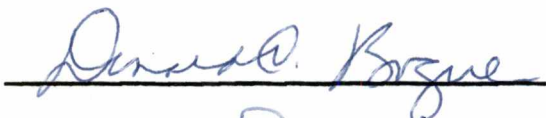


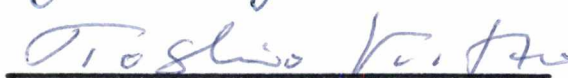
To the Graduate Council:

I am submitting herewith a thesis written by Hideki Yamane entitled "Rheological Properties and Processing of Thermally Degraded Polyolefins." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

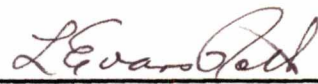

James L. White, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:


Vice Chancellor
Graduate Studies and Research

RHEOLOGICAL PROPERTIES AND PROCESSING
OF
THERMALLY DEGRADED POLYOLEFINS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Hideki Yamane

August 1982

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ABSTRACT

Thermally degraded polypropylene and polybutene-1 were studied in a series of rheological and processing experiments.

The materials were rheologically characterized in steady shear measurements which include steady shear viscosity measurements and the first normal stress difference measurements. The rheological properties in shear flow indicated not only a molecular weight lowering but a narrowing of the molecular weight distribution.

Studies of elongational flow indicated that the degraded melt could be drawn out into uniform filaments and gave elongational viscosities roughly three times the zero shear viscosity. The untreated and mildly degraded filaments developed defects and failed at small elongations.

Extrudate swell during isothermal extrusion was measured by a photographic method. Degradation reduces the swell at constant shear rate, shear stress and normal stress - shear stress ratio.

Diameter and velocity profile were measured during isothermal melt spinning and spinline elongational viscosity was estimated. Studies of instability in isothermal melt spinning indicated that thermal treatment stabilized the spinline.

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CHAPTER I

INTRODUCTION

Since the polymerization of propylene with Ziegler-type catalysts, polypropylene has become one of the most important polymeric materials which is used for plastics and fibers.

While commercially polymerized polypropylene by Ziegler-Natta catalyst have a range of molecular weight distributions, truly narrow molecular weight distribution materials have not been prepared as in the case of polystyrene, polybutadiene and polyisoprene where anionic polymerization is possible.

Relatively narrow molecular weight distribution materials of polypropylene can be usually prepared by a post polymerization process involving degradation of high molecular weight materials by random chain scission. This process is called viscracking. As the molecular weight distribution of polypropylene is initially broad ($\bar{M}_w/\bar{M}_n \sim 10$), the molecular weight is not only lowered but its distribution is narrowed, and tends to a most probable distribution with $\bar{M}_w/\bar{M}_n = 2$. Patents by Kowalski and his coworkers (85, 86, 146) indicate that the viscracking process makes the polypropylene more suitable for processing such as for melt spinning of fibers or the production of film.

Molecular weight and its distribution have a strong effect on rheological properties and processing including melt spinning. While process engineers in the polymer industries have long noted this problem, there has been little direct study of molecular weight distribution effects on melt spinning. The most thorough study seems to be that of Minoshima, White and Spruiell (112, 114, 115) who found that molecular weight

distribution influences spinline elongational viscosity and stability of the fiber spinline.

The purpose of the present work are to determine the influence of thermal degradation on the melt spinning and rheological properties of polypropylene and polybutene-1.

CHAPTER II

BACKGROUND

A. DEGRADATION OF POLYOLEFINS

A-1. Experimental Study of degradation of polyolefins

In the middle 60's, Sheehan and Cole (142) investigated the molecular weight and its distribution of thermally degraded isotactic polypropylenes. In their experiments a polypropylene was heated for 2.5 hr. at 280°C in the presence of oxygen and then extruded. Another polypropylene was heated for 0.75 hr. at 235°C under a vacuum and then extruded also under vacuum. The original polypropylene has $\bar{M}_w/\bar{M}_n$ value of about 10. After these processing the polymer degraded under a presence of oxygen tended to have $\bar{M}_w/\bar{M}_n$ value of 2.1 ~ 2.5 while that degraded under a vacuum had $\bar{M}_w/\bar{M}_n$ value of 8.5 ~ 9.3.

The thermal degradation of polypropylene has been critically discussed by Kowalski et al. (85, 86, 146) in a series of patents. Their patents mainly consist of an extruder reactor, a rheometer and a feed-back loop system. The molecular weight and its distribution of polypropylene were changed by degradation in the extruder at high temperatures between 300°C and 500°C in the presence of oxygen. The polymers were then investigated with a rheometer. The temperature was controlled by a feed-back system which was connected with a rheometer. They indicated that the viscracking process makes the polypropylene suitable for processing such as for melt spinning of fibers or the production of film since the molecular weight is not only lowered but its distribution is narrowed by this process.

Sakai and coworkers (139) determined the processing conditions

required to change the molecular weight and its distribution of polypropylene using several commercial processing machines. They included two kind of single screw extruders, a double screw mixer, and a continuous intensive mixer. Using a gel permeation chromatograph (GPC) they found that the high molecular weight region tended to shift to the low molecular weight region and the distribution becomes narrower. They also indicated that the polypropylene treated in this way has several differences in processing characteristics from that prepared as polymerized.

The thermal and thermo-oxidative degradation of high density polyethylene (HDPE) and low density polyethylene (LDPE) was studied by Holmström and Sörvic (67, 68, 69). Changes in molecular weight distribution and degree of branching (LCB) were followed by GPC and intrinsic viscosity measurements. In their experiments they suggested that HDPE and LDPE are not degraded according to a random scission type of mechanism. They found that $\bar{M}_w/\bar{M}_n$ tended to increase from ~ 3 to ~ 5 for LDPE and that it decreased from ~ 13 to ~ 5 for HDPE. They postulated that this value is considerably higher than the value 2 expected from random scission theory and is due to concurrently occurring molecular weight enlargement and diminishing reaction.

In the middle 70's, Iring and coworkers, and Fuzes and coworkers (76) investigated the thermoxidative degradation of polyethylene and polypropylene at various oxygen pressures and temperatures. The changes in molecular weight distribution (MWD), weight average molecular weight ($\bar{M}_w$), and average number of chain scissions were measured by GPC. In the case of polyethylene at atmospheric oxygen pressure and increase of the reaction time resulted in a shift of MWD peaks towards lower molecular

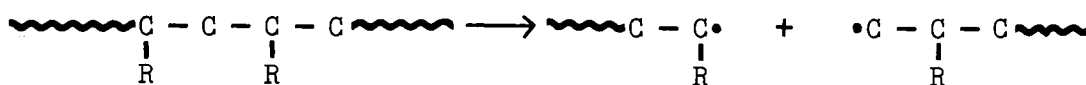
weight. This tendency become more obvious increasing temperature. At lower degradation temperatures, with an increase of reaction time, the initial, at least bimodal, distribution was gradually converted into a unimodal distribution and MWD curves showed a strongly narrowing trend. In the case of PP, the change in MWD produced a distribution much narrower and more homogeneous than for PE.

A-2. Theoretical Studies of the Degradation of Polymers

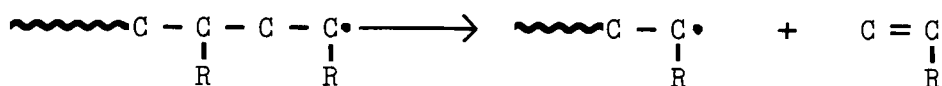
In the process of viscracking, polypropylene is exposed not only to high temperature and shear force, but also to the influence of oxygen.

The detailed mechanism and kinetics of thermal degradation of hydrocarbon polymers was developed by Simha, Wall and their coworkers (143, 165). According to these authors the pyrolysis is a radical chain reaction comprising initiation, depropagation, hydrogen transfer and termination.

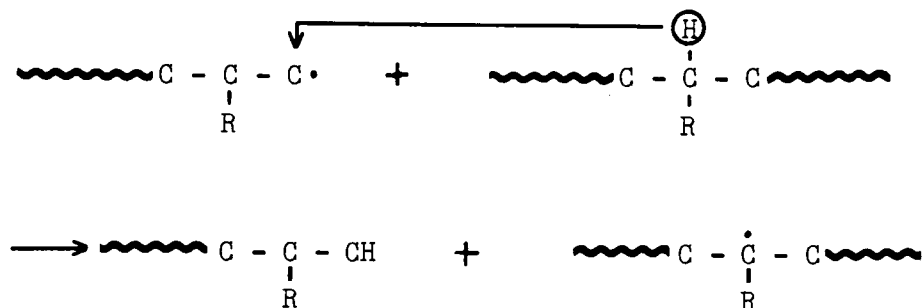
The initiation reaction is primarily the thermal cleavage of the polymer backbone into two radicals.



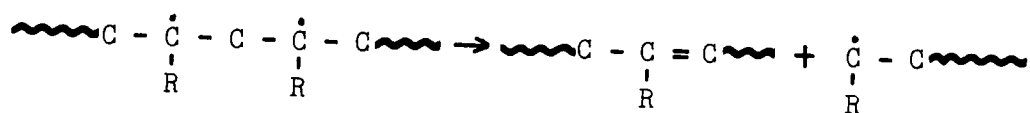
When these radicals decompose under β -scission, monomers are split off.



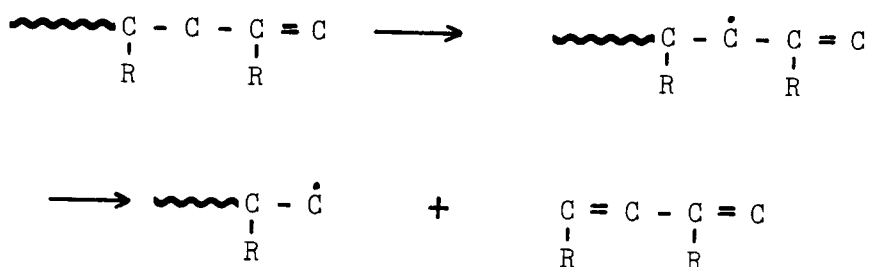
The hydrogen transfer reactions may be intermolecular or intramolecular. Intermolecular hydrogen transfer will preferentially abstract tertiary hydrogen atoms.



The radical formed may decompose, giving an α -olefin and a new radical:

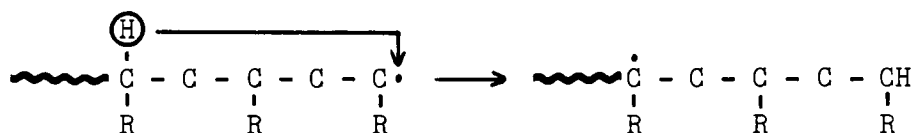


The α -methylenic hydrogen in the α -olefin is even more easily abstracted than a tertiary hydrogen and by a second intermolecular hydrogen abstraction an allyl radical may be formed, which on β -scission gives a substituted butadiene, showing up as a methyl alkane in hydrogenation.

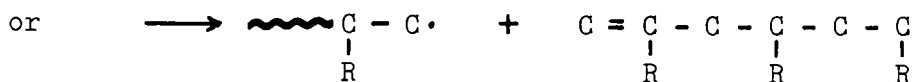
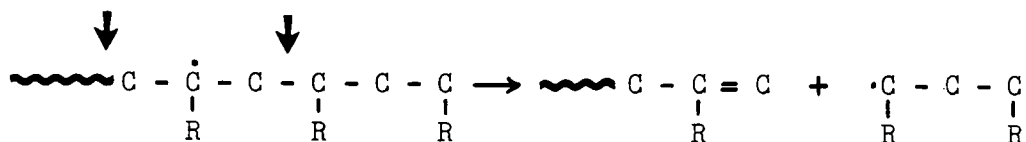


Since C - C bonds in a β -position to a double bond are appreciably weaker than normal saturated C - C bonds the α -olefin may also decompose and give a substituted allyl radical $\cdot\text{C} - \underset{\text{R}}{\text{C}} = \text{C}$, which yields a methyl alkane on hydrogenation.

Intramolecular hydrogen transfer has also been taken into consideration by Wall et al. (166) in discussing the kinetics of the pyrolysis of branched polyethylenes and other polymeric hydrocarbons. Here



The newly formed radical may then be decomposed by β -scission into volatile fragments:



Polymers for which the rate of unzipping or depropagation is high compared with the initiation and transfer reactions give a high yield of monomer on pyrolysis and volatilize to a great extent.

Later, Bailey and coworkers (6, 7), van Schooten and Evenhuis (157) and Tsuchiya and Sumi (156) have pointed out that an intramolecular hydrogen abstraction (backbiting) running parallel to the intermolecular

one must be considered in order to explain both the immediate formation of volatile material and its composition.

A statistical treatment describing the chain length distribution after a given degree of random degradation of an initially monodisperse system was developed by Montroll and Simha (117). Their treatment leads to the following equations

$$W_{t,a} = t a(1-a)^{t-1} (W_{p,o}/p) [(p-1-t)a + 2] \quad t < p \quad (2.1a)$$

$$W_{t,a} = W_{p,o} (1-a)^{p-1} \quad t = p \quad (2.1b)$$

where $W_{t,a}$ is the weight of polymer of chain length, t , existing after a degree of degradation, a , of $W_{p,o}$ grams of original polymer of chain length, p . The chain length as used here refers to the number of chain subunits joined by breakable links. The degree of degradation, a , is defined as the fraction of original links which have been broken. If the original polymer is polydisperse, contributions are made to the weight of polymer, $W_{t,a}$ of chain length, t , in the degraded material by all species in the original sample of chain length, $p \geq t$. If one assumes that there are no specific interactions between species, the weight of polymer of chain length, t , in the degraded sample can be obtained by summation over all contributing species in the original material.

$$W_{t,a} = t a(1-a)^{t-1} \sum_{p=t+1}^{p=p_m} (W_{p,o}/p) [(p-1-t)a + 2] + W_{t,o} (1-a)^{t-1} \quad (2.2)$$

Montroll (116) has derived an expression for $W_{t,a}$ for initial distributions which are sufficiently near normal to be expressible as a product of a Gaussian error function and a linear combination of the zero, first, second and third Hermite polynomial.

A-3. Stress Induced Degradation

In the processing of polymer melts, mechanical degradation must be considered as well as the thermal and oxidative degradation. The phenomenon has long been known in cis-1,4 polyisoprene.

The influence of temperature is a fundamental variable for the mechanical processes of high polymers. However, it is generally recognized that the effect of temperature in this process is not always direct, as in normal chemical reactions which increase in rate with temperature (Arrhenius equation), but is mainly indirect, involving change in the rheological properties (principally elastic and viscous), change in the physical state of the system, and consequently changes in the mechanism of rupture. Busse (20) first identified the degradation of cis-1,4 polyisoprenes with the presence of oxygen and the formation of peroxides.

Kauzman and Eyring (83) in 1940 postulated that molecules, caused to flow by high shear fields, undergo bond rupture due to mechanical forces alone to form free radicals. According to this theory, at low temperatures, large stresses are developed in the fluid owing to its high viscosity, causing mechanical bond rupture. Oxygen or other radical accepters terminate the chains. Since the viscosity decreases with temperature, the degree of degradation is reduced as the shear

strain is relieved at the molecular level. This negative temperature effect can be seen in the mastication of natural rubber. It has long been known that natural rubber mastication efficiency passes through a minimum at a temperature of approximately 115°C . Pike and Watson (132) suggested that the curve of mastication efficiency can be divided into two branches and that these branches are applied to two distinct and different processes separately important at low and high temperatures and have combined effect at temperatures near the minimum. The branch for lower temperature represents the efficiency due to mechanical degradation and that for higher temperature is caused by oxidative degradation. The negative temperature coefficient has been considered as a prime criterion of a mechanochemical reaction by Casale, Porter and Johnson (22).

The softening of polymer system on rising the temperature results in the imposition of less shear energy at a given shear rate, and consequently, in a reduction in reaction and a higher critical molecular weight below which rupture will not occur. At lower temperatures, thermal motion is reduced, the relaxation process is slower, and the disentangling process is longer. As a result of these effects, reaction rate in mechanically induced degradation is higher at lower temperatures (21). As postulated by Bestul (12), the probability that a chain bond will get the activation energy for rupture is the sum of the mechanical and thermal energy contributions. At lower temperatures, the thermal contribution is negligible, while the opposite is true at higher temperatures.

B. THEORETICAL STUDIES ON RHEOLOGICAL BEHAVIOR OF POLYMER MELTS

B-1. Theory of Viscoelastic Fluid

Polymeric melts exhibit a combined behavior of the properties of elastic solid and of Newtonian fluid and show not only viscous but also elastic responses or memory effects to applied stresses. They are thus viscoelastic fluids. The responses of the viscoelastic fluid depend on the time scale of the experiment. If the rate of deformation is larger than that of relaxation, the material generally behaves more like an elastic solid and if the deformation rate is smaller, they behave more like a viscous liquid. This rate dependent response is one of the most important features of the viscoelastic fluid.

B-1-a. Constitutive Equation

The theory of viscoelasticity, which originated in Maxwell's one dimensional model for small strains, has been generalized to three dimensional large strain models (13, 15, 60, 65, 98). These generalized constitutive equations are of two types: differential models which relate the stress tensor to deformation as a differential equation, and integral type models which represent the stress response to the integrated deformation history.

The total stress tensor is usually divided into two parts.

$$\underline{\sigma} = - p \underline{I} + \underline{P} \quad (2.3)$$

where p is a hydrostatic pressure and $\underline{P}$ is an extra stress tensor associated with deformation.

The historical development of the differential type constitutive equation is based on Maxwell's equation (98).

$$P + \tau \frac{dP}{dt} = G \tau \frac{d\gamma}{dt}, \quad G \tau = \eta \quad (2.4a.b)$$

where P is the stress, γ is the strain, G is the elastic modulus, and τ is the relaxation time. This is the simplest viscoelastic fluid model in one dimensional linear form. In this model the viscosity η is $G\tau$ which is independent of the deformation rate. Phenomena such as normal stresses do not exist in such a one dimensional theory.

The first generalization of equation (2-4) in three dimensional form was first done by Zaremba in 1903 (186). He suggested that Maxwell's equation represents the behavior in a coordinate system which translates and rotates with the fluid. Zaremba considered a rigid embedded coordinate system. His constitutive equation is of form

$$\underline{P} + \tau \frac{\partial \underline{P}}{\partial t} = 2G \tau \underline{d} \quad (2.5a)$$

where

$$\frac{\partial \underline{P}}{\partial t} = \frac{\partial \underline{P}}{\partial t} + \underline{V} \cdot \nabla \underline{P} - \nabla \underline{W} \cdot \underline{P} - \underline{P} \cdot (\nabla \underline{W})^T \quad (2.5b)$$

$\underline{d}$ is the deformation rate tensor

$$\underline{d} = \frac{1}{2} \left[\nabla \underline{V} + (\nabla \underline{V})^T \right] \quad (2.5b)$$

and $\underline{w}$ is the vorticity tensor

$$\underline{w} = \frac{1}{2} \left[\nabla \underline{V} - (\nabla \underline{V})^T \right] \quad (2.5c)$$

Zaremba's equation predicts non-Newtonian viscosity and normal stresses in simple shear flow. In 1950, Oldroyd (124) proposed a coordinate system which translates, rotates and deforms with the fluid as the convected coordinate system. Oldroyd developed a differential model similar to the Maxwell's formulation. In succeeding years, other generalizations of non-linear Maxwell type equation were developed by Noll (122), White and Metzner (171), Williams and Bird (175) and Spriggs and Bird (144, 145).

When one tries to apply these constitutive equations for various flow problems, one encounters a number of difficulties. First, the stress can not be expressed exactly except for the simplest flows. Secondly, they contain too many material constants to be used in practical problems. The expression developed by White and Metzner (171) is the simplest but still describes many important features of the non-linear viscoelastic behavior at large deformations. This has a form

$$\underline{P} + \tau \frac{\delta \underline{P}}{\delta t} = 2G \tau \underline{d} \quad (2.6a)$$

where

$$\frac{\delta \underline{P}}{\delta t} = \frac{\partial \underline{P}}{\partial t} + \underline{V} \cdot \nabla \underline{P} - \nabla \underline{V} \cdot \underline{P} - \underline{P} \cdot (\nabla \underline{V})^T \quad (2.6b)$$

is the Oldroyd contravariant convective derivative. The relaxation time, τ , is considered as a function of the second invariant of the deformation rate tensor, $\underline{d}$.

$$\tau(\text{II}_{\underline{d}}) = \tau(\text{tr } \underline{d}^2) \quad (2.7)$$

Ide and White (73, 74) and Minoshima, White and Spruiell (112, 114, 172) have used a form of τ following Bogue (14, 15, 26).

$$\tau = \frac{\tau_0}{1 + a \tau_0 \text{II}_{\underline{d}}^{\frac{1}{2}}} \quad (2.8)$$

where τ_0 is the zero deformation rate relaxation time and "a" is a material parameter which represents the deformation rate dependence.

Integral theories are based on Boltzmann's superposition principle (17) which represents the stress response to a series of infinitesimal strains.

$$\underline{P}(t) = \sum_i G(t-t_i) \Delta \underline{Y} = \int_{-\infty}^t G(t-s) \frac{d\underline{Y}}{ds} ds \quad (2.9)$$

where $G(t)$ is a relaxation modulus at time t , $\underline{Y}$ is the infinitesimal strain tensor and s is the time. The above equation can be rewritten as

$$\underline{p}(t) = \int_{-\infty}^t \phi(t-s) \underline{\gamma}(s) ds \quad (2.10a)$$

where

$$\phi(t) = - \frac{d G(t)}{dt} \quad (2.10b)$$

This formulation is equivalent to a Maxwell model (Eq. 2.2) if:

$$G(t) = G e^{-t/\tau} \quad (2.11)$$

$$\phi(t) = \frac{G}{\tau} e^{-t/\tau} \quad (2.12)$$

More generally we may write

$$\phi(t) = \sum_i \frac{G_i}{\tau_i} e^{-t/\tau_i} = \int_{-\infty}^{\infty} \frac{H(\tau)}{\tau} e^{-t/\tau} d \ln \tau \quad (2.13)$$

The first generalization to finite strains was given by Oldroyd (125) and more specifically by Lodge (91). At about same time Yamamoto (183, 184, 185) and Lodge (92, 93) developed non-linear generalization of Boltzmann's equation based on network theories of flexible polymer chains. A general constitutive theory accounting for non-linear effects was developed by Green and Rivlin (57) presuming that the stress is general hereditary functional of the deformation history. An equivalent but more elegant formulation of the Green and Rivlin concept has been given by Noll (122) and later by Coleman and Noll (29). The stress on an incompressible material can be expressed as a functional of strain

history

$$\underline{P} = \underline{F} \left[\underline{e}(t-s) \right]_{s=-\infty}^{s=t} \quad (2.14)$$

Here $\underline{e}(t)$ is a strain tensor which measures deformation from the present state to some past time. This may be taken as the Finger strain tensor.

$$e_{ij} = \frac{1}{2} \left[c_{ij}^{-1} - \delta_{ij} \right] = \frac{1}{2} \left[\frac{\partial x_i}{\partial X_m} \frac{\partial x_j}{\partial X_m} - \delta_{ij} \right] \quad (2.15)$$

where x_i is the instantaneous state and X_m is the position of material at time, s . The F functional of Eq.(2-14) may be expressed by a Frechet expansion of the functional yielding a multi-integral form. If the kernel functions of the multiple integrals are products of a single relaxation function and Dirac delta function, the multi-integral form may be simplified to a single integral theory using the Cayley-Hamilton theorem as follows: (see White and Tokita (1974))

$$\begin{aligned} \underline{P}(t) = \int_{-\infty}^t & \left[a_1(t-s, I_e, II_e) \underline{e}(s) \right. \\ & \left. + a_2(t-s, I_e, II_e) \underline{e}^2(s) \right] ds \end{aligned} \quad (2.16)$$

Here relaxation moduli $a_1(t-s, I_e, II_e)$ and $a_2(t-s, I_e, II_e)$ are dependent on time and deformation invariants, $I_e = \text{tr } \underline{e}$ and $II_e = \text{tr } \underline{e}^2$. Single integral constitutive equations are often written in the equivalent form:

$$\underline{P}(t) = \int_{-\infty}^t \left[m_1(t-s) \underline{c}^{-1}(t-s) - m_2(t-s) \underline{c}(t-s) \right] ds \quad (2.17)$$

where $\underline{c}^{-1}$ is the Finger deformation tensor and $\underline{c}$ is the Cauchy deformation tensor.

$$c_{ij}^{-1} = \frac{\partial x_i}{\partial X_m} \frac{\partial x_j}{\partial X_m} \quad (2.18)$$

$$c_{ij} = \frac{\partial X_m}{\partial x_i} \frac{\partial X_m}{\partial x_j} \quad (2.19)$$

The memory function $m_1(t-s)$ and $m_2(t-s)$ have been variously taken as dependent upon the invariants of $\underline{c}^{-1}$, $\underline{c}$, $\underline{d}$, or $\underline{P}$. Many constitutive equations of this type have been proposed. Bernstein, Kearsley and Zapas (BKZ) equation forms a strain energy motivation in memory functions (10).

$$m_1(t-s) = 2 \frac{\partial U}{\partial I_{\underline{c}^{-1}}} \quad (2.20a)$$

$$m_2(t-s) = 2 \frac{\partial U}{\partial II_{\underline{c}^{-1}}} \quad (2.20b)$$

where U is the rate of strain energy production and $I_{\bar{C}}$ and $II_{\bar{C}}$ are the first and the second invariants of the Finger deformation tensor.

Wagner (163, 164) proposed a constitutive equation whose memory function is a product of the memory function of Lodge's rubber-like liquid theory and a damping function of the invariant of the Finger deformation tensor. His expression is

$$m_1(t-s, I_{\bar{C}}, II_{\bar{C}}) = m_0(t-s) h(I_{\bar{C}}, II_{\bar{C}}) \quad (2.21a)$$

$$m_2 = 0 \quad (2.21b)$$

where $h(I_{\bar{C}}, II_{\bar{C}}) \leq 1$ is called the damping function, and $m_0(t-s)$ is identical with the rubber-like liquid memory function.

Another important form of the memory function of this type of constitutive equation has been proposed by Bogue (14) and later modified by Bogue and White (15). These forms have been successfully tested by Chen and Bogue (26), Chen et al. (27), Takaki and Bogue (151), Furuta, Lobe and White (46) and Ide and White (73, 75) in a wide range of experiments on polyethylene, polystyrene and polypropylene melts. These forms are:

$$m_1(t-s) = \left(1 + \frac{\epsilon}{2}\right) \sum_i \frac{G_i}{\tau_{ieff}} e^{-t/\tau_{ieff}} \quad (2.22)$$

$$m_2(t-s) = -\left(\frac{\epsilon/2}{1 + \epsilon/2}\right) m_1(t-s) \quad (2-23)$$

where G_i are the relaxation moduli, ϵ is a constant, and τ_{ieff} are the effective relaxation times dependent upon time averaged invariants of the rate of deformation suggested by Bogue (26).

$$\tau_{ieff} = \frac{\tau_i}{1 + a \tau_i \langle II_d^{\frac{1}{2}} \rangle} \quad (2.24)$$

$$\langle II_d^{\frac{1}{2}} \rangle = \frac{1}{z} \int_0^z (2 \operatorname{tr} \underline{d}^2)^{\frac{1}{2}} dz \quad (2.25)$$

where $z = t - s$ is the back running time from the present.

B-2. Behavior of Polymer Melt in Some Flow Fields

B-2-a. Simple Shear Flow

i. General

The most widely studied basic flow is simple shear flow.

For simple shear flow, the imposed kinematics can be written as

$$\underline{v} = [v_1(x_2), 0, 0] \quad (2.26)$$

where "1" denotes the flow direction, "2" the normal direction, and "3" the neutral direction. This includes a flow in a long tube (Poiseuille flow), flow between coaxial cylinders (Couette flow) and flow between two plates or plate and cone. The stress tensor can be represented as follows

$$\sigma_{12} = \eta \dot{\gamma} \quad (2.27a)$$

$$N_1 = \sigma_{11} - \sigma_{22} = \Psi_1 \dot{\gamma}^2 \quad (2.27b)$$

$$N_2 = \sigma_{22} - \sigma_{33} = \Psi_2 \dot{\gamma}^2 \quad (2.27c)$$

where $\dot{\gamma}$ is the shear rate dv_1/dx_2 , η the shear viscosity, N_1 the principal and N_2 the second normal stress differences and Ψ_1 the principal and Ψ_2 the second normal stress difference coefficients. The constitutive equations of the previous subsection are able to predict stress fields. For the differential type constitutive equations such as the Zaremba model

$$\eta = \frac{\eta_0}{1 + \tau \dot{\gamma}^2} \quad (2.28a)$$

$$N_1 = \frac{2\eta_0 \tau \dot{\gamma}^2}{1 + \tau \dot{\gamma}^2} \quad (2.28b)$$

$$N_2 = -\frac{1}{2} N_1 \quad (2.28c)$$

and the White-Metzner model

$$\eta = G \tau(\dot{\gamma}) \quad (2.29a)$$

$$N_1 = 2G \tau^2 \dot{\gamma}^2 \quad (2.29b)$$

$$N_2 = 0 \quad (2.29c)$$

For the single integral constitutive equation

$$\eta = \int_0^{\infty} z \left[m_1(z) + m_2(z) \right] dz \quad (2.30a)$$

$$N_1 = \Psi_1 \dot{\gamma}^2 = \dot{\gamma}^2 \int_0^{\infty} z^2 \left[m_1(z) + m_2(z) \right] dz \quad (2.30b)$$

$$N_2 = \Psi_2 \dot{\gamma}^2 = \dot{\gamma}^2 \int_0^{\infty} z^2 m^2(z) dz \quad (2.30c)$$

The shear viscosity is well known as a decreasing function of shear rate for polymer melts and solutions. Less rheological data are available for N_1 , N_2 , Ψ_1 and Ψ_2 .

At low shear rates, the stress field can be represented by the theory of second order fluids (29, 122). The principal normal stress difference can be written according to this theory as

$$N_1 = \Psi_{10} \cdot \dot{\gamma}^2 = 2 \text{ Je} \cdot \sigma_{12}^2 \quad (2.30)$$

where Ψ_{10} is the principal normal stress difference coefficient as

$$\Psi_{10} = 2 \text{ Je} \eta^2 \quad (2.31)$$

and Je is the steady state compliance.

Generally N_1 should be proportional to the square of shear stress at low shear stress. Oda, White and Clark (123) found that the first normal stress difference, N_1 , in commercial polystyrene melts is a unique function of shear stress, independent of temperature and molecular weight.

Several reserchers have investigated the relative magnitude of the second normal stress difference, N_2 , generally finding it to be negative and of the order of one tenth of N_1 (48, 108, 153). Sakamoto and Porter (140) have attempted to measure N_1 and N_2 independently using cone- and prallel-plate instruments and have found N_2 to be zero within experimental error. Han and Charles (61, 62) have reported large positive values of N_2 for melts based on capillary experiments,

but later (63) they have backed from this and argued that N_2 is negative. Lee and White (89) experimentally determined N_1 and N_2 in a Weissenberg rheogoniometer using cone- and parallel-plate geometries. They found that the mean N_2 function is negative and about 0.1 ~ 0.3 the value of N_1 . Similar magnitudes are found for polymer solutions.

ii. Experimental Studies

The most studied and well documented rheological property is the shear viscosity. The shear viscosity function, $\eta(\dot{\gamma})$, is found in polymer melts to be a constant η_0 at low shear rates and decreases at high shear rates. The viscosity decreases with increasing temperature and increases with molecular weight and the non-Newtonian character becomes more pronounced. In the low molecular weight region, $M < M_c$, the viscosity linearly depends on the molecular weight, and shows Newtonian behavior. In the high molecular weight region, $M > M_c$, the viscosity depends on both molecular weight and shear rate, and shows non-Newtonian behavior (10, 114, 133, 147). The transition point, which is referred to as the critical molecular weight, M_c , is sometimes called the entanglement transition and considered to represent the molecular weight at which entangling of the flexible polymer chain occurs.

The influence of molecular weight distribution on viscosity-shear rate behavior has received considerably study. Generally broadening molecular weight distribution increases deviations from Newtonian flow at low shear rates (66, 114, 133). To quantitatively examine the effect of molecular weight distribution on linear polymers, a method of data reduction is required. Porter et al. (133) proposed reduced

plots of η/η_0 as a function of shear stress σ_{12} multiplied by absolute temperature and reduced by concentration (for solutions). Later, Vinogradov and Malkin (158) plotted a relative viscosity, η/η_0 , against a relative stress, $\eta\dot{\gamma}$, for many polymer systems. This procedure gives a temperature independent universal plot, but there is some scatter. Following Vinogradov and Malkin's procedure, Minoshima et al. (114) found that the relative viscosity is only function of the molecular weight distribution but not the molecular weight nor the temperature. They showed that η/η_0 for broad molecular weight distribution polymers fall off more rapidly than for narrow molecular weight distribution polymers. The narrow molecular weight distribution polymers show after first exhibiting a slow decrease in η/η_0 , a sudden rapid decrease.

Investigations of the influence of molecular weight and its distribution on the first normal stress difference, N_1 , and the first normal stress difference coefficient, Ψ_1 , have been reported from the University of Tennessee group (114, 123, 170). White and Kondo (170) reported that Ψ_1 varies with about the 6th power of molecular weight for polystyrene at a shear rate of 1 sec^{-1} . They surmise that at very low shear rates where both Ψ_1 and η are constants Ψ_{10} is proportional to the square of η_0 . This suggests that Ψ_{10} depends on about 7th power of molecular weight.

Oda, White and Clark (123) have shown that the N_1 depends on shear stress, σ_{12} , through a power law which is independent of temperature and molecular weight but not the molecular weight distribution. They indicated that the broader the molecular weight distribution the higher N_1 and the lower $d \log N_1 / d \log \sigma_{12}$, i.e., the

values for monodisperse PS are 2.0 and those for commercial PS are 1.58 to 1.73. This was confirmed for polypropylenes by Minoshima et al.(114). Racin and Bogue (137) showed that there are distinct trends with molecular weight distribution, with the exponent in $N_1 = A \sigma_{12}^b$ varying from about 1.8 for narrow molecular weight distribution samples to about 1.4 to 1.6 for broad molecular weight distribution ones.

Ψ_{10} is related to J_e through Eq. (2-31). In the low molecular weight region J_e is small. Above the critical molecular weight J_e is constant for monodisperse polymer (2, 109, 110, 126, 135, 136). The elastic properties of broad molecular weight distribution system show more complicated effects (14, 95, 110, 135, 136), especially in blended system. Mills and Nevin (108, 109) and Mieras and van Rijn (107) from normal stress measurements found that the steady state compliance is proportional to the 3.7th power of $\bar{M}_z/\bar{M}_w$. Minoshima et al.(112, 114) have correlated characterized PS data by dynamic experiments and normal stress measurements found that steady state compliance is proportional to the 3.5th power of $\bar{M}_z/\bar{M}_w$ and the first normal stress difference is to the 3.5th power of $\bar{M}_z \cdot \bar{M}_w$.

B-2-b. Uniaxial Elongational Flow

i. General

Polymeric liquid and melts can be deformed by tensile stresses as well as by the more conventional shear stress. The occurrence of elongational flow in polymer processing operations as melt spinning, film casting and tubular blown film extrusion makes it an important area of study.

The kinematics of simple uniaxial elongational flow can be expressed by

$$\underline{v} = [v_1(x_1), v_2(x_2), v_3(x_3)] \quad (2.32)$$

with $v_2(x_2) = v_3(x_3)$. The rate of deformation tensor takes the following form after applying the continuity equation:

$$\underline{d} = \frac{1}{2} \left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right] = \begin{vmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{vmatrix} \quad (2.33)$$

where $E = \partial v_1 / \partial x_1$ is the elongational rate. If the elongational rate is constant with time, the cylinder deforms according to

$$L(t) = L(0) e^{Et}, \quad R(t) = R(0) e^{-E/2 \cdot t} \quad (2.34)$$

where L is the filament length and R is its radius.

The stress field in a stretching filament may be expressed as

$$\underline{\sigma} = -p \underline{I} + \begin{vmatrix} P_{11} & 0 & 0 \\ 0 & P_{22} & 0 \\ 0 & 0 & P_{33} \end{vmatrix} \quad (2.35)$$

A true elongational viscosity can be defined

$$\chi = \frac{\sigma_{11}}{E} \quad (E = \text{constant}) \quad (2.36a)$$

and the transient elongational viscosity is

$$\chi(t) = \frac{\sigma_{11}(t)}{E} \quad (2.36b)$$

As early as 1906, Trouton (155) showed that the elongational viscosity of Newtonian fluid is three times the shear viscosity in his study of tensile stretching of Newtonian filaments as well as continuous gravity spinning. This result is equivalent to Young's modulus for an incompressible solid being three times the shear modulus.

Since there were often difficulties in measuring the elongational viscosity under controlled kinematics, various methods of elongational viscosity measurements have been developed for highly viscous melts from the mid 1960's. Ballman (8) observed transient stress build-up for a PS melt setting the elongational rate constant and showed that the elongational viscosity remained constant and its magnitude is around three times zero shear viscosity, although the shear viscosity decreases with shear rate. Constant stress measurements of elongational viscosity have also been reported by Cogswell (28) and Munstedt (118). A creep experiment using a constant force coupled with a cam to make it respond as a constant stress is utilized. The apparatus of Cogswell involves a filament being extended vertically on top of bath, while that of Munstedt involves a vertical sample immersed in a bath. Meissner (99,

100, 101, 102, 103)), using his constant elongational rate apparatus for low density polyethylene (LDPE) and high density polyethylene (HDPE), observed slow stress build-up to a steady state at low elongational rates. At high elongational rates, LDPE showed unbounded stress growth, while HDPE did not. Vinogradov et al. (159), Stevenson (148), Ide and White (74, 75) and Minoshima, White and Spruiell (112, 114) observed similar behavior in other polymers including polyisobutylene, polyisoprene, PS, polymethyl methacrylate (PMMA), LDPE, HDPE and polypropylene (PP). PS resembled LDPE and PP resembled HDPE.

In 1952 ~ 4, Yamamoto (176, 177, 178, 179, 180, 181, 182) described the nonlinear character of the elongational viscosity. Considering the structural viscosity of concentrated solutions of chain polymers, he treated this cause as the result of the network formation due to physical entangling among the chain polymers, and showed that, depending upon the constitutive equation used, the elongational viscosity first increases with elongational rate and then either goes to infinity at finite elongational rate or decreases after exhibiting a maximum. It was, however, pointed out by Denn and Marrucci (31) that the infinite stress indicates a never achievable steady state and one should rather consider the transient stress build-up. Later Chen, Hagler, Abbott, Bogue and White (27), Takaki and Bogue (151), Ide and White (73, 74, 75) and Wagner (164) experimentally and theoretically described transient stress development in polymer melts using material parameters obtained from shear experiments.

Generally, nonlinear viscoelastic constitutive equations are tested using shear experiments. The behavior of polymer melts in

elongational flow also should be predicted by these constitutive equations. Chang and Lodge (24) applied the Lodge fluid to describe Meissner's stress build-up data at least semiquantitatively using relaxation parameters obtained by fitting a small elongational rate experiment.

Later Chen et al. (27), Takaki and Bogue (151) and Ide and White (75) described transient stress based upon the material parameters obtained in shear experiments using the Bogue-White model with τ_0 taken as zero. Ide and White (73, 75) also compared their experimental results with the White-Metzner model which has a relaxation time defined by Eq. (2-8) using the material parameters obtained in shear experiments and stress relaxation experiments. There was good agreement between experimental data and predictions, even in the one time constant White-Metzner model. Minoshima, White and Spruiell (112, 114), comparing their experimental data, studied the relationship between steady state elongational viscosity and the time average deformation dependent relaxation in the prediction by the White-Metzner model. They suggested that this relationship is due to the value of the deformation rate softening parameter, "a". It may be shown that using a relaxation time of form defined by Eq. (2-8)

$$\frac{\chi}{3\eta_0} = \frac{\sqrt{3} a \tau_0 E + 1}{[(\sqrt{3} a - 2) \tau_0 E + 1][(\sqrt{3} a + 1) \tau_0 E + 1]} \quad (2.37)$$

(1) $0 \leq "a" \leq 0.3 \sim 0.6$, X is a monotonous increasing function of elongational rate. At low elongational rates, X is equal to $3\eta_0$. At τ_{eff}^E of $1/2$, X reaches infinity. (2) $0.3 \sim 0.6 \leq "a" \leq 2\sqrt{3}$, shows a minimum value, and then monotonously increases to infinity at τ_{eff}^E of $1/2$. (3) $"a" = 2\sqrt{3}$, X monotonously decreases from $3\eta_0$ to $2\eta_0$ and does not show unbounded stress. (4) $"a" > 2\sqrt{3}$, X monotonously decreases from $3\eta_0$.

ii. Failure Phenomena

Studies of stability on uniaxial elongational flow considering nonlinear viscoelastic behavior of polymer melts were initiated by Chang and Lodge (24) and Ide and White (73, 74, 75). The latter authors distinguish three types of mechanism of failure of filaments. These are, (1) capillarity, defects propagated by surface tension, (2) ductile failure, growth of necks and gradual thinning down due to higher stresses causing elevated local deformation rates, and (3) catastrophic failure due to a brittle or cohesive fracture when the applied stress exceed the tensile strength.

Ide and White (74, 75, 169) and Minoshima et al. (114) have studied the failure mechanism of different types of commercial polymer melts. Low density polyethylenes generally pull out in uniform filaments and eventually fail by catastrophic "brittle fracture". Commercial polystyrene filaments also commonly exhibit catastrophic failure. Commercial high density polyethylenes and polypropylenes exhibit necking and ductile failure.

Ide and White (73, 74, 75, 169) showed in a stability analysis based on the White-Metzner model that for large $"a"$ the defects grow

and ductile failure results. The relaxation time, τ , was given by expression similar to Eq. (2-8) where τ depends on II_d through a parameter "a". They reported that filament stability and elongation to break depend on $\tau_0 E$ and "a". At small "a", stability increases with increasing $\tau_0 E$ while for "a" $> 1/\sqrt{3}$, stability decreases with increasing $\tau_0 E$. For smaller "a", ductile failure can occur for small $\tau_0 E$, but cohesive fracture should be the case of failure at large $\tau_0 E$.

iii. Molecular Structure Effects

Studies of the effect of molecular parameters on the rheological response of polymer melts in elongational flow have been strongly related to instabilities and failure studies.

Ide and White (73, 74, 75, 169, 168) and Minoshima, White and Spruiell (112, 114) have studied the failure mechanisms of different types of commercial polymer melts. LDPE generally pulled out in uniform filaments and eventually fail by catastrophic "brittle" fracture. Commercial PS filaments also exhibit catastrophic failure as do narrower molecular weight distribution polypropylene (112, 114).

It would appear that necking and ductile failure are associated with a decreasing elongational viscosity function. This is enhanced by broadening the molecular weight distribution of linear polymers and by addition of particles. It is inhibited by introducing long chain branching as in LDPEs and narrowing of molecular weight distribution. These results were explained by Ide and White's (73, 74), and Minoshima, White and Spruiell's interpretation (112, 114) and by deformation rate dependent relaxation time.

Steady state elongational viscosities have been measured on PS, LDPE, narrow molecular weight distribution PP and some other systems. The PS may be considered as a linear narrow molecular weight distribution melt. The LDPE has long chain branching. At low deformation rates, η is a constant $3\eta_0$. At higher deformation rates, it becomes an increasing function of stretch rate. The broad molecular weight distribution melts do not achieve steady states. The maximum transient elongational viscosity of these systems is a decreasing function of stretch rate.

C. THE EFFECT OF MOLECULAR STRUCTURE ON RHEOLOGICAL BEHAVIOR

C-1. Shear Flow

C-1-a. Theoretical Studies of Shear Flow

By analogy with rubber elasticity, entanglement effects have been considered theoretically in terms of a temporary cross-linked network. Green and Tobolsky (56) considered the properties of rubber like network in which the junctions are being continually broken and reformed. They showed that under certain circumstances the stress could be expressed as a function of the strain history. Later, Yamamoto (176, 177, 178, 179, 180, 181, 182) and Lodge (90) showed that a wide range of properties of flowing polymer melts could be described quantitatively through the concept of a transient network of flexible random coil elements, the junction points being specifically identified as chain entanglement.

Another type of theory is based on the friction or bead spring

model which originated in dilute solution theories. Bueche (19) proposed a first model for the extra frictional drag conferred by entangling interactions and used it to calculate the molecular weight dependence of melt viscosity for linear chains. Bueche, using a modified model, recalculated zero shear viscosity, η_0 , and obtained a result equal to the empirical relation, η_0 is proportional to the 3.5th power of weight average molecular weight (39, 44, 53, 112, 114, 170).

Different molecular theories for the viscoelastic behavior in the entanglement region, based on chain slippage, were proposed by Graessly (50, 52). Using this theory, Graessly and Segal (54) found that the shear rate dependence of the viscosity can be reasonably predicted not only for narrow molecular weight distribution samples but also for blended systems.

Doi and Edwards (33, 34, 35, 36) used DeGennes theory of primitive chains. The real chain wriggles around the primitive chain within a distance, a (the diameter of the DeGennes tunnel). The primitive chain is a sequence of discrete steps, each represented by a vector, $\underline{r}$. The vector, $\underline{r}$, may be considered as the end to end vector of the subchains. Doi and Edwards assumed that all subchains behave as Gaussian chains. Their final form of the constitutive equation is similar to the BKZ equation (Eq. 2-17 to 2-20).

$$\sigma_{ij} = -p \delta_{ij} + \int_{-\infty}^t m'(t-s) Q_{ij}(\underline{E}(t-s)) ds \quad (2.38)$$

where $\underline{E}$ is the deformation gradient tensor, and $m'(t-s)$ and $Q_{ij}(\underline{E})$ are the function of time, t , and tensor, $\underline{E}$, respectively.

D. PROCESSING

D-1. Extrudate Swell

When polymer solutions and melts emerge from dies, the fluid generally swells to a diameter "d" greater than the diameter "D" of the holes from which it emerged. We speak of extrudate swell

$$B = d/D \quad (2.39)$$

Nickell et al. (121) and Tanner (154) carried out a numerical solution using finite element methods for the case of Newtonian creeping flow. They predicted the extrudate swell of 1.13 for long tubes.

Extrudate swell is observed to increase with extrusion rate and die wall shear rate. For a given shear rate, the extrudate swell decreases as the length to diameter ratio of the capillary increases (5, 18, 138). The reason for this is because much of the molecular orientation in capillary flow actually is the result of the elongational flow in the entrance region to the capillary and not as a result of the shear deformation within the capillary. At a constant shear rate, the extrudate swell often tends to decrease somewhat as the temperature is raised.

When extrudate swell and the first normal stress difference for polystyrene melts are plotted against shear stress, the curves do not depend on the temperature, the elastic property being seen here is independent of temperature (55, 60, 105).

Several investigators (55, 58, 60, 112, 115, 106, 135, 160, 161, 162) have systematically studied well characterized materials of narrow molecular weight distribution and their blends, as well as commercial samples. Since the rheological properties of polymer melts depend on molecular parameters, such as molecular weight, its distribution and the degree of branching, one may expect that the extrudate swell would also depend on these parameters. Vlachopoulos and coworkers (161, 162) and Racine and Bogue (137) using well characterized polystyrene samples and their blends, and Minoshima et al. (115) using well characterized polypropylene samples found that the extrudate swell is strongly dependent on the molecular weight distribution and that the broader the molecular weight distribution, the larger the extrudate swell at the same shear stress. The extrudate swell generally increases as the molecular weight increases at the same shear rate and temperature. However, some contradictory results have also been reported. Mendelson and Finger (105, 106) reported that the extrudate swell of high density polyethylene decreases with broadening molecular weight distribution or increasing molecular weight. They also reported that long chain branching in polyethylene caused a reduction in elasticity and that linear polymers have higher elastic deformability than branched polymers with the same molecular weight.

Various expressions have been proposed for correlating extrudate swell. In most cases researchers have considered a fully developed flow. There are two distinct types of models: the elastic type and viscoelastic type. In the elastic type model the energy stored in the polymer melt is released in a solid like recovery. To this group belong

the expressions of Nakajima and Shida (119), Bagley and Duffey (4), Graessley et al. (54), Vlachopoulos et al. (162), Mendelson et al. (104) and Funatsu and Mori (45). The key early paper of the theory which involves unconstrained elastic recovery of a viscoelastic fluid model has been developed by Tanner (152). Using a nonlinear integral constitutive equation containing c^{-1} only and with a Maxwellian relaxation function, he obtained

$$B = \left\{ \frac{\int_0^R (N_1 + G - \sigma_{12}/G) r \, dr}{\int_0^R G r \, dr} \right\} \quad (2.40)$$

where G is the modulus. If G is constant:

$$B = \left[1 + \frac{1}{2} \left(\frac{N_1}{2 \sigma_{12} w} \right)^2 \right]^{\frac{1}{6}} = \left[1 + \frac{1}{2} \left[\bar{\tau}(\gamma) \cdot \gamma \right]_w^2 \right]^{\frac{1}{6}} \quad (2.41)$$

This equation reveals a strong dependence of $\left(\frac{N_1}{2 \sigma_{12}} \right)$ on B compared with the elastic theories. Since it is well known that B approaches a value of about 1.10 for creeping flow (55, 162), Tanner suggested a modification of Eq. (2.41) by a simple additive correction :

$$B = \left[1 + \frac{1}{2} \left(\frac{N_1}{2 \sigma_{12}} \right)^2 \right]^{\frac{1}{6}} + 0.1 \quad (2.42)$$

Racin and Bogue (137) showed that the low stress asymptote extrudate swell is about 1.1 in the case of narrow molecular weight distribution PS, is more than this in the case of broad molecular weight distribution PS and Eq. (2-42) apparently modified to

$$B = \left[1 + \frac{1}{2} \left(\frac{N_1}{2\sigma_{12}} \right)^2 \right]^{\frac{1}{6}} + C \quad (2.43)$$

where C is the extrudate swell correlation at a shear stress or shear rate at zero.

White and Roman (173) developed a modified formulation of Tanner's theory where the melt recovers from Poiseuille flow into a state of uniaxial flow. They found that the swell decreases rapidly with increasing applied take-up force. They also found that the frozen extrudate swell data and melts extruded into air account for theory reasonably well but the annealed and isothermal data are much higher.

Huang and White (70) presented a comparative experimental and theoretical study for the extrudate swell and dies of various geometries such as slit, capillary, rectangular and trapezoidal dies, and length. They found that at low die wall shear rates the swell of homogeneous melts goes to a value of about 1.2 for slit dies as opposed to about 1.1 for capillary dies and that the swell from a short die of $L/D = 0$ is greater than the swell from long dies.

D-2. Steady State Spinline Behavior

D-2-a. Isothermal Melt Spinning

A force balance for a fiber spinline was first developed by Ziabicki (190). The forces acting on the spinline include the applied tension, F_L , the vertical downward force of gravity, F_{grav} , the force due to frictional air drag, F_{drag} , and force due to surface tension, F_s . If we make a balance between the take-up roll and an arbitrary position on the spinline, the rheological force, F_{rheo} , acting to deform the descending fiber is the resultant of the applied forces, and momentum fluxes.

$$F_L + F_{\text{grav}} - F_{\text{drag}} - F_s - F_{\text{rheo}} = Q(V_L - V_1) \quad (2.44)$$

In the force balance equation, inertia and surface tension forces are generally small. Gravitational and frictional drag forces tend to counterbalance each other; the former is important at low take-up velocities and the latter at high take-up velocities. The take-up force is approximately equal to rheological force over a wide range of take-up velocities, that is

$$\sigma_{11}(x_1) = \frac{4F_L}{\pi d^2(x_1)} = \frac{F_L}{Q} V_1(x_1) \quad (2.45)$$

where $d(x_1)$ is the diameter of fiber at an arbitrary position, x_1 , and Q is the volumetric flow rate.

The steady state spinline dynamics away from the extrudate swell region were first considered by Ziabicki and Kedzierska (188, 189) who made a detailed analysis for isothermal case where the fluid has constant properties along the spinline. They predicted an exponential velocity distribution for the case of a constant elongational viscosity.

There have been more extensive investigations of modelling for viscoelastic fluids. The earliest study of this type is probably that of Matovich and Pearson (96) for a second order fluid. A more realistic modelling for viscoelastic fluids was given by Acierno, Dalton, Rodriguez and White (1) who used a nonlinear integral model. This was extended by Chen, Hagler, Abbott, Bogue and White (27) using a Bogue-White model. These studies involved numerical solutions and related diameter profiles to spinline tensions. Zeichner (187) in his unpublished MS thesis, presented an analysis of the isothermal spinline for a convected Maxwell model and gave an analytical solution for this problem. The efforts of Zeichner were extended in succeeding years by Denn, Petrie and Avenas (32). Analyses for a convected Maxwell model with a deformation rate dependent relaxation time have been reported by Fisher and Denn (40, 41, 42, 43) and by White and Ide (73, 169). White and Ide (169), taking the relaxation time to be given by the function of Eq. (2-8), showed that the shape of the spinline velocity profile is strongly affected by the "a" parameter. For small "a" the spinline velocity tends to be linear.

D-2-b. Non-isothermal Melt Spinning

The simplest consistent theory of non-isothermal melt spinning is that published by Kase and Matsuo (80, 81). They combined a one

dimensional Newtonian fluid model for the spinline with only applied take-up forces acting with a one dimensional energy balance with forced convection heat transfer. Hamana, Matsui and Kato (59) presented more concise formulation of the non-isothermal melt spinning problem which includes air drag, gravitation and momentum flux forces assuming the melt behaves as a Newtonian fluid.

Lamonte and Han (88) made a significant improvement in the model of Hamana et al. by including non-Newtonian effects on the spinline elongational viscosity. The use of differential viscoelastic models to analyze non-isothermal melt spinning was initiated by Fisher and Denn (43). These authors used a special form of the convected Maxwell model developed by Marrucci (94) from considerations of the rheological behavior of systems of dumbbell molecules. They also described detailed calculations for the spinline velocity and temperature profile dependent upon the heat transfer.

Modelling of non-isothermal melt spinning using a viscoelastic integral model was by Matsui and Bogue (97). They considered both flow in the spinneret and in the spinline as well as accounting for temperature variations in polymer properties. Matsui and Bogue compared their theory to a set of experimental results and had good agreement.

D-3. Unstable Melt Spinning

Melt spun filaments are generally non-uniform exhibiting a fluctuating diameter along their length. These diameter fluctuations may be due to heterogeneities or forced oscillations of the system induced by temperature, extrusion rate, or tension variations. True

instabilities, in the sense of hydrodynamic instabilities, also occur which give rise to a periodically fluctuating diameter of high amplitude known as draw resonance.

D-3-a. Theoretical Studies of Unstable Melt Spinning

Theoretical analyses of the mechanism of draw resonance were by Kase, Matsuo and Yoshimoto (83), Pearson and Matovich (128) and Gelder (47). These analyses were carried out for isothermal melt spinning of a Newtonian fluid. They performed a linear perturbation analysis combining force and continuity balances in the absence of inertial, gravitational and surface tension effects, all of which may usually be neglected for melt spinning, and it was shown that the spinline becomes unstable to infinitesimal perturbations at a critical draw ratio of 20.21, beyond which steady spinning can not be maintained.

A different approach was made by Hyun (71, 72), based on the competition between a throughput wave velocity and the actual material velocity. He predicted a critical draw ratio 19.74 instead of 20.21.

The influence of non-Newtonian rheological characteristics in the stability of isothermal melt spinning was considered by Shah and Pearson (141), Ishihara and Kase (77), Zeichner (187), Fisher and Denn (42), White and Ide (168) and Chang and Denn (23). The work of Shah and Pearson (141) and Ishihara and Kase (77) concerns power law fluids and commonly shows that the spinline becomes more stable as the power law exponent increases. Zeichner (187) considered the stability of a spinline for a constant relaxation time convected Maxwell model and found that the stability increased with $\tau V_1/L$, the Weissenberg number.

Fisher and Denn reported a stability analysis for a convected Maxwell model with a variable relaxation time based on a power law representation. They showed the critical draw ratio dependent on the power law exponent, n , and a viscoelastic parameter, α , defined as

$$\alpha = \frac{3^{\frac{n-1}{2}} K}{G} \left(\frac{V_0}{L} \right)^n \quad (2.46)$$

where V_0 is the velocity at the maximum extrudate swell and L is the length of the melt zone. It is found that decreasing n or making the relaxation time, τ , decreases more rapidly with deformation rate (equivalent to a larger Yamamoto number) makes the spinline unstable.

White and Ide (73, 169) and later Minoshima, White and Spruiell (112, 115) argue that draw resonance in a spinline is the analogue of ductile failure of an extending filament.

The influence of spinline temperature gradient was modelled by Shah (64), Kase (79), Pearson, Shah and Mhaskar (129) and Fisher and Denn (43) using a range of rheological models. While Shah and Pearson, and Kase considered Newtonian fluid models, Han et al. made calculations for a viscous non-Newtonian fluid and Fisher and Denn for a convected Maxwell model. For the Newtonian case, decreases in the ratio $T(\text{air})/T(\text{melt})$ increases the stability of the spinline, provided that extreme Stanton numbers, N_{st} , are avoided. The Stanton number is defined as

$$N_{st} = \frac{h}{\rho C_p V} \left(\frac{L}{D} \right) \quad (2.47)$$

where h is the heat transfer coefficient at thread surface, ρ is the density of polymer melt, C_p is the specific heat of melt, D is the diameter of fiber at spinneret, V is the thread velocity at spinneret, and L is the spinline length. Solidification of samples stabilize the spinline even in a high Stanton number region.

Fisher and Denn (43) have solved the same problem for a viscoelastic fluid represented by a convected Maxwell model with temperature dependent properties. They also found that the cooling of the spinline is stabilizing and the critical draw ratio increases with increasing Stanton number.

D-3-b. Experimental Studies of Unstable Melt Spinning

Ishihara and Kase (77) have studied the onset of draw resonance in polyethylene terephthalate (PET) under isothermal condition and found that is at a value of V_L/V_0 about 20 which is what should be expected for a melt with non-Newtonian properties.

Minoshima, White and Spruiell (112, 115) in a series of well characterized polypropylene found that narrowing the molecular weight of polypropylenen stabilizes the spinline. Comparative studies on a range of different polymer melts are reported by White and Ide (169). The ordering observed by White and Ide, and Minoshima et al. in order of the value of the critical draw ratio was

CHAPTER III

MATERIALS AND EXPERIMENTAL PROCEDURES

A. MATERIALS

The materials used in this study are Hercules polypropylene, Profax 6823, Shell polybutene-1, 1600SA, and Phillips high density polyethylene, Marlex 6009. These are listed in Table III-1.

These samples were heated in the barrel of an Instron Capillary Rheometer at several conditions under which degradation would occur. These conditions are listed in Table III-2. The polymers were then extruded. During the extrusion the apparent shear rate was 2.87 sec^{-1} . Following this treatment 0.1 weight percent of butylate hydroxytoluene (BHT) was added as stabilizer.

Weight average molecular weight of the degraded polypropylene samples were measured by Ube Industrial Cooperation using Gel Permeation Chromatography. These are listed in Table III-2.

B. EXPERIMENTAL PROCEDURES

B-1. Shear Flow Measurements

Rheological Measurements were carried out at 180°C and 200°C on a Rheometrics Mechanical Spectrometer using a cone-plate mode in the low shear rates and on an Instron Capillary Rheometer in the higher shear rate range.

The cone-plate apparatus was used to measure the shear stresses, σ_{12} , and the first normal stress differences, N_1 . The cone has a

Table III-1. Polymers Used in the Experiments

Polypropylene

Hercules Polypropylene Profax 6823

MFI 0.33

Density 0.902

Polybutene-1

Shell Polybutene-1 1600A

High Density Polyethylene

Phillips High Density Polyethylene Marlex 6009

MFI 0.9

Table III-2. Conditions of Thermal Treatment

Polymer	Temperature	Time	$\bar{M}_w$
PP	no treatment	-	6.84×10^5
	260°C	0.5 hr	5.44×10^5
	260°C	1.0 hr	5.14×10^5
	260°C	1.5 hr	4.54×10^5
	280°C	0.5 hr	4.16×10^5
	280°C	1.0 hr	3.29×10^5
	280°C	1.5 hr	2.93×10^5
	300°C	0.5 hr	2.13×10^5
	300°C	1.0 hr	1.54×10^5
	300°C	1.5 hr	-
PB-1	no treatment		
	240°C	1.0 hr	
	260°C	1.0 hr	
	280°C	1.0 hr	
HDPE	no treatment		
	240°C	1.0 hr	
	260°C	1.0 hr	
	280°C	1.0 hr	

diameter of 25 mm and a 0.1 radian cone angle. The shear stress and the first normal stress difference are determined by measuring the torque, T , and the thrust force, F . To obtain the shear stress and the first normal stress difference the following equation developed for this geometry was used (15, 30).

$$\gamma = \Omega/a \quad (3.1)$$

$$\eta = \sigma_{12}/\dot{\gamma} = \frac{3T}{\dot{\gamma} 2 \pi R^3} \quad (3.2)$$

$$N_1 = \sigma_{11} - \sigma_{22} = \frac{2F}{\pi R^2} \quad (3.3)$$

where Ω is the angular velocity of the cone, a is the cone angle, T is the torque, F is the thrust force, and R is the radius of the cone. Sheet samples to be placed in the gap were prepared on a hot press at 200°C.

In the higher shear rate region an Instron Capillary Rheometer was used to measure the shear viscosity. A close-fitting plunger was driven through the barrel at constant speed between 5.08×10^{-2} cm/min. to 50.8 cm/min. extruding the melt through a capillary die fixed to the bottom of the barrel. By recording the plunger force from the load cell and knowing the plunger speed, a total pressure drop and volumetric flow rate are obtained.

The basic theory of measurement of viscosity of a fluid in a capillary rheometer was developed by Weissenberg (15, 37, 38).

$$\Delta P_{\text{total}} = \Delta P_{\text{end}} + 4(\sigma_{12})_w \frac{L}{D} \quad (3.2a)$$

$$\gamma_w = \left(\frac{3n' + 1}{4n'} \right) \frac{32 Q}{\pi D^3} \quad (3.2b)$$

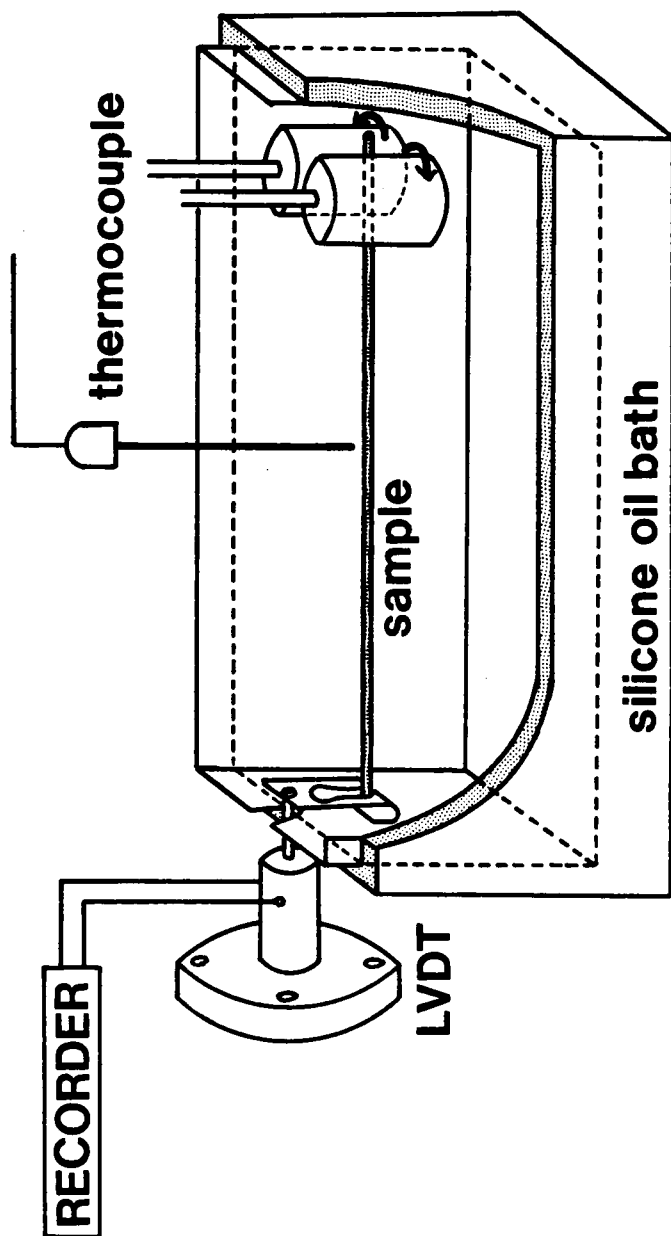
$$n' = \frac{d \log \left(\frac{32 Q}{D^3} \right)}{d \log (\sigma_{12})_w} \quad (3.2c)$$

where Q is the flow rate, L is the length of capillary, and D is the diameter of capillary.

Capillaries of diameter 1.47 mm were used to measure the total pressure drop. The L/D ratios were 10, 20, 30 and 40.

B-2. Elongational Flow Measurement

Elongational viscosity measurements were carried out on a constant elongational rate rheometer recently built by W. Minoshima, Y. Suetsugu and the author. It consists of a constant temperature silicone oil bath which is controlled by a heater and a temperature controller, an transducer, and a take-up system (Figures III-1 and III-2). The transducer used is a linear variable differential transformer (LVDT) (FTA-G-50, Schaevitz Co., Pennsauken, N.J.). The take-up system has two rotating gears which have been used by Meissner (99, 100, 101, 102, 103). These gears prevent the slippage of the sample, and make the region of elongation clear. These gears were driven by a motor



ELONGATIONAL RHEOMETER

Figure III-1. Schematic Diagram of the Elongational Flow Apparatus

a) Overall View of the Apparatus

b) Close Up View of the Sample Clamp and the Take Up Rolls

Figure III-2. Experimental Set Up of Constant Elongational Stretching

with a controller. Two motors were used in this study, one (1/15 Hp., B and B motor, 1.6 r.p.m.) for low speeds, and the second (1/15 Hp., B and B motor, 12 r.p.m.) for high speeds. The motor speed was controlled by a controller. A stretch rate range of $5.10 \times 10^{-3} \text{ sec}^{-1}$ to $1.68 \times 10^{-1} \text{ sec}^{-1}$ was obtained. The silicone oil used was Dow Corning 200 fluid with a kinematic viscosity of 100 centistokes.

Filament samples were prepared by extrusion with a Brabender single screw extruder (C. B. Brabender Co. 3/4 in. diameter and $L/D = 10$). Dies with diameter of 3 mm and L/D of 11.5 was used. The extrusion speed was usually 10 r.p.m. and the semi-solidified filament was taken up at almost the same velocity as at die exit to avoid stretching and orienting the samples. For each material, the measured diameter of the filaments at room temperature was corrected to 200°C using specific volume temperature data and a shrinkage factor.

The filament was attached between LVDT and the gears. After thermal equilibration in the silicone oil bath was reached, the filament was stretched by the rotating gears.

The elongational rate, E , is determined by

$$E = \frac{1}{L} \frac{dL}{dt} = \frac{V_L}{L} \quad (3.3)$$

In the present experiment, deformation length, L , and rotation speed, V_L remain constant with time, t , thus providing constant stretch rate conditions. As long as the filament deforms uniformly, the tensile stress, $\sigma_{11}(t)$, and the (apparent) elongational viscosity, $\chi(t)$, can be determined by

$$\sigma_{11}(t) = \frac{4 F(t)}{\pi d_o^2} \exp (Et) \quad (3.4a)$$

$$\chi(t) = \frac{\sigma_{11}(t)}{E} \quad (3.4b)$$

where $F(t)$ is the total force, and d_o is the diameter before stretching.

B-3. Observation of Failure of Stretched Filaments

The filament samples were prepared by extrusion with an Instron Capillary Rheometer. The solidified extrudates were given two notches. Then the samples were inserted into a hot silicone oil bath at 200°C for polypropylene and at 180°C for polybutene-1, and subsequently removed and stretched.

B-4. Extrudate Swell Measurement

Extrudate swell measurements were carried out using the Instron Cappollary Rheometer at 200°C for polypropylene and at 180°C for polybutene-1. A die with L/D of 53.88 and the diameter of 0.74 mm was used to obtain extrudate swell. The polymer melt was extruded into a 2.54 cm inner diameter by 7.62 cm long heated chamber shown in Figure III-3. Two sets of heaters were used to heat the chamber and were controlled by a two temperature controller with the control thermocouples at 0.64 cm and 3.18 cm from the die exit. This chamber has two glass windows so that the extrudate can be observed. The photographs of extrudate were taken from one of these windows when the extrudate became 2.54 cm length. The resulting slides were enlarged by a slide projector. The diameter of the extrudates were measured at 1.0 cm from

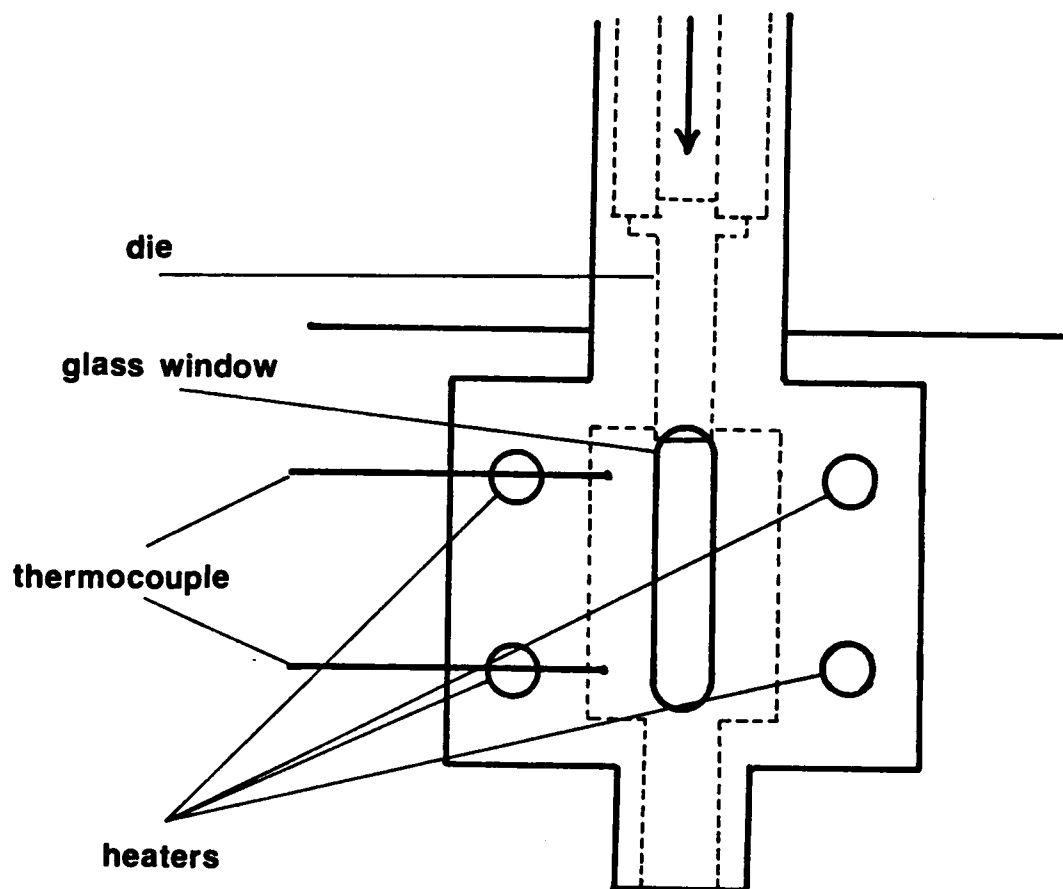


Figure III-3. Schematic Diagram of the Isothermal Chamber for Extrudate Swell Measurements

the initially extruded end.

Since the atmosphere in the heated chamber was kept at the same temperature as that of the polymer melt, the thermal expansion correction was not required.

B-5. Measurements of Diameter Profile and Spline Elongational Viscosity

Isothermal melt spinning experiments were carried out using an Instron Capillary Rheometer in order to measure the elongational viscosity. The polymer melt was extruded at 200°C through a die of diameter of 7.37 mm and L/D ratio 53.88. The extrudate passed into a heated chamber which was used in the extrudate swell measurement and finally into a water quench bath of shown in Figure III-4. The diameter of the take-up roll was 8.8 cm which was driven by a 1/15 Hp. B and B motor (12 r.p.m. maximum speed). The take-up velocity was chosen as 2.3 cm/sec and flow rate was always $1.508 \times 10^{-3} \text{ cm}^3/\text{sec}$. A Rothschild tensiometer (4g full scale) was placed near the take-up device. The calibration procedure to obtain the spline tension followed Minoshima (112). The measured tension was recorded by a Strip Chart Recorder (Model EV-205-11, Heath Co., Benton Harbor, Mich.) and a potentiometric amplifier (Model EV-200-01, Heath Co.)

Photographs were taken to measure the changing diameter along the spline. Bright spot lights were located on the both side of the camera. The resulting slides were enlarged by a slide projector in order to make measurements of the diameter profile by comparing the spline with a reference scale.

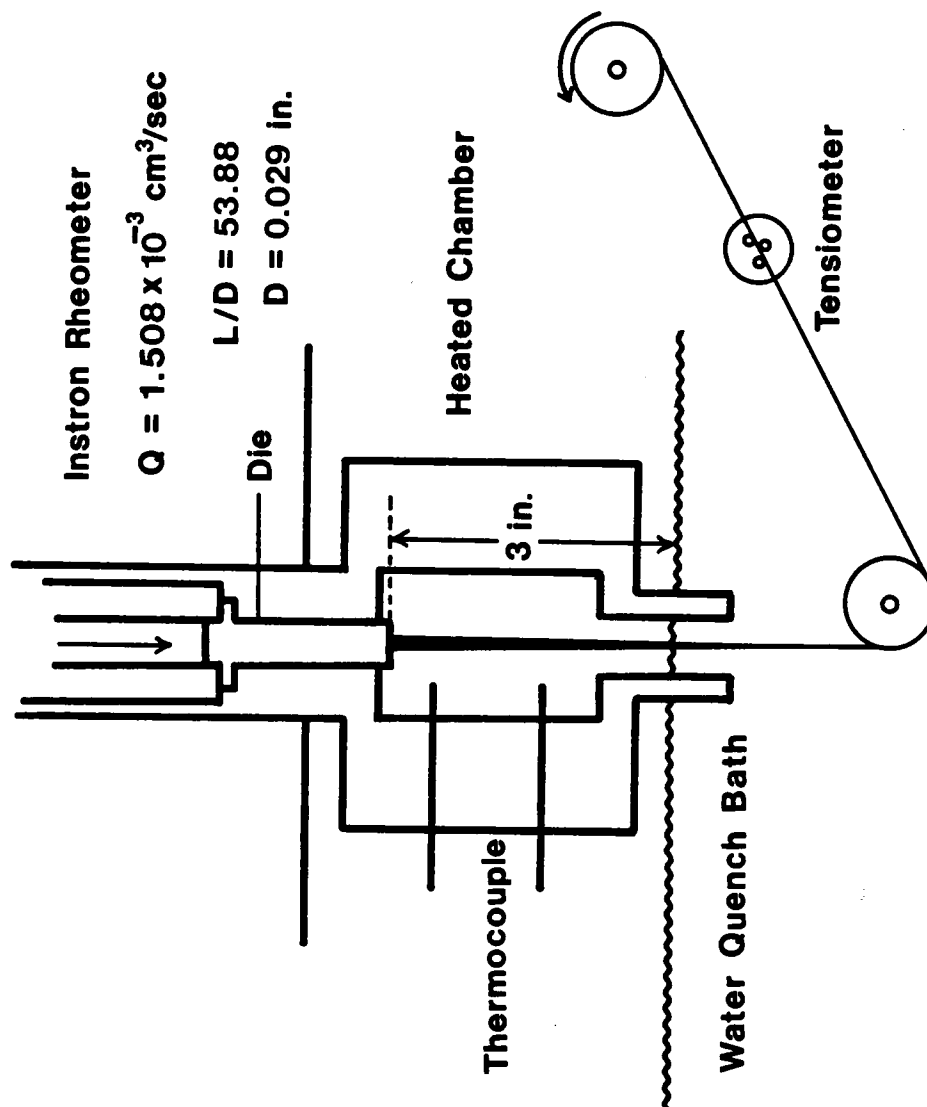


Figure III-4. Schematic Diagram of the Isothermal Chamber for Isothermal Melt Spinning

The spinline elongational viscosity, χ_{sp} , can be calculated from

$$\chi_{sp} = \frac{F_{rheo}/A(x)}{dV_1(x)/dx} \quad (3.5a)$$

$$V_1(x) = \frac{Q}{\pi[r(x)]^2} \quad (3.5b)$$

where F_{rheo} is the actual force, $A(x)$ is a cross sectional area of the fiber, $V_1(x)$ is the longitudinal velocity of fiber, r is the radius of the fiber, and Q is the volumetric flow rate.

B-6. Melt Spinning Instability under Isothermal Condition

The experimental set-up and conditions, except for take-up speed, were exactly the same as those for spinline elongational viscosity measurement. The occurrence of variation of diameter along the fiber was detected by tension measurement. The variation of diameter along fiber was measured directly with a thickness gage.

CHAPTER IV

SHEAR FLOW RHEOLOGICAL MEASUREMENTS

In this chapter, the steady shear viscosity, η , and the first normal stress difference, N_1 , are discussed.

A. STEADY SHEAR VISCOSITY

A-1. Results

In Figure IV-1, the changes of the zero shear viscosity of untreated and thermally treated polypropylene (PP), polybutene-1 (PB-1), and high density polyethylene (HDPE) as a function of degradation temperature are shown. The zero shear viscosity of the PP and PB-1 decrease with the extent of thermal treatment. The effects on HDPE are minor but seem to indicate a viscosity increase. Figure IV-2 shows a similar plot for PP as a function of treatment time at 260°C, 280°C and 300°C. The viscosity decrease increases with increasing temperature and time.

The steady shear viscosity of untreated and thermally treated PP measured at 180°C and 200°C as a function of shear rate are presented in Figures IV-3 and IV-4. In Figure IV-5, similar plots for PB-1 measured at 180°C are shown. Both PP and PB-1 exhibit a strong and similar dependence on the thermal treatment condition.

A-2. Discussion

A-2-a. Degradation vs Temperature and Time

If the thermal treatment involves chain scission, the process makes the molecular weight lower. With increasing treatment temperature

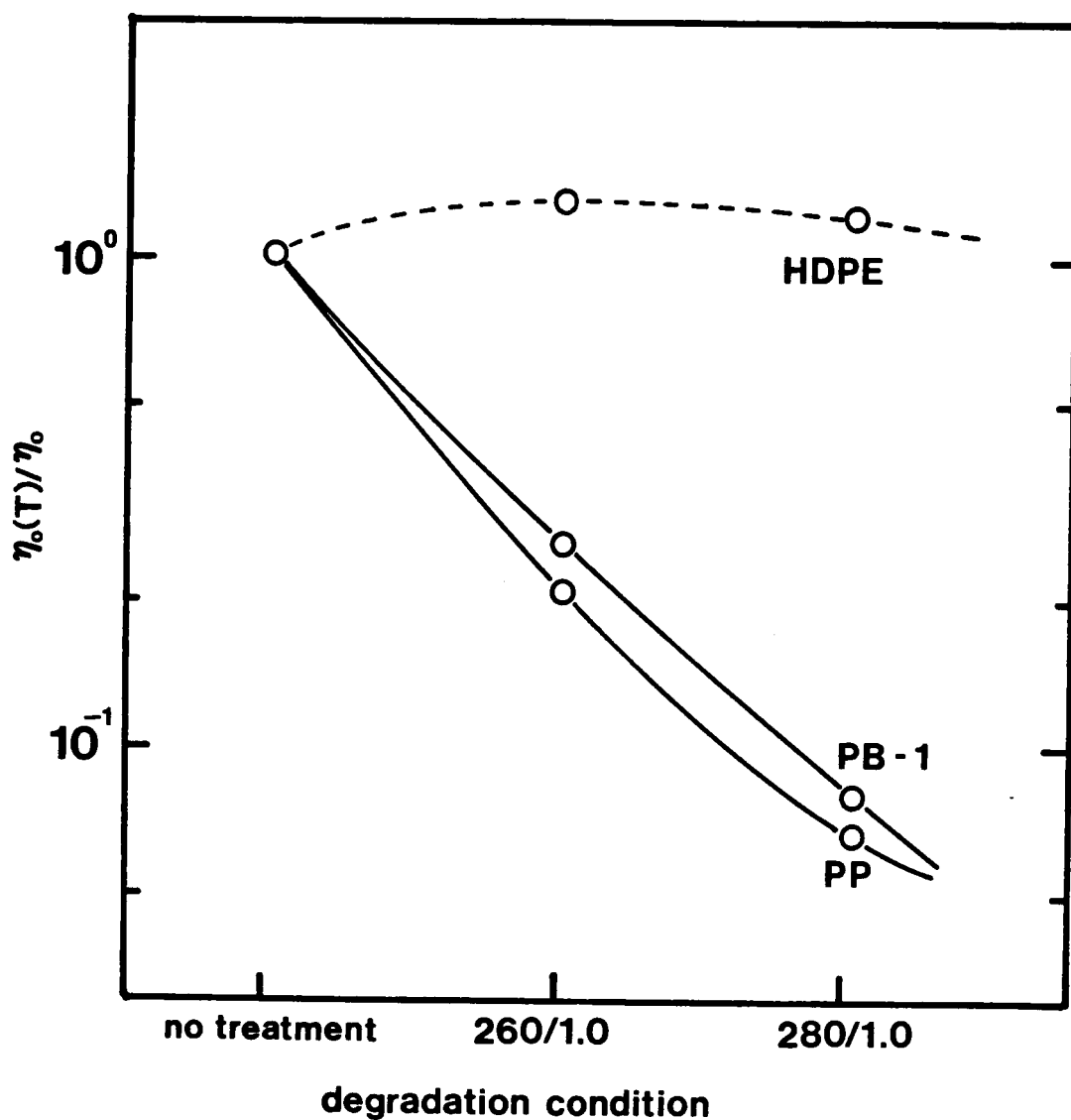


Figure IV-1. Comparisons of Thermal Treatment on Zero Shear Viscosity (η_0) of HDPE, PP and PB-1

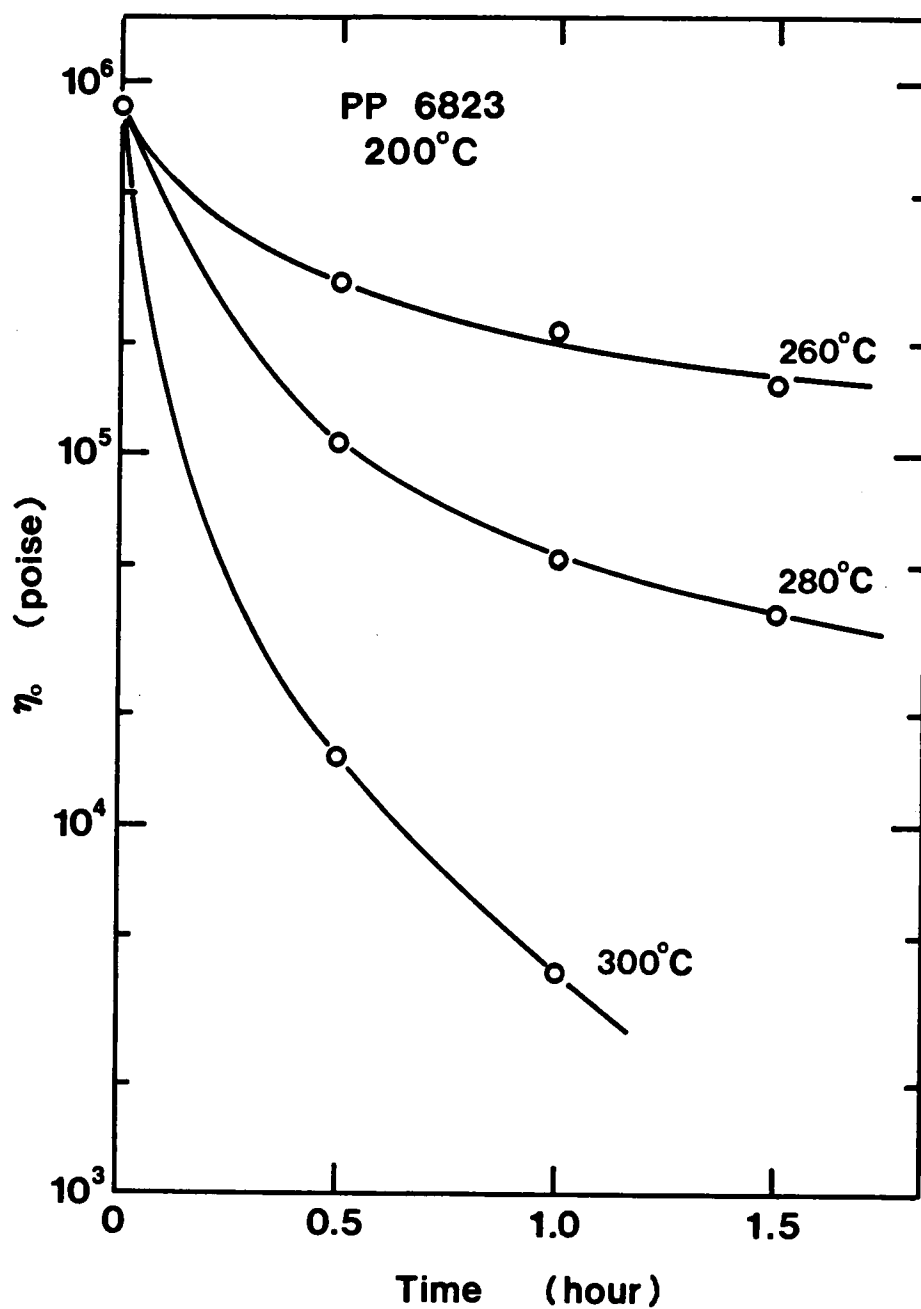


Figure IV-2. Changes of Zero Shear Viscosity (η_0) as a Function of Treatment Time at 260°C, 280°C and 300°C for PP

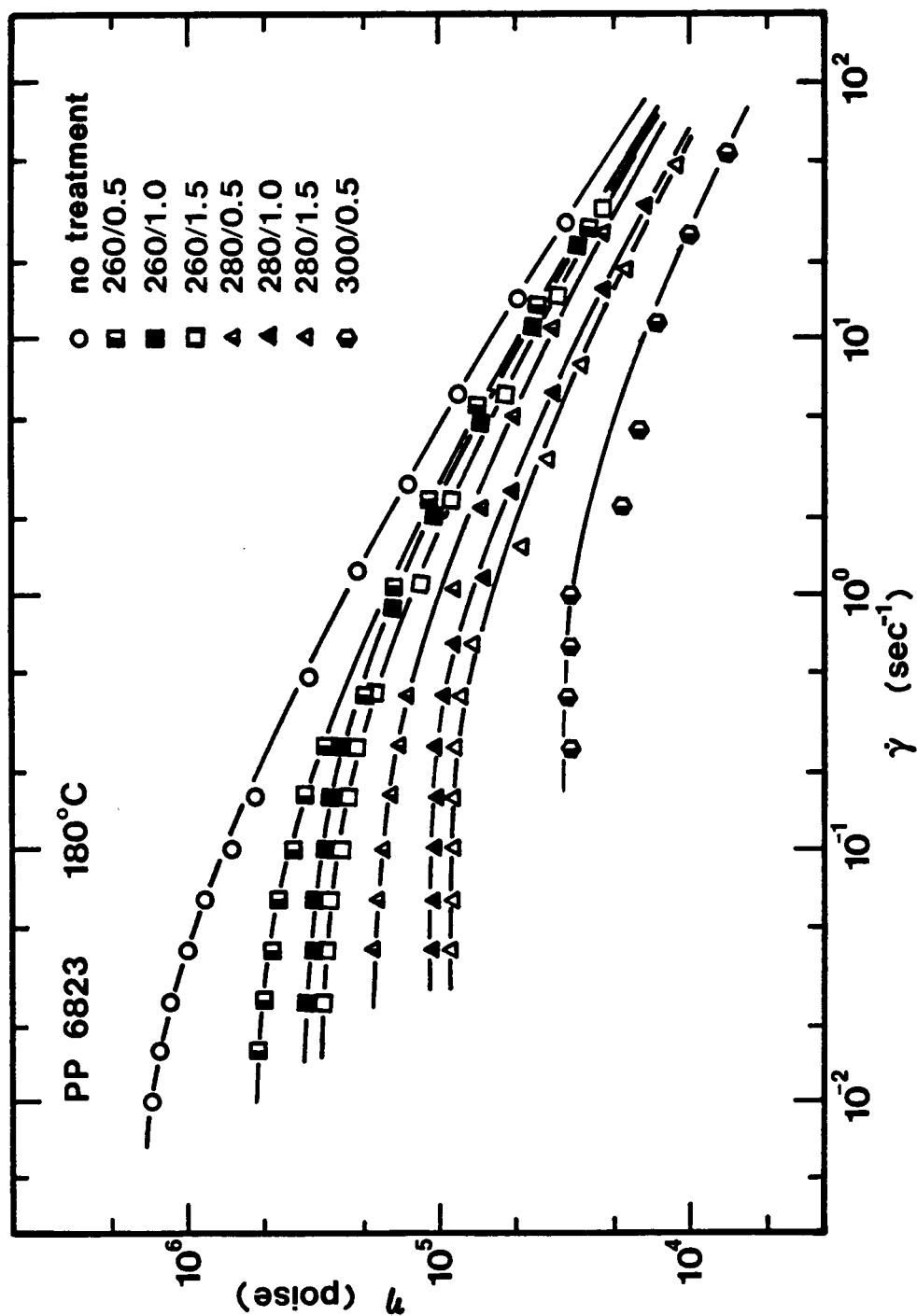


Figure IV-3. Viscosity (η) - Shear Rate ($\dot{\gamma}$) Behavior of Untreated and Thermally Treated PP Measured at 180°C

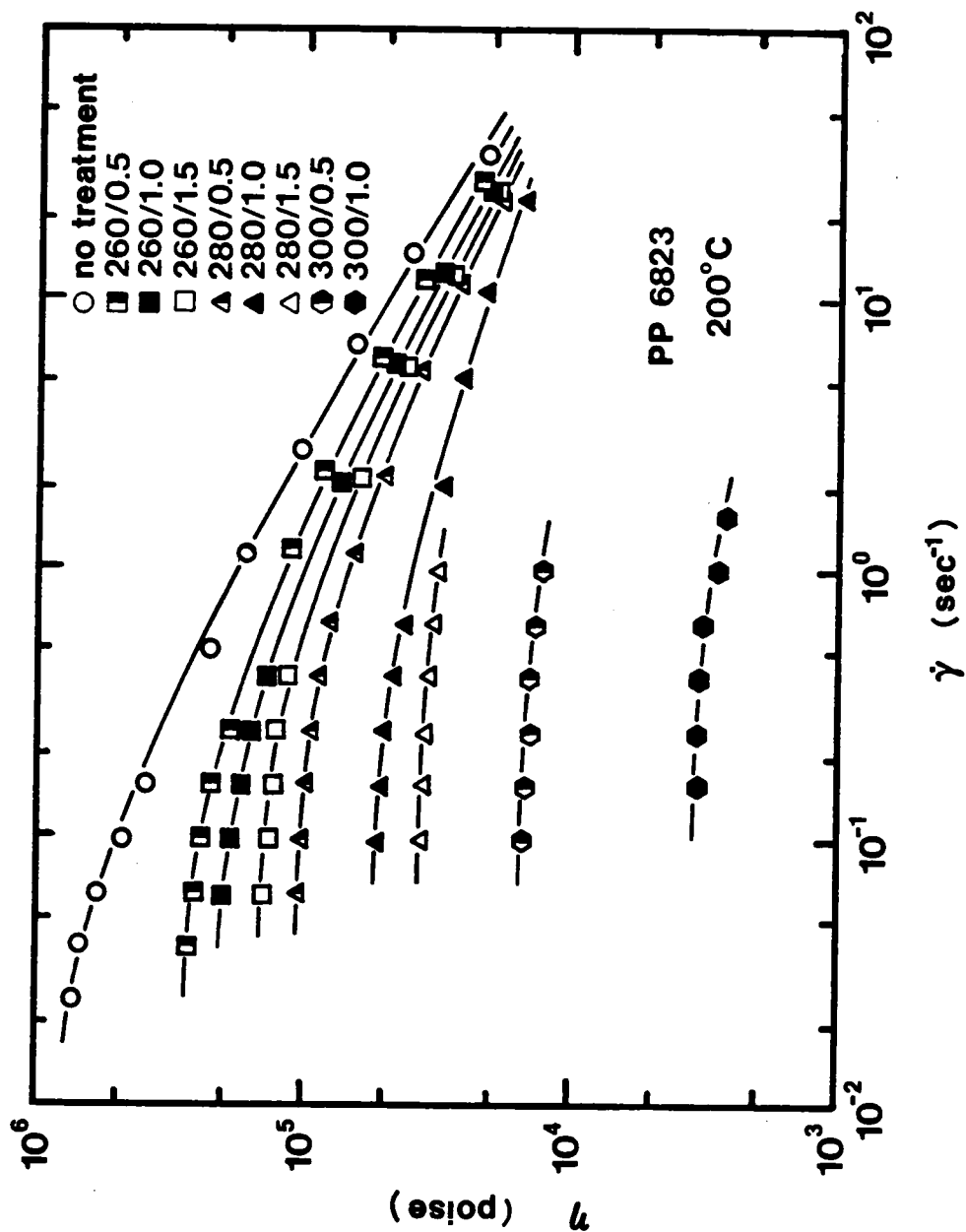


Figure IV-4. Viscosity (η) - Shear Rate ($\dot{\gamma}$) Behavior of Untreated and Thermally Treated PP Measured at 200°C

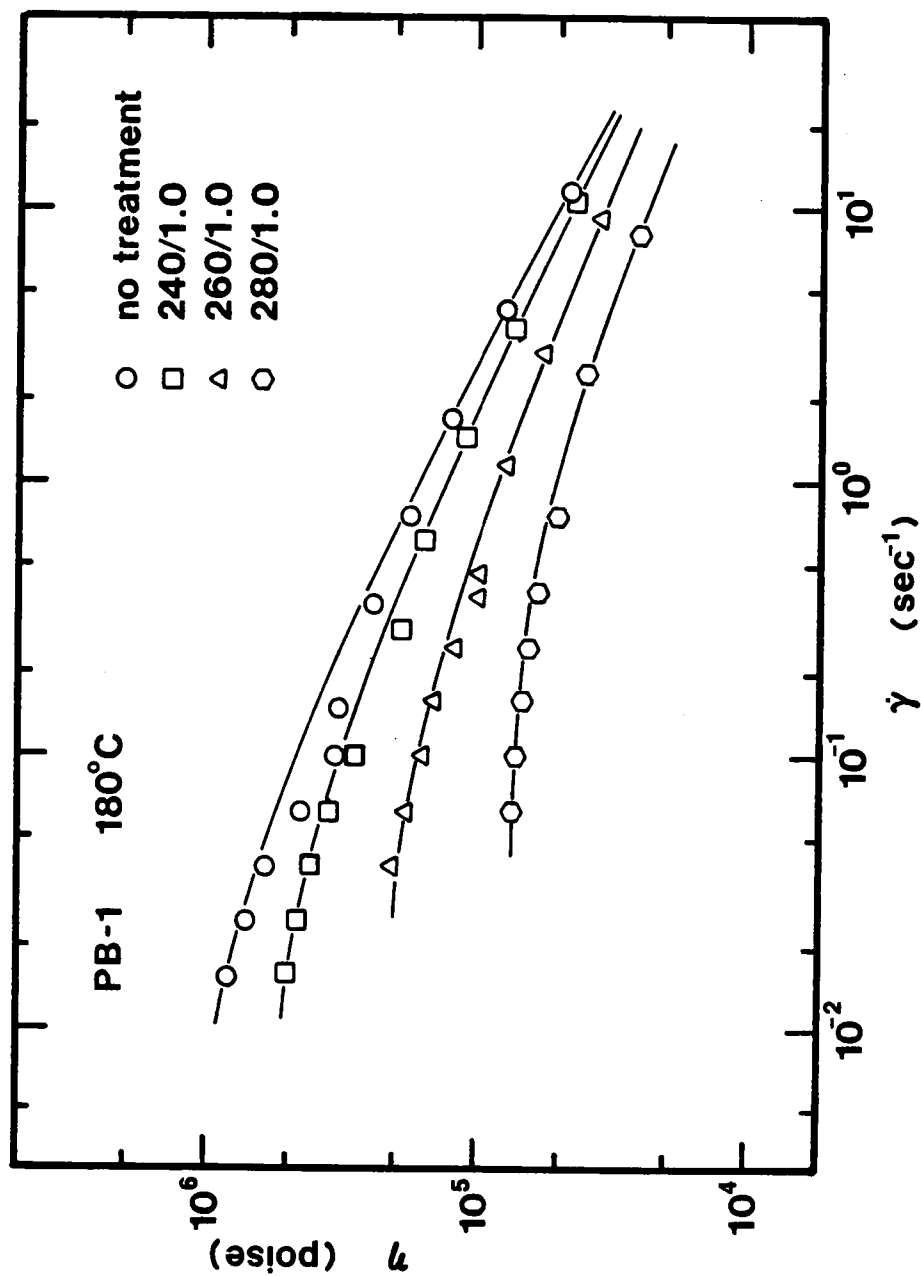


Figure IV-5. Viscosity (η) - Shear Rate ($\dot{\gamma}$) Behavior of Untreated and Thermally Treated PB-1 Measured at 180°C

the zero shear viscosity of PP and PB-1 decrease. The HDPE does not exhibit a decreasing viscosity.

A-2-b. η_0 vs $\bar{M}_w$ for Polypropylene

It is well known that the zero shear viscosity, η_0 , is proportional to the 3.5th power of the weight average molecular weight, $\bar{M}_w$, above a critical molecular weight (96, 128). Figure IV-6 shows a correlation between zero shear viscosity and the weight average molecular weight for PP. A straight line is obtained representing a correlation with a slope of 3.5. This is in agreement with earlier data for polypropylene (11, 130, 148).

A-2-c. η/η_0 vs $\eta_0\dot{\gamma}$

To quantitatively examine the effect of molecular weight distribution on linear polymers, a method of data reduction is required. Several procedures of reduction have been proposed by Porter et al. (134), Vinogradov and Malkin (158) and Graessley (51).

Following Vinogradov and Malkin's method, Minoshima et al. (112, 114) found that the relative viscosity, η/η_0 , plotted against a relative stress, $\eta_0\dot{\gamma}$, exhibits the effect of molecular weight distribution. They suggested that the broader the molecular weight distribution the lower the relative viscosity, η/η_0 , at fixed relative stress, $\eta_0\dot{\gamma}$. The relative viscosity of broad molecular weight distribution material decreases more rapidly than that of the narrow molecular weight distribution material.

Figure IV-7 shows the relative viscosity, η/η_0 , of untreated and thermally treated PP as a function of relative stress, $\eta_0\dot{\gamma}$.

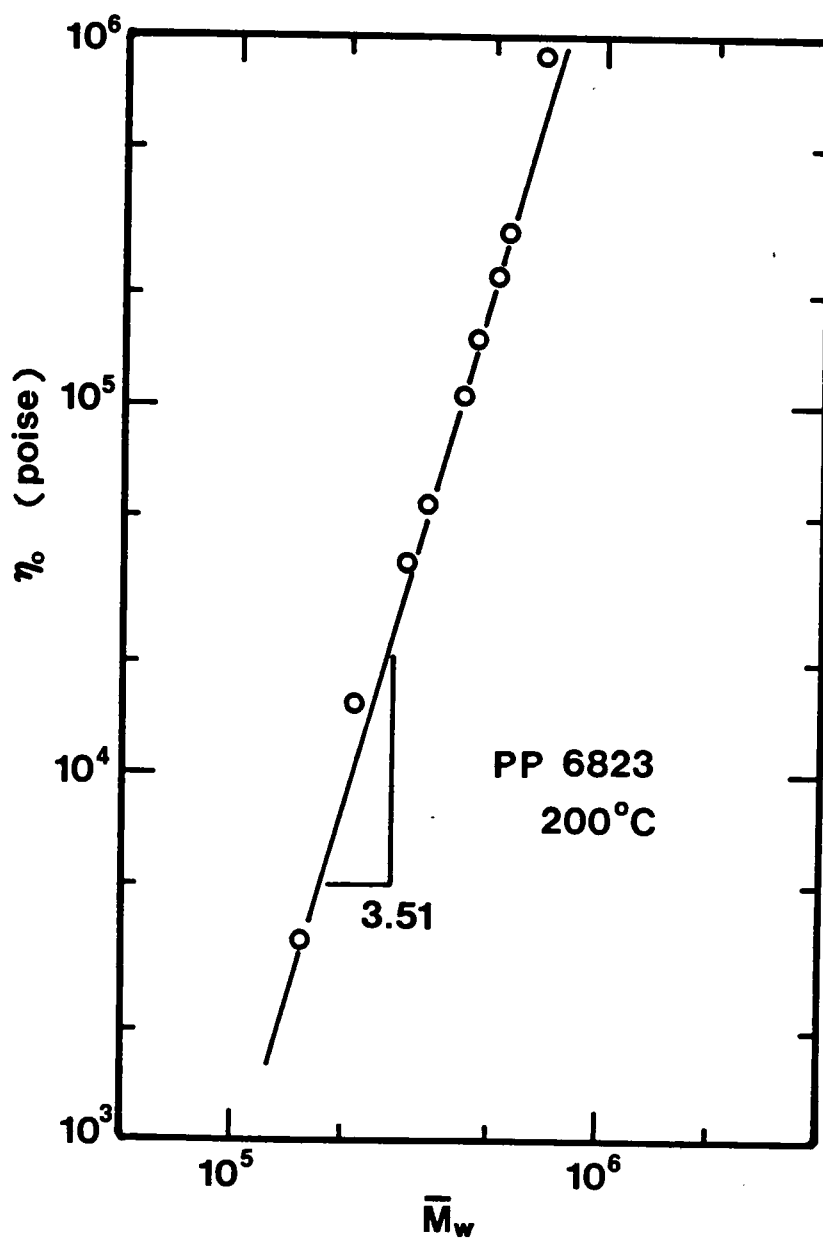


Figure IV-6. Zero Shear Viscosity (η_0) of Thermally Treated PP as a Function of Weight Average Molecular Weight ($\bar{M}_w$)

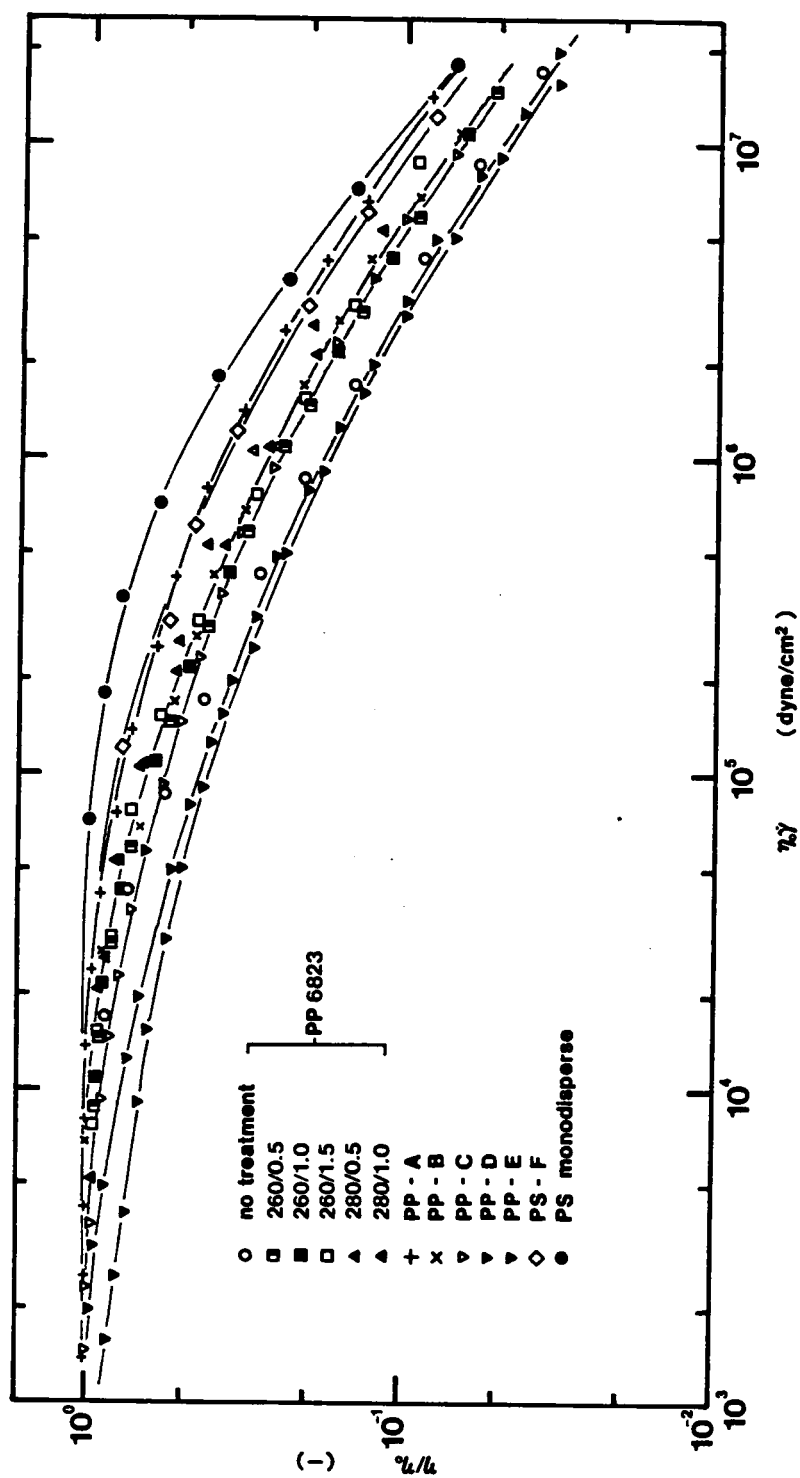


Figure IV-7. Relative Viscosity (η/η_0) as a Function of Relative Stress $(\eta_0 \dot{\gamma})$ for PP Samples and Well Characterized Samples

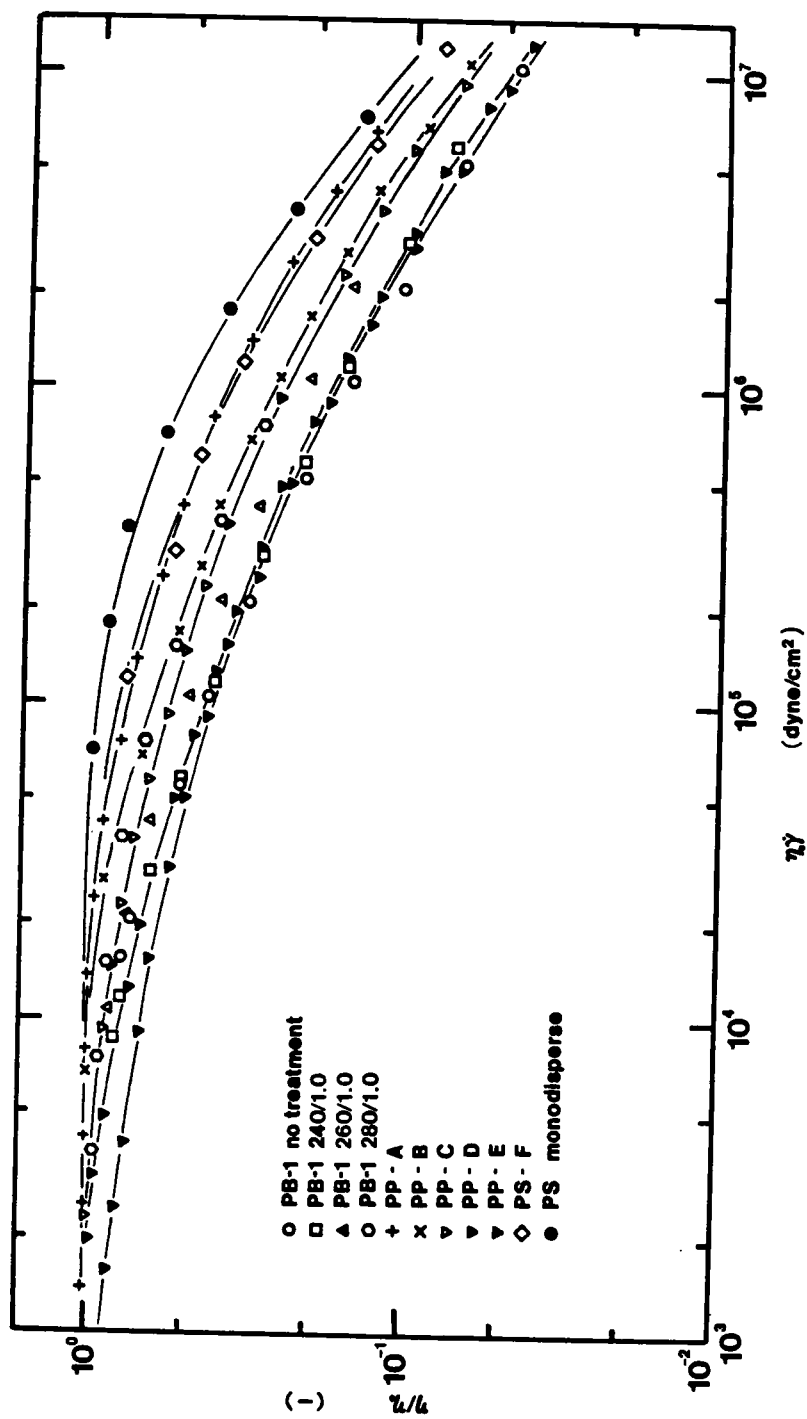


Figure IV-8. Relative Viscosity (η/η_0) as a Function of Relative Stress ($\eta_0 \dot{\gamma}$) for PB-1 Samples and Well Characterized Samples

Table IV-1. η/η_o and $\bar{M}_w/\bar{M}_n$ of Well Characterized Materials

Polymer	$\bar{M}_w/\bar{M}_n$	η/η_o ($\eta_o \dot{\gamma} = 10^6$ dyne/cm ²)
1. monodisperse PS	1.06	0.515
2. PS - F	2.6	0.375
3. PP - A	3.5	0.380
4. PP - B	4.6	0.270
5. PP - C	6.7	0.255
6. PP - D	9.0	0.180
7. PP - E	9.0	0.173

Table IV-2. η/η_0 and Estimated $\overline{M}_w/\overline{M}_n$ of Untreated and Thermally Treated Polypropylene and Polybutene-1

Polymer	$\overline{M}_w/\overline{M}_n$	η/η_0
		$(\eta_0 \dot{\gamma} = 10^6 \text{ dyne/cm}^2)$
1. monodisperse PS	1.06	5.15
2. PP - A	3.5	3.80
3. PS - F	2.6	3.75
4. PP 280/1.0	(3.5 ~ 4.0)	3.15
5. PP 280/0.5	(4.0 ~ 4.5)	2.85
6. PP 260/1.5	(4.5 ~ 5.0)	2.70
7. PP - B	4.6	2.70
8. PB-1 280/1.0	(4.5 ~ 6.5)	2.65
9. PP - C	6.7	2.55
10. PP 260/1.0	(6.5 ~ 7.0)	2.45
11. PP 260/0.5	(6.5 ~ 7.0)	2.45
12. PB-1 260/1.0	(7.0 ~ 8.0)	2.20
13. PP notreatment	(8.0 ~ 9.0)	1.90
14. PP - D	9.0	1.80
15. PB-1 240/1.0	(10.0 ~ 15.0)	1.75
16. PP - E	17.0	1.73
17. PB-1 notreatment	17.0	1.60

A similar plot for PB-1 is shown in Figure IV-8. For comparison, curves for monodisperse PS, commercial PS, and a series of PP, whose $\bar{M}_w/\bar{M}_n$ values are known, are added in these Figures. Comparing η/η_0 values at fixed $\eta_0\gamma$ value of our samples with those of well characterized samples, $\bar{M}_w/\bar{M}_n$ values can be estimated. The η/η_0 values and $\bar{M}_w/\bar{M}_n$ values for the known samples are listed in Table IV-1. Then unknown $\bar{M}_w/\bar{M}_n$ values are estimated and listed in Table IV-2.

B. FIRST NORMAL STRESS DIFFERENCE

B-1. Results

The first normal stress differences, N_1 , of untreated and thermally treated PP are shown in Figure IV-9 as a function of shear stress, σ_{12} . Similar plots for PB-1 are shown in Figure IV-10. Both PP and PB-1 exhibit a strong dependence of N_1 on the thermal treatment conditions. Increasing treatment time and temperature decrease the value of N_1 at a fixed σ_{12} .

B-2. Discussion

It is well known that the normal stress dependence upon shear rate exhibits a strong dependence on molecular weight distribution. It was found by Oda, White and Clark (123) that the dependence of the first normal stress difference, N_1 , plotted against shear stress is a function of molecular weight distribution but not the molecular weight. Racine and Bogue (137) and Minoshima et al. (114) have shown that the broader molecular weight distribution material has a higher first normal stress difference but possesses a smaller $d\log N_1/d\log \sigma_{12}$. Oda et al. (123) and Racine and Bogue (137) considered polystyrene melts while

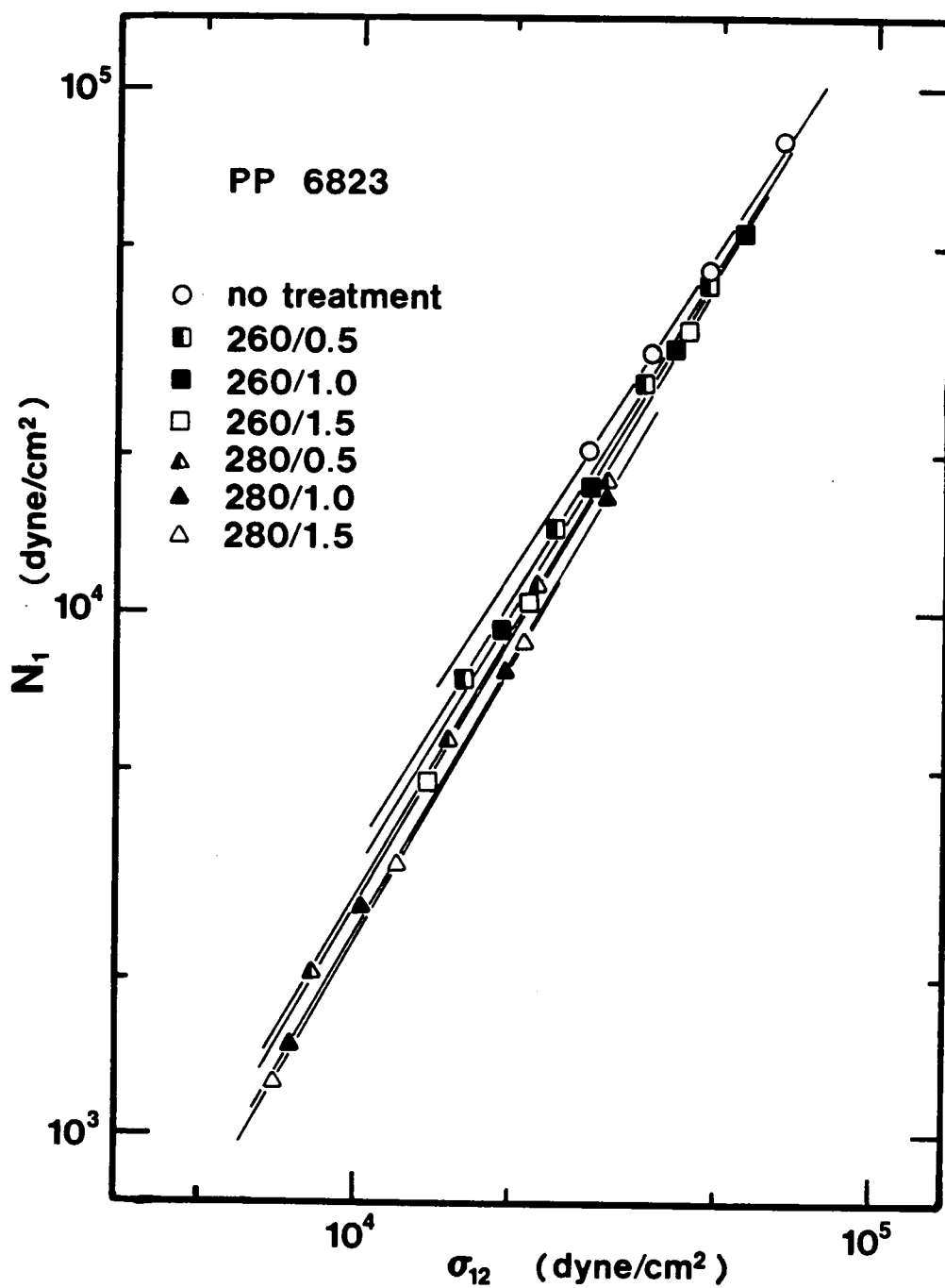


Figure IV-9. First Normal Stress Difference (N_1) as a Function of Shear Stress (σ_{12}) for PP Samples

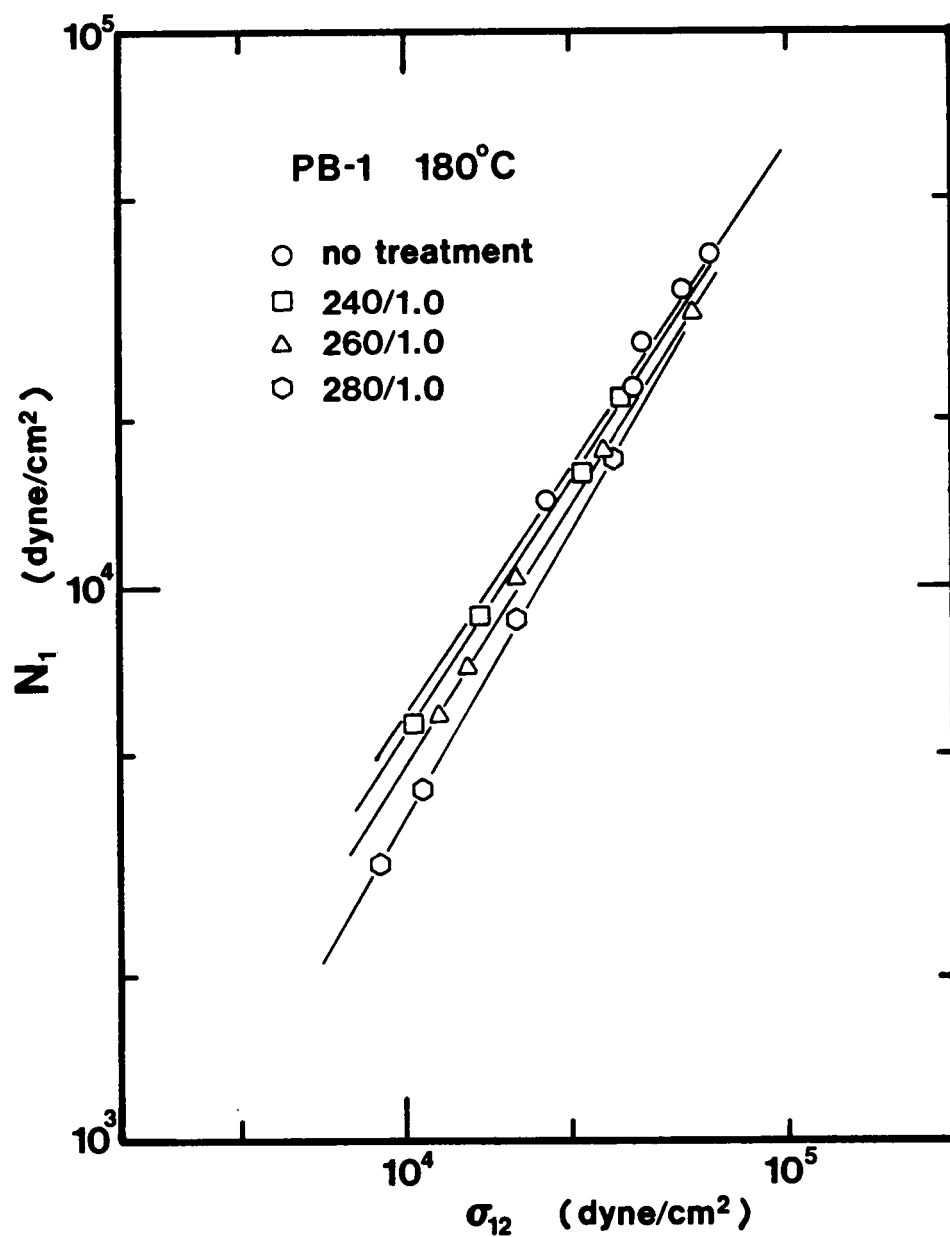


Figure IV-10. First Normal Stress Difference (N_1) as a Function of Shear Stress (σ_{12}) for PB-1 Samples

Minoshima et al. (114) investigated polypropylenes.

In Figure IV-11, the N_1 vs σ_{12} relation of PP and PB-1 which are untreated and thermally treated at 280°C for 1 hour, and those for well characterized PP and commercial and monodisperse PS are shown. Values of N_1 at fixed σ_{12} (10^4 dyne/cm²) are listed in Table IV-3.

We assume the empirical power law relation between N_1 and σ_{12} as

$$N_1 = A\sigma_{12}^b \quad (4.1)$$

then

$$d \log N_1 / d \log \sigma_{12} = b \quad (4.2)$$

In Table IV-3, the values of A and b are listed. The values of N_1 at fixed σ_{12} are almost in the exact order of the values of $\bar{M}_w/\bar{M}_n$ computed from η/η_0 vs $\eta_0\dot{\gamma}$ plots.

Table IV-3. The Values of A, b and N_1 at Fixed σ_{12} (10^4 dyne/cm²), and Estimated $\bar{M}_w/\bar{M}_n$ of Polypropylene and Polybutene-1

Polymer	$\bar{M}_w/\bar{M}_n$	A	b	$N_1 \times 10^3$ ($\sigma_{12} = 10^4$ dyne/cm ²)
PP no treatment	(8.0 ~ 9.0)	2.6×10^{-3}	1.6	4.05
PP 260/0.5	(6.5 ~ 7.0)	1.1×10^{-3}	1.6	3.50
PP 260/1.0	(6.5 ~ 7.0)	7.1×10^{-4}	1.7	3.15
PP 260/1.5	(4.5 ~ 5.0)	2.2×10^{-4}	1.8	2.75
PP 280/0.5	(4.0 ~ 4.5)	5.2×10^{-4}	1.7	2.90
PP 280/1.0	(3.5 ~ 4.0)	3.2×10^{-4}	1.7	2.57
PB-1 no treatment	(>17.0)	7.5×10^{-3}	1.5	5.90
PB-1 240/1.0	(10.0 ~ 15.0)	5.0×10^{-3}	1.5	5.45
PB-1 260/1.0	(7.0 ~ 8.0)	2.7×10^{-3}	1.6	4.75
PB-1 280/1.0	(4.5 ~ 6.5)	5.9×10^{-4}	1.7	3.82
PP - B	9.0	1.5×10^{-2}	1.4	7.20
PP - D	4.6	1.5×10^{-3}	1.6	2.72
monodisperse PS	1.06	2.3×10^{-6}	2.0	0.299

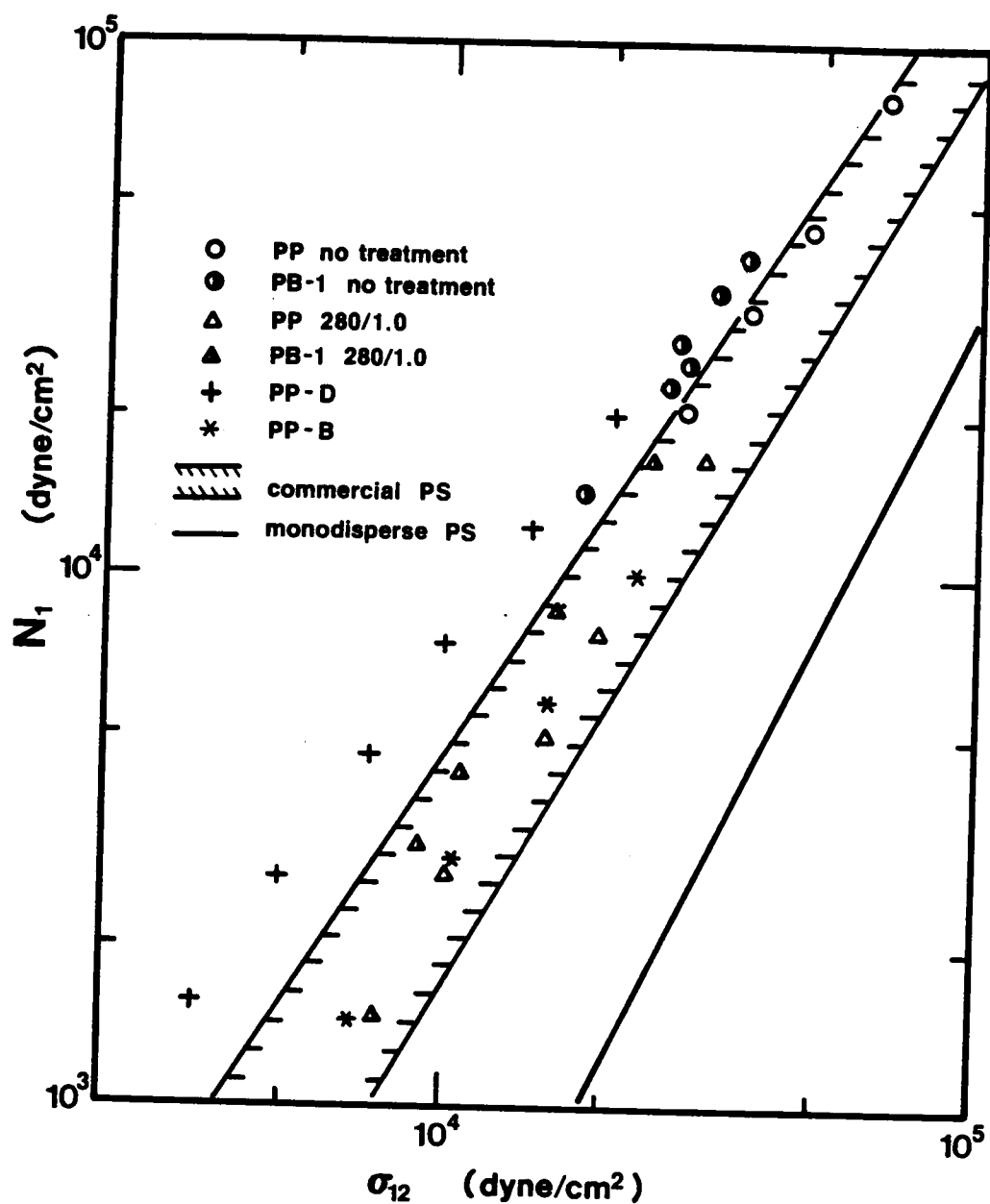


Figure IV-11. First Normal Stress Difference (N_1) as a Function of Shear Stress (σ_{12}) for Untreated and Thermally Treated PP and PB-1 and Comparisons with Well Characterized Samples

CHAPTER V

ELONGATIONAL FLOW RHEOLOGICAL MEASUREMENTS

In this chapter, the rheological behavior of polypropylene and polybutene-1 filaments in uniaxial elongational flow are represented. The transient elongational viscosity, $\lambda(t)$, and steady state elongational viscosity, λ , are discussed.

A. Transient Elongational Viscosity

A-1. Results

The transient elongational viscosity of untreated and degraded polypropylenes measured at 200°C are shown in Figures V-1 to V-6. Similar plots for polybutene-1 are shown in Figures V-7 to V-10. The Trouton prediction of viscosity which is three times the zero shear viscosity is indicated in these Figures. These Figures show that the higher the molecular weight the higher the elongational viscosity. The shape of transient elongational curve depends on the molecular weight distribution.

Comparing these transient elongational viscosity curves of polypropylene, one can separate these into two groups. In one group, at low elongational rates, the transient elongational viscosity increases to much more than $3\eta_0$ and then after reaching the maximum values the sample fails. At higher elongational rates, the sample achieves a value around $3\eta_0$ when the sample breaks. In the second group, at low elongational rates, λ increases more gently to $3\eta_0$ or to a large value.

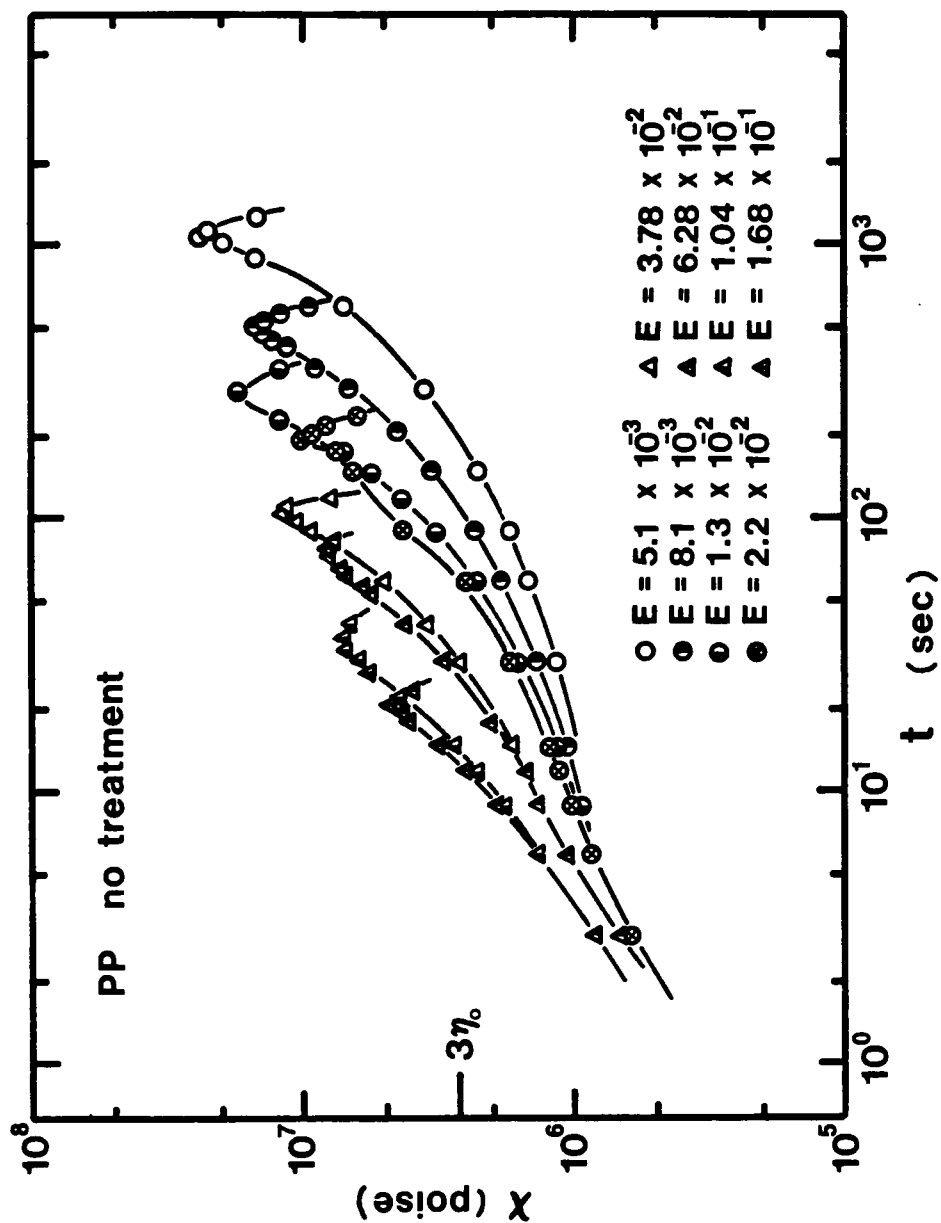


Figure V-1. Transient Elongational Viscosity ($\chi(t)$) as a Function of Elongational Rate (E) and Time (t) for Untreated PP

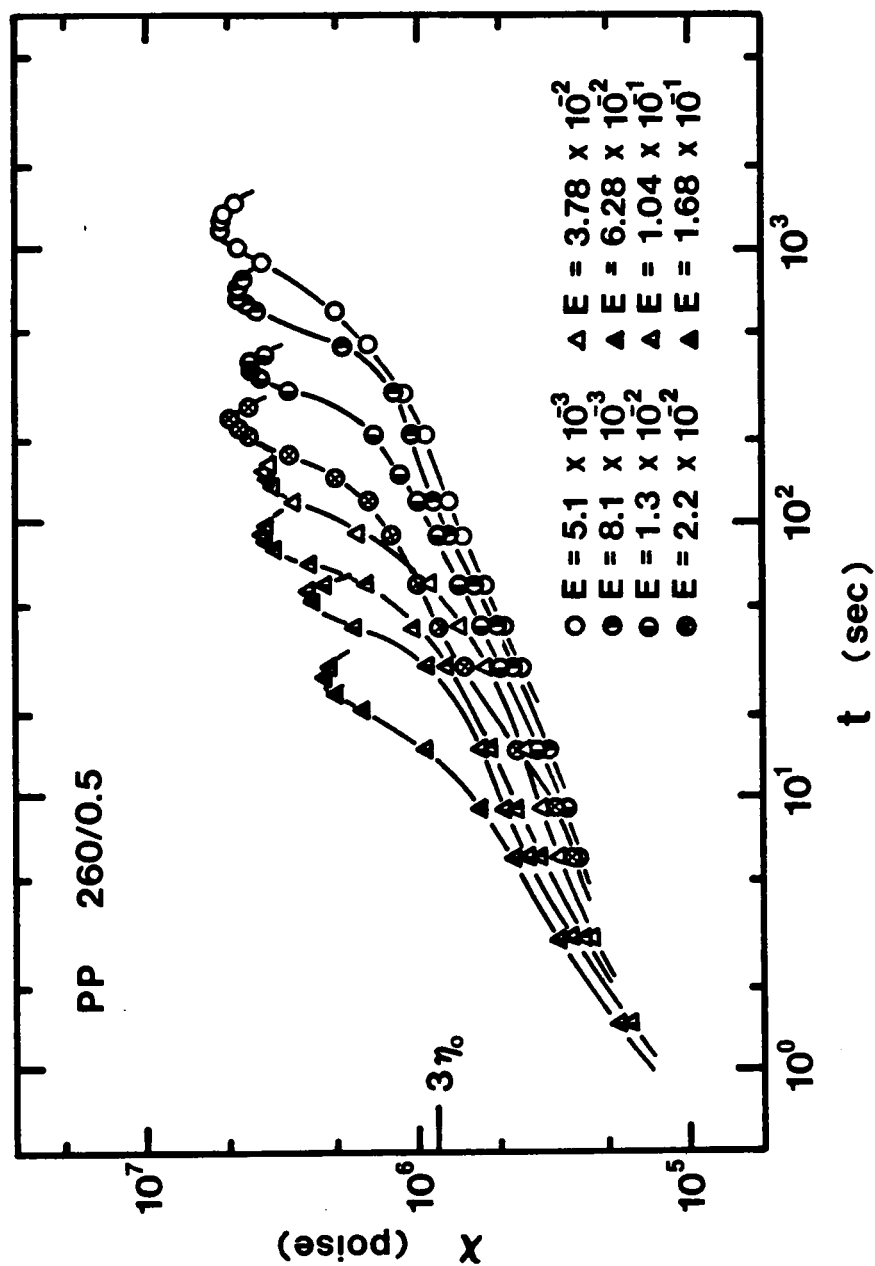


Figure V-2. Transient Elongational Viscosity ($X(t)$) as a Function of Elongational Rate (E) and Time (t) for PP 260/0.5

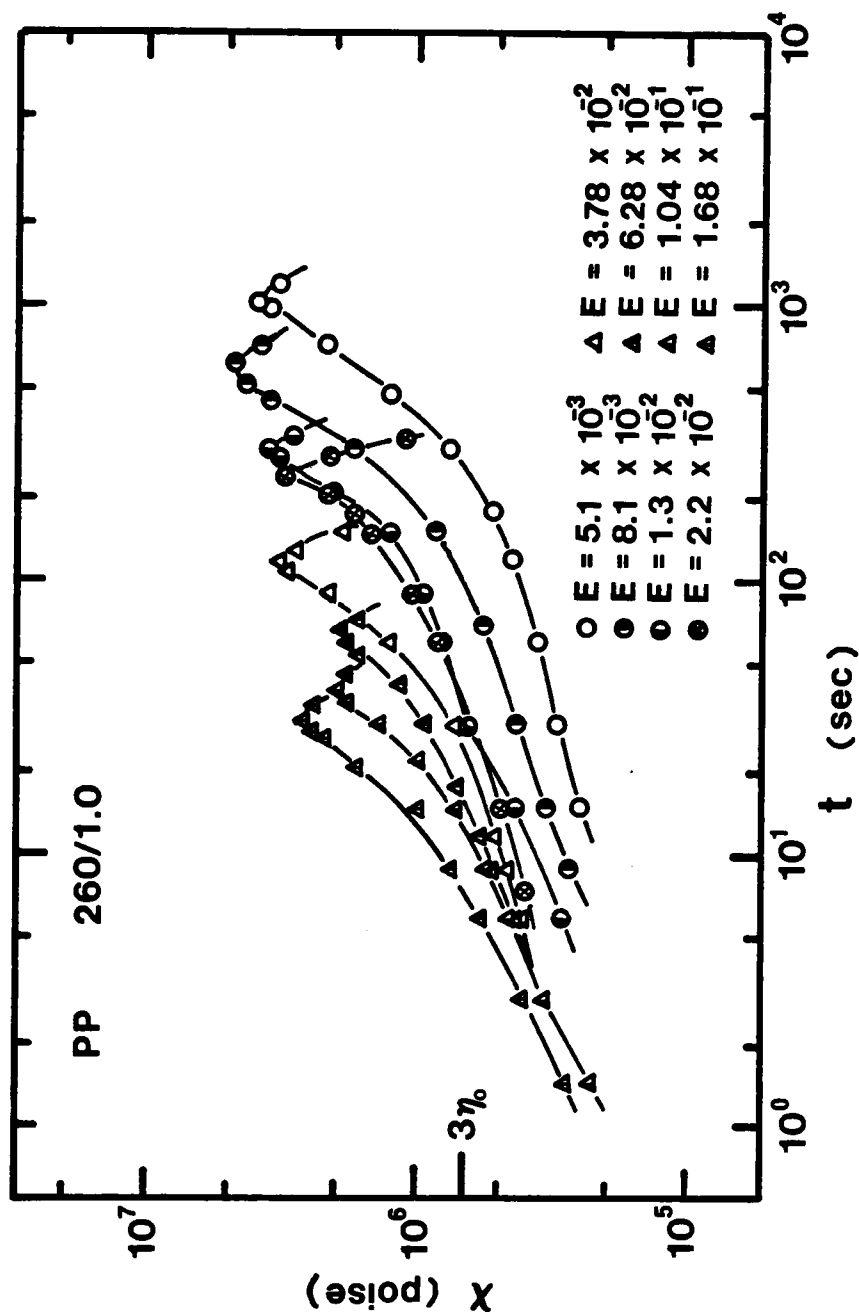


Figure V-3. Transient Elongational Viscosity ($\chi(t)$) as a Function of Elongational Rate (E) and Time (t) for PP 260/1.0

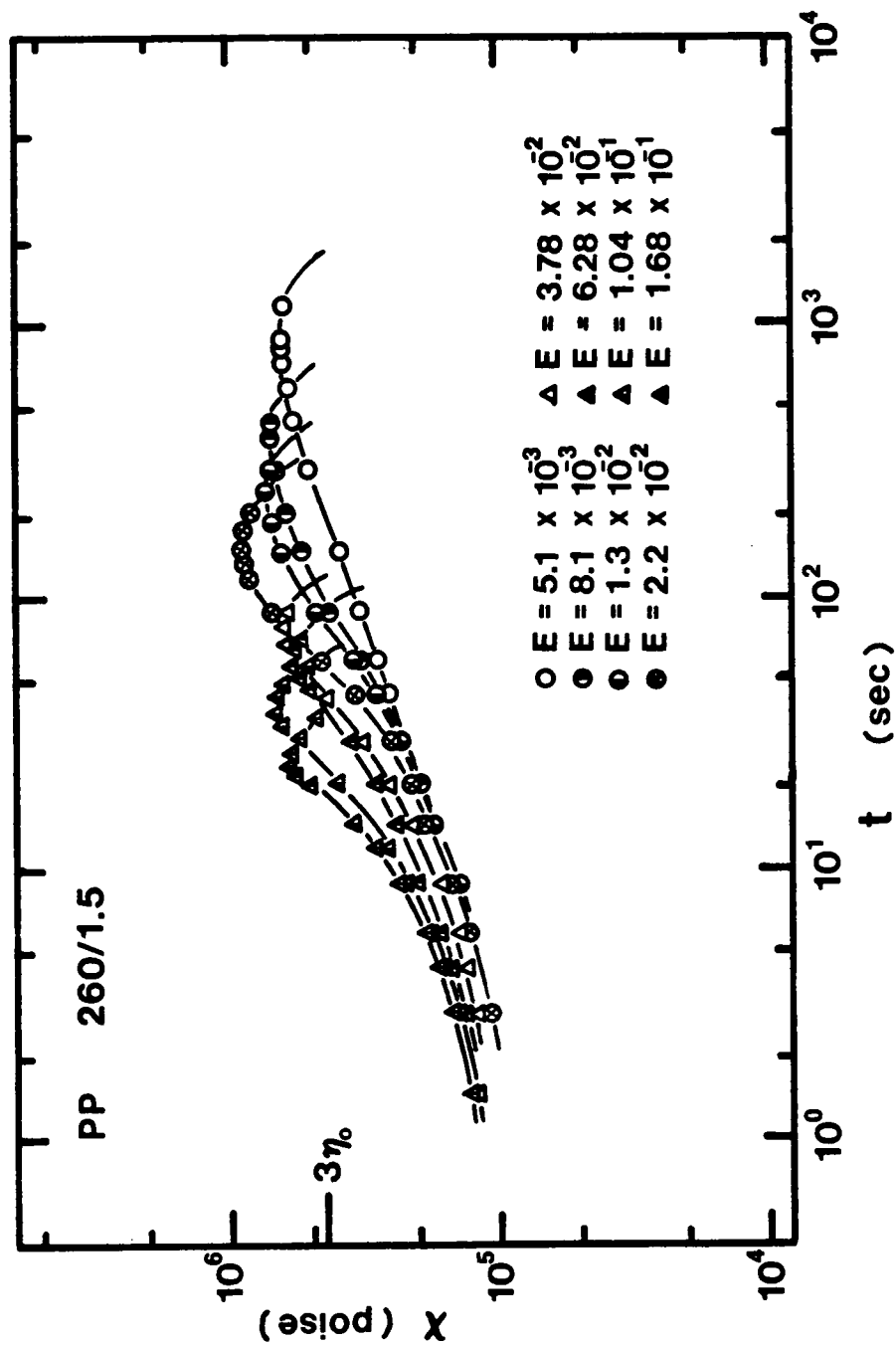


Figure V-4. Transient Elongational Viscosity ($\chi(t)$) as a Function of Elongational Rate (E) and Time (t) for PP 260/1.5

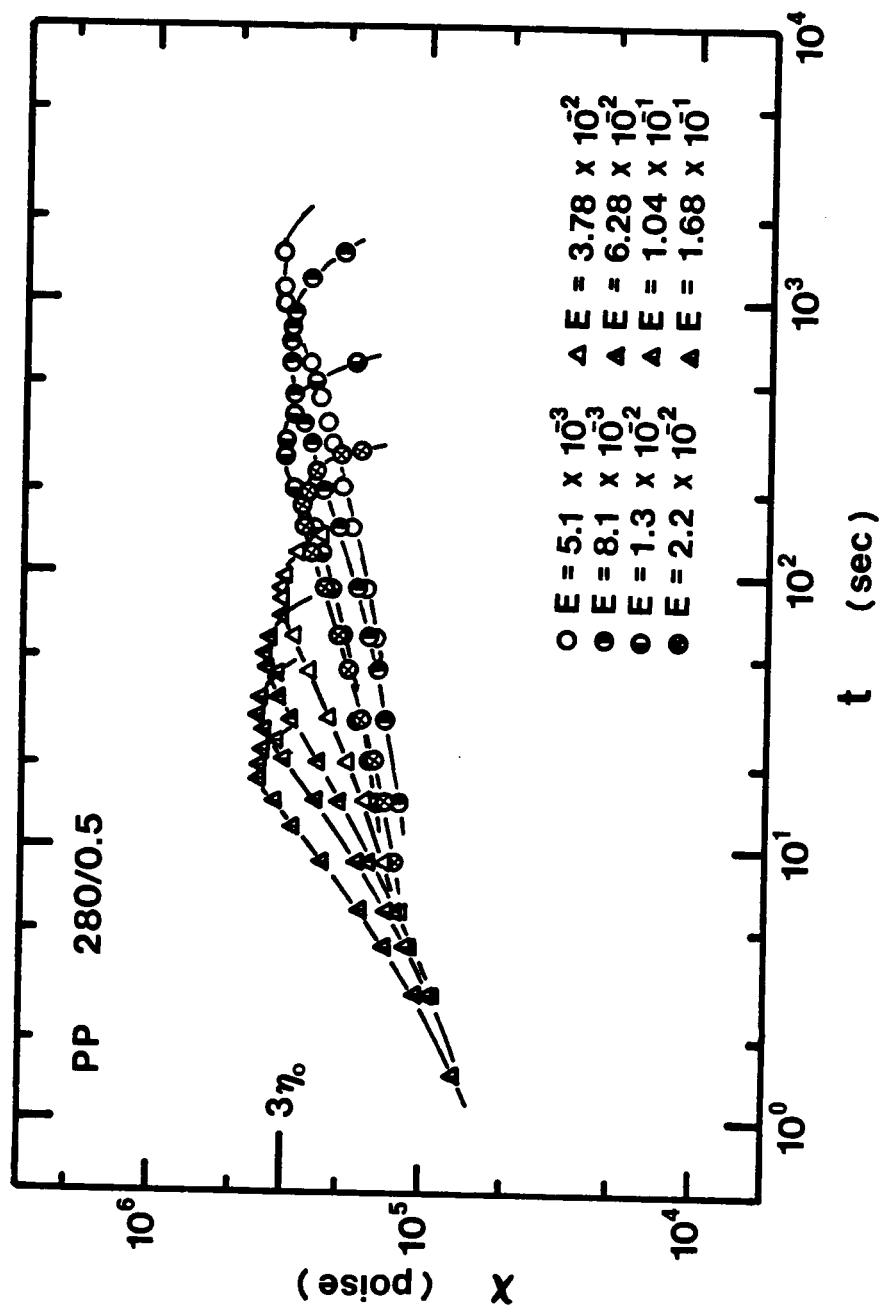


Figure V-5. Transient Elongational Viscosity ($X(t)$) as a Function of Elongational Rate (E) and Time (t) for PP 280/0.5

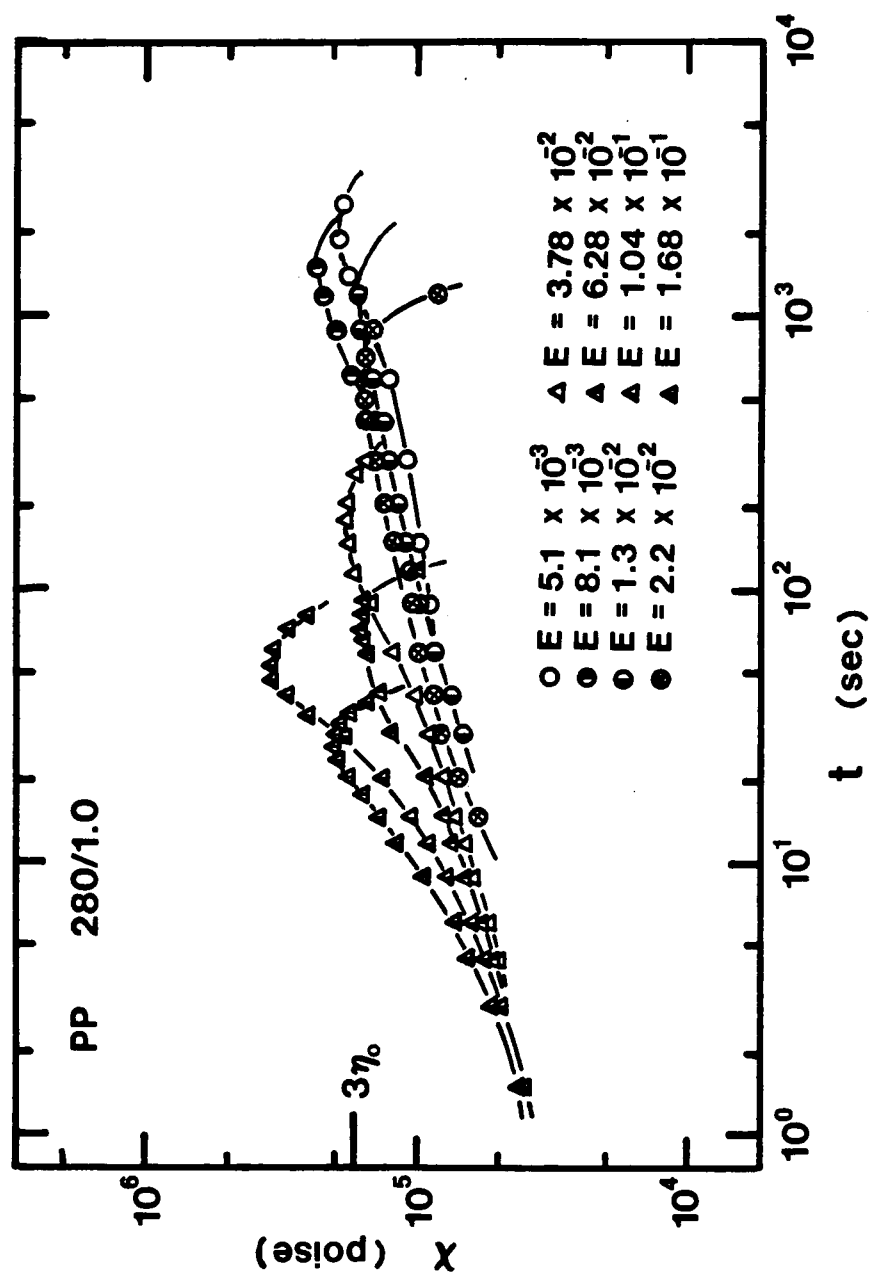


Figure V-6. Transient Elongational Viscosity ($\chi(t)$) as a Function of Elongational Rate (E) and Time (t) for PP 280/1.0

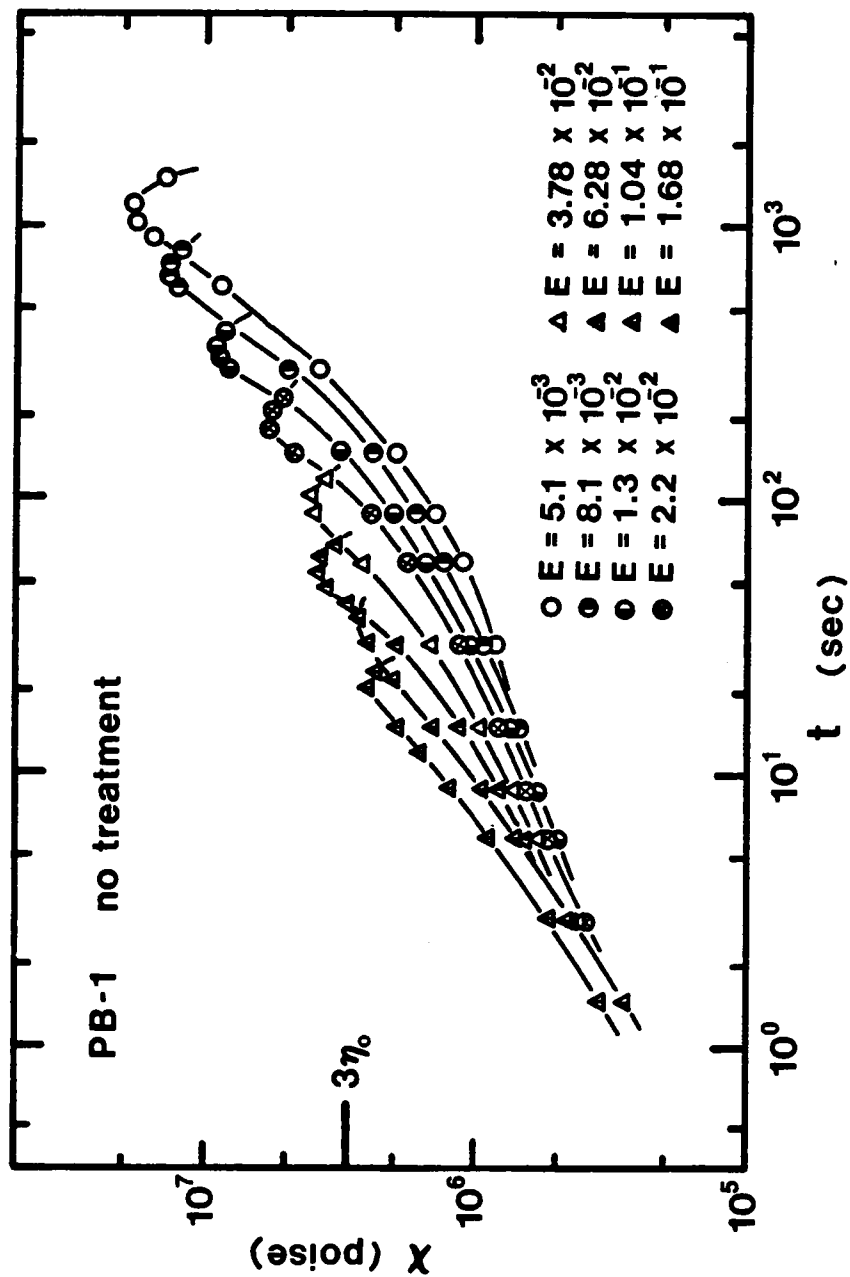


Figure V-7. Transient Elongational Viscosity ($\chi(t)$) as a Function of Elongational Rate (E) and Time (t) for Untreated PB-1

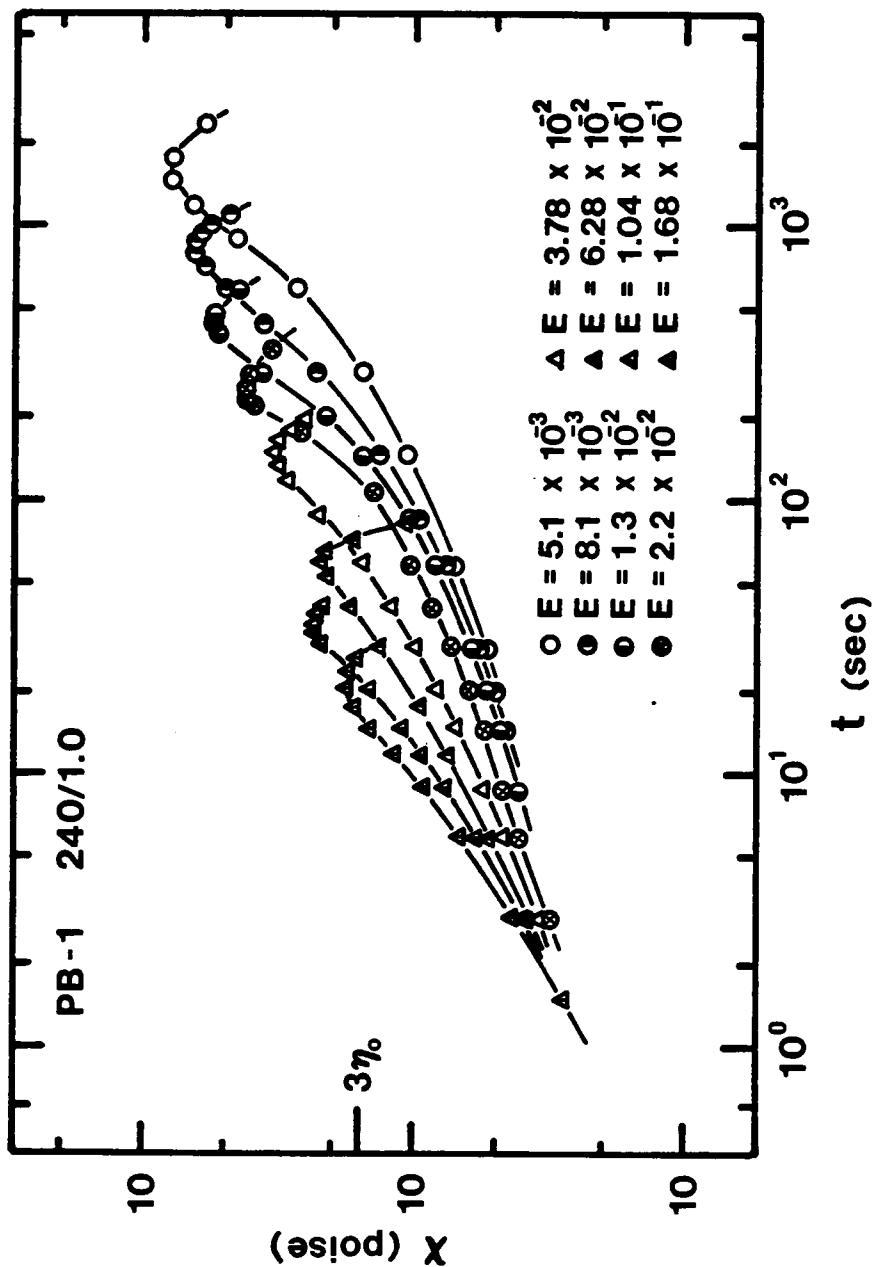


Figure V-8. Transient Elongational Viscosity ($X(t)$) as a Function of Elongational Rate (E) and Time (t) for PB-1 240/1.0

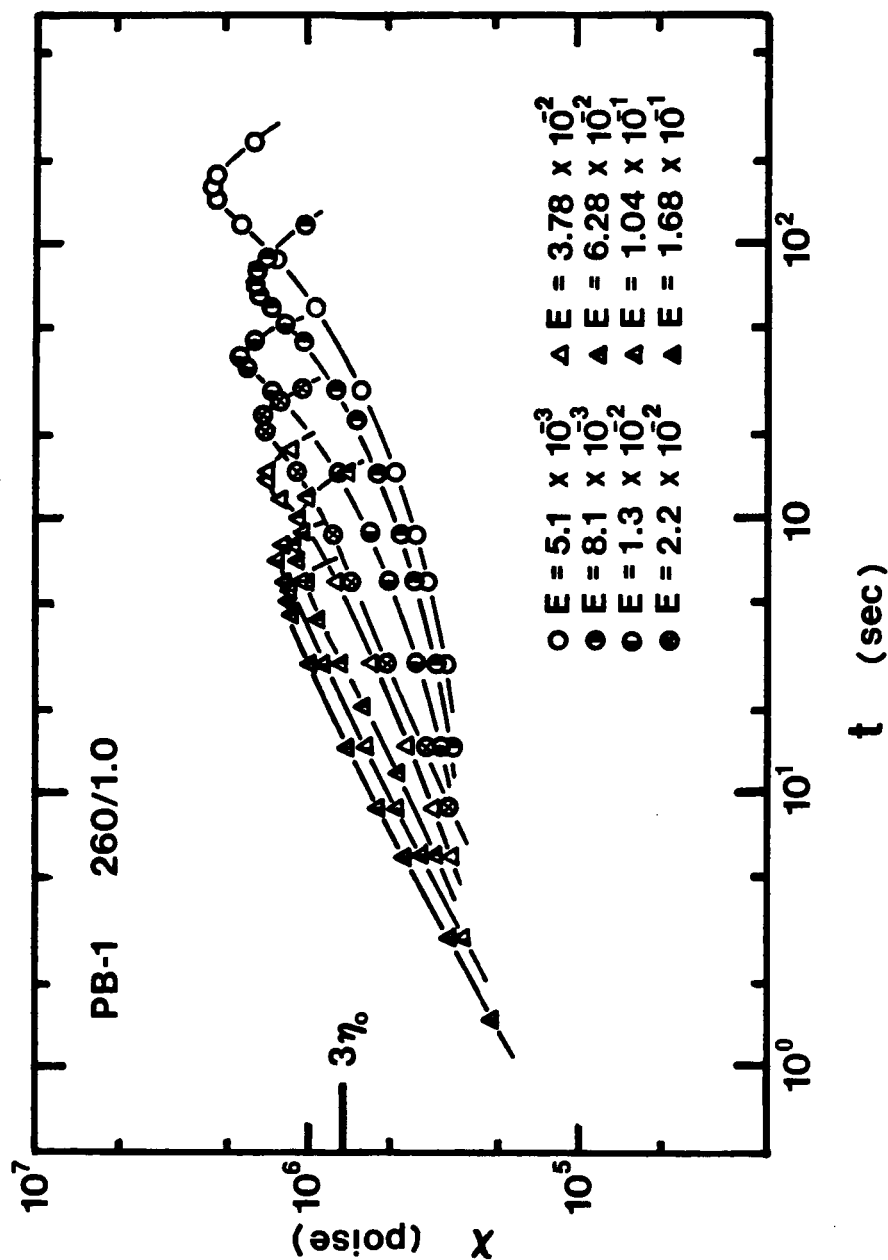


Figure V-9. Transient Elongational Viscosity ($\chi(t)$) as a Function of Elongational Rate (E) and Time (t) for PB-1 260/1.0

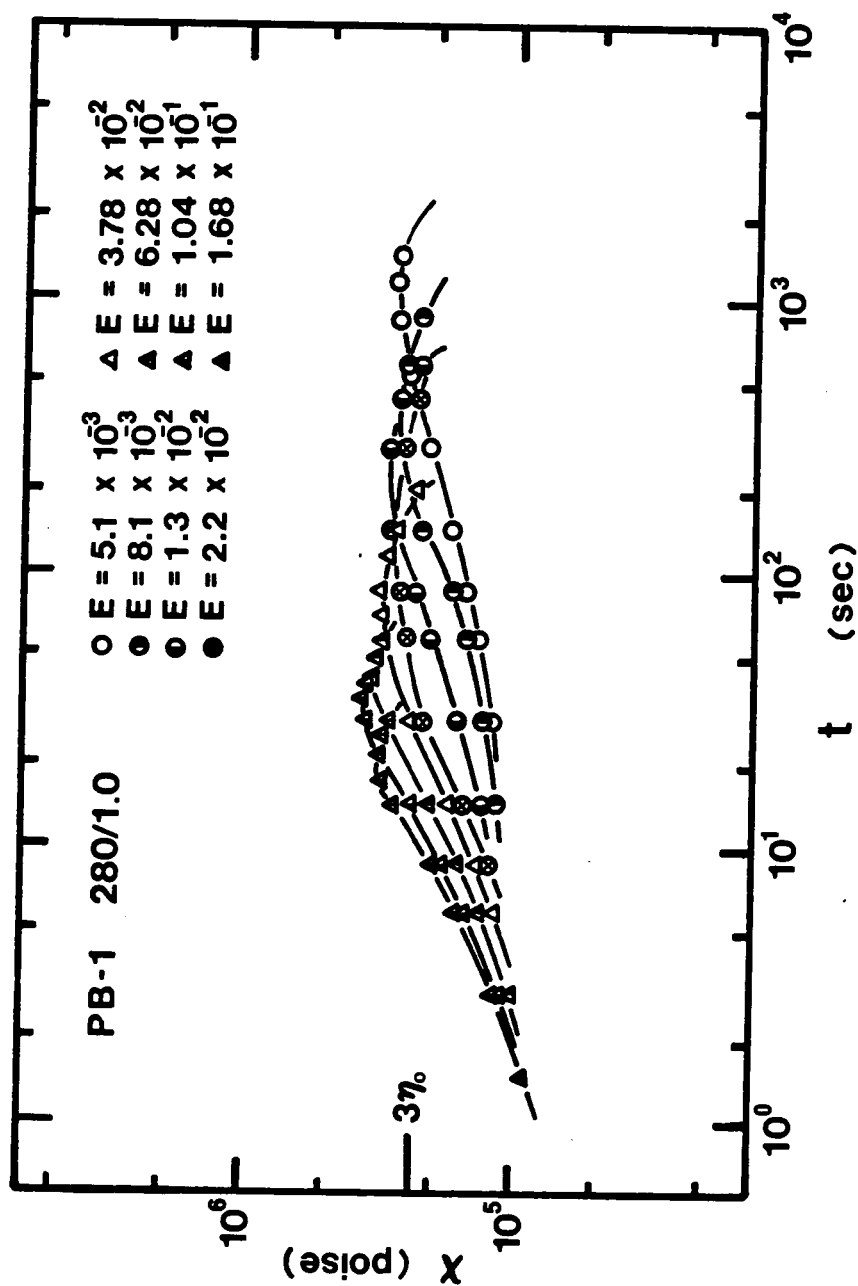


Figure V-10. Transient Elongational Viscosity ($X(t)$) as a Function of Elongational Rate (E) and Time (t) for PB-1 280/1.0

A-2. Discussion

Similar observations were made by Minoshima et al. (114). The first group was found to belong to polypropylenes having broad molecular weight distribution and the second group belongs to polypropylenes having narrower molecular weight distributions. Our data for polybutene-1 shows similar behavior.

B. STEADY STATE ELONGATIONAL VISCOSITY

B-1. Results

As mentioned previously, the transient elongational viscosity of narrow molecular weight distribution materials measured at low elongational rates achieves a steady state for long periods of time. However, broad molecular weight distribution materials measured at all elongational rates do not achieve steady states.

Following Ide and White (75), and Minoshima et al. (114), we will plot maximum values of transient elongational viscosity as steady state elongational viscosity. The elongational viscosity of the untreated and thermally treated polypropylenes as a function of elongational rate are shown in Figure V-11. Similar plots for polybutene-1 are shown in Figure V-12.

B-2. Discussion

From the Figures V-11 and V-12, one can see the higher the molecular weight the higher the steady state elongational viscosity. However, the correlation is not clear as for shear viscosity. While the steady state elongational viscosity of narrow molecular weight distribution sample is close to $3\eta_0$ through wide elongational rate range,

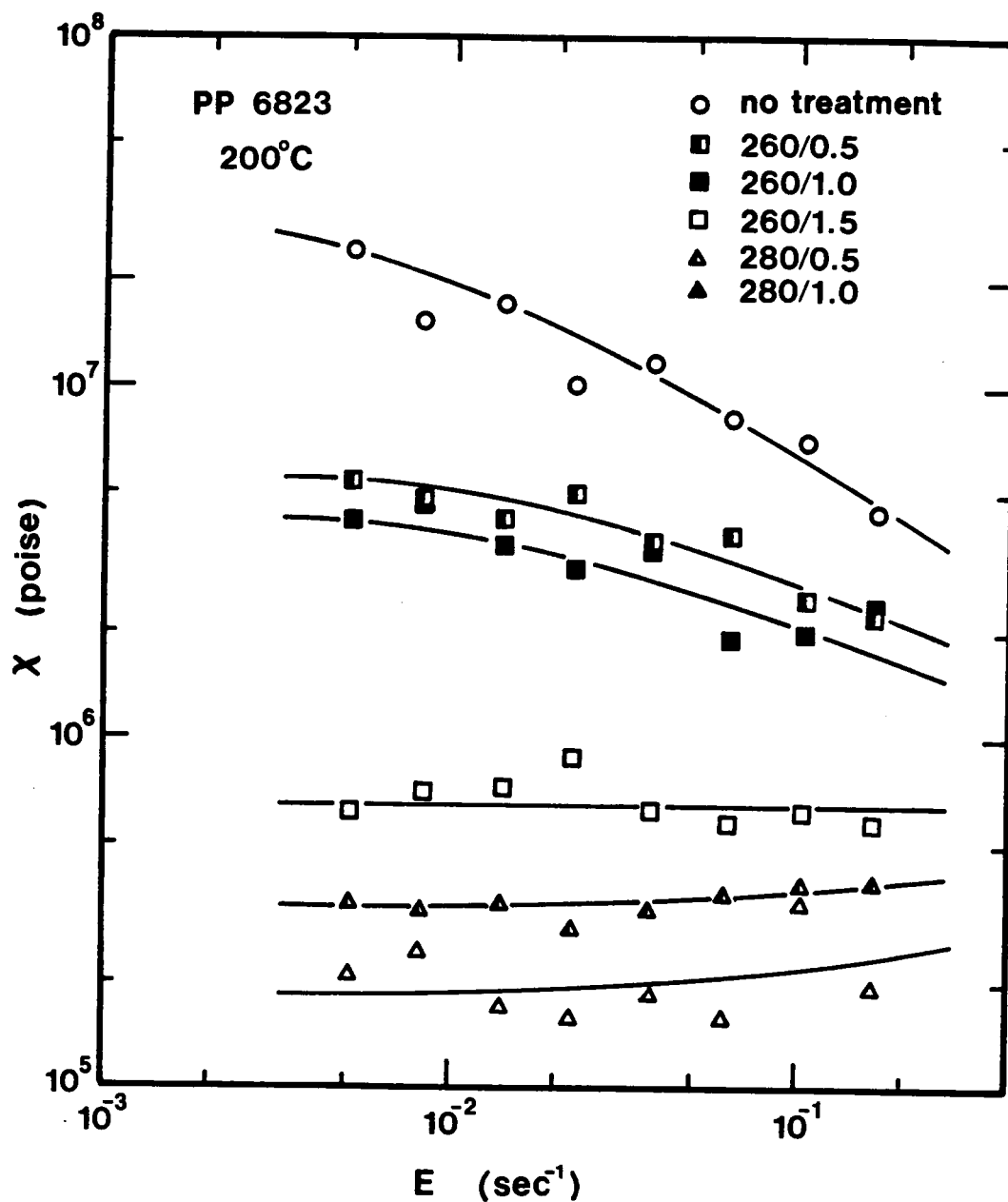


Figure V-11. Steady State Elongational Viscosity (χ) as a Function of Elongational Rate (E) for PP

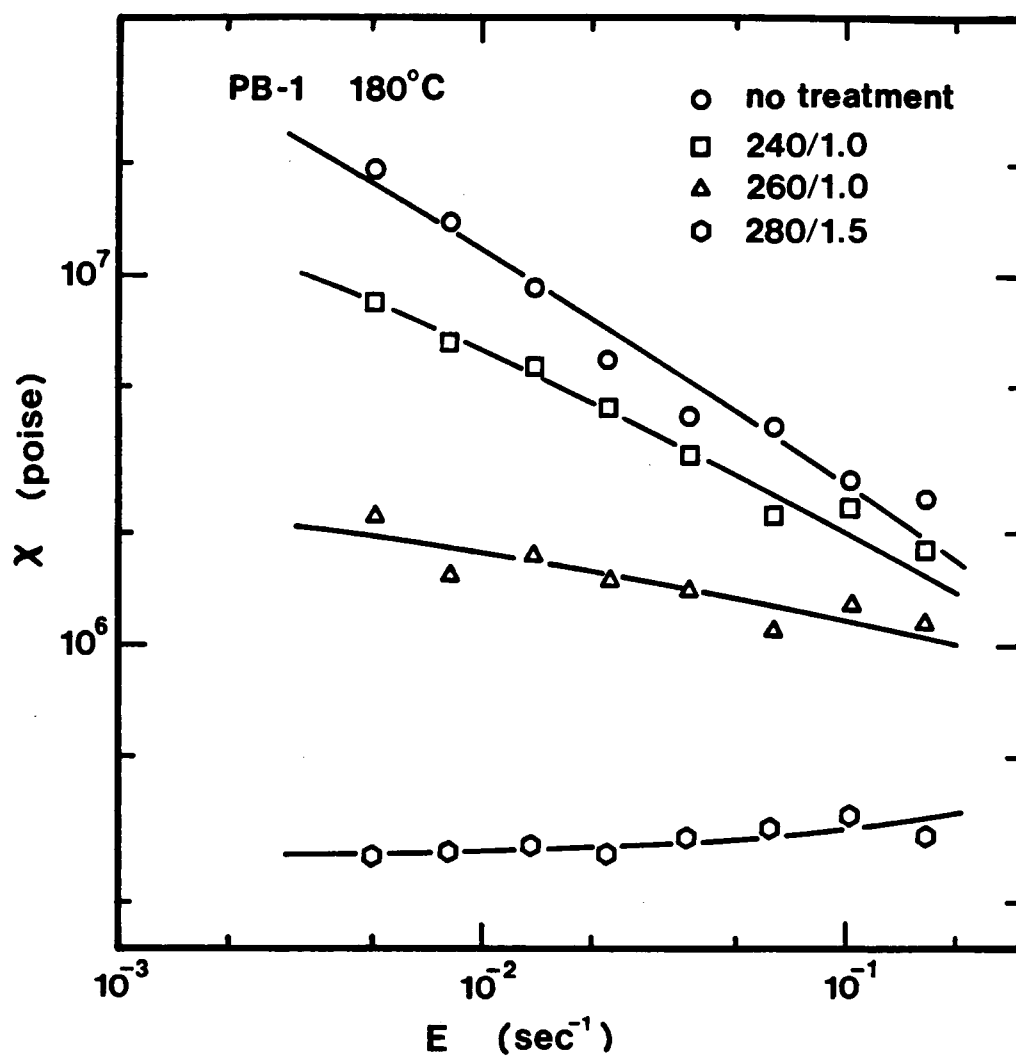


Figure V-12. Steady State Elongational Viscosity (χ) as a Function of Elongational Rate (E) for PB-1

that of broad molecular weight distribution sample measured at low elongational rate is much higher than $3\eta_0$.

For comparison purposes, the steady state elongational viscosities reduced by their Trouton viscosities are plotted in Figure V-13 for polypropylenes and in Figure V-14 for polybutene-1. From these Figures one can see that the separation of materials into two groups according to molecular weight distribution can be applied again to these results. The first group, which belongs to broad molecular weight distribution materials, exhibits a decreasing steady state elongational viscosity with increasing elongational rate. The second group, which belongs to narrow molecular weight distribution materials, shows constant or slightly increasing steady state elongational viscosity.

In this work, both polypropylene and polybutene-1 show the same trends which were observed by Minoshima et al. (114). The untreated, 260/0.5 and 260/1.0 polypropylenes, and the untreated, 240/1.0 and 260/1.0 polybutene-1 are in the first group (broad molecular weight distribution). However the dependence of $\lambda/3\eta_0$ upon the elongational rate seems to be stronger for the untreated polypropylene and polybutene-1 than for the thermally treated samples belonging to the first group (260/0.5 and 260/1.0 PP, and 240/1.0 and 260/1.0 PB-1). The shapes of $\lambda/3\eta_0$ curves of polypropylenes and polybutene-1 in this work, and those of polystyrene and low density polyethylene measured by Ide and White (75) are shown in Figure V-15. Those are summarized in Table V-1.

Ide and White (75) found that polystyrene and low density polyethylene have strongly increasing $\lambda/3\eta_0$ with increasing elongational rate, while commercial PPs and high density polyethylene exhibited decreasing function. Minoshima et al. (114) have shown that $\lambda/3\eta_0$ of

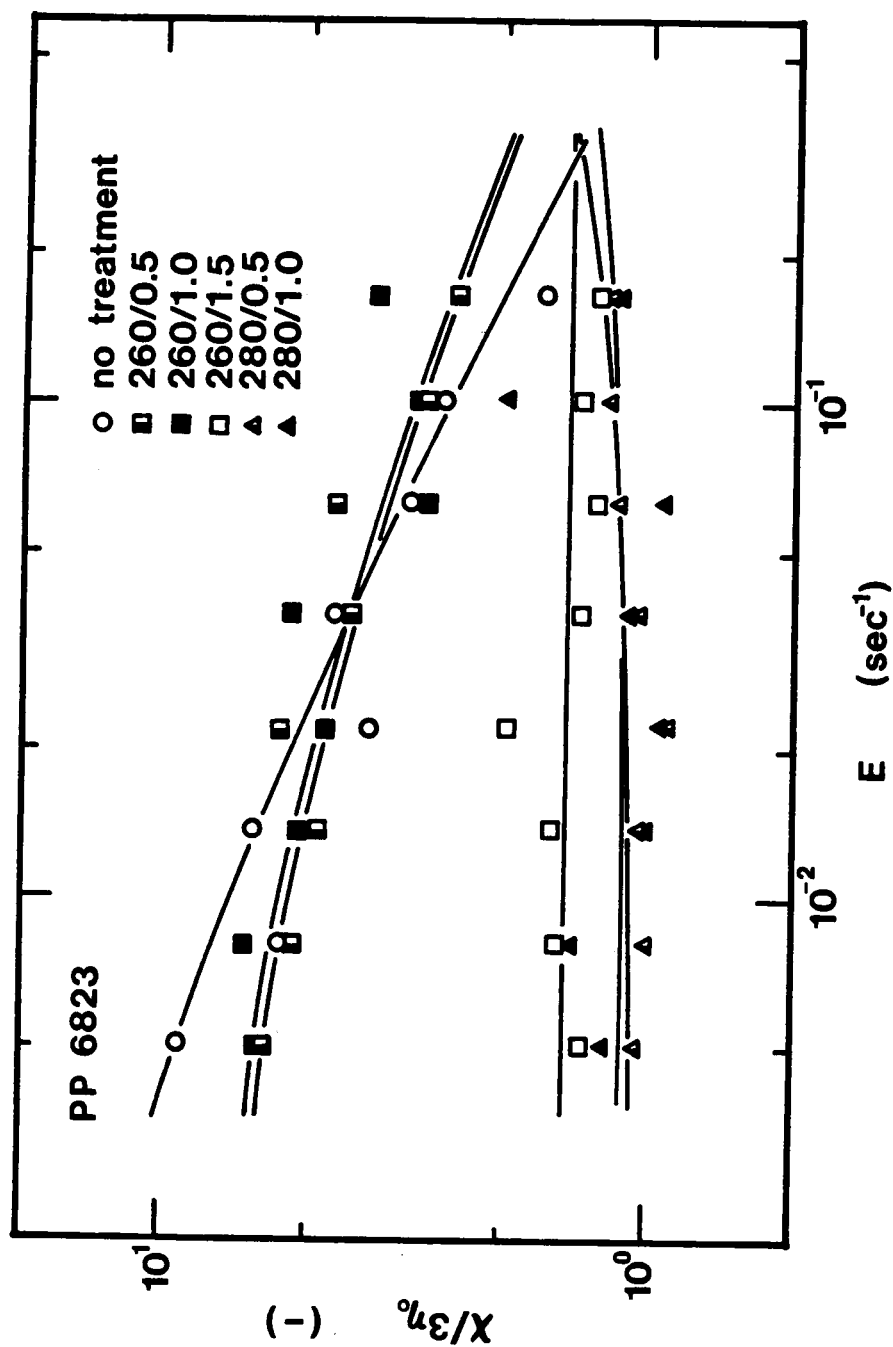


Figure V-13. Reduced Steady State Elongational Viscosity ($X/3\eta_0$) as a Function of Elongational Rate (E) for PP

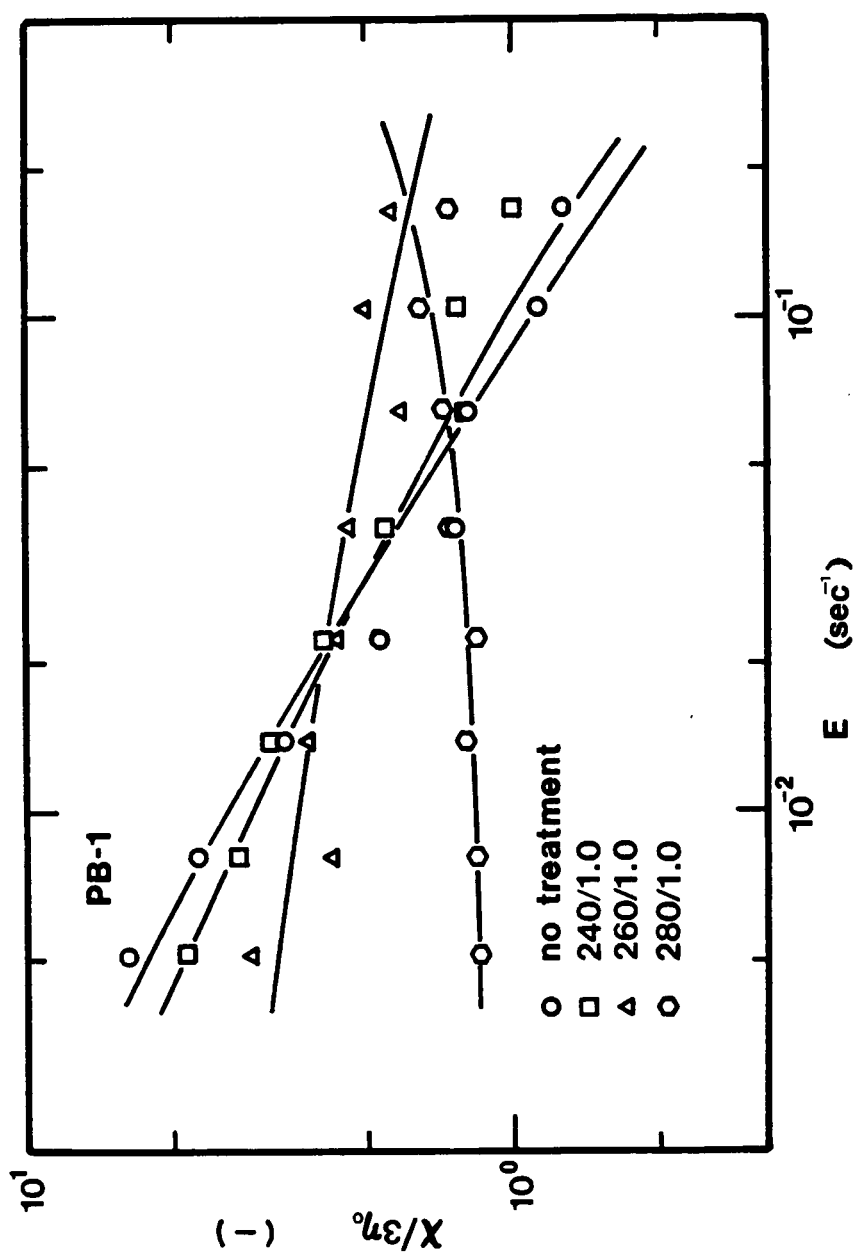


Figure V-14. Reduced Steady State Elongational Viscosity ($X/3\eta_0$) as a Function of Elongational Rate (E) for PB-1

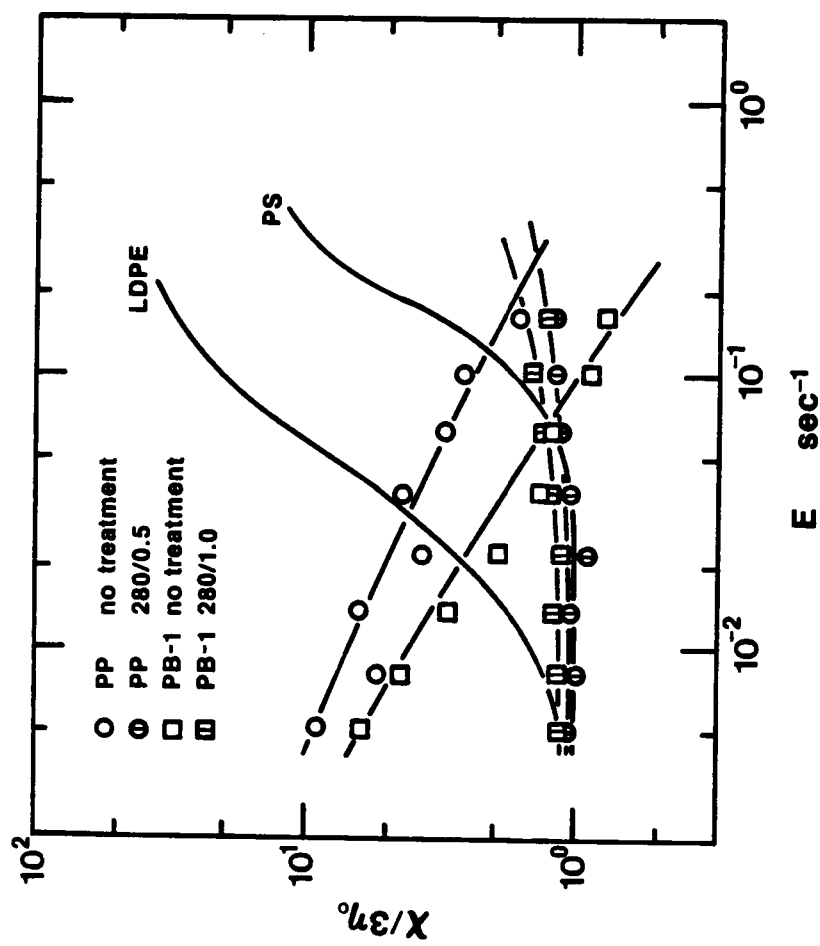


Figure V-15. Reduced Steady State Elongational Viscosity ($X/3\eta_0$) as a Function of Elongational Rate (E) for Untreated and Thermally Treated PP and PB-1 and Comparisons with PS and LDPE

Table V-1. Summary of the Manner of Elongational Viscosity for
PP, PB-1, PS and LDPE

Polymer	$\chi/3\eta_0$
PP no treatment	decreasing
260/0.5	decreasing (more gently)
260/1.0	
260/1.5	constant or slightly increasing at high elongational rate
280/0.5	
280/1.0	
PB-1 no treatment	decreasing
240/1.0	decreasing (more gently)
260/1.0	
280/1.0	constant or slightly increasing at high elongational rate
PS	
LDPE	strongly increasing

narrow molecular weight distribution polypropylene is almost constant and that of broad molecular weight distribution polypropylene is decreasing with elongational rate. Polybutene-1's show the same trend as well as polypropylenes in this work. Also the decreasing rate of change of $\chi/3\eta_0$ of broad molecular weight distribution polypropylene and polybutene-1 depends on the broadness of the molecular weight distribution.

CHAPTER VI

ELONGATIONAL FLOW INSTABILITY

In this chapter, the elongation to break, $L(t_b)/L(0)$, and the manner of failure of stretched filaments of polypropylene (PP) and polybutene-1 (PB-1) will be considered. The growth of disturbances in stretched filaments will be contrasted for untreated and thermally treated samples.

A. THE ELONGATION TO BREAK OF STRETCHED FILAMENTS

A-1. Results

The elongation to break, $L(t_b)/L(0)$, of the stretched filaments of untreated and thermally treated PP are shown in Figure VI-1. Similar plots are shown in Figure VI-2 for untreated and thermally treated PB-1.

The most degraded samples of PP and PB-1 have the highest elongation to break, while the less degraded and untreated samples have low elongations to break. Both PP and PB-1 show similar failure behavior which depends on the extent of degradation.

A-2. Discussion

The samples can be divided into two groups. For PP the $L(t_b)/L(0)$ of the more degraded samples is 10 ~ 100 times greater than the untreated and mildly degraded samples. For PB-1 the $L(t_b)/L(0)$ of the more degraded samples is 100 ~ 500 times higher than that of untreated and mildly degraded samples.

Comparing the data with apparent $\bar{M}_w/\bar{M}_n$ values estimated in Chapter IV, one can say that the smaller the $\bar{M}_w/\bar{M}_n$ value the higher the $L(t_b)/L(0)$

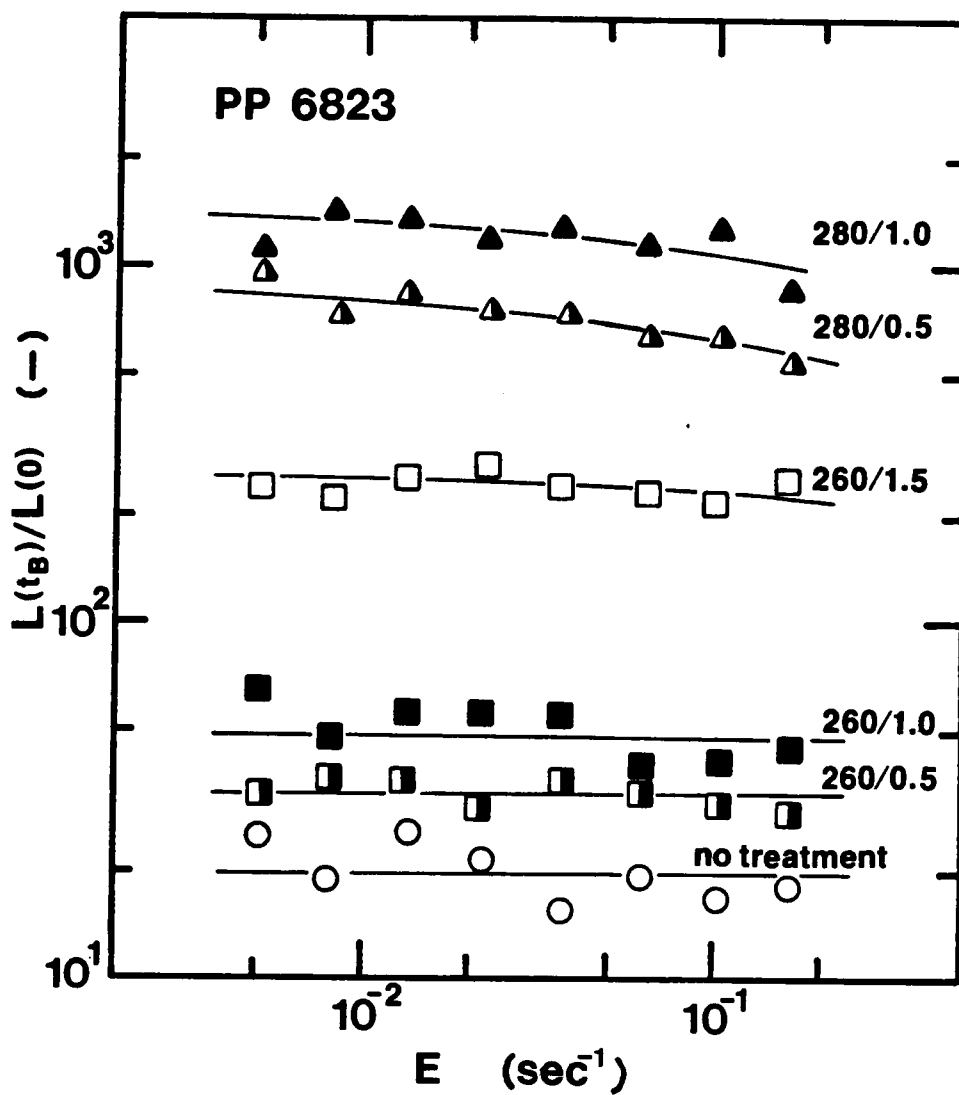


Figure VI-1. Elongation to Break ($\ln L(t_B)/\ln L(0)$) as a Function of Elongational Rate (E) for PP

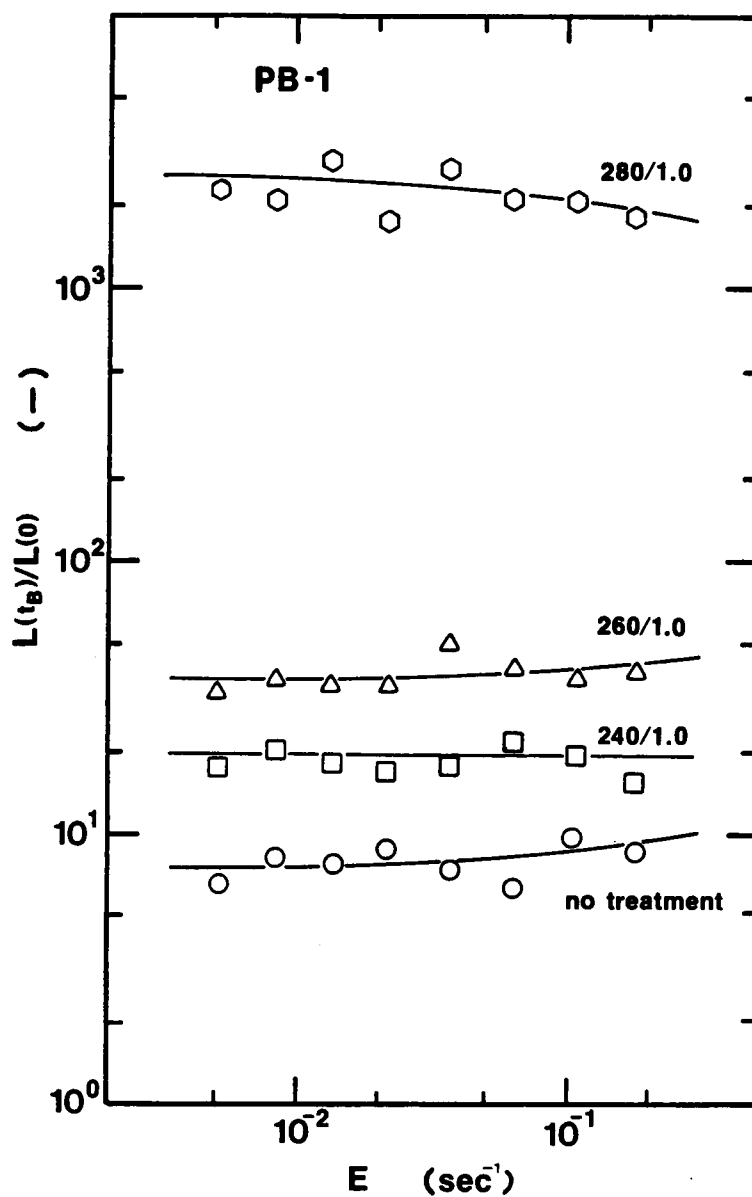


Figure VI-2. Elongation to Break ($\ln L(t_B)/\ln L(0)$) as a Function of Elongational Rate (E) for PB-1

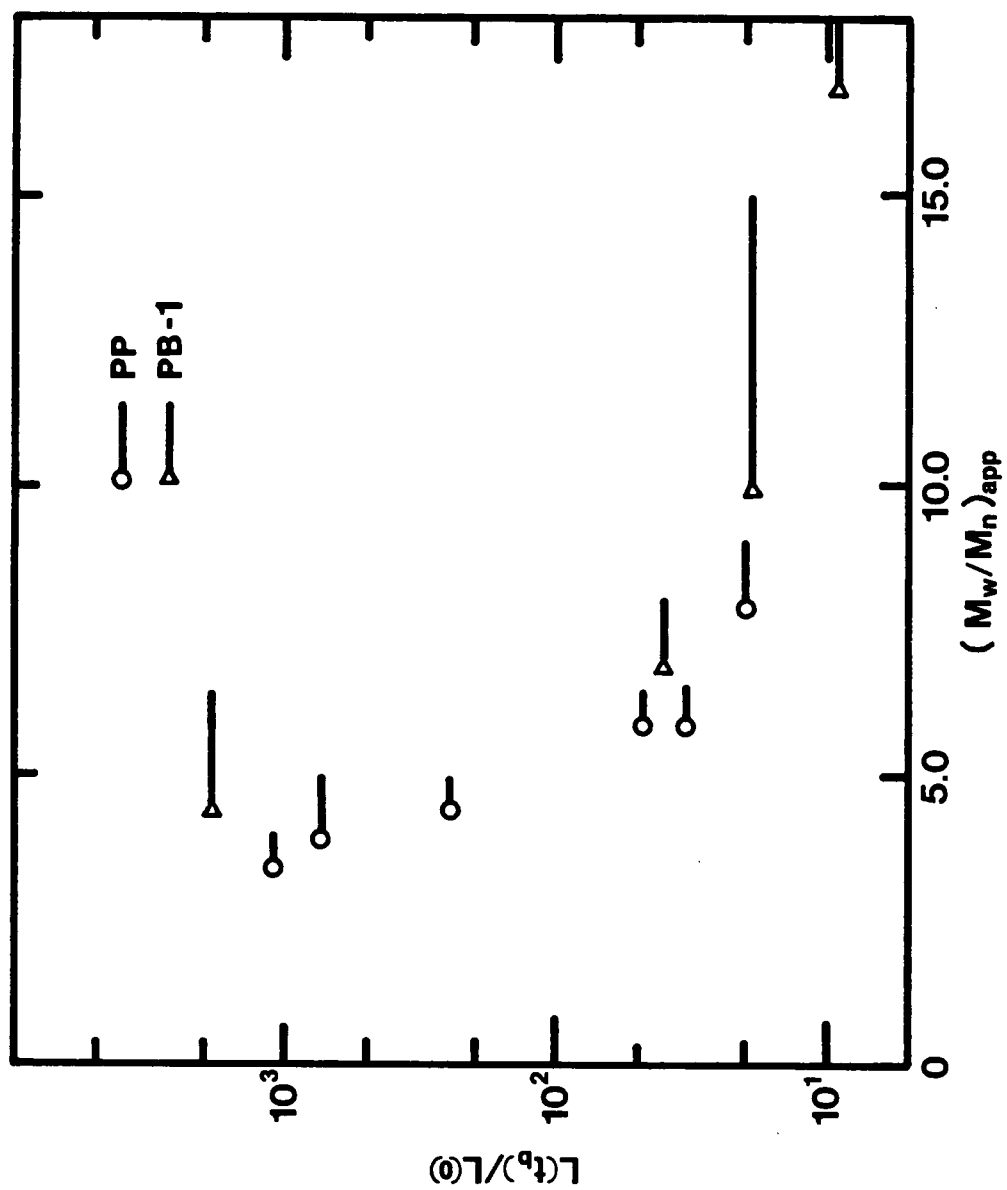


Figure VI-3. Elongation to Break $(\ln L(t_b)/\ln L(0))$ of PP and PB-1 Samples as a Function of Apparent Molecular Weight Distribution $(\bar{M}_w/\bar{M}_n)_{app}$

for both PP and PB-1. This result is an agreement with that obtained by Minoshima et al. (114). Our data show that the order of $L(t_p)/L(0)$ is exactly in the order of $\bar{M}_w/\bar{M}_n$ values. This is shown in Figure VI-3.

B. GROWTH OF DISTURBANCES IN STRETCHED FILAMENTS

B-1. Results

The shape of the initial sample and the stretched samples are illustrated in Figure VI-4. The initial sample contain two notches. Figures VI-5 to VI-7 show photographs of stretched PP filaments. Figure VI-8 and VI-9 contain similar photographs for PB-1.

When the filaments of untreated and mildly degraded PP and PB-1 are stretched, necking starts at the notches and then grows. The both ends and the center portion between notches do not deform, and the sample takes on the shape shown in Figure VI-4. When the applied force is removed, the sample shows "snap back".

The filaments of more degraded samples are stretched uniformly and the notches heal. When the applied force is removed, the sample remains uniform.

B-2. Discussion

For both PP and PB-1, the untreated samples show necking clearly and the stretched region and unstretched region are easily distinguished. As the extent of thermal treatment increases, the necking becomes less marked. Comparing these results with the apparent $\bar{M}_w/\bar{M}_n$ values, we see that the samples having larger $\bar{M}_w/\bar{M}_n$ (> 6.5) show growth of necks. For samples having smaller $\bar{M}_w/\bar{M}_n$ (< 6.5) the disturbances do not grow and become unclear. The most degraded samples, which have the lowest

Initial Sample



Stretched Sample

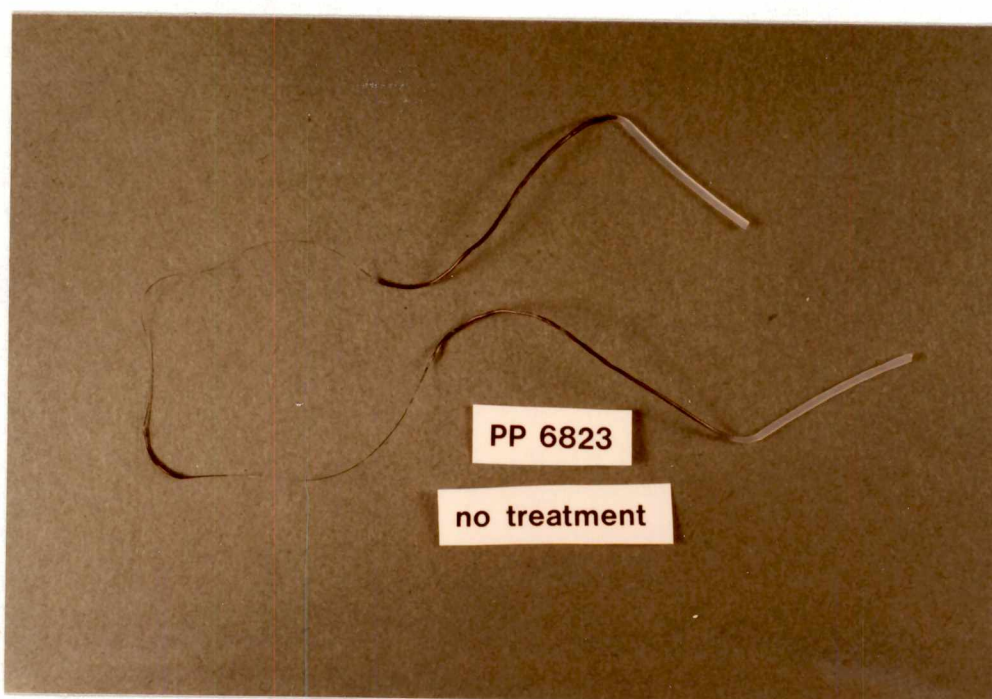
Untreated and Mildly Degraded Sample



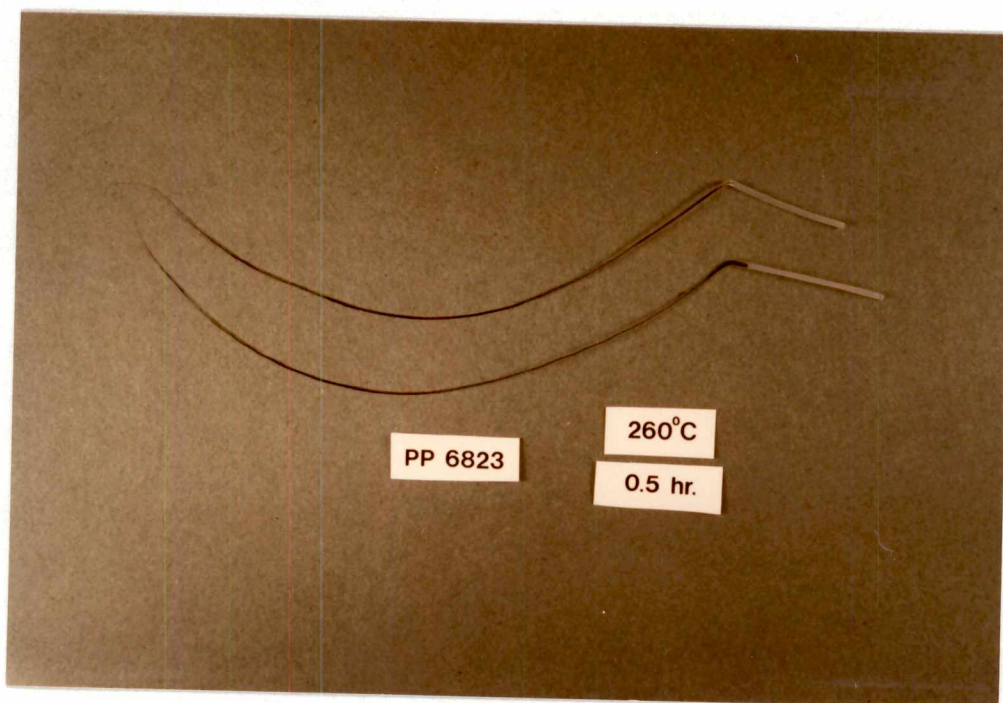
Degraded Sample



Figure VI-4. Stretched Manners of Untreated and Thermally Treated PP and PB-1

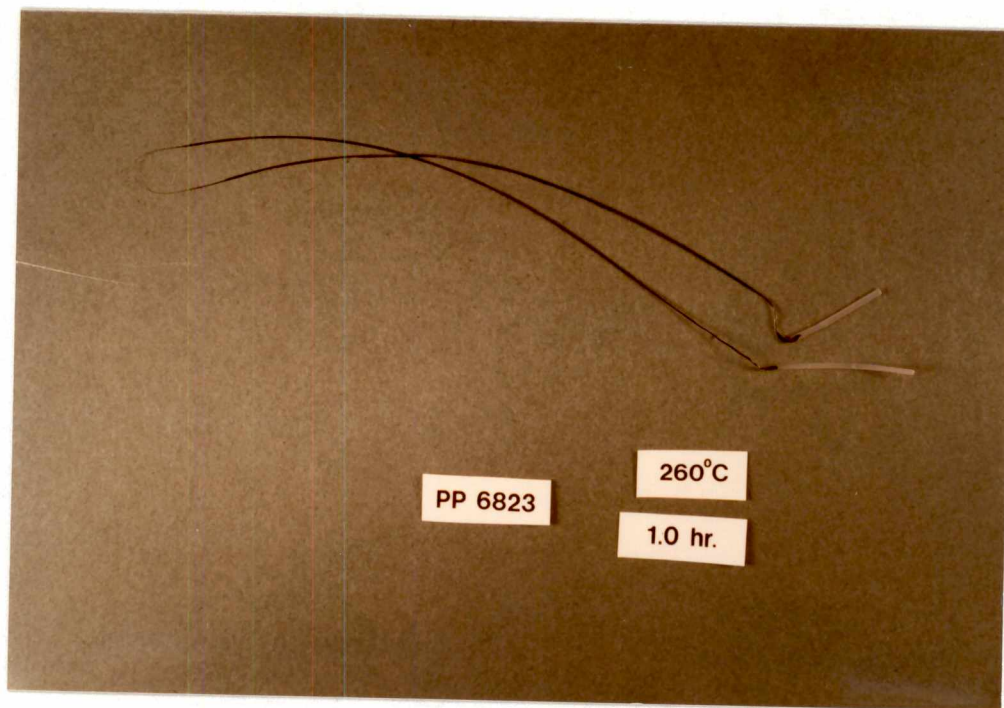


a) Untreated PP

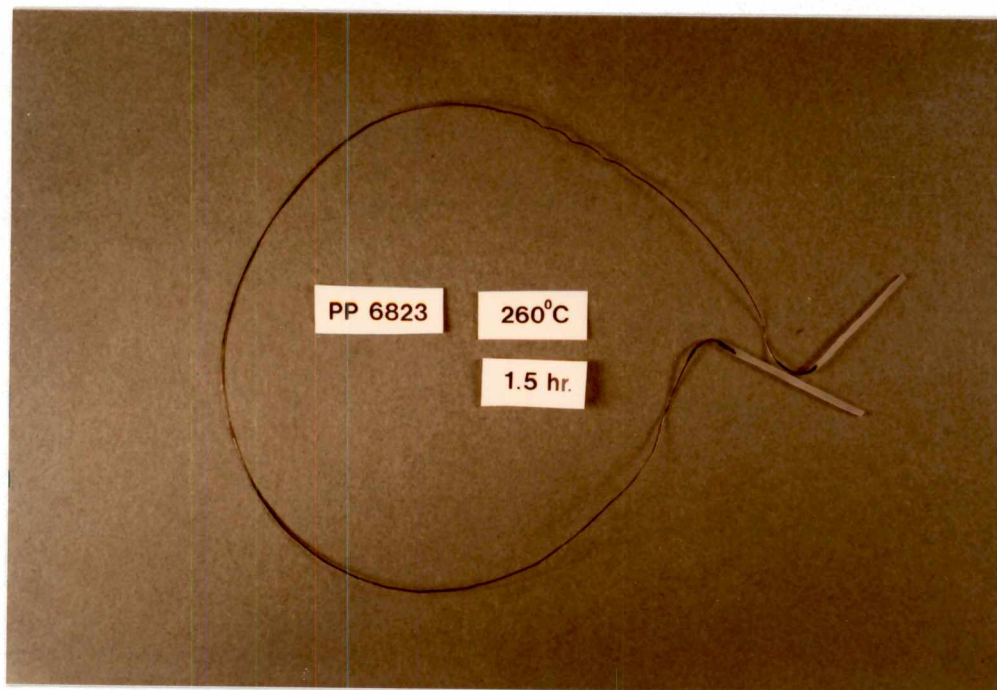


b) PP 260/0.5

Figure VI-5. Photographs of Stretched Filaments of Untreated PP and PP 260/0.5

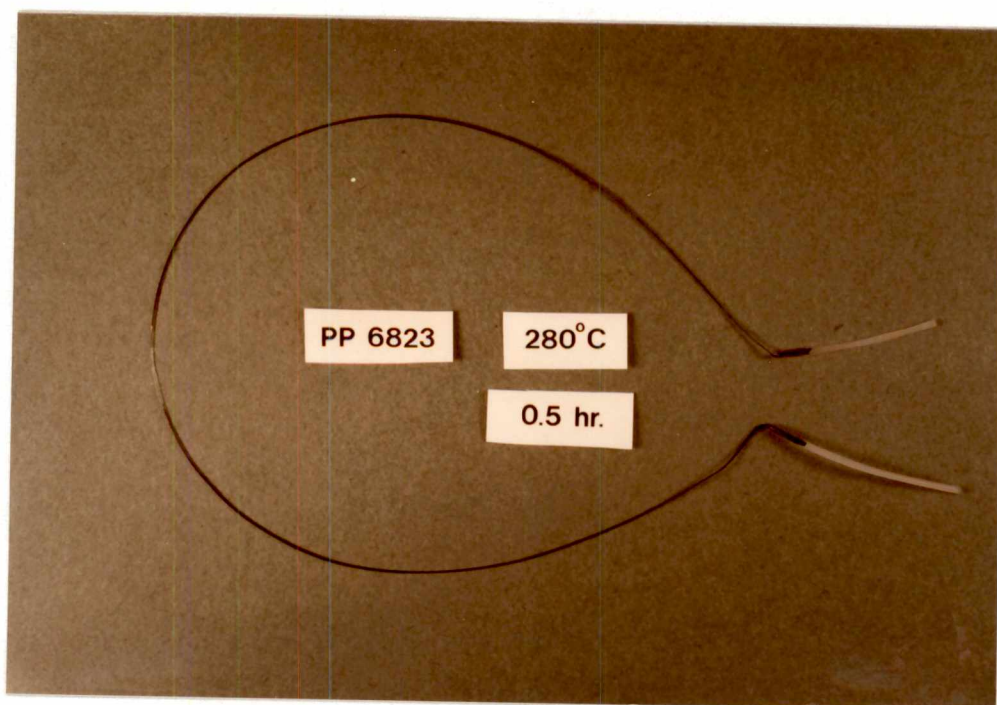


a) PP 260/1.0

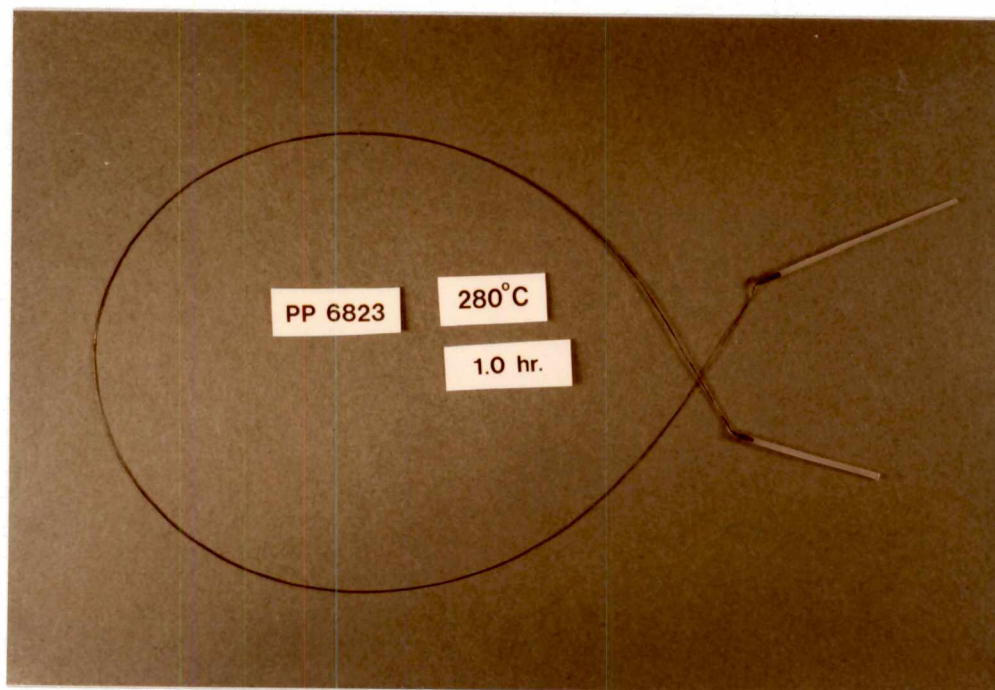


b) PP 260/1.5

Figure VI-6. Photographs of Stretched Filaments of PP 260/1.0 and PP 260/1.5

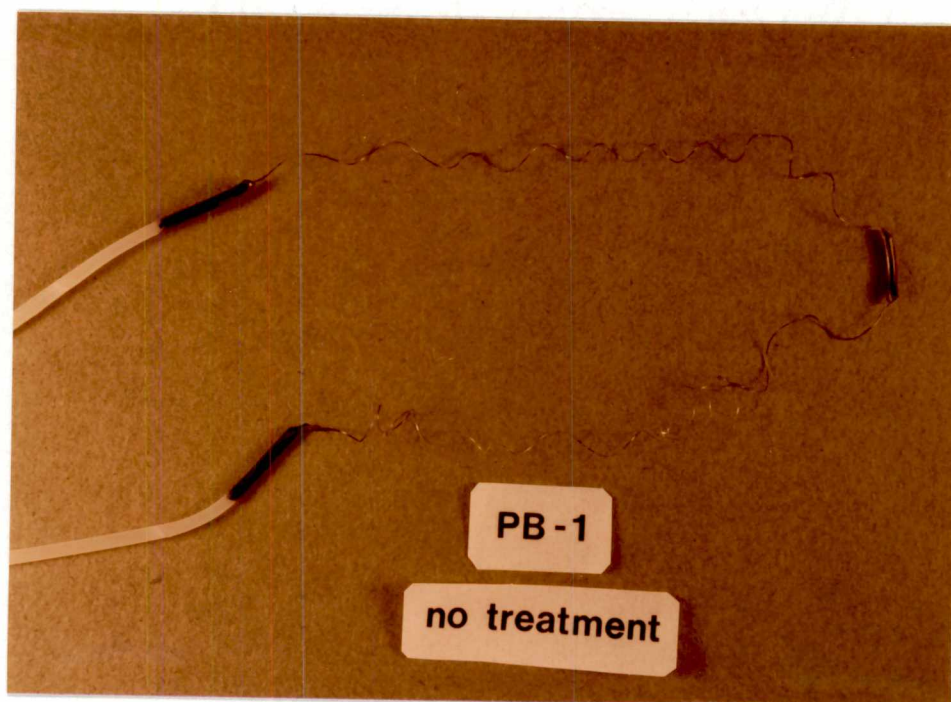


a) PP 280/0.5

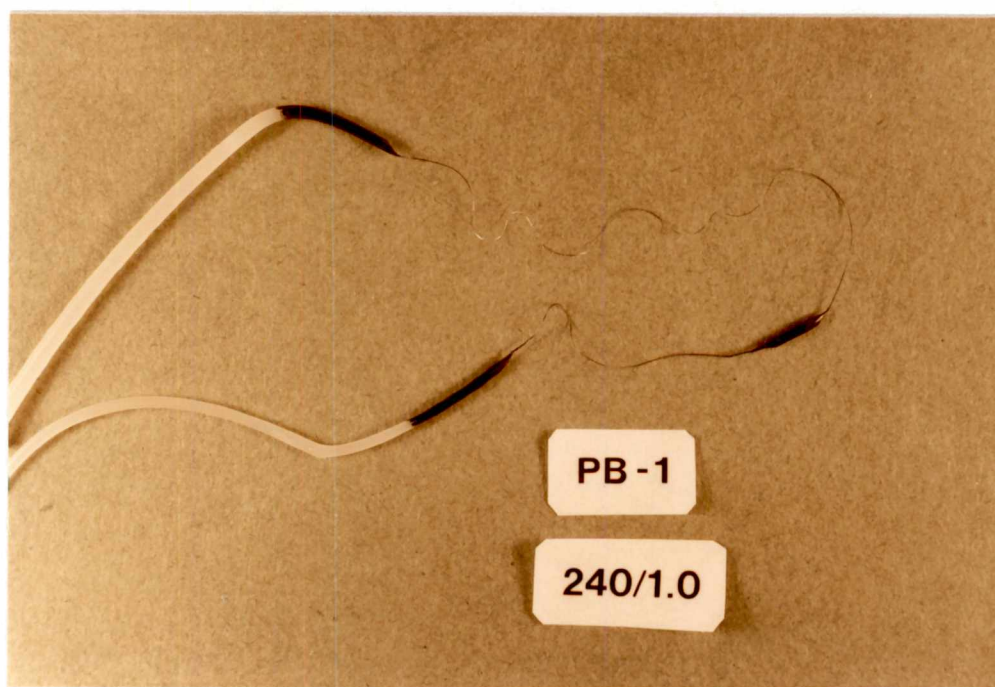


b) PP 280/1.0

Figure VI-7. Photographs of Stretched Filaments of PP 280/0.5 and PP 280/1.0

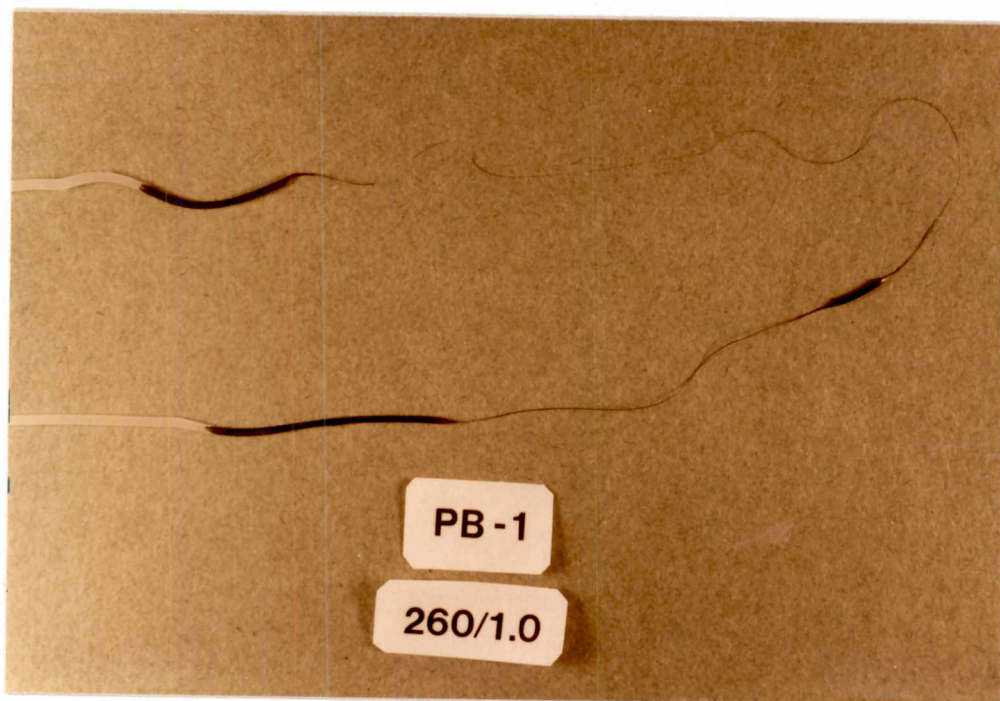


a) Untreated PB-1

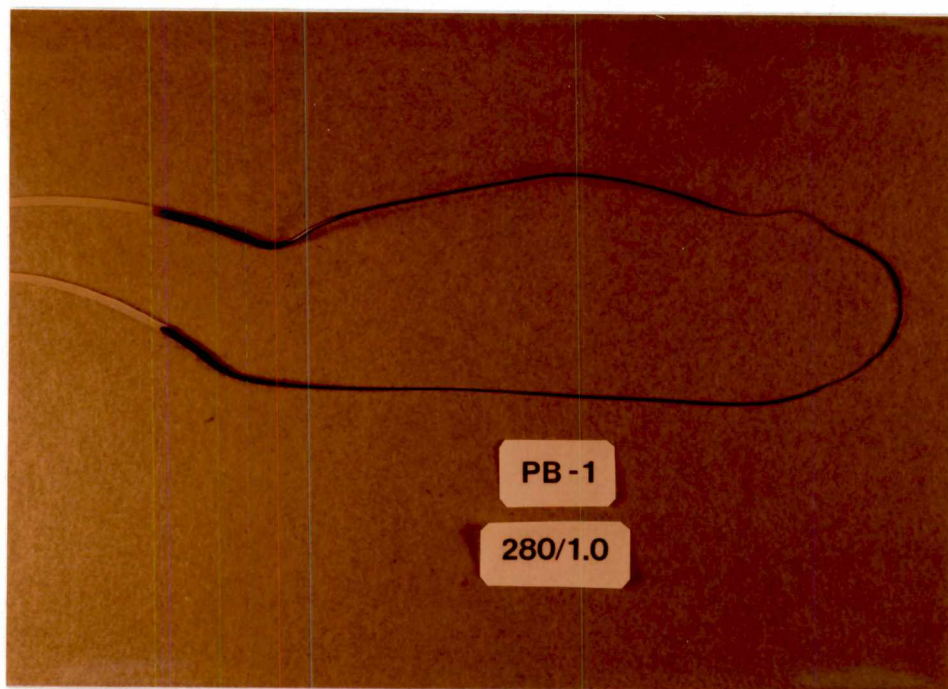


b) PB-1 240/1.0

Figure VI-8. Photographs of Stretched Filaments of Untreated PB-1 and PB-1 240/1.0



a) PB-1 260/1.0



b) PB-1 280/1.0

Figure VI-9. Photographs of Stretched Filaments of PB-1 260/1.0 and PB-1 280/1.0

$\overline{M}_w/\overline{M}_n$ values for both PP and PB-1, show that the disturbances are completely healed as can be seen in the photographs.

The manner of growth of the disturbances in the stretched filaments and its dependence upon the molecular weight distribution is essentially the same as that found by Minoshima et al. (114).

CHAPTER VII

EXTRUDATE SWELL MEASUREMENTS

A-1. Results

In Figure VII-1, the extrudate swell $B (= d/D)$ of untreated and thermally treated PP are plotted as a function of shear stress, where "d" is the diameter of the extrudate and "D" is the inner diameter of the capillary die. In Figure VII-2, similar plots for PB-1 are shown. Both PP and PB-1 exhibit similar dependence of extrudate swell on the extent of thermal treatment. For both PP and PB-1, the magnitude of the extrudate swell, B , increases with shear stress σ_{12} and with the extent of thermal treatment. The rate of increase in B with σ_{12} decreases with the extent of thermal treatment.

A-2. Discussion

Generally the observed extrudate swell is strongly dependent upon the method of measurement. However most experimental data in the literatures show the same trend that the extrudate swell, B , increases with increasing molecular weight and increases with broadning molecular weight distribution at constant shear rate. A similar but less pronounced trend is observed in plots versus die wall shear stress (70, 115, 137). As mentioned in earlier chapters, thermal treatment (viscracking) produces PP and PB-1 having lower molecular weight and narrower molecular weight distribution. Those changes in molecular parameters make the extrudate swell smaller as one can see in Figures VII-1 and VII-2. This agrees with the findings of Racin and Bogue for polystyrene melts and Minoshima et al. (115) for polypropylene melts.

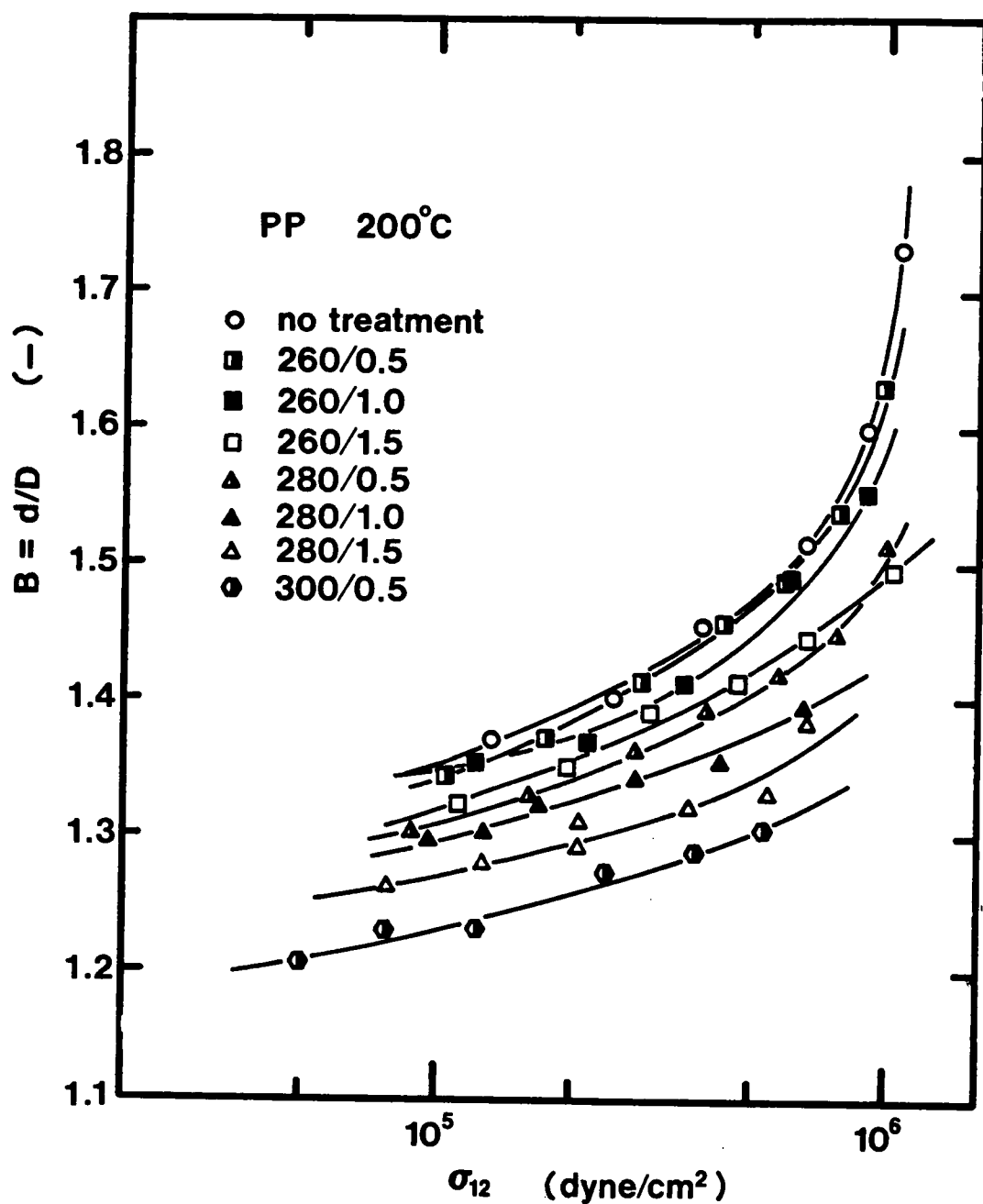


Figure VII-1. Extrudate Swell (B) as a Function of Shear Stress (σ_{12}) for PP

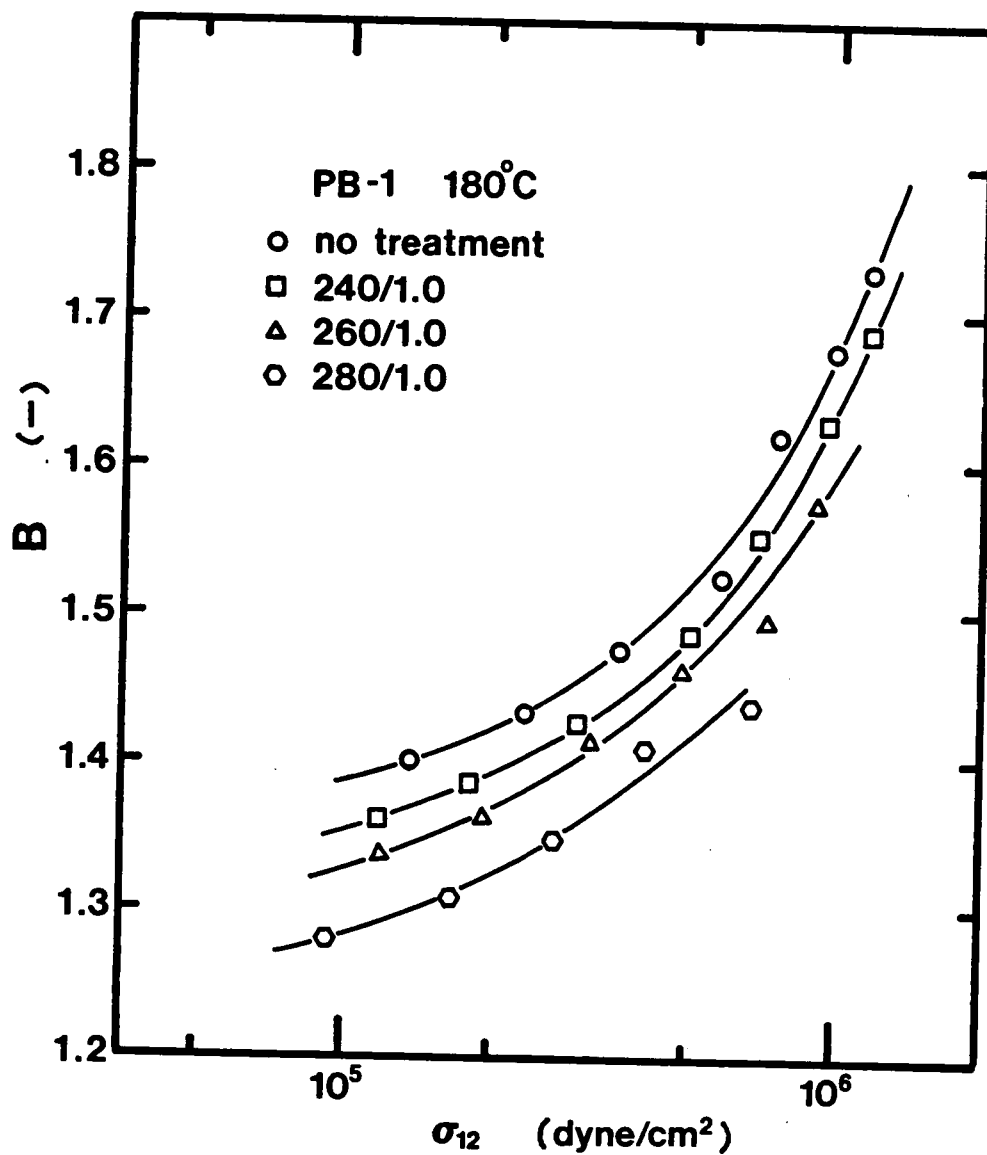


Figure VII-2. Extrudate Swell (B) as a Function of Shear Stress (σ_{12}) for PB-1

To formulate the extrudate swell problems, it is useful to examine data in terms of dimensional analysis. If a viscoelastic fluid's rheological behavior is specified by a Maxwell model with a constant relaxation time, τ , the velocity fields is specified by a dimensionless group, the Weissenberg number, N_{ws} (74).

$$N_{ws} = \tau \frac{U}{L} \quad (7.1)$$

where U and L are the characteristic velocity and length, respectively. Thus

$$B = F (N_{ws}) \quad (7.2)$$

In Figures VII-3 and VII-4, the extrudate swell, B , of PP and PB-1 are plotted against the Weissenberg number, N_{ws} . From the second order fluid theory, N_{ws} can be expressed as (167)

$$N_{ws} = \tau \frac{U}{L} = \frac{N_1}{2\sigma_{12}} \quad (7.3)$$

To represent the variations of the first normal stress difference, N_1 , the empirical power law may be useful.

$$N_1 = A \sigma_{12}^b \quad (7.4)$$

The values of A and b were obtained in Chapter IV. In the plots of B vs N_{ws} , PP and PB-1 still show the same trend as in Figure VII-1 and VII-2, the greater the extent of thermal treatment, the lower the extrudate swell at fixed N_{ws} and the lower the increasing rate of B especially in the high N_{ws} region.

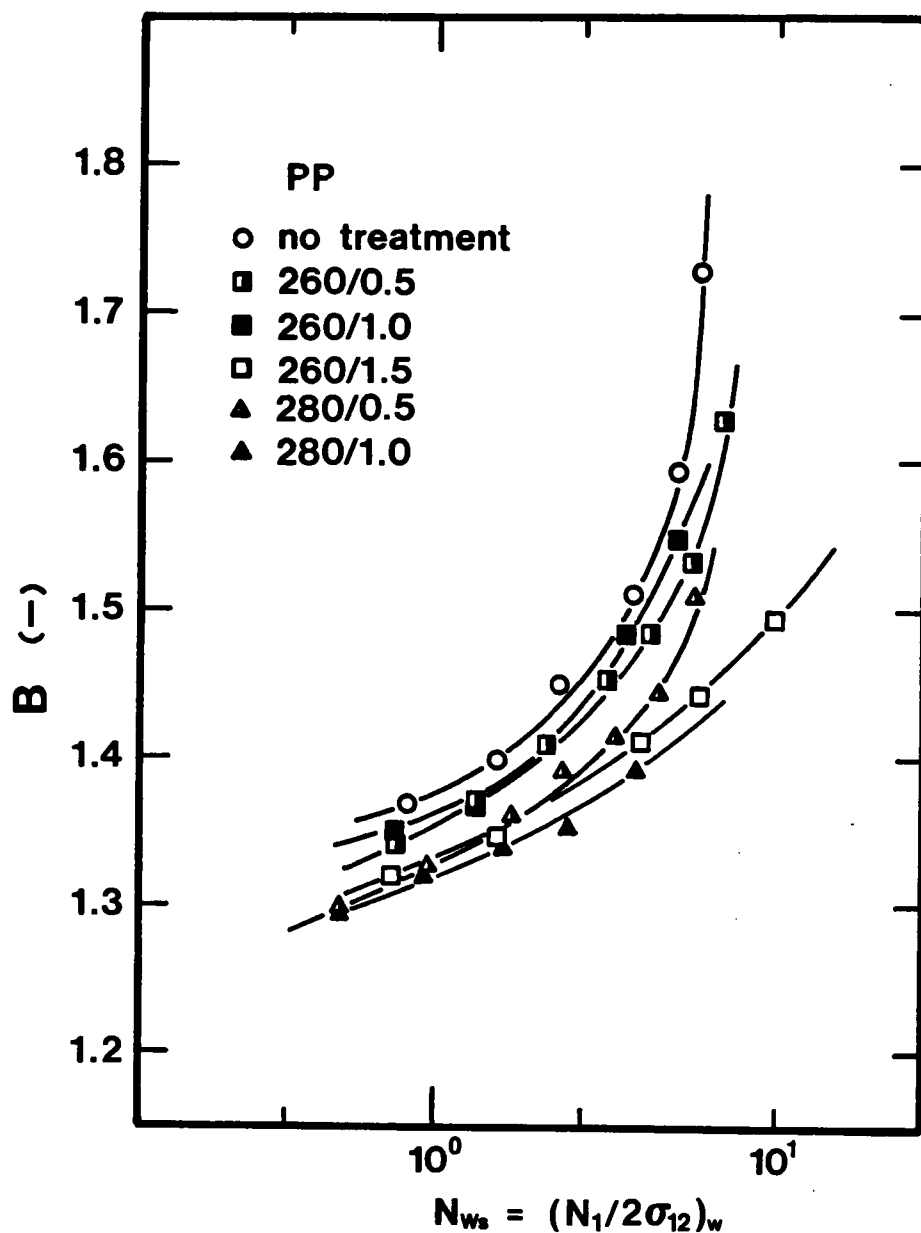


Figure VII-3. Extrudate Swell (B) as a Function of Weissenberg Number (N_{ws}) for PP

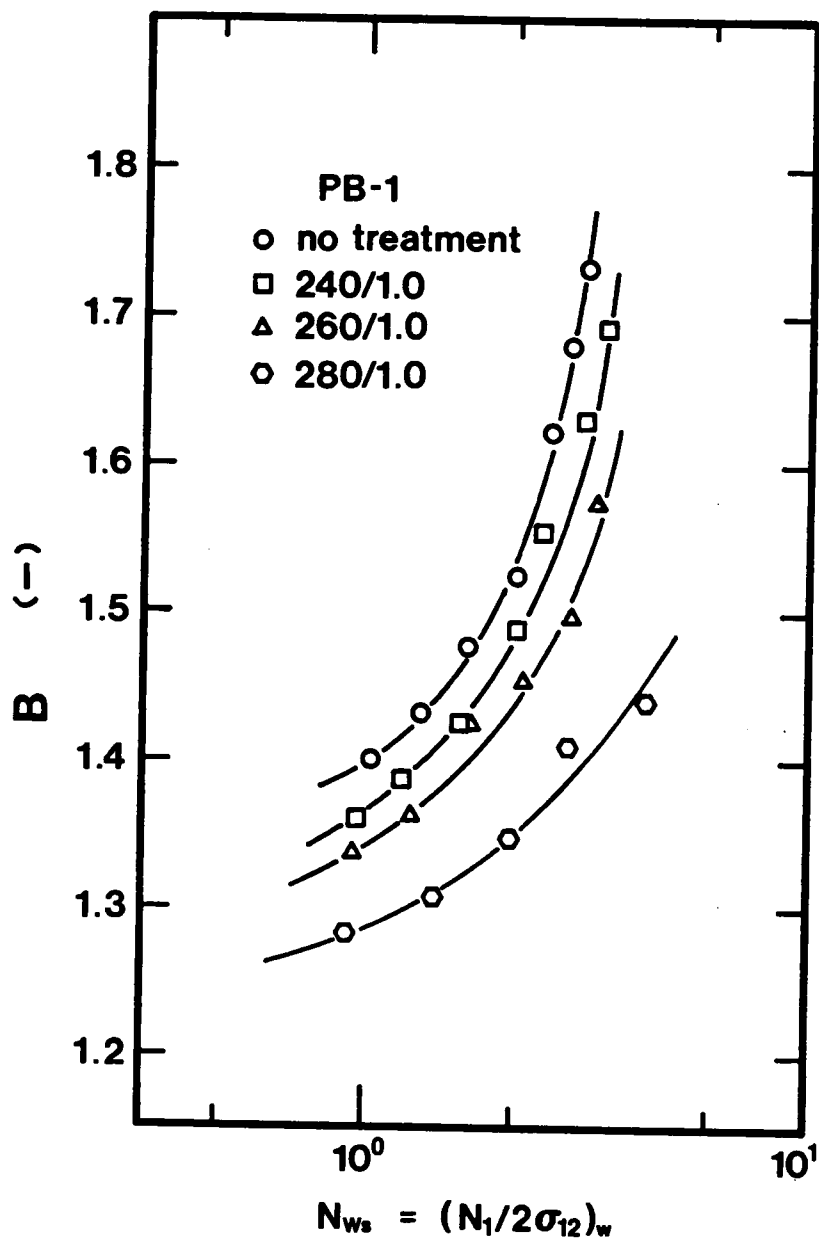


Figure VII-4. Extrudate Swell (B) as a Function of Weissenberg Number (N_{ws}) for PB-1

The simplest consistent theory of the extrudate swell of a Maxwell fluid with constant ν is that developed by Tanner (152) based on unconstrained recovery from Poiseuille flow from a very long tube. This leads to

$$B = \left[1 + \frac{1}{2} \left(\frac{N_1}{2\sigma_{12}} \right)^2 \right]^{\frac{1}{6}} + C \quad (7.5)$$

where C is a constant, which is 0.1 for a Newtonian fluid. In Figures VII-5 and VII-6, the extrudate swell data of untreated and thermally treated PP and PB-1 are plotted with a theoretical curve. The values of B for both untreated PP and PB-1 are well above those of the theoretical predictions. The values of B deviate from theoretical curve at all N_{ws} . Thermally treated PP and PB-1 show lower values of B , but are still much higher than theoretical curve at lower N_{ws} . Similar trends can be seen in the data of Minoshima et al. (115) who noted that the Tanner's equation (Eq. (7-5)) underestimates the extrudate swell even for narrow molecular weight distribution PP. However, our results show that B seems to cross the theoretical prediction line for the degraded samples at higher N_{ws} .

The assumption is made in Tanner's analysis that all materials should behave in a Newtonian fashion at very low stresses giving low stress asymptote 1.1. Racin and Bogue (137) noted that it seemed to be more than 1.1 for broad molecular weight distribution materials. For both untreated PP and PB-1, the correction factor, C , in Eq. (7-5) is 0.3. For degraded PP and PB-1, this is between 0.2 ~ 0.3. This result

is agreement with that of Racin and Bogue (137) since the degraded samples have similar narrow molecular weight distribution, but is higher than that of Minoshima et al. (115) who estimated that C is 0.1 for narrow molecular weight distribution PP. This difference may be caused by the different method of measurement.

If we take the relaxation time, τ , to depend on the deformation rate, we would predict

$$B = F (N_{ws}, \tau(\dot{\gamma})/\tau_0) \quad (7.6)$$

Racin and Bogue (137) and Huang and White (70) considered modified forms of Tanner's theory with

$$B = \left[1 + f(b) N_{ws}^2 \right]^{\frac{1}{6}} + C \quad (7.7)$$

In Figures VII-5 and VII-6 , the comparisons of experimental results and theoretical predictions of Huang and White (70)

$$B = \left[1 + \frac{1}{b} N_{ws}^2 \right]^{\frac{1}{6}} + C \quad (7.8)$$

This result predicts an increasing B with broadening molecular weight distribution, but not enough to correlate the data as is seen in Figure VII-5 .

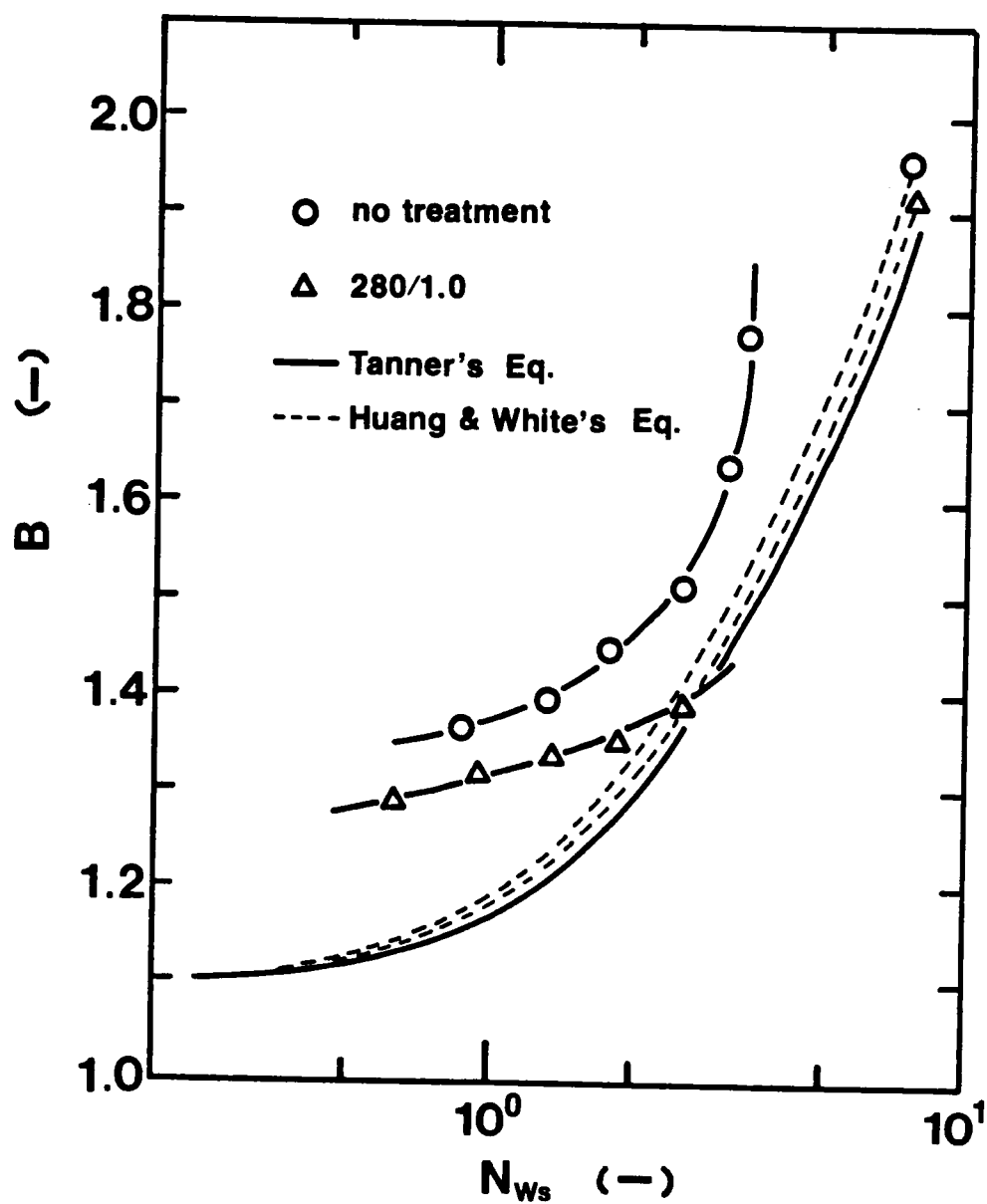


Figure VII-5. Comparisons of Experimental Data to Theories of Extrudate Swell (B) as a Function of Weissenberg Number (N_{ws})

CHAPTER VIII

MELT SPINNING

In this chapter, the apparent spinning elongational viscosity measured by melt spinning and spinline instabilities will be considered.

A. APPARENT ELONGATIONAL VISCOSITY BY ISOTHERMAL MELT SPINNING

A-1. Results

The apparent spinline elongational viscosity, X_{sp} , was measured for untreated and thermally treated (degraded) polypropylene (PP).

Figure VIII-1 shows the diameter of the spinline as a function of distance from the die (spinneret). The data were obtained from photographs. From these data, profiles of the thread line velocity were calculated and are shown in Figure VIII-2.

Apparent spinline elongational viscosity, X_{sp} , and $X_{sp}/3\eta_0$ are plotted as a function of elongational rate, E , in Figures VIII-3 and VIII-4 respectively.

After polymer melt is extruded from a die, the velocity continues to increase from the velocity at the die to take-up velocity. In Figure VIII-2, one can see that the velocity of untreated PP is strong increasing function of spinline length, and the more degraded samples show a lower rate of increase in velocity. The untreated and mildly degraded samples are drawn down more rapidly than other degraded samples.

In Figure VIII-3, it is seen that untreated sample and mildly degraded samples exhibit strongly decreasing X_{sp} with elongational rate while highly degraded samples exhibit slightly decreasing or constant

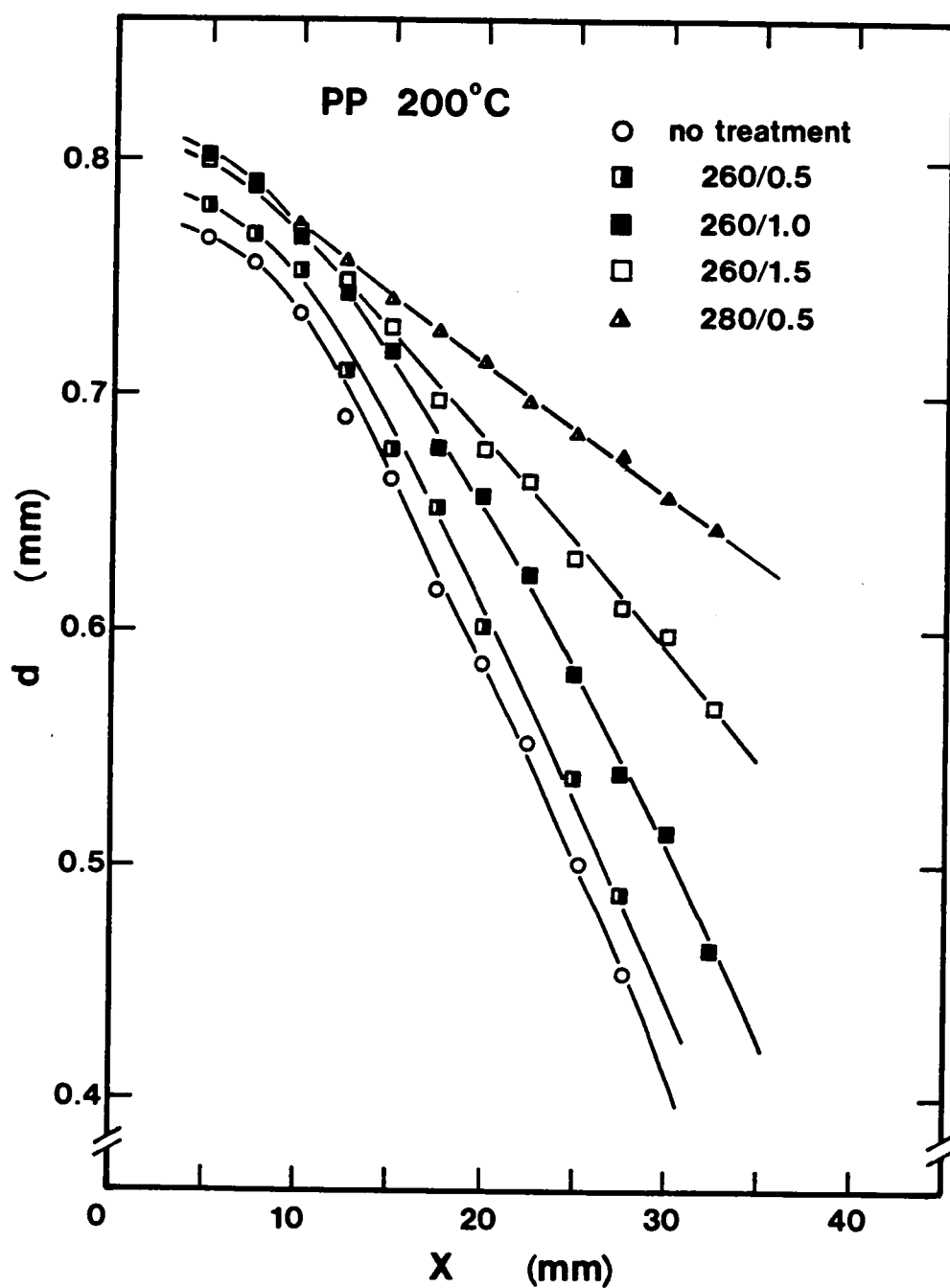


Figure VIII-1. Profiles of Thread Diameter ($d(x)$) as a Function of Distance (x) along Spinline Way for PP under Isothermal Condition

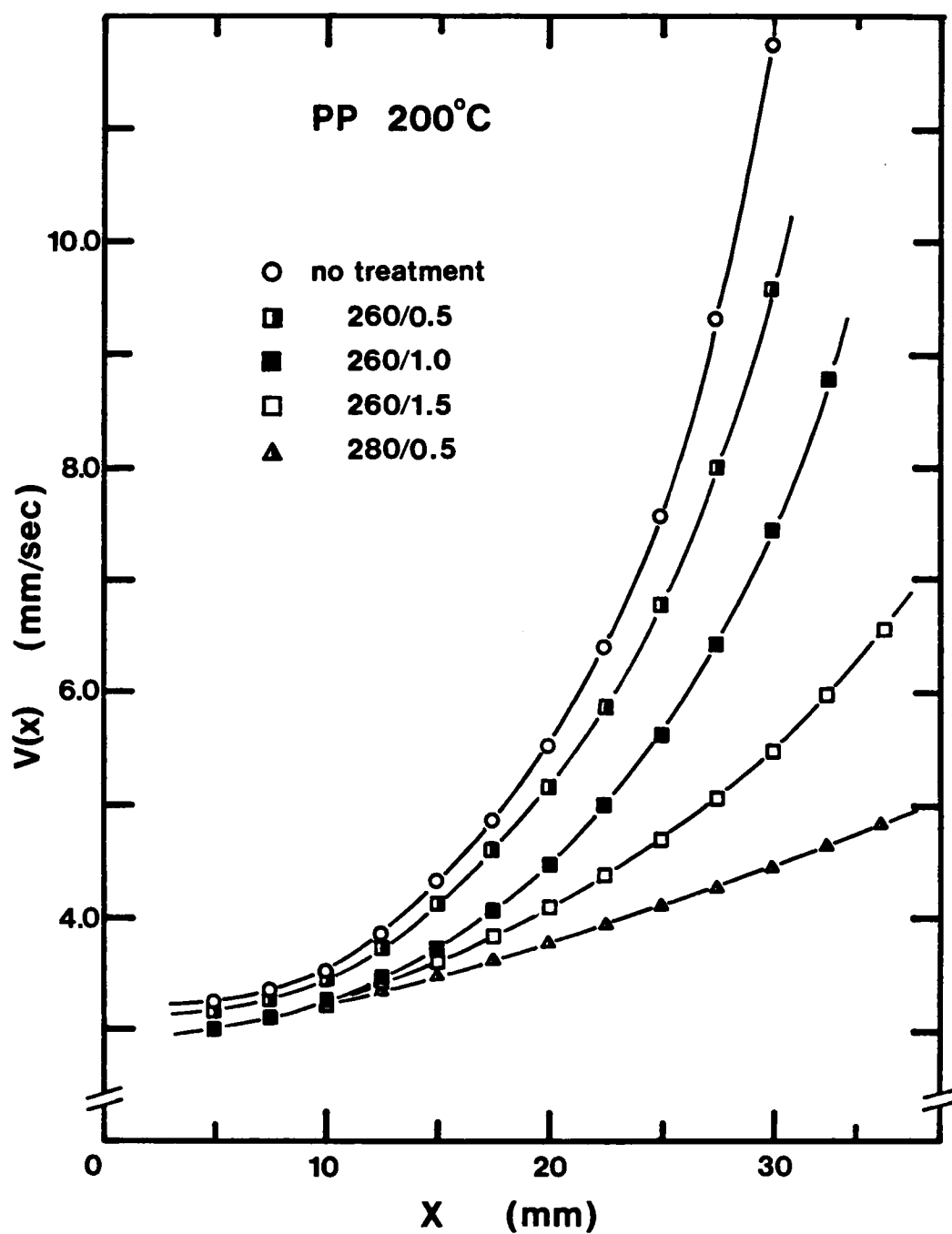


Figure VIII-2. Profiles of Thread Velocity ($V(x)$) as a Function of Distance (x) along Spinline Way for PP under Isothermal Condition

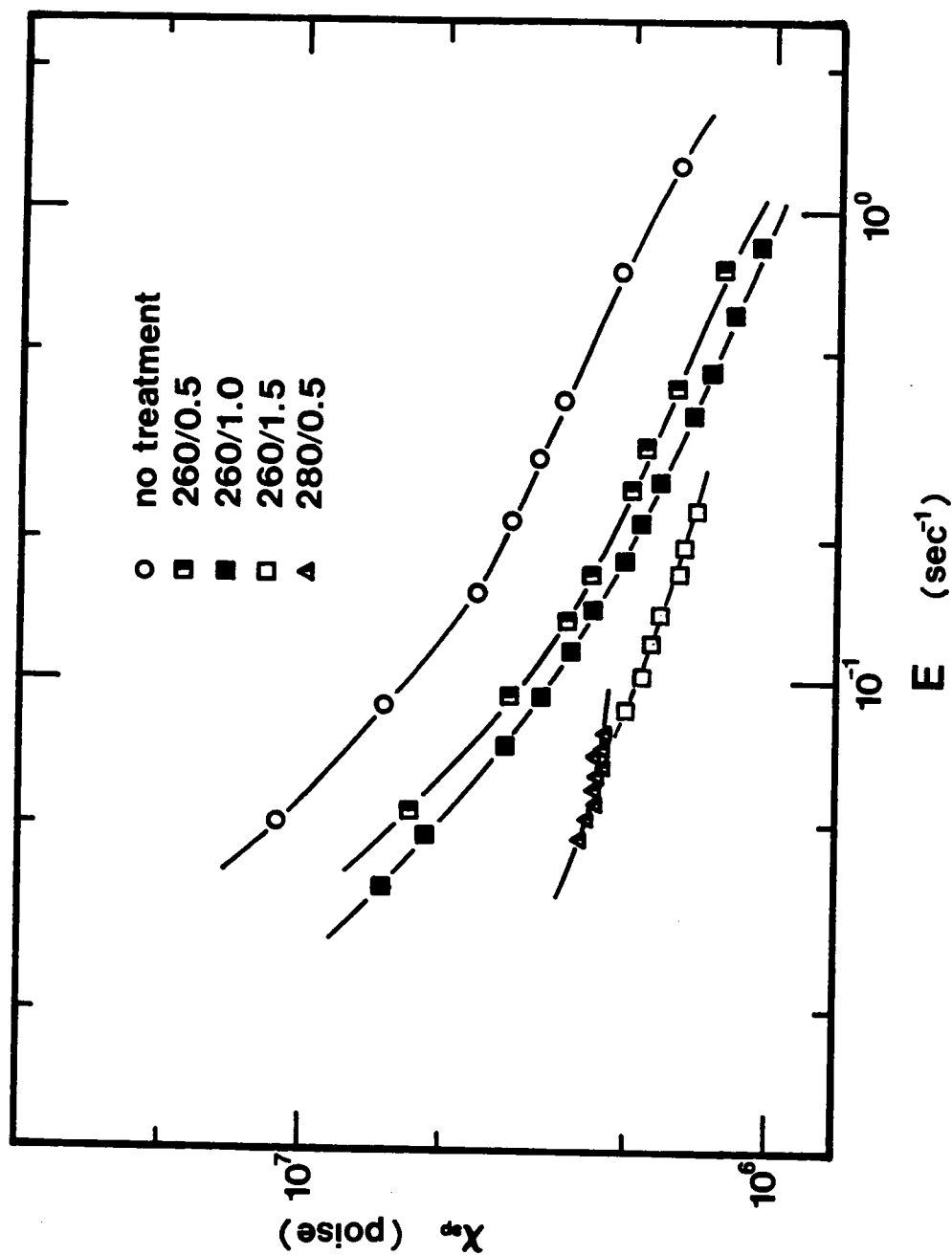


Figure VIII-3. Spinline Elongational Viscosity (X_{sp}) as a Function of Elongational Rate (E) for PP

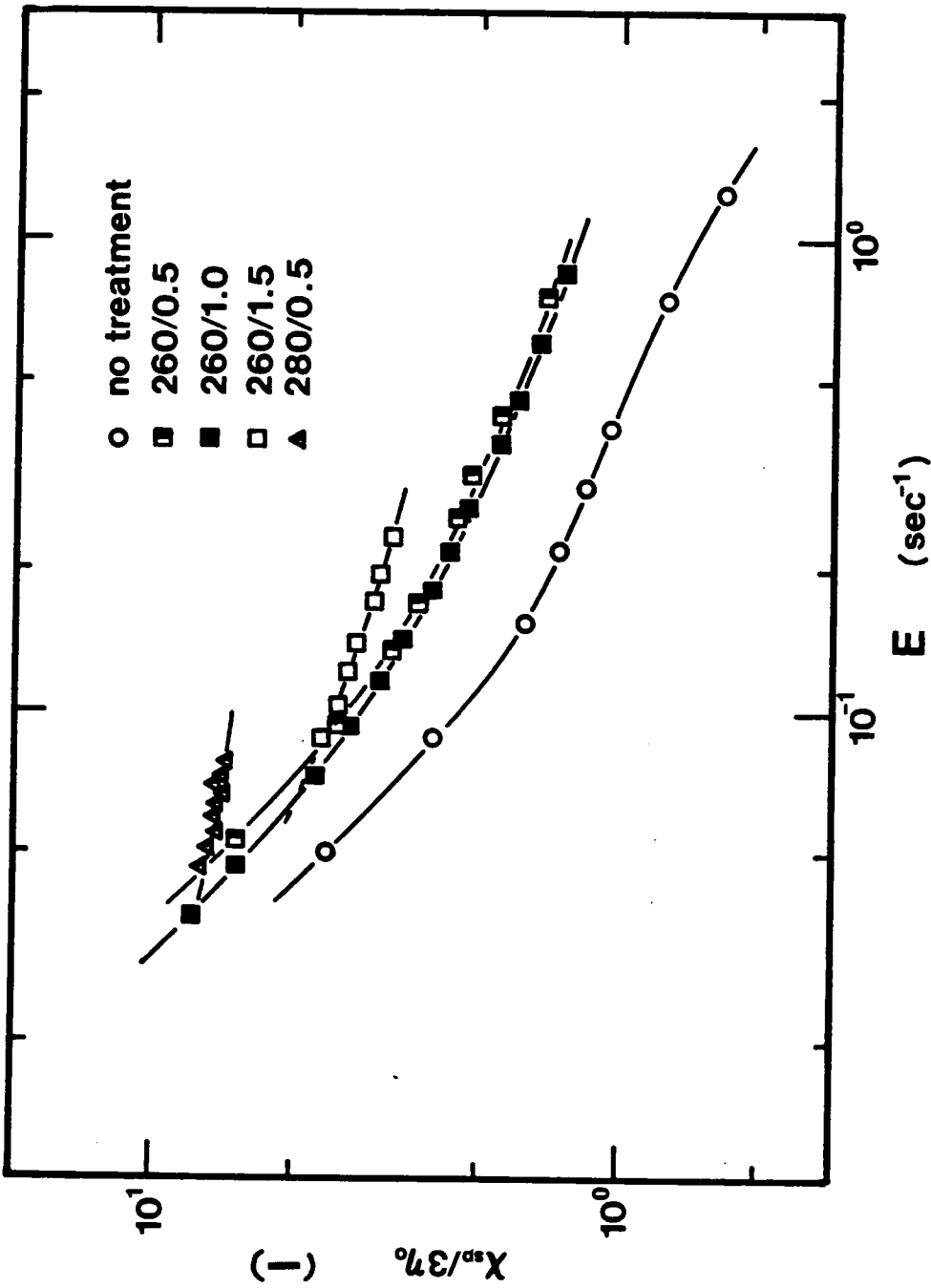


Figure VIII-4. Reduced Spinline Elongational Viscosity ($X_{sp}/3\eta_0$) as a Function of Elongational Rate (E) for PP

χ_{sp} . The range of elongational rate, E , in the isothermal chamber for the former is much larger than that for the latter.

A-2. Discussion

Comparing our results with those for other PP measured by Minoshima et al. (115), the untreated and mildly degraded samples have similar χ_{sp} to broad molecular weight distribution PP. Highly degraded samples behave as narrow molecular weight distribution PP in elongational flow. The shapes of our χ_{sp} are similar to those of Minoshima et al. of the same value of $\bar{M}_w/\bar{M}_n$. The $\bar{M}_w/\bar{M}_n$ of our samples are those estimated from the $\eta/\eta_0 - \eta_0 \dot{\gamma}$ plots.

It is of interest to contrast the apparent spinline elongational viscosity, χ_{sp} , with the results of more basic experiments which are described in Chapter VI. In Figure VIII-5, the $\chi_{sp}/3\eta_0$ and $\chi/3\eta_0$ are plotted as a function of elongational rate, E . The samples which show strongly decreasing $\chi_{sp}/3\eta_0$ show decreasing $\chi/3\eta_0$ in simple elongational flow and the magnitudes are almost the same for $\chi_{sp}/3\eta_0$ and $\chi/3\eta_0$. The samples which show slightly decreasing or constant $\chi_{sp}/3\eta_0$ show constant or slightly increasing $\chi/3\eta_0$. The magnitudes of $\chi_{sp}/3\eta_0$ is much higher than $\chi/3\eta_0$. The latter is at most 1.5.

B. ELONGATIONAL FLOW INSTABILITY DURING ISOTHERMAL MELT SPINNING

B-1 Results

Filament diameter fluctuations of two types are observed. One of these is random in character and seems to occur to varying extents under all spinning conditions in which the threadline is drawn down. The second type of diameter fluctuations has a well defined wavelength

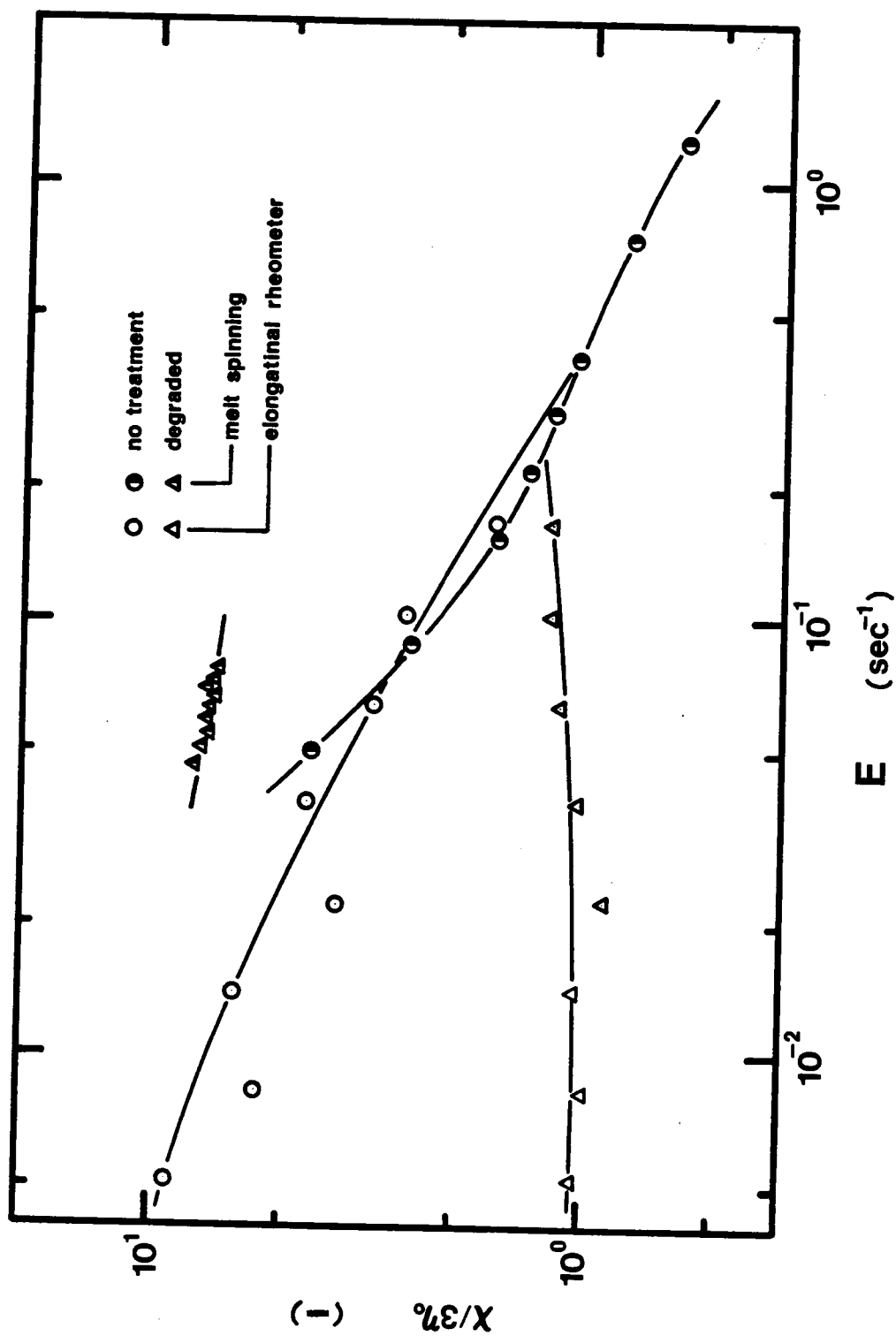


Figure VIII-5. Comparisons of Reduced Spinline Elongational Viscosity ($X_{sp}/3\eta_0$) to Reduced Elongational Viscosity ($X/3\eta_0$) Measured in Simple Elongational Flow for PP

or period and a much larger amplitude. The two types of diameter fluctuations are shown in Figures VIII-6 and VIII-7. These deameter fluctuations were measured directly with a thickness gage. In Figure VIII-6, the diameter fluctuations of untreated PP at two different draw down ratios, and in Figure VIII-7, those of untreated and degraded PP are shown.

The second type of diameter fluctuations occurs when draw down ratio, V_L/V_O , exceeds a critical value. The critical draw down ratio at the onset of the second type of diamter fluctuations is listed in Table VIII-1 for untreated and degraded PP and PB-1. As the extent of thermal treatment increases the critical draw down ratio increases.

B-2. Discussion

There are two types of phenomena giving rise to deameter fluctuation in the spinline. One of these is induced by random fluctuation in spinline tension, output, cooling condition, etc. as proposed by Kase and Matsuo (80), which may be termed "forced oscillations". The second type is called "draw resonance" or "natural oscillations" which is hydrodynamic instability first described by Kase, Matsuo and Yoshimoto (83) and Pearson and Matovich (128).

White and Ide (169) argued that draw resonance is a continuous spinline form of the neck development ductile failure instability. Polymer melts exhibiting ductile failure should tend to exhibit draw resonance at low V_L/V_O . The data obtained by Minoshima et al. (115) and our data show good agreement with the theory of White and Ide. According to Minoshima et al. (114, 115), polypropylenes which tend to show the necking phenomena have broad molecular weight distribution,

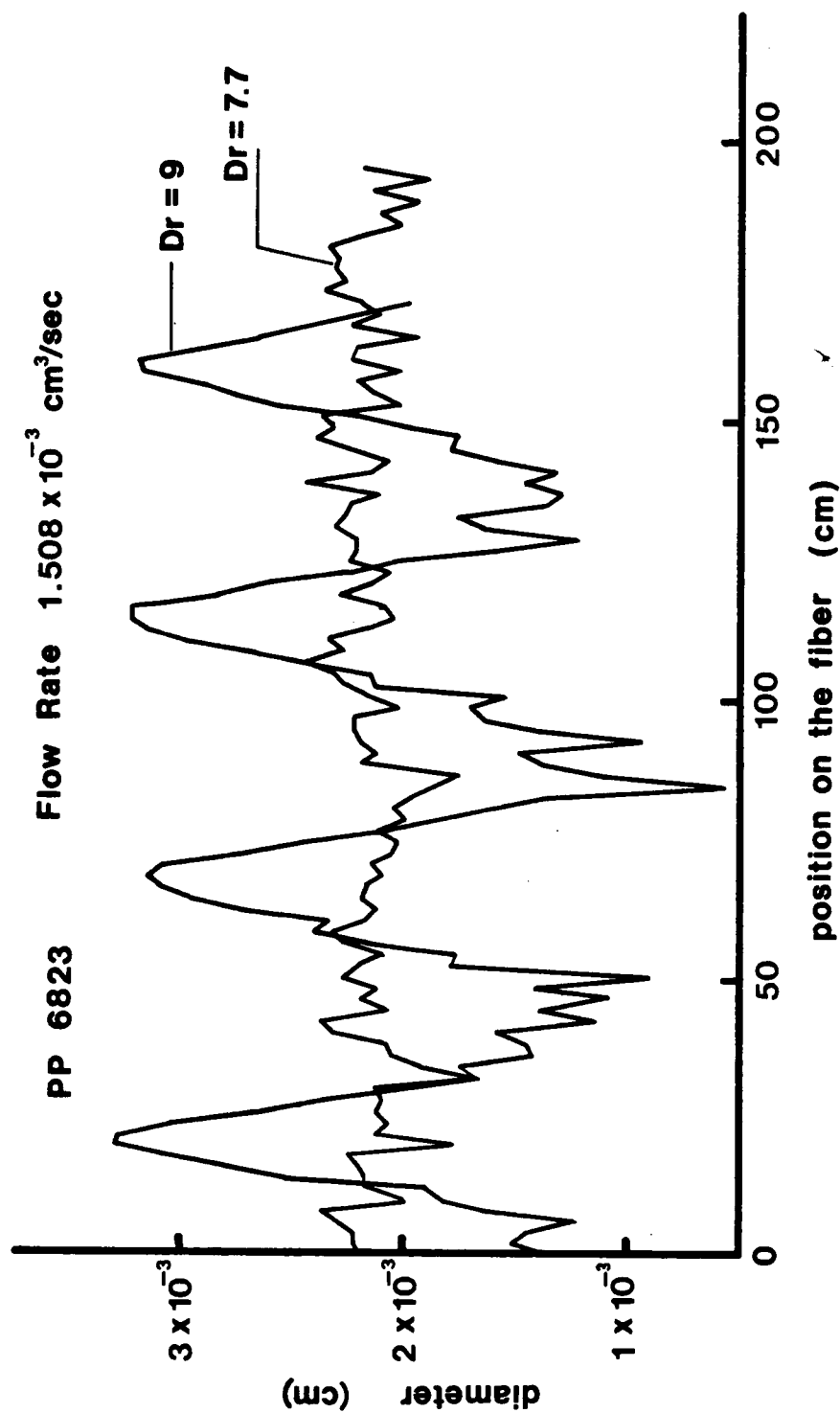


Figure VIII-6. Thread Diameter Fluctuations of PP at Two Different Draw Down Ratios

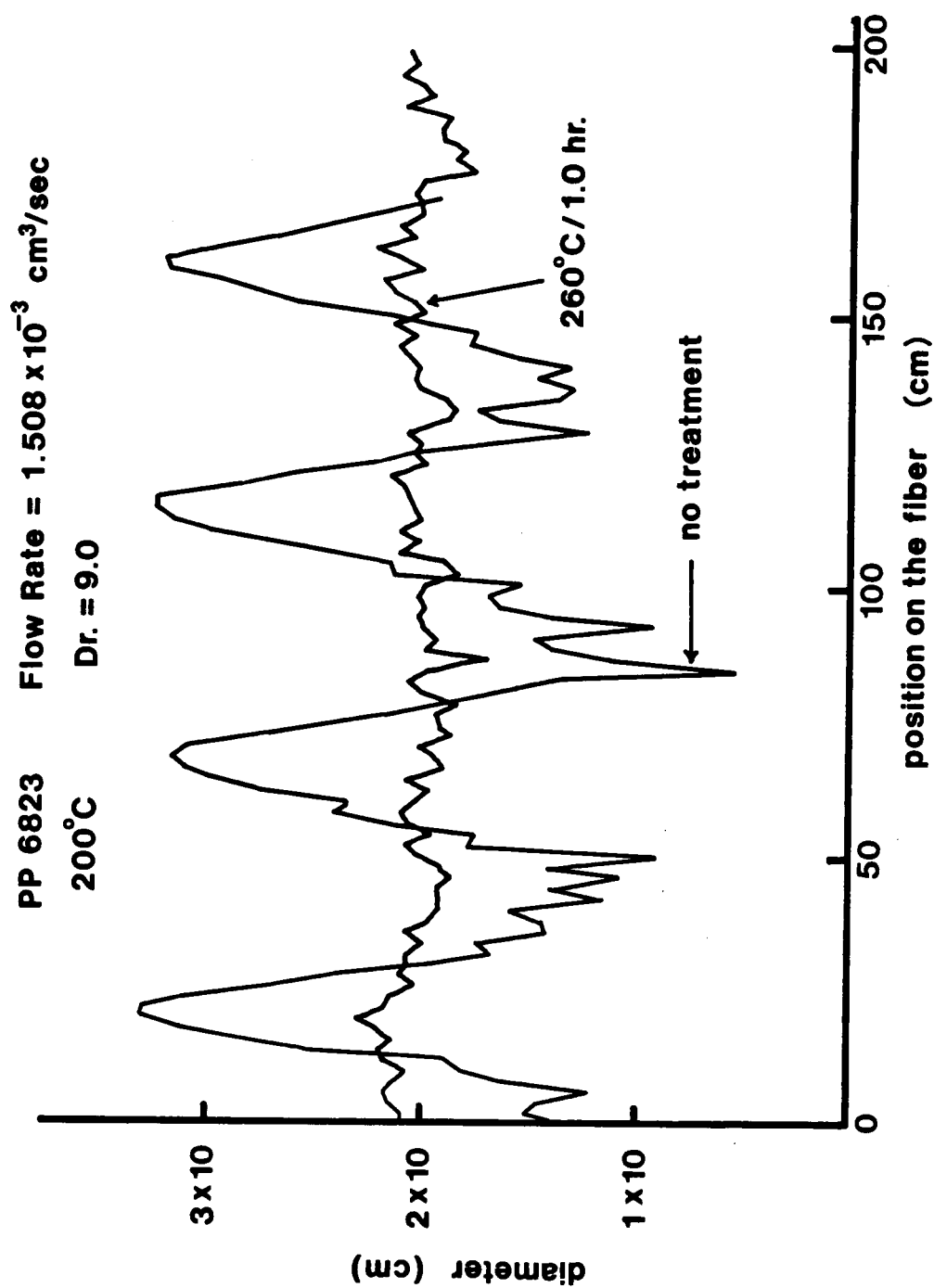


Figure VIII-7. Thread Diameter Fluctuations of Untreated and Thermally Treated PP

Table VIII-1. Onset of Draw Resonance in Isothermal Melt Spinning

$$(V_o = 3.54 \times 10^{-1} \text{ cm/sec})$$

Polymer		Onset (V_o/V_L)
PP	(200°C)	
	no treatment	6.3
	260/0.5	8.3
	260/1.0	8.6
	260/1.5	8.9
	280/0.5	9.8
	280/1.0	10.1
	280/1.5	not spinnable
PB-1	(180°C)	
	no treatment	8.2
	240/1.0	8.45
	260/1.0	9.0
	280/1.0	9.9

and such materials tend to exhibit draw resonance at low V_I/V_O . Polypropylenes not showing necking phenomena have narrow molecular weight distributions, and are more stable in melt spinning.

As mentioned in Chapter IV, thermal treatment (viscracking) makes the molecular weight lower and the distribution narrower. The critical draw down ratio is increasing with increasing the extent of thermal treatment. In our case we can not separate the effect of narrowing molecular weight distribution from the lowering molecular weight. Minoshima et al. (114, 115) however have been able to conclude that narrowing molecular weight distribution and not absolute molecular weight is the stabilizing factor.

CHAPTER IX

REPRESENTATION OF EXPERIMENTAL DATA IN TERMS OF A CONVECTED MAXWELL MODEL

A. CONSTITUTIVE EQUATION

In this chapter, we will seek to represent our experimental data in terms of the differential Maxwell model of White and Metzner (172) which is of form

$$\sigma = -p \underline{I} + \underline{P} \quad (9.1)$$

$$\underline{P} = 2G\tau(\text{II}_{\underline{d}}) \underline{d} - \tau(\text{II}_{\underline{d}}) \frac{\delta \underline{P}}{\delta t} \quad (9.2)$$

where p is the pressure, $\underline{P}$ is the extra stress, $\underline{I}$ is the unit tensor, G is the modulus and τ is the relaxation time which depends upon the rate of deformation tensor, $\underline{d}$, specifically $\text{II}_{\underline{d}} = 2 \text{tr } \underline{d}^2$. The convected derivative is of form

$$\frac{\delta \underline{P}}{\delta t} = \frac{D \underline{P}}{Dt} - \nabla \underline{V} \cdot \underline{P} - \underline{P} \cdot \nabla \underline{V} \quad (9.3)$$

following Ide and White (73, 74) we have used the form of relaxation time which was proposed by Bogue (14, 15, 26).

$$\tau = \frac{\tau_0}{1 + a \tau_0 \text{II}_{\underline{d}}^{\frac{1}{2}}} \quad (9.4)$$

where τ_0 is the zero deformation rate relaxation time and "a" is a material parameter which represents the deformation rate dependence.

Eqs. (9.1) to (9.3) are in no sense the best fitting of all constitutive equations but represent rather the best approximate compromise form for developing a constitutive equation simple enough to develop a fluid mechanics.

For the convected Maxwell model, we may write the viscosity, η , the first and second normal stress differences, N_1 and N_2 , and the elongational viscosity, χ , as

$$\eta = \frac{\sigma_{12}}{\dot{\gamma}} = G \tau_0 \left(\frac{\tau}{\tau_0} \right) \quad (9.5a)$$

$$N_1 = 2G \tau_0^2 \left(\frac{\tau}{\tau_0} \right)^2 \dot{\gamma}^2 \quad (9.5b)$$

$$N_2 = 0 \quad (9.5c)$$

where

$$\frac{\tau}{\tau_0} = \frac{1}{1 + a \tau_0 \dot{\gamma}} \quad (9.6)$$

and

$$\chi = \frac{3G \tau_0 (\tau/\tau_0)}{[1 + (\tau/\tau_0) \tau_0 E] [1 - 2(\tau/\tau_0) \tau_0 E]} \quad (9.7)$$

where

$$\frac{\tau}{\tau_0} = \frac{1}{1 + \sqrt{3} a \tau_0 E} \quad (9.8)$$

Here $\dot{\gamma}$ is the shear rate and E is the elongational rate.

In Eqs. (9.4) to (9.8), there are three material parameters, τ_0 , G and "a", to be determined. To obtain these parameters, we propose three procedures.

- (1) The modulus, G , can be obtained by combining Eqs. (9.5a) and (9.5b).

$$G = \frac{2\sigma_{12}^2}{N_1} \quad (9.9)$$

We may then determine G from a $N_1 - \sigma_{12}$ plot.

- (2) If we combine Eqs. (9.4) and (9.5) we have

$$\frac{1}{\eta} = \frac{1}{\eta_0} + a \frac{\tau_0}{\eta_0} \dot{\gamma} \quad (9.10a)$$

or

$$\frac{G}{\eta} = \frac{G}{\eta_0} + a \dot{\gamma} \quad (9.10b)$$

where τ_0 is the zero shear viscosity. Plots of $1/\eta$ or G/η vs $\dot{\gamma}$ for G values obtained in procedure (1) give "a" and τ_0 since $G/\eta_0 = \tau_0$.

- (3) Best fit "a" and G values are obtained by trying to optimize the fit in both (1) and (2).
- (4) "a" and τ_0 may be obtained in another procedure. Combining Eqs. (9.4), (9.5) and (9.6), we have

$$\frac{2\sigma_{12}\dot{\gamma}}{N_1} = \frac{1}{\tau} = \frac{1}{\tau_0} + a \dot{\gamma} \quad (9.11)$$

Table IX-1. Procedures to Obtain τ_o , G and "a"

	(1) $N_1 - \sigma_{12}$	(2) $G/\eta - \dot{\gamma}$	(4) $2\sigma_{12}\dot{\gamma}/N_1 - \gamma$	(5) $\chi/3\eta_o - \tau_o E$
τ_o	-	Yes	Yes	τ_o known
G	Yes	G known	-	-
"a"	-	Yes	Yes	Yes

(1) Determine G values from $N_1 - \sigma_{12}$ plot.

(2) Determine τ_o and "a" from $G/\eta - \dot{\gamma}$ plot.

(3) Optimize G for reasonable τ_o and "a" from (1) and (2).

(4) Determine τ_o and "a" from $1/\tau - \dot{\gamma}$ plot.

(5) Check "a" values using $\chi/3\eta_o - \tau_o E$ plot.

If we plot $2 \sigma_{12} \dot{\gamma} / N_1$ against $\dot{\gamma}$, the intercept gives $1/\tau_0$ and the slope gives "a".

- (5) We can check "a" values determined in procedures (2), (3) and (4) using data of $\chi/3\eta_0$ vs $\tau_0 E$. Using the theory of Ide and White (74) only filaments with low "a" may be stretched in a stable manner. If a material shows that $\chi/3\eta_0 \approx 1$ at low $\tau_0 E$ and $\chi/3\eta_0$ is constant or increasing function of $\tau_0 E$, it should have small "a". If the filaments extend in a non-uniform manner usually leading to $\chi/3\eta_0 > 1$ at low $\tau_0 E$ and $\chi/3\eta_0$ is decreasing function of $\tau_0 E$, it should have larger "a".

These procedures are summarized in Table IX-1.

B. VALUES OF τ_0 , G AND "a"

We first proceeded by applying this approach to a series of well characterized polymer melts discussed in the literature. In Table IX-2 the standard materials, two polypropylenes (PP-B, PP-N), two polyethylene (HDPE, LDPE) and a Polystyrene (PS), and the sources from which the data were taken are listed.

N_1 increases less rapidly than σ_{12} . $1/\eta$ and $1/\tau$ do not increase exactly linearly with $\dot{\gamma}$. In Figures IX-1 to IX-3, plots of $1/\eta$ vs $\dot{\gamma}$ and $1/\tau$ vs $\dot{\gamma}$ are shown for PP-B, LDPE and PS. The resultant estimated τ_0 , G and "a" of the standard materials are listed in Tables IX-3 to IX-5. To determine the values of G, we considered data at $\sigma_{12} = 10^4$ and 10^5 (dyne/cm²). As the formulation is expected to fit experimental data best at low σ_{12} , it seems more reasonable to accept these values.

Table IX-2. Standard Materials Used for Determination of
Material Parameters

Polymer	Code	Temp.	Reference
Broad MWD PP	PP - B	180°C	Minoshima et al. (72, 112)
Narrow MWD PP	PP - N	180°C	Minoshima et al. (72, 112)
HDPE (Marlex 6001)	HDPE	180°C	Minagawa & White (111) Ide & White (73)
LDPE (Tenite 800)	LDPE	160°C	Chen & Bogue (26) Ide & White (73)
PS (Styron 678U)	PS	180°C	Suetsugu (149)

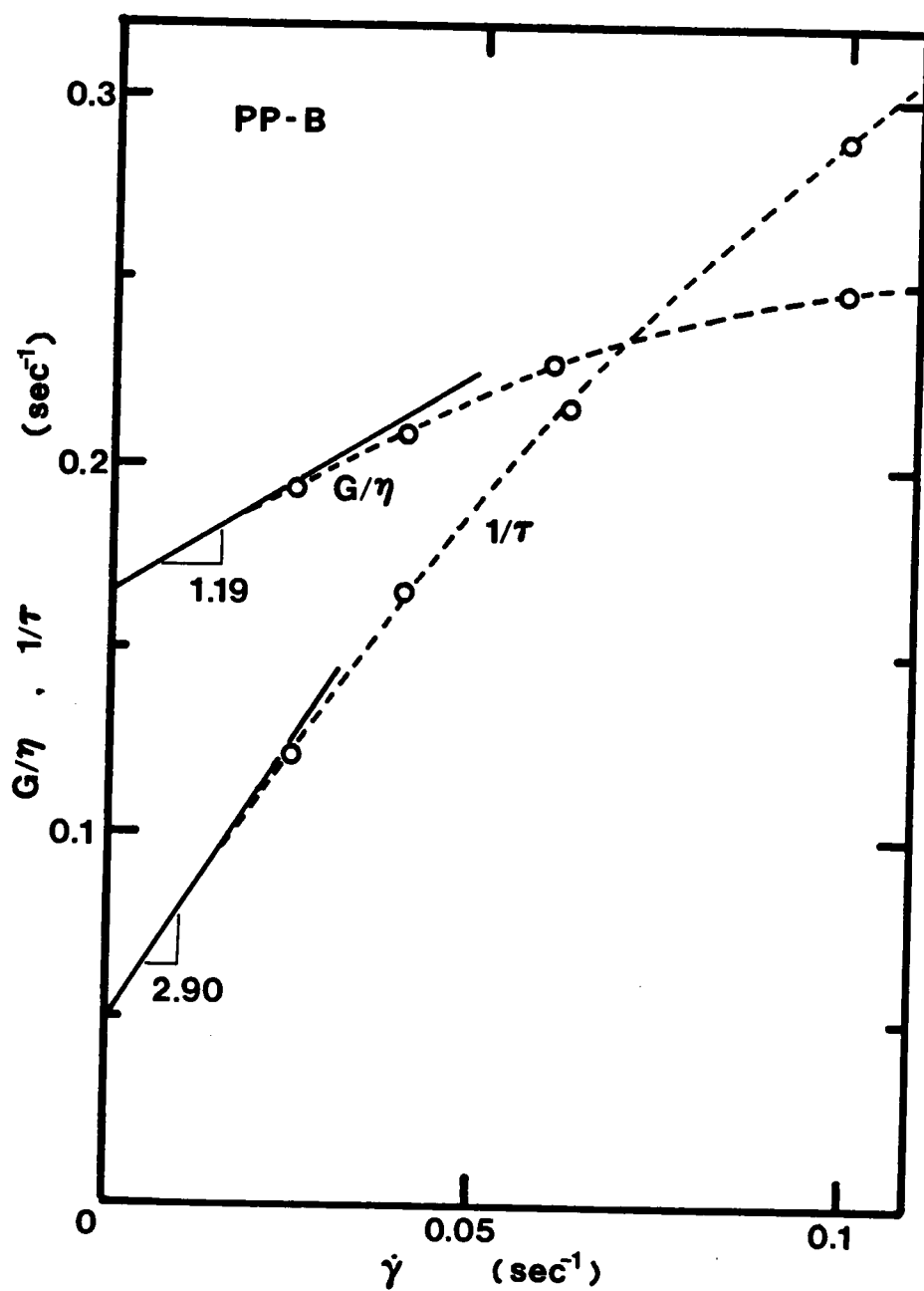


Figure IX-1. Plots of G/η vs $\dot{\gamma}$ and $1/\tau$ vs $\dot{\gamma}$ for PP-B

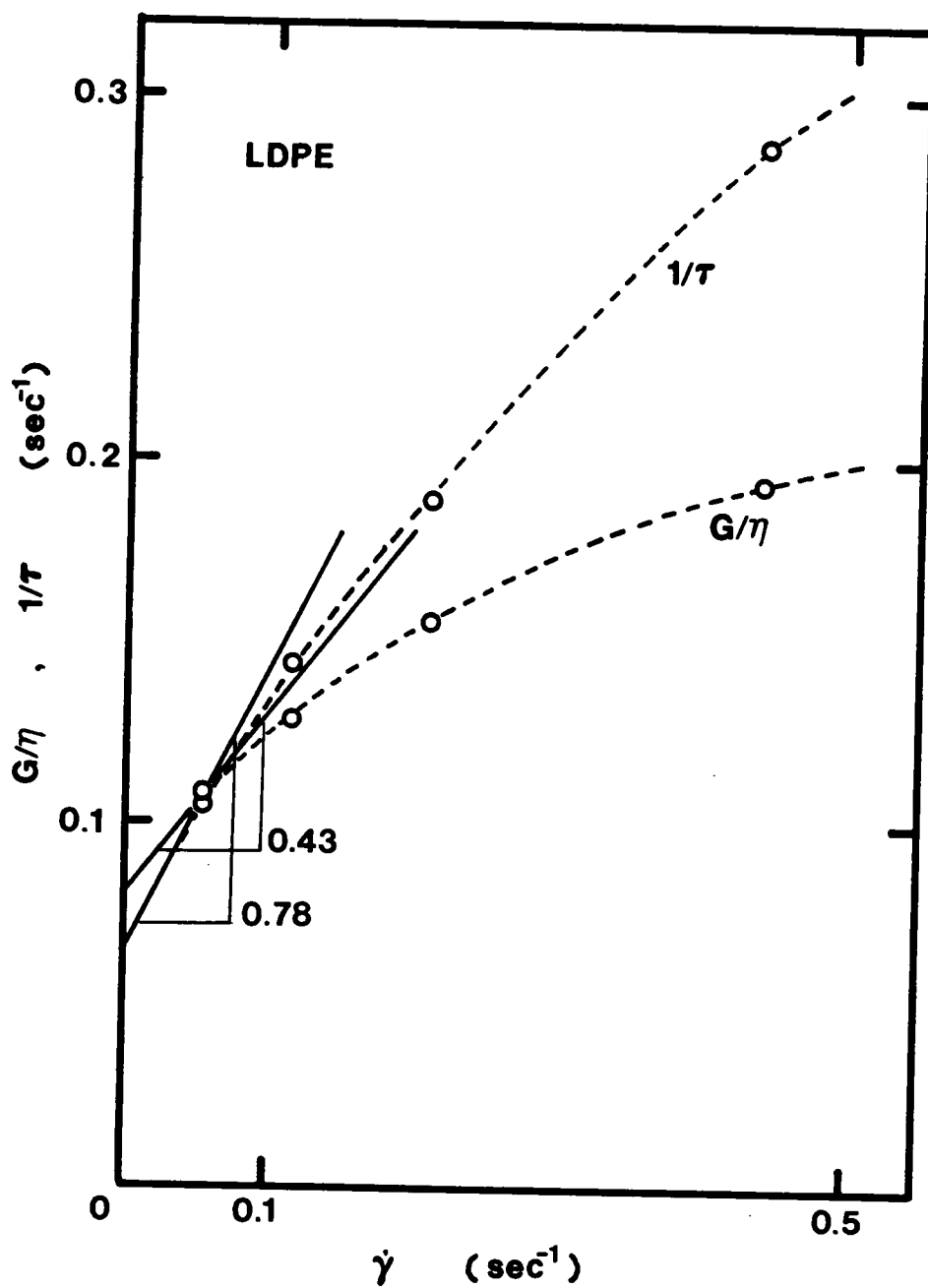


Figure IX-2. Plots of G/η vs $\dot{\gamma}$ and $1/\tau$ vs $\dot{\gamma}$ for LDPE

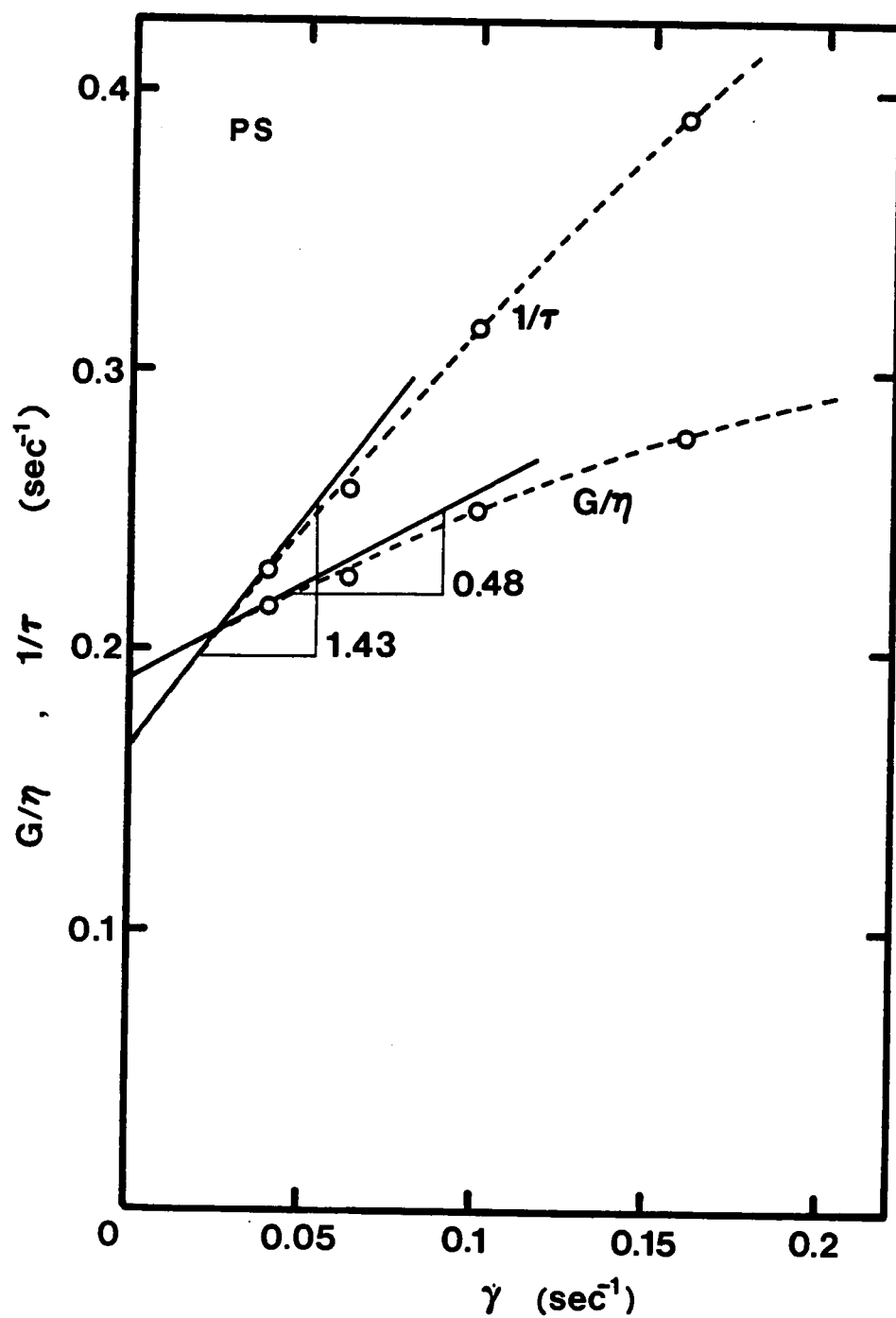


Figure IX-3. Plots of G/η vs $\dot{\gamma}$ and $1/\tau$ vs $\dot{\gamma}$ for PS

Table IX-3. G Values Obtained from $N_1 - \sigma_{12}$ Plot.

Polymer	G at $\sigma_{12} = 10^4$ dyne/cm ² (dyne/cm ²)	G at $\sigma_{12} = 10^5$ dyne/cm ² (dyne/cm ²)
PP - B	3.33×10^4	1.12×10^5
PP - N	5.48×10^4	1.79×10^5
HDPE	2.71×10^4	7.15×10^4
LDPE	2.33×10^4	4.59×10^4
PS	5.13×10^4	1.11×10^5

Table IX-4. τ_o and "a" Obtained from $G/\eta - \dot{\gamma}$ plot.

Polymer	τ_o (sec) (G at $\sigma_{12} = 10^4$ dyne/cm ²)	"a" (G at $\sigma_{12} = 10^5$ dyne/cm ²)	τ_o (sec)	"a"
PP - B	6.06	1.10	1.68	2.75
PP - N	0.86	0.69	0.27	1.24
HDPE	100	1.26	29.0	1.88
LDPE	12.5	0.43	6.06	0.81
PS	5.18	0.48	2.38	5.18

Table IX-5. τ_0 and "a" Obtained from $1/\tau - \gamma$ plot.

Polymer	τ_0 (sec)	"a"
PP - B	33.3	2.90
PP - N	2.44	1.96
HDPE	100	1.96
LDPE	15.4	0.78
PS	5.99	1.43

In addition the data based on $\sigma_{12} = 10^5$ (dyne/cm²) gave very large values of "a" inconsistent with elongational viscosity behavior and Ide and White's filament stability theory. Procedure (4) gave much higher values of "a" especially when only small were considered. Similarly determined values of τ_0 , G and "a" for the untreated and thermally treated PP and PB-1 are summarized in Table IX-6.

The material parameters, τ_0 , G and "a" determined in procedures (1) and (2) at $\sigma_{12} = 10^4$ (dyne/cm²) will be considered best fit. These "a" values obtained in these procedures are very good agreement with those reported for the same standard materials by Ide and White (73, 74) and White and Minoshima (172). PP-B and HDPE have "a" values of 1.17 ~ 1.26, while PP-N has "a" value of 0.69. LDPE and PS have much smaller "a" values which are 0.4 ~ 0.5. Specifically

$$\text{HDPE} > \text{PP-B} > \text{PP-N} > \text{PS} > \text{LDPE}$$

The G values order as

$$\text{PP-N} > \text{PS} > \text{PP-B} > \text{HDPE} > \text{LDPE}$$

and the τ_0 as

$$\text{HDPE} > \text{LDPE} > \text{PP-B} > \text{PS} > \text{PP-N}$$

In figures IX-4 to IX-6, the theoretical predictions and the experimental data of η and N_1 as a function of $\dot{\gamma}$ for the five standard materials are plotted. For the materials which have small "a" values, there are good agreement between theory and experimental results of η . For large "a" materials the theoretical curves deviate from the data in

Table IX-6. G, τ_o and "a" Parameters for Untreated and Thermally Treated PP and PB-1

Polymer	$\frac{G}{\eta} = \frac{G}{\eta_o} + a\dot{\gamma}$				$\frac{G}{\eta} = \frac{G}{\eta_o} + a\dot{\gamma}$				$\frac{1}{\tau} = \frac{1}{\tau_o} + a\dot{\gamma}$			
	(G at $\sigma_{12} = 10^4$ dyne/cm ²)		(G at $\sigma_{12} = 10^5$ dyne/cm ²)		(G at $\sigma_{12} = 10^4$ dyne/cm ²)		(G at $\sigma_{12} = 10^5$ dyne/cm ²)		(G at $\sigma_{12} = 10^4$ dyne/cm ²)		(G at $\sigma_{12} = 10^5$ dyne/cm ²)	
	G	τ_o	"a"	(sec)	G	τ_o	"a"	(sec)	G	τ_o	"a"	(sec)
PP												
no treatment	4.86×10^4	25.0	1.21		1.37×10^5	6.33	2.82		23.3		2.73	
260/0.5	5.82×10^4	5.05	1.17		1.22×10^5	2.50	2.64		8.47		2.75	
260/1.0	6.30×10^4	4.00	1.19		1.37×10^5	1.71	2.71		5.40		2.68	
260/1.5	7.35×10^4	2.08	0.75		1.25×10^5	1.22	1.68		2.70		1.92	
280/0.5	6.89×10^4	1.59	0.90		1.42×10^5	3.33	1.99		2.50		2.74	
280/1.0	7.42×10^4	0.74	0.69		1.38×10^5	0.43	1.71		1.06		2.03	
PB-1												
no treatment	3.39×10^4	33.0	1.23		1.14×10^5	14.7	2.67		37.0		2.48	
240/1.0	3.67×10^4	16.6	1.18		1.14×10^5	5.00	2.48		18.5		2.24	
260/1.0	4.21×10^4	5.26	1.15		1.16×10^5	1.96	2.25		8.33		2.18	
280/1.0	5.19×10^4	1.47	0.78		1.03×10^5	0.78	1.54		2.13		1.80	

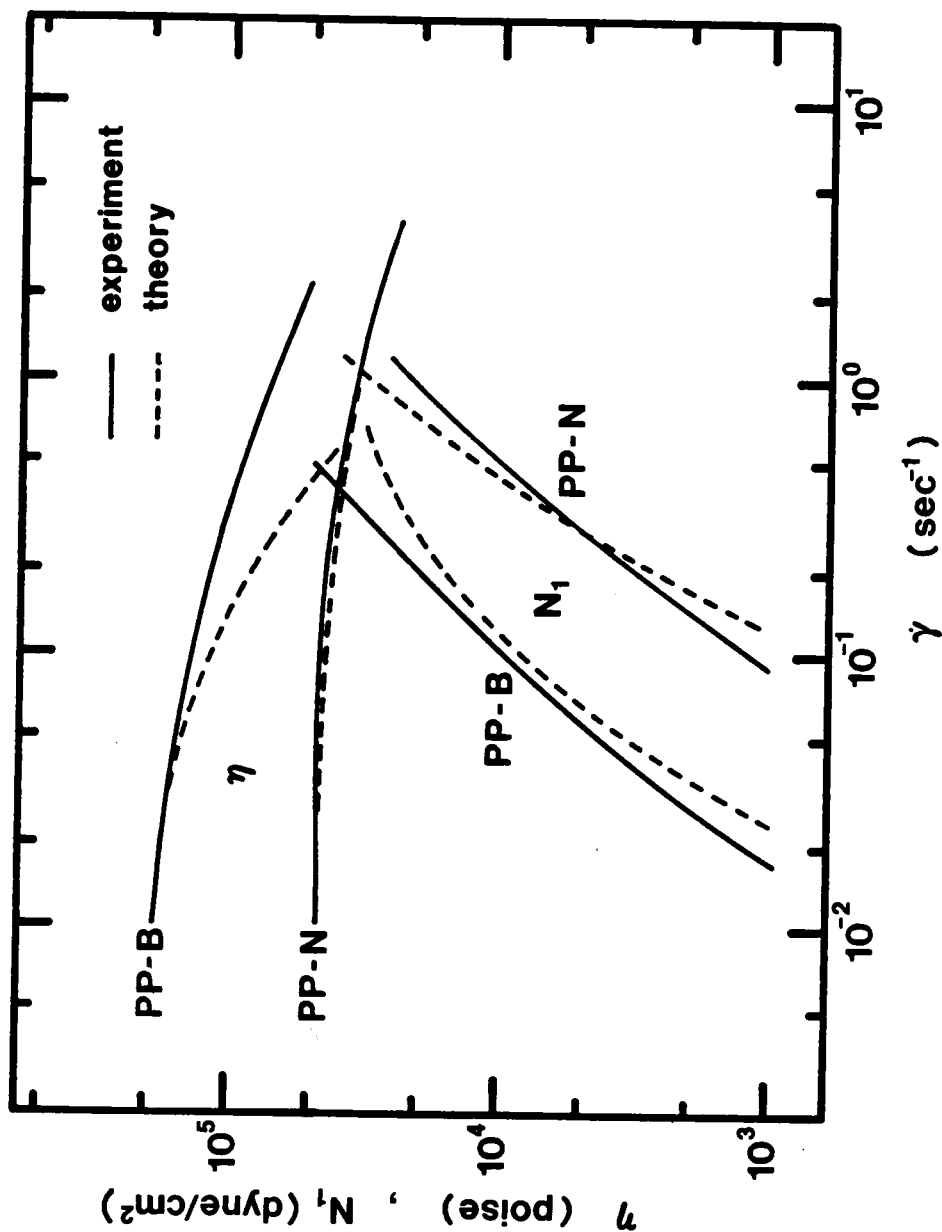


Figure IX-4. Comparisons of Experimental Data to the Theoretical Predictions of Shear Viscosity (η) and the First Normal Stress Difference (N_1) as a Function of Shear Rate ($\dot{\gamma}$) for PP-B and PP-N

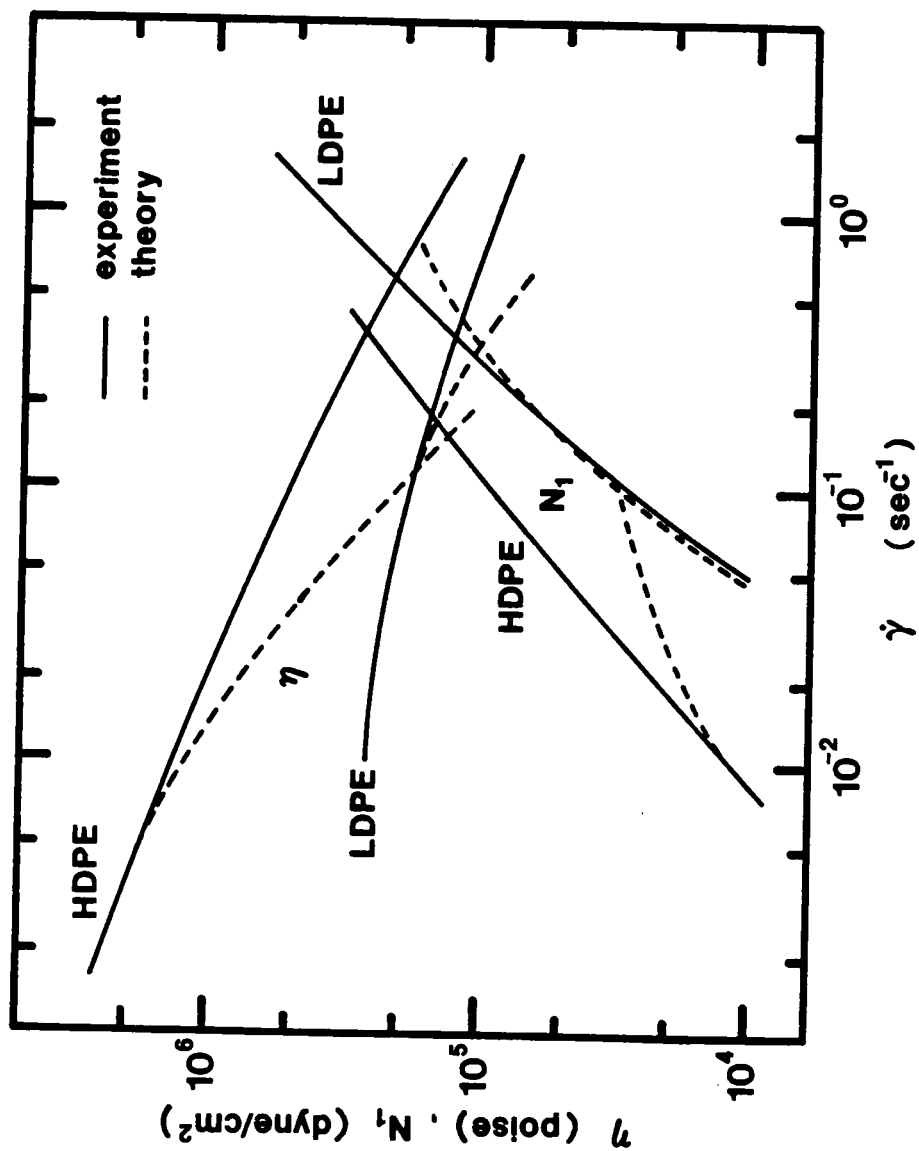


Figure IX-5. Comparisons of Experimental Data to the Theoretical Predictions of Shear Viscosity (η) and the First Normal Stress Difference (N_1) as a Function of Shear Rate ($\dot{\gamma}$) for HDPE and LDPE

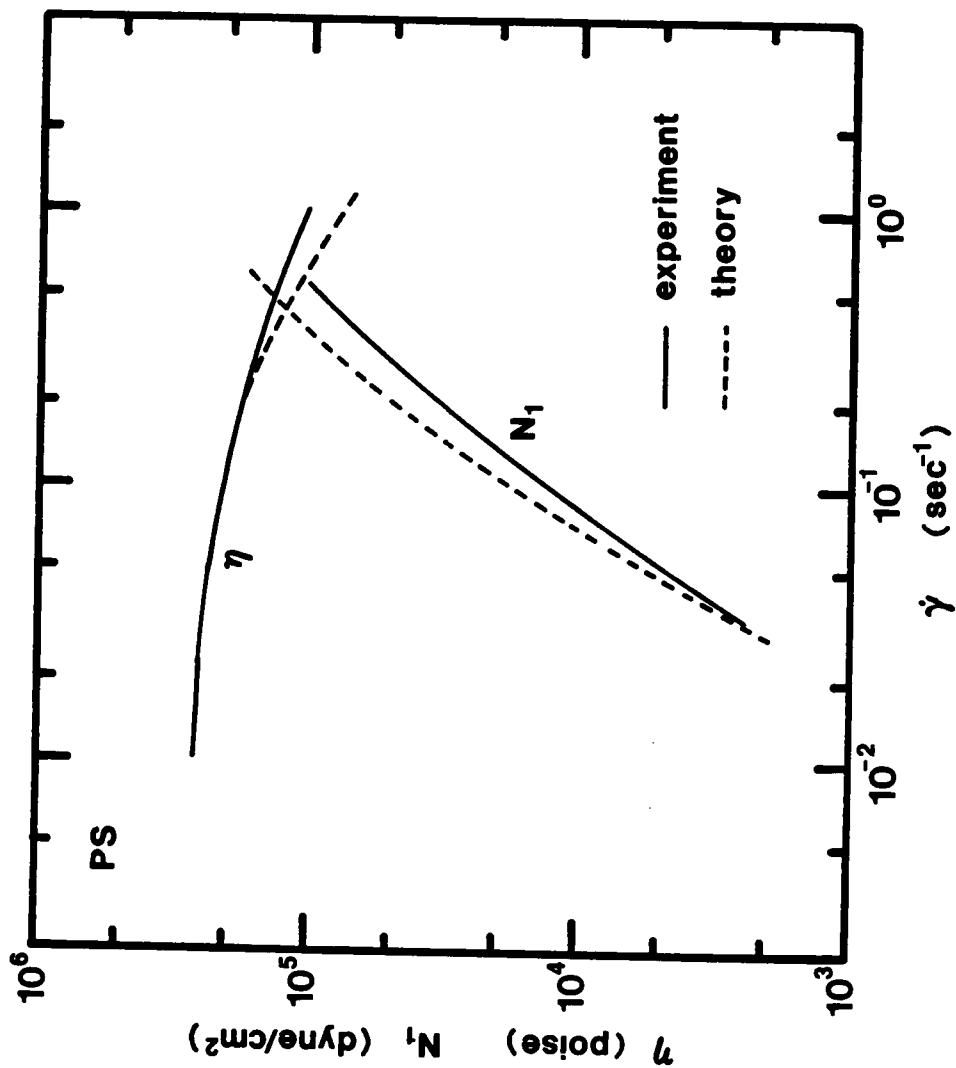


Figure IX-6. Comparisons of Experimental Data to the Theoretical Predictions of Shear Viscosity (η) and the First Normal Stress Difference (N_1) as a Function of Shear Rate ($\dot{\gamma}$) for PS

the high shear rate region. There seems to be good agreement between theory and data of N_1 if these are plotted against $\dot{\gamma}$. N_1 of HDPE does not seem to be good agreement with theory. This is because the G value was determined at $\sigma_{12} = 10^4$ (dyne/cm²) which is at very low shear rate for this HDPE and the theory and the data show good agreement at low which is not contained in Fig. IX-4. Oda, White and Clark (123) and Racin and Bogue (137) using commercial PS and Minoshima, White and Spruiell (144) using PP have found in plots of N_1 vs σ_{12} that the broader the molecular weight distribution, the higher the N_1 at fixed σ_{12} and the larger the $d \log N_1 / d \log \sigma_{12}$. Using a convected Maxwell model we have $d \log N_1 / d \log \sigma_{12}$ of 2 for all materials. As one can see in Figure IX-7, this theory is reasonably good approximation for $N_1 - \sigma_{12}$ plots except for the slope.

For untreated and thermally treated PP and PB-1, parameters, τ_0 , G and "a", were determined and listed in Table IX-7. For both PP and PB-1, the greater the extent of thermal treatment, the higher the G value which was obtained at $\sigma_{12} = 10^4$ (dyne/cm²). Untreated and mildly degraded PP and PB-1 have "a" values of about 1.2 which is close to those of PP-B and HDPE in the standard materials, while greatly degraded PP and PB-1 have "a" values about 0.7 which is close to that of PP-N. If we compare the G and "a" values with apparent $\bar{M}_w / \bar{M}_n$ values, for the linear polymers (PP, HDPE, PS), it can be found the larger the $\bar{M}_w / \bar{M}_n$, the smaller the G and larger the "a" value. The PP and PB-1 which have $\bar{M}_w / \bar{M}_n$ of more than 6.5 have "a" values of about 1.2 while those which have $\bar{M}_w / \bar{M}_n$ of less than 6.5 have "a" values of about 0.7. Similar effects on "a" are found in the degraded PP and PB-1, but are not obvious in the

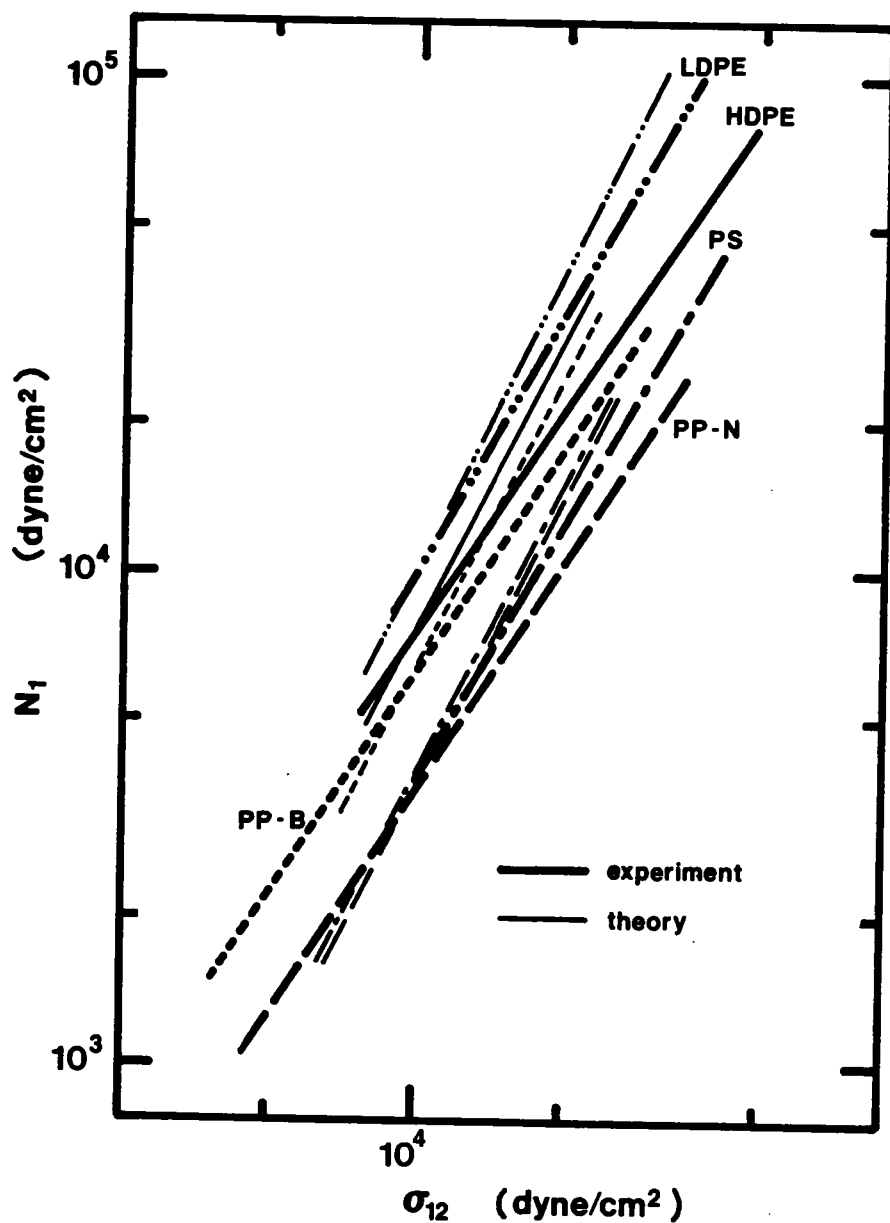


Figure IX-7. Comparisons of Experimental Data to the Theoretical Predictions of the First Normal Stress Difference (N_1) as a Function of Shear Stress (σ_{12})

G values. The PS and HDPE data are also consistent if we consider them respectively as narrow and broad molecular weight distribution materials.

C. COMPARISON TO IDE-WHITE FILAMENT FAILURE THEORY

Ide and White (73, 74) developed an equation which represents the elongation to break, $L(t_b)/L(0)$, of steadily stretched filaments.

Applying stability theory to a convected Maxwell model which has a deformation rate dependent relaxation time, they computed $L(t_b)/L(0)$ as a function of $\tau_0 E$ and "a".

$$\ln \frac{L(t_b)}{L(0)} = \frac{1}{1 - \tau_0 E(2 - \sqrt{3}a)} \left[(1 - \tau_0 E) \ln \frac{R(0)}{\xi(0)} - \tau_0 E \frac{1 - \tau_0 E}{1 - \tau_0 E(2 - \sqrt{3}a)} \right] \quad (9.12)$$

where $\xi(0)/R(0)$ is the initial defect size. For the case of $\tau_0 E = 1$,

$$\ln \frac{L(t_b)}{L(0)} = \frac{1}{\sqrt{3}a - 1} \ln \left[1 + (\sqrt{3}a - 1) \ln \frac{R(0)}{\xi(0)} \right] \quad (9.13)$$

When "a" = $1/\sqrt{3}$, the ductile instability is always more severe than for Newtonian fluids and maximum elongation is limited for infinitesimal disturbances to

$$\ln \frac{L(t_b)}{L(0)} = \frac{1}{(2 - \sqrt{3}a)\tau_0 E - 1} \ln \frac{\tau_0 E}{(\sqrt{3}a - 1)\tau_0 E} \quad (9.14)$$

Figure IX-8 shows the plots of $L(t_b)/L(0)$ as a function of $\tau_0 E$ for PP-B and HDPE in standard materials and untreated PP and PB-1 in this study. Previously we determined "a" values of these materials which are between 1.19 and 1.26. To calculate $L(t_b)/L(0)$ of these materials, "a" value of 1.2 and the initial disturbances $\xi(0)/R(0)$ of 0.01, 0.02 and 0.04 were chosen. For comparison $L(t_b)/L(0)$ at "a" of 0.7 and $\xi(0)/R(0)$ of 0.01 is added in this figure. At lower $\tau_0 E$, $\tau_0 E < 1$, $L(t_b)/L(0)$ is strongly affected by initial disturbances, but at higher $\tau_0 E$, $\tau_0 E > 1$, it goes to an asymptotic value. The fact that with the increasing "a" value, $L(t_b)/L(0)$ decreases is explained in this theory. However, the magnitudes of experimental data are much higher than those of theoretical prediction.

The materials which have smaller "a" values such as LDPE, PS and narrow molecular weight distribution PP and PB-1 have higher $L(t_b)/L(0)$. As determined previously, τ_0 of these materials are much smaller than those of large "a" materials. If one plots $L(t_b)/L(0)$ of these small "a" materials against $\tau_0 E$, $L(t_b)/L(0)$ will be in low $\tau_0 E$ region. Therefore the theoretical predictions can fit the experimental data if proper $\xi(0)/R(0)$ is chosen.

D. ISOTHERMAL MELT SPINNING VELOCITY PROFILE

D-1. Limitations in Isothermal Melt Spinning

White and Ide (169) showed how the material parameters affect the velocity profile in isothermal melt spinning using a convected Maxwell model which has a deformation rate dependent relaxation time neglecting the radial component of the constitutive equation. They developed an

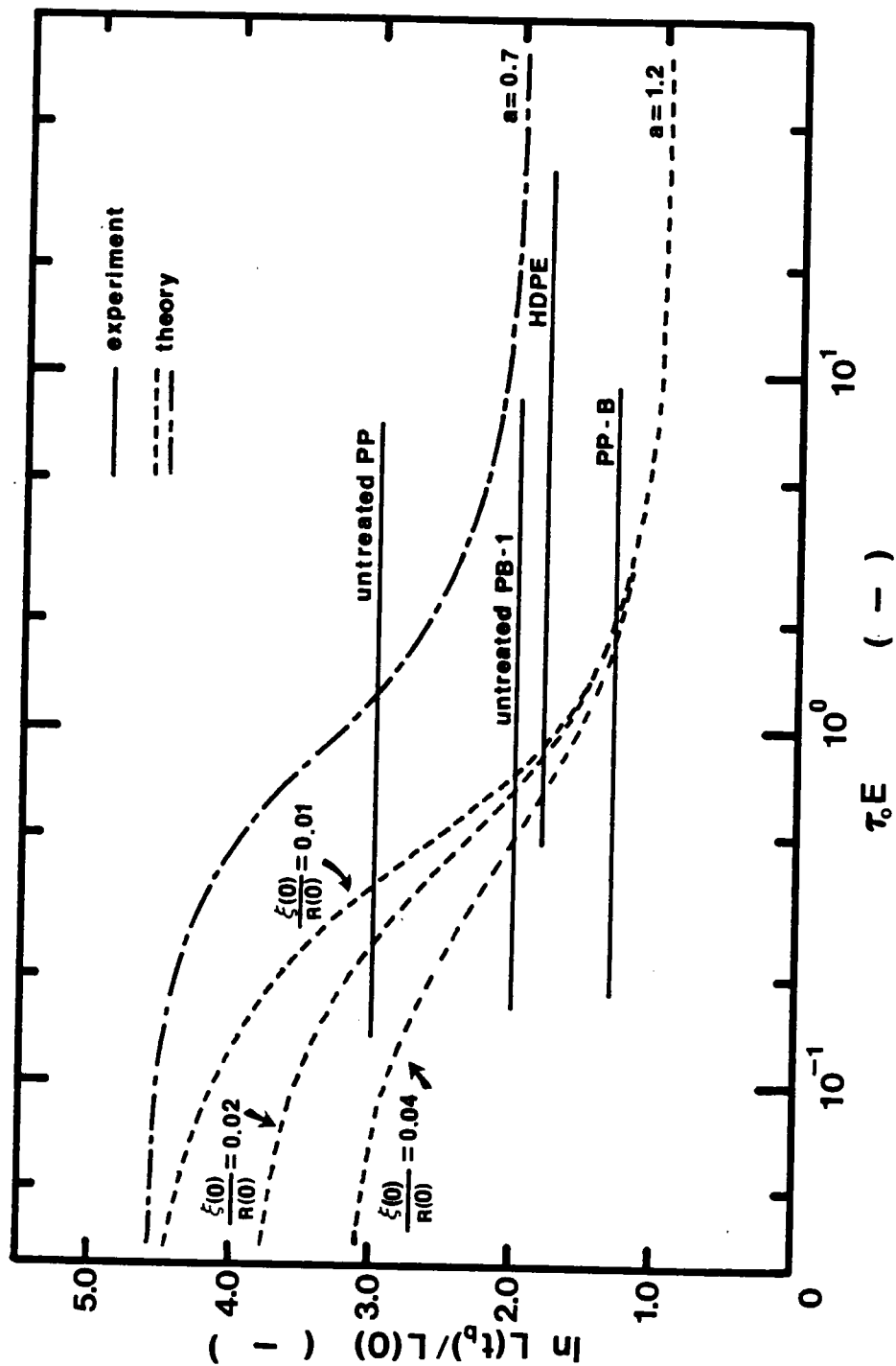


Figure IX-8. Comparisons of Ide-White Filament Failure Theory to the Experimental Data

analytical equation which represents the velocity profile in the spinline for viscoelastic fluids. This is

$$\frac{F}{Q} \left[x - (1-\sqrt{3}a) \tau_0 [V(x) - V(0)] \right] = 2G \tau_0 \ln \frac{V(x)}{V(0)} \quad (9.15)$$

where F is the spinline tension and Q is the volumetric flow rate.

Eq. (9.15) can be rearranged to give two equations (9.16) and (9.17).

Following Nam (120) this can be put in dimensionless form.

$$F^* = \frac{N_{ws} \ln V^*}{x^* - a(V^*-1)} \quad (9.16)$$

and

$$x^* = a(V^*-1) + \frac{1 - a(D-1)}{\ln D} \ln V^* \quad (9.17)$$

where

$$x^* = \frac{x}{L} \quad (9.18a)$$

$$V^* = \frac{V(x)}{V(0)} \quad (9.18b)$$

$$F^* = \frac{FV(0)}{2QG} = \frac{\sigma_{11}(0)}{2G} \quad (9.18c)$$

and

$$a = (1-\sqrt{3}a) \tau_0 \frac{V(0)}{L} = (1-\sqrt{3}a) \cdot N_{ws} \quad (9.19)$$

$$D = \frac{V(L)}{V(0)} \quad (9.20)$$

can be considered as a effective Weissenberg number.

Zeichner (187) and Denn, Petrie and Avenas (32) imply that there are unobtainable regions because of the development of infinite stresses. Pearson (127) noted the existence of specific discontinuities at $x^* = 0$. This point has been emphasized by Nam (120). The general matter of discontinuities in Eq. (9.17) has been further considered by Minoshima (113) and the present author. In Figure IX-9, Eq. (9.17) is plotted. At

$$\alpha = \frac{1}{D - 1} \quad (9.21)$$

a linear velocity profile results. As α decreases from this value, the dependence becomes exponential.

In Eqs. (9.16) and (9.17), one needs to add two limitations; (1) the take-up force must be finite, and (2) the velocity must change continuously along spinline. From limitation (1) and Eq. (9.16)

$$x^* - \alpha(V^* - 1) > 0 \quad (9.22)$$

When $\alpha \leq 0$, this is always satisfied. When $\alpha \geq 0$, this limitation is necessary. According to Nam (120) and Minoshima (113), this can be explained by using D and N_{ws} and is shown in Figure IX-10. From limitation (2) and Eq. (9.17)

$$\frac{\partial V^*}{\partial x^*} = \frac{V^* \ln D}{1 - \alpha(D - 1 - V^* \ln D)} \quad (9.23)$$

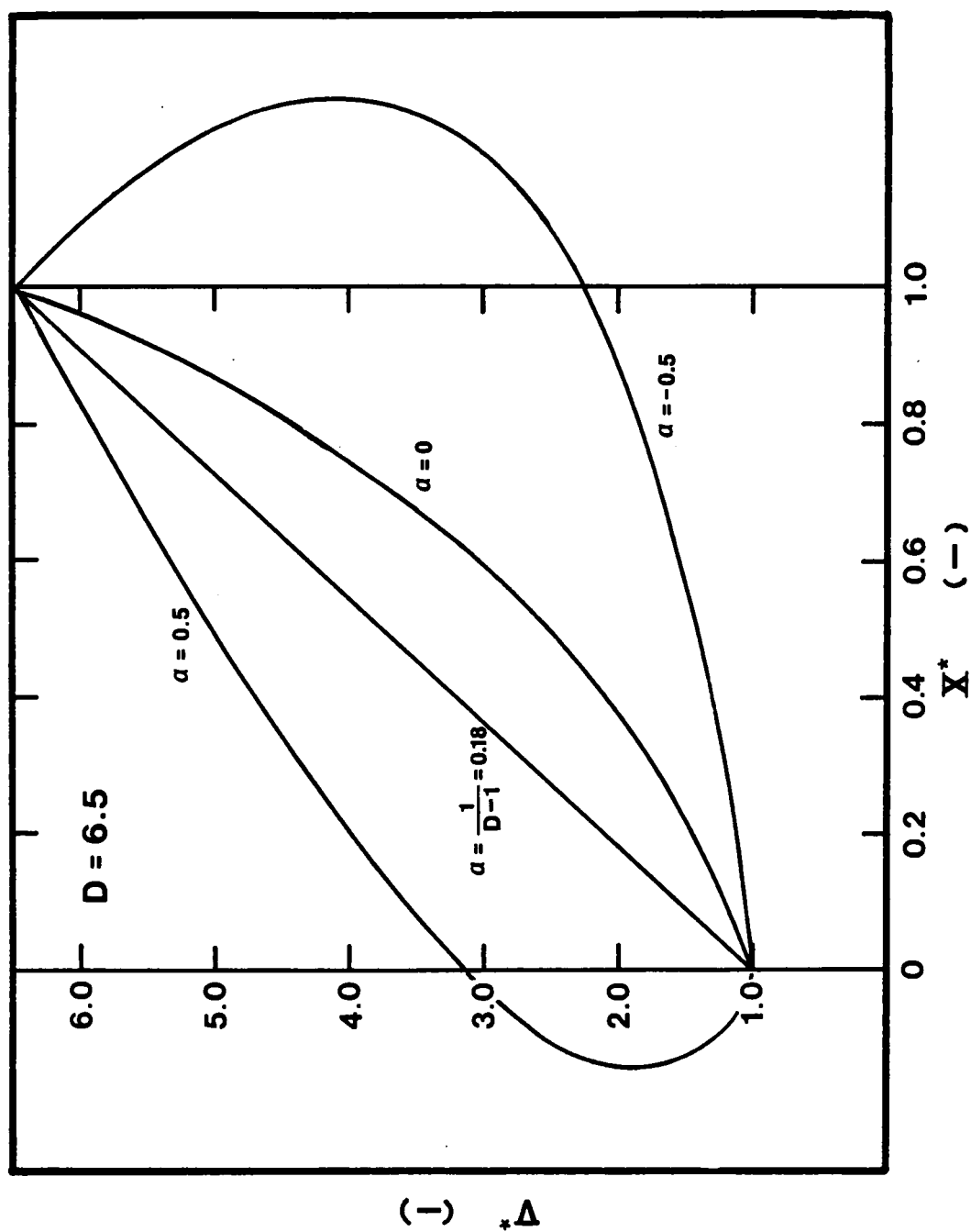


Figure IX-9. Theoretical Predictions of Velocity Profile for Various α

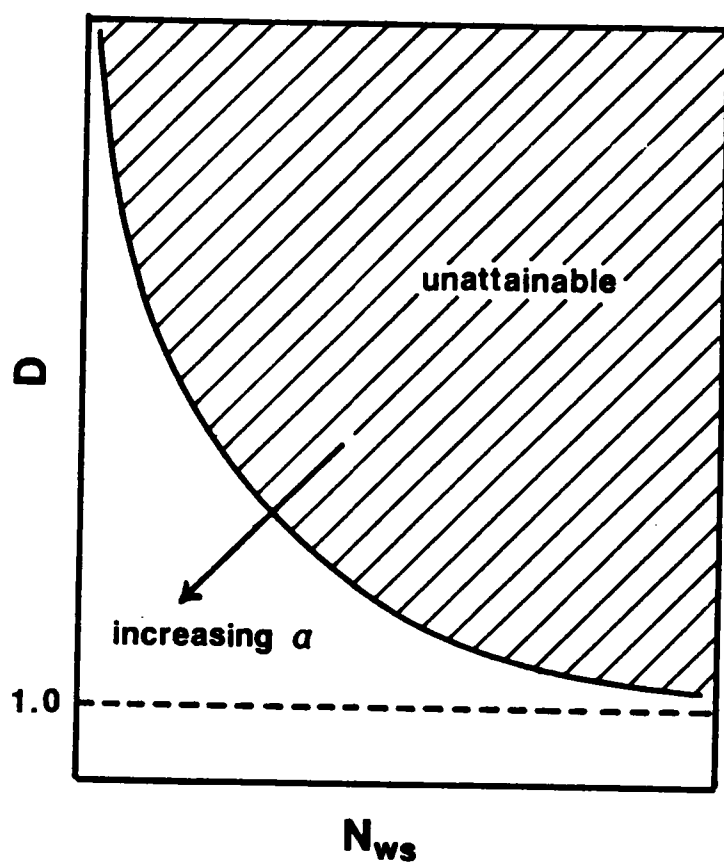


Figure IX-10. Limitations in the Conditions of Isothermal Melt Spinning

For $\alpha > 0$, a discontinuity may happen at $x^* = 0$ (113, 120, 127).

Therefore

$$1 - (D - 1 - \ln D) > 0 \quad (9.24)$$

For $\alpha < 0$, a discontinuity can occur at $x^* = 1$. Therefore

$$1 - \alpha(D - 1 - D \ln D) > 0 \quad (9.25)$$

The limitation of Eq. (9.24) is less severe than that of Eq. (9.21).

Finally the limitation can be written as

$$\frac{1}{D - 1 - D \ln D} < \alpha < \frac{1}{D - 1} \quad (9.26)$$

D-2. Comparison to White-Ide Theory

In our melt spinning experiments (chapter VIII), the velocity at die exit, $V(0)$, was 3.54×10^{-1} cm/sec, the spinline path length, L , was 7.62 cm and the draw down ratio, D , was 6.5. To compare the experimental results to the theory, one has to consider the extrudate swell effect. In Figure IX-11, the velocity profiles of untreated and thermally treated PP during isothermal melt spinning and the theoretical predictions are plotted with extrudate swell correction. For thermally treated PP which has small " α " (0.75), this theory fits the experimental results pretty well. However, α of untreated PP has large negative value and the theoretical curve has a discontinuity at $x^* = 1$. In our experiments, the velocity of large " α " material increases at higher rate

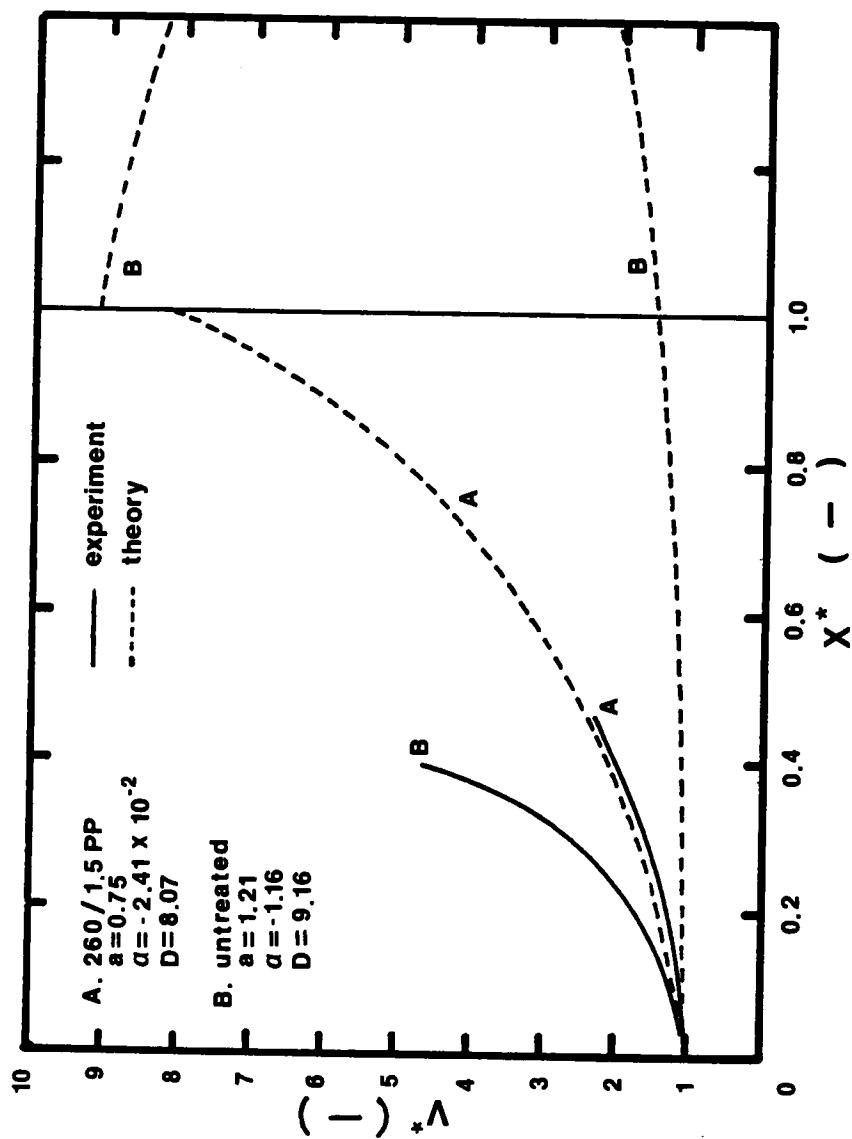


Figure IX-11. Comparisons of Experimental Data to the Theoretical Predictions of the Velocity Profiles

than that of small "a" material. This seems opposite to what the theory describes. Similar experimental results have been obtained by Minoshima et al. (115) who used the same equipments and Ishizuka, Koyama and Nokubo (78).

Fisher and Denn (42) made similar analysis using a convected Maxwell model with a power law viscosity and a constant shear modulus. They obtained similar theoretical predictions to those of White and Ide's which show the more the material is deformation rate softening, the more the velocity profile is exponential, and that the initial increasing rate is lower for more deformation rate softening materials. Their theory fits reasonably well to the data for polystyrene which is less deformation rate softening material similar to the degraded PP (compare to the remarks of Section IX-B).

The disagreement between our theory and the data for the untreated PP may be due to following effects. Theoretically, (1) to develop Eq. (9.15) we assume that P_{22} is very small compared to P_{11} and then $\sigma_{11} \sim P_{11}$, and as shown by Petrie (130), (2) prehistory of polymer melt due to shearing in the die is important. Also experimentally, (3) the apparatus may not achieve completely isothermal condition near the quench bath.

CHAPTER X

CONCLUSIONS

The influence of thermal treatment (viscracking) on the rheological properties and the processing characteristics of polypropylene (PP) and polybutene-1 (PB-1) were determined as follows:

- (1) With increasing thermal treatment, the molecular weight becomes lower and the distribution becomes narrower. This was found in PP and PB-1 which have tertiary hydrogen atoms, but not in high density polyethylene (HDPE). Presumably random degradation occurs on the polymer chain back bone, which preferentially induce scission in the back bone.
- (2) Steady shear viscosities of PP and PB-1 are affected by thermal treatment. The zero shear viscosity, η_0 , becomes lower due to the lowering the molecular weight, $\bar{M}_w$. The rate of decrease of viscosity, η/η_0 , becomes lower and the nonlinear character decreases.
- (3) The molecular parameters, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$, can be estimated from zero shear viscosity, η_0 , and reduced viscosity, η/η_0 , respectively.
- (4) The extent of thermal treatment decreases the first normal stress difference, N_1 , of PP and PB-1 at fixed shear stress, σ_{12} , and increases $d \log N_1 / d \log \sigma_{12}$.
- (5) The shape of the transient elongational viscosity, $X(E, t)$, is dependent on the extent of thermal treatment and the samples can be divided into two groups, one belongs to untreated and less degraded PP and PB-1 which have broader

molecular weight distribution and another belongs to more degraded PP and PB-1 which have narrower molecular weight distribution.

- (6) The elongational viscosity of untreated and less degraded PP and PB-1 does not reach a steady state. At low elongational rates, the maximum value is much higher than $3\eta_0$ and decreases with elongational rate. The more degraded samples achieve a steady state elongational viscosity which is close to $3\eta_0$ through wide elongational rate range.
- (7) The elongation to break, $L(t_b)/L(0)$, of untreated and less degraded PP and PB-1 is much lower than that of more degraded samples.
- (8) The growth manner of disturbances in stretched filaments varies. The behavior of untreated and less degraded PP and PB-1 is ununiform and the neck grows at the disturbances. The more degraded samples is more uniform and the disturbances are healed.
- (9) Narrowing of the molecular weight distribution and lowering of the molecular weight due to the thermal treatment decreases the extrudate swell, B , at fixed shear rate, shear stress and normal stress-shear stress ratio.
- (10) The spinline elongational viscosity, $X_{sp}(E)$, of untreated and less degraded PP is decreasing function of the elongational rate, E , and the magnitude is similar but greater than that measured by an elongational rheometer (constant E). X_{sp} of more degraded PP is slightly decreasing

or constant, and the magnitude is much higher than that measured by the elongational rheometer.

(11) The stability in melt spinning of PP and PB-1 increases with increasing extent of thermal treatment. Untreated PP and PB-1 readily exhibit draw resonance at lower draw down ratio compared to thermally treated samples.

(12) The material parameters, G , τ_0 and "a" of the convected Maxwell model of White and Metzner as modified by Ide and White were estimated in various ways. The order of "a" value is

$$\text{HDPE} > \text{PP and PB-1 (broad MWD)} > \text{PP and PB-1 (narrow MWD)} \\ > \text{PS} > \text{LDPE}$$

"a" values of HDPE and broad MWD PP and PB-1 are about 1.2 while those of narrow MWD PP and PB-1 are about 0.7 and those of PS and LDPE are about 0.4. These values are consistent with Ide-White filament failure theory.

(13) The White-Ide isothermal melt spinning theory predicts the velocity profile for small "a" materials well if one makes the extrudate swell correction. Discrepancies arise for the larger "a" melts.

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