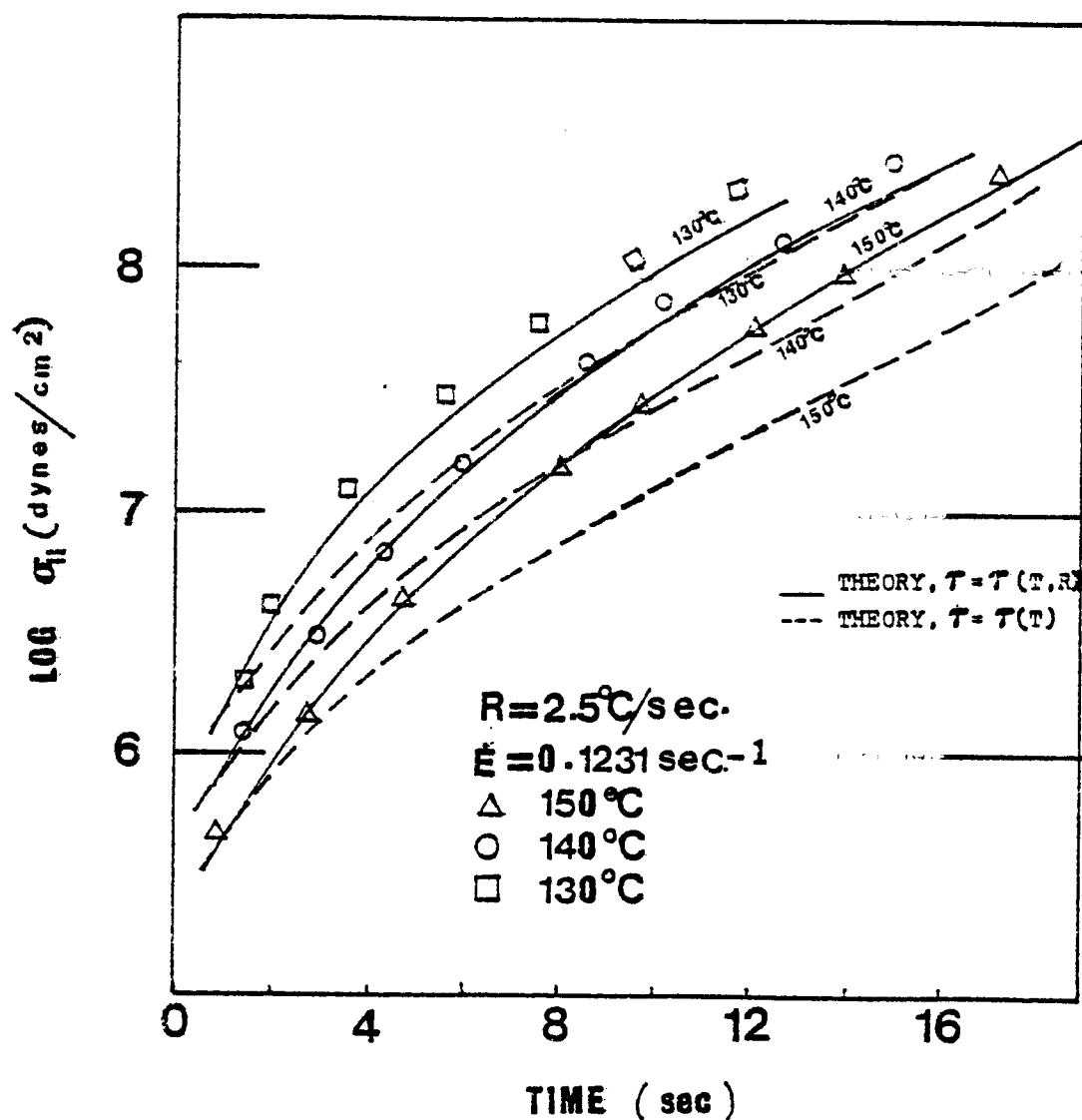


Figure 24. Comparison of a modified theory based on a cooling-rate-dependent a_T with experimental data ($R = 2.5^\circ\text{C/sec.}$).

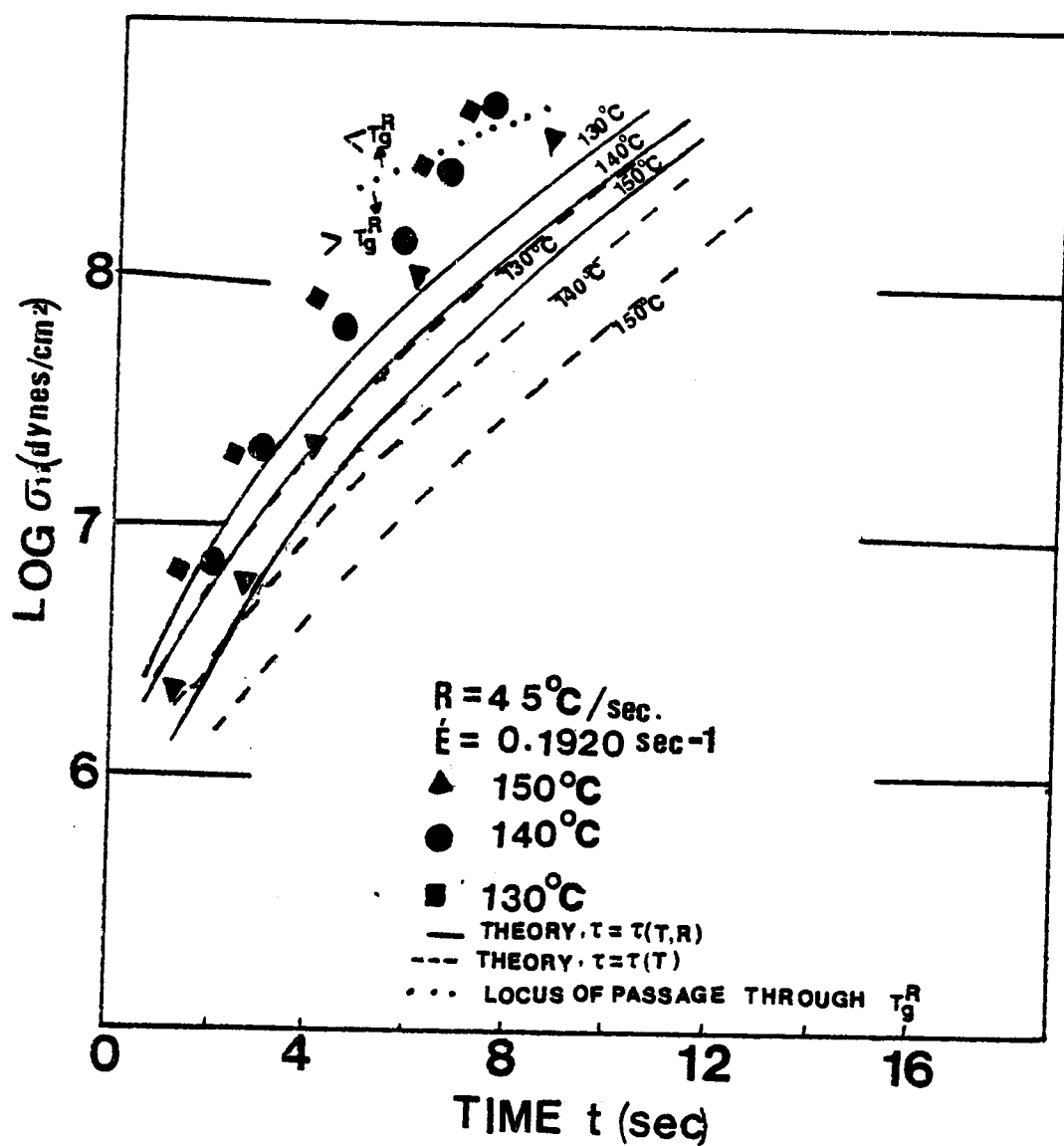


Figure 25. Comparison of a modified theory based on a cooling-rate-dependent a_T with experimental data ($R = 4.5^{\circ}\text{C/sec.}$).

modified theory appears to match the experimental results rather well. Figure (25) presents data at much higher cooling rates, and although the modified theory makes a shift in the right direction, it is clearly not enough to match the experimental stresses. These results seems to confirm the idea that at those high cooling rates, one has both a rubbery-like and glassy-like contribution to the stresses. The present theory is mostly showing the rubbery-like stress.

CHAPTER VI

SUMMARY OF IMPORTANT RESULTS

In this chapter the major results of the experimental and theoretical studies will be summarized. The work can be divided into two parts: (1) In the principal part of the work oriented polystyrene fibers were prepared under various deformation and thermal histories and their mechanical and optical properties measured. While subjecting the fiber to uniaxial extensions, both isothermal and non-isothermal histories were imposed in the rubbery state and the resulting samples quenched rapidly to the glassy state. And (2) in supplementary work a theoretical analysis of the non-isothermal rubbery deformation was carried out.

In preparing highly oriented samples, both isothermal and non-isothermal histories were imposed. In the isothermal tests it was found that conditions intermediate between those which gave very fluid-like response and those which gave solid-like (glassy) response produced the optimum orientation. This optimum was found to be about 105°C , which is approximately 10°C above the equilibrium T_g for the polystyrene being studied. The pulling was carried out in an Instron Tensile Tester at a crosshead speed of 1.67 cm/sec . (initial $\dot{\epsilon} \approx 0.55\text{ sec.}^{-1}$); the stress so induced was $2.0 \times 10^8\text{ dynes/cm}^2$. Higher stresses could be induced under non-isothermal conditions (cooling from about 140°C at a constant elongational rate of $0.13 - 0.21\text{ sec.}^{-1}$ at cooling rate of

2.5 - 4.5°C/sec.). However, the highest stress could not be taken into the glassy state due to very rapid relaxation, even under conditions of very rapid quenching.

It was possible, however, to produce samples with frozen-in stresses of about 2.80×10^8 dynes/cm² by non-isothermal processing. It is suggested that perhaps high temperatures provide conditions for "massaging-out" defects or micro irregularities that later lead to cohesive failure, while lower temperature are needed to create high orientations. Apparently, a non-isothermal cooling history provides the right balance between these two competing mechanisms.

Whether the samples were prepared isothermally or non-isothermally, the resulting frozen-in orientation (birefringence) correlated well with the stress induced in the rubbery state. A nearly linear relationship between stress and birefringence was found, in agreement with prior work. However, some deviation from linearity was observed at high stress levels. The only major effect, then, of the non-isothermal histories was to allow one to produce somewhat higher stresses before failure in the rubbery state.

The mechanical properties (Young's modulus, torsional modulus, yield stress, tensile strength and elongation-to-break) correlated well with orientation (birefringence). The young's modulus and yield stress increased with increasing birefringence. Elongation-to-break increases enormously with a very small degree of orientation; this

is followed by a moderate decrease in the elongation-to-break as the birefringence continues to increase. There is also a moderate increase in the torsional modulus as the orientation increases, this modulus being essentially three times the Young's modulus in the samples studied.

The second part of the study dealt with an analysis of non-isothermal rheology response above T_g . The basic theoretical structure is an integral viscoelastic theory using the generalized time-temperature superposition principle introduced in earlier work (Matsui and Bogue). By using a cooling rate-dependent T_g one can obtain good agreement with stress development curves at moderate cooling rates. However, at high cooling rates ($4.5^{\circ}\text{C}/\text{sec.}$) it is not possible to explain the experimental data accurately. Although the cooling rate-dependent T_g produces a shift in the right direction, the predicted stresses are clearly lower than the experimental ones. This is most likely due to a "glassy-like" contribution to the stress, which the present theory is not considering.

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APPENDICES

APPENDIX A

TABLE I

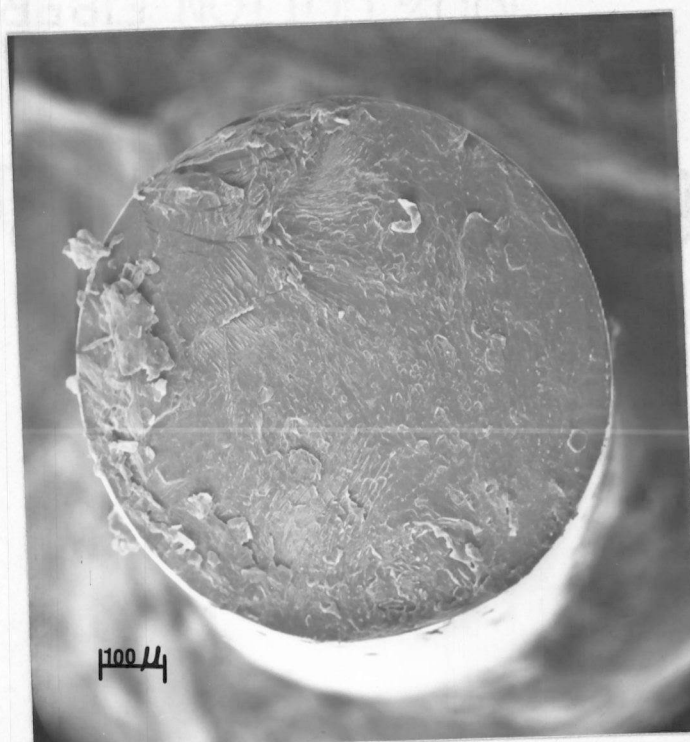
COOLING PARAMETERS USED IN EQUATION (V-10)

Initial Temp. (°C)	Cooling Rate (R) (°C/sec.)	$\alpha_{o,*}^{-1}$ (deg. ⁻¹)	$\alpha_{R,*}^{-1}$ (deg. ⁻¹)	Cooling Rate $\alpha_{o,*}^{-1}$ (sec. ⁻¹)	Cooling Rate $\alpha_{R,*}^{-1}$ (sec. ⁻¹)
130	2.5	0.30	0.484	0.75	1.21
140	2.5	0.25	0.425	0.63	1.06
150	2.5	$T_g = 93.5^\circ C$ 0.22	$T_g = 105^\circ C$ 0.39	0.55	0.975
130	4.5	0.30	0.616	1.35	2.77
140	4.5	0.25	0.53	1.125	2.38
150	4.5	0.22	0.48	0.99	2.16

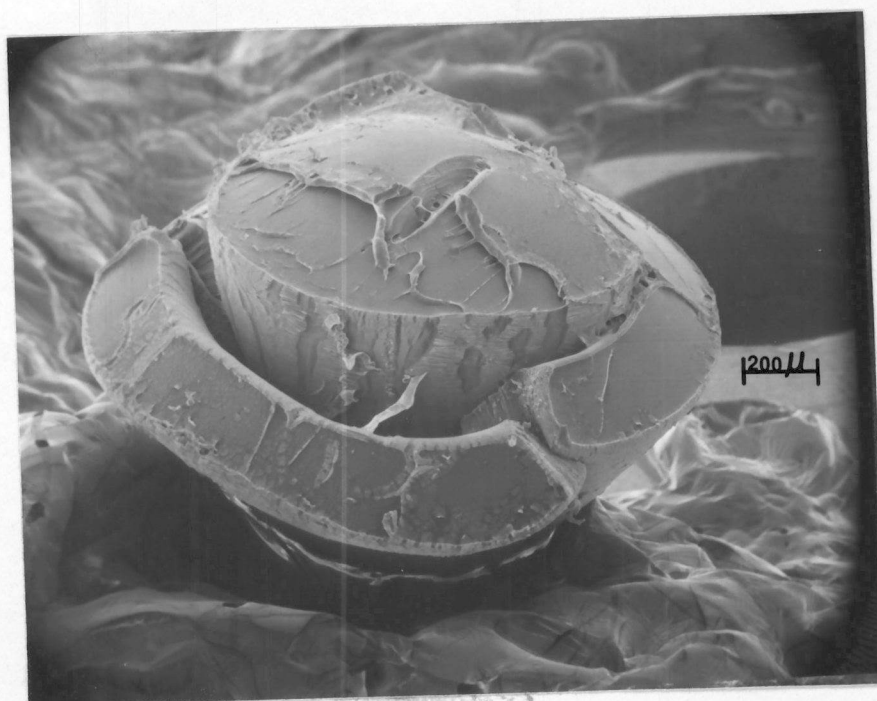
APPENDIX B

FRACTURE SURFACES OF POLYSTYRENE SAMPLES

Figures (26a) and (26b) show the fracture surfaces of polystyrene fiber as observed under a scanning electron microscope. Figure (26a) shows the surface of a typical fiber that has been extruded from an Instron Capillary Rheometer and annealed. This photograph shows a homogeneous cross-section, of the sort that was seen visually in all the samples reported in the main part of the thesis (whether annealed or not). Figure (26b) shows the cross-section of a hand drawn fiber, obtained accidentally while cleaning the Instron Capillary Rheometer. The cross-section of this particular fiber is clearly non-homogeneous, possibly due to a "squeezing effect" from a hard core which forms upon rapid cooling. While the observed structure is certainly an interesting one, more work is needed to identify the variables responsible for forming such a non-homogeneous structure.



(a)



(b)

Figure 26. Fracture surfaces of polystyrene.

APPENDIX C

LIST OF VARIABLES

a_T	shift factor
$a_T^{O,*}$	defined by Equation V-6
$a_T^{R,*}$	defined by Equation V-11
b	nonlinearity
C_1	constant used in Equations V-6 and V-11
C_2	constant used in Equations V-6 and V-11
C_{ij}	relative Cauchy strain tensor
C_{ij}^{-1}	relative Finger strain tensor
C	stress-optical coefficient
d	fiber diameter
E	Young's modulus
F	Herman's orientation factor
G	shear modulus
$H(T)$	continuous spectrum of relaxation times
J	moment of an inertia of the fiber
L	fiber length
$m_1(t-t')$	deformation dependent memory function
$m_2(t-t'')$	deformation dependent memory function
n	birefringence
p	pressure
R	cooling rate
t	time
t'	past time (integration variable)

t''	past time (integration variable)
T	temperature
T^*	initial temperature
T_0	reference temperature
T_g^0	glass transition temperature at zero cooling rate
T_g^R	cooling-rate-dependent glass transition temperature
δ_{ij}	kronecker delta
ϵ	strain
α	approximated shift factor
II_d	second invariant of the deformation rate
σ_{ij}	stress
σ_{11}	rheological tensile stress
τ	relaxation time
$\dot{E}$	elongation rate
σ_B	tensile strength
	Poisson's ratio

APPENDIX D

COMPUTER PROGRAM

Following is the computer program used for predicting the stress development of polystyrene undergoing elongational flow in the presence of changing temperatures. In order to have a full understanding of this program the reader is asked to refer to Chapter V and particularly Equation (V-10) in the chapter.

```

C      TAU      RELAXATION  $\tau(t)$ 
C      G        ELASTIC MODULUS
C      AR       COOLING RATE MULTI. BY SHIFT FACTOR  $(\alpha_0 \cdot R)$ 
C      A        NON-LINEARITY FACTOR  $\rightarrow b$  in eq. V-4)
C      RB       B (SEE EQUATION V-4)
C      AA       A (SEE EQUATION V-4)
C      DEX      STEP SIZE
C      KK       NUMBER OF STEP
C      T1       REAL TIME
C      SS       LN S (SEE EQUATION V-6)
C      ATMIN    MINIMUM VALUE OF LN S
C      E        ELONGATION RATE
C      STRESS   STRESS
C      REAL N
C      DIMENSION TAU(6), G(6)
C      G(1) = 8.6E6
C      G(2) = 1.0E6
C      G(3) = 6.E5
C      G(4) = 8.0E5
C      G(5) = 4.0E5
C      G(6) = 1.6E5
1111 READ(5,100,END=999) E, AR, A
100  FORMAT(8F10.5)
      WRITE (6,200) E, AR, A
200  FORMAT(1H0/ 5X, 8F10.3/)
      WRITE (6,11)
11   FORMAT (10X, 'THE VALUES OF TAU ARE ')
      READ (5,12) TAU
12   FORMAT (6F12.6)
      WRITE (6,20)
20   FORMAT (5X, 'REAL TIME', 8X, 'STRESS' )
      SQ=SQRT(3.)
      AA=2.-SQ*A       $A = 2 - \sqrt{3} b$ 
      BB=1.+SQ*A       $b = 1 + \sqrt{3} A$ 
      DEX=10.**.25 = 1.8
      T1 = 0.1/DEX = 0.06
      KK = 100
      AKK=KK
      DO 3 J=1,10
      T1=T1*DEX = 0.1
      STRESS = 0
      DO 4 I = 1,6
      ATMIN = ALOG (TAU(I)/AKK) =  $\ln \left( \frac{TAU(I)}{AKK} \right)$ 
      D=(ALOG(T1)-ATMIN)/AKK =  $(\ln(T1) - ATMIN)/AKK$ 
      SS=ATMIN-D/2.
      TV=0
      DO 2 K=1, KK

```

$$t = \ln t - \ln \left(\frac{\tau(t)}{100} \right)$$

ATMIN = minimum value of $\ln t$

$$\ln \eta_T = \ln \left(\frac{\eta_0}{T} \right) - \frac{D}{T} = 0 \quad 78$$

```

SS=SS+D
S = EXP(SS)
P=AR*T1 → P = α0*R.t
IF(P.GT.100.) P=100.
Q=AR*(T1-S) → Q = α0*R.(t-s)
IF(Q.GT.100.) Q=100
X = AA*E*S → X = AĒS
IF(X.GT.100.) GO TO 1111
IF(X.LT.-100.) X=-100
Y=BB*E*S → Y = BĒS
IF(Y.GT.100.) Y=100.
C=C*EXP(X)+EXP(-Y) → C = 2*P(AĒS)+2*P(-BĒS)
ARGI = (EXP(-P)-EXP(-Q))/(AR*TAU(I)) → ARG I =  $\frac{\exp(-\alpha_0 R t) - \exp(-\alpha_0 R (t-s))}{\alpha_0 R \cdot \tau(x)}$ 
IF (ARGI .GT. 100.) ARG I =100
IF (ARGI .LT. -100) GO TO 30
FM = EXP(ARGI) → FM = exp(
GO TO 40
FM = 0
30 TV=TV+FM*C*D*S
40 2 CONTINUE
STRESS = STRESS + TV*G(I)*E
N = STRESS/E
4 CONTINUE
WRITE (6,300) T1,STRESS,N,AR,E
300 FORMAT(5X,8E13.4)
3 CONTINUE
GO TO 1111
999 STOP
END

```

$$S = 100$$

$$C = 1$$

VITA

Delroy A. Carey was born in St. Catherine, Jamaica on March 26, 1954. He attended elementary school there. In 1968 he and his family left Jamaica to assume residency in the United States. He graduated from Glade Central high, Belle Glade Fla. in 1973. Upon his graduation he entered W.Va. State College, from which he received a Bachelor of Science degree in Chemistry in 1977. The same year he entered the University of Tennessee; in August 1979 he received a Master of Science degree in Polymer Engineering.