

To the Graduate Council:

I am submitting herewith a dissertation written by Hari P. Nadella entitled "Quiescent and Stress Induced Crystallization Studies of Nucleated and Nonnucleated Polyolefins." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Polymer Engineering.

Joseph E. Spruiell

Joseph E. Spruiell, Major Professor

We have read this dissertation
and recommend its acceptance:

DeBogus

K E. Ducloux

Edward S. Clark

James L. White

Accepted for the Council:

L Evans

Vice Chancellor
Graduate Studies and Research

QUIESCENT AND STRESS INDUCED CRYSTALLIZATION STUDIES OF
NUCLEATED AND NONNUCLEATED POLYOLEFINS

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Degree
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ABSTRACT

Isothermal crystallization studies of nucleated and nonnucleated polypropylene and high density polyethylene were conducted under quiescent and stress induced conditions (SIC). For SIC case, the samples were subjected to both elongational and shear flow deformations on a Rheometrics Mechanical Spectrometer over a range of crystallization temperatures. Changes in the sample viscosities were recorded as function of time at constant temperature and deformation rate. Induction times, defined as the time from start of deformation to the point where they increase from a steady state value, were obtained. These induction times were interpreted as proportional to the nucleation rates. In the case of quiescent crystallization studies, the differential scanning calorimeter was used and the sample exotherms were recorded under isothermal conditions.

Quiescent crystallization results were analyzed using the Avrami approach. The results showed an increase in the crystallization rates with decreasing temperature in both control and nucleated polypropylenes and polyethylene. Avrami index was found to be approximately 3 for all the samples. Under quiescent conditions, addition of 0.5 wt % of sodium benzoate nucleating agent to polypropylene increased the maximum crystallization temperature by about 20°C over the control. The talc nucleated sample crystallized only at slightly higher temperature. The effect of sodium benzoate

concentration was nonlinear and seems to saturate as the concentration is increased.

SIC results in polypropylenes and polyethylenes showed increases in nucleation rates with increase in the stress (shear or tensile) and decrease in crystallization temperature. In polypropylene at low shear rates ($\dot{\gamma} \leq 0.1 \text{ sec}^{-1}$) the nucleation rates approached the quiescent values at higher crystallization temperatures. Nucleated polypropylenes under shear flow conditions showed additional (compared to sheared control sample) enhancement in their nucleation rates. Depending on the temperature at which the sample is being stressed, addition of nucleating agent (at $\dot{\gamma} = 0.1 \text{ sec}^{-1}$) increased the maximum crystallization temperature by 7 to 19°C (overall increase in $T_{Cr,Max} \sim 44^\circ\text{C}$ over control quiescent case).

Expressions for SIC relating nucleation rates to $Tr_{\tilde{\gamma}}^P$ were successfully developed using classical nucleation theories following Jarecki and Ziabicki's analysis. In addition an equation relating nucleation rate to molecular orientation in the melt was proposed from intuitive arguments. SIC results were analyzed using the above two approaches. In both polypropylene and polyethylene the differences in the nucleation rates between the samples crystallized under shear and elongational flow are significant when the nucleation results for a given crystallization temperature were plotted as a function of stress (shear or tensile). Replots of the same results as function of $Tr_{\tilde{\gamma}}^P$ or $\sigma_x - \sigma_y$ showed a unique correlation independent of mode of deformation but dependent on the sample molecular weight

distribution and temperature. This suggests that the high molecular weight species in the broader distribution samples are important in determining the crystallization behavior of the sample.

Predictions of nucleation rates from theoretical considerations showed similar trends and temperature sensitivity as the experimental results. However, they were lower than the experimental values for given ΔG_{def} due to under predictions in ΔG_{def} ($\Delta G_{\text{def}} = \frac{1}{2} \text{Tr} P_{\lambda}$) in Marrucci's analysis. The results also showed overprediction of nucleation rates when the rubber elasticity theory (affine deformation) was used to estimate ΔS_{def} .

Our experimental results were successfully curve fitted by a simplified Jarecki and Ziabicki relation. The constant $a_{11}(\Delta G_{\text{def}} = \sigma_{11} \text{Tr} P_{\lambda})$ ranged from 50 to 80 and was found to be dependent on the sample molecular weight distributions.

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CHAPTER I

INTRODUCTION

In commercial fabrication operations, polymer melts are generally sheared and stretched at high rates before being crystallized. Crystallization then takes place in a molecularly oriented state. As a result, quiescent crystallization experiments are not representative models of polymer crystallization in commercial processes.

The rate of crystallization is a major factor in determining the extent of crystallization in a particular sample. Indeed, polymers which crystallize slowly (e.g., polyethylene terephthalate) can often be quenched rapidly enough to retain the amorphous, super-cooled liquid phase, while other polymers which crystallize rapidly (e.g., polyethylene) cannot be prevented from crystallizing during quenching. Further, the mechanical and physical properties of a polymer are closely related to its detailed structural state (i.e., morphology) and this state is controlled by the interaction of crystallization kinetics and processing conditions (180, 214). For these reasons crystallization kinetics are of primary importance in studies of structure-property-processing relations.

Until recently most of the studies of crystallization of molten polymers have been performed on quiescent unoriented melts. There are fewer detailed quantitative studies of the effect of stress on crystallization kinetics because of experimental difficulties. Recent studies (50,180,214) of nonisothermal crystallization kinetics during

the melt spinning of polypropylene and polyethylene showed orders of magnitude increase in crystallization rates over quiescent rates.

Analysis of crystallization kinetics under quiescent isothermal conditions following the general approach of Avrami (15-17) are well established. But analyses of crystallization kinetics under the influence of molecular orientation have not been considered until recently (263-265,269,271,219,260,139).

Studies of melt spun polypropylene fibers here at The University of Tennessee, Knoxville (180,214), suggested a unique correlation between morphology and orientation and the state of the stress existing during crystallization. In order to pursue these ideas further it is necessary to understand the kinetics of "stress-induced crystallization" and the morphology developed by it. It is with these thoughts in mind that the present study of stress-induced crystallization was undertaken.

In the present research work major emphasis is placed on studies of enhanced crystallization rates in polyolefins by melt orientation. An attempt is made to assess the relation of melt stress to orientation and crystallization kinetics through studies of different modes of deformation (shear and elongation) under isothermal conditions. The effects of additives such as fillers and nucleating agents on the nucleation rates in both the quiescent and the stress induced cases are also considered. In all these studies polypropylene was the main experimental polymer though some limited experiments on high density polyethylene were also carried out.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

A. NUCLEATION THEORY

1. Quiescent Nucleation Rates

a. Homogeneous nucleation. In the present chapter a brief historical review of the classical nucleation theories will be given. Detailed development of the nucleation rate expressions from these theories will be presented in the following chapter.

The basic concepts and equations of nucleation rate theory were developed primarily for condensation from vapor phase (27,57,242). Volmer and Weber (242) were the first to treat the formation of nuclei assuming that they form by a series of bimolecular reactions. Improvement of the Volmer-Weber theory was made by Becker and Doring (27) in 1935. Frenkel (62) in 1939 presented a quantitative theory of heterogeneous fluctuations which he applied to condensation from vapor, pre-melting and crystallization phenomena. The theory of nucleation in crystals was first considered by Becker (26) in 1938. Considering the nucleation as a local process, Becker (26) analyzed the kinetics of forming well-defined noninteracting microclusters of the new phase. For nucleation in condensed phases the free energy of activation for motion across the embryo-matrix interface must be included in the rate expression. This was done by Becker (26). Later Turnbull and Fisher (230) by

combining absolute reaction rate theory (56) with the Becker-Doring (27) approach derived an expression for the steady state nucleation rate which is now commonly used for interpretation of nucleation phenomena in the condensed state. For the case of a solid nucleating from a liquid Turnbull and Fisher obtained the rate of formation of critical size clusters of atoms, i.e., nuclei as follows :

$$\dot{N} = \dot{N}_0 \exp[-(\Delta F_i^* + \Delta G_i^*)/kT] \quad (\text{II-1})$$

where $\dot{N}_0$ is a term dependent on molecular parameters and ΔF_i^* is the activation energy barrier affecting transport of material across the crystal-liquid interface; ΔG_i^* is the critical free energy required for the formation of the critical size cluster.

The overall nucleation rate as shown in Eq. II-1 is controlled by the rate of transport of material to the nucleation site and the rate of formation of the crystalline nucleus. The rates of these two processes have opposite temperature dependencies. This gives a maximum in nucleation rate at an intermediate temperature between the melting point (rate of formation of nuclei = 0) and the glass transition temperature (rate of material transport to the nucleation site = 0) (148,160).

In order to use the classical nucleation theory to make quantitative predictions, the specific mechanism of nucleation must be specified in order to fix the form of the second exponent in Eq. II-1. A convenient expression for ΔG_i^* derived by several investigators

has the form (99,230,197,167),

$$\Delta G_i^* = \frac{K\gamma^2\gamma_e}{\Delta G_v^2} \quad (\text{II-2})$$

where K is a constant, the value of which depends on the shape of the nucleus, γ and γ_e are the surface interfacial free energies per unit area γ is for side surface of the embryo, γ_e is for end surface and ΔG_v is the bulk free energy difference between the embryo and the melt per unit volume.

Substitution of Eq. II-2 into Eq. II-1 results in the following form for the rate of nucleation of crystals from the quiescent melt :

$$\dot{N} = \dot{N}_0 \exp\left[-\left(\frac{\Delta F_i^*}{kT} + \frac{K\gamma^2\gamma_e}{kT\Delta G_v^2}\right)\right] \quad (\text{II-3})$$

b. Heterogeneous nucleation. The discussion in the above section is for homogeneous nucleation in the absence of foreign material. Commercial polymers usually contain residual heterogenities or purposefully added nucleating agents for modifying their properties. As a result, in polymer melts and solutions crystallization is initiated almost exclusively by heterogeneous nucleation. Analysis of the heterogeneous nucleation process requires introduction of interfacial free energies for the catalyst in contact with the polymer melt (or solution) and the crystal (63,197). Since these free energies are rarely known, they become, in effect, adjustable parameters.

Several important papers have dealt with heterogeneous nucleation theory (51,165,166,197,228). Following the suggestions of Volmer in 1950 (240), Turnbull (228) published his theory of heterogeneous nucleation in phase changes in which he reviewed the experimental work of several investigators who studied the effect of added impurities upon the rate of phase change in solid-liquid nonpolymeric systems. Based on the theories of homogeneous nucleation, Turnbull (228, 229) developed the kinetics of nucleation by solid phase material retained in conical and cylindrical pits in adventitious nucleating agents. Devoy and Mandelkern (51) specifically dealt with the theory of heterogeneous nucleation of long chain molecules. Their treatment of the process was an extension of Turnbull's development to a system of long chain molecules which could not form nucleus embryos because of the molecular geometry.

2. Stress Effects on Nucleation Rates

Assuming similar nucleus type, mass transport term and pre-exponential factor for both the stress induced and quiescent cases, the nucleation rate for the SIC case can be written as (139,188,259),

$$\dot{N}(\text{stressed}) = \dot{N}_0 \exp\left| -\frac{\Delta F_i^*}{kT} \right| \exp\left| -\frac{K_r^2 \gamma_e}{kT |\Delta G_v + \Delta G_{\text{def}}|^2} \right| \quad (\text{II-4})$$

where ΔG_{def} is the elastically stored free energy resulting from the deformation of the polymer chains.

Kobayashi and Nagasawa (139) and recently Yeh and Hong (259) assuming similar nucleus type in both the quiescent and the stressed case

evaluated the ratio of the stressed to quiescent nucleation rates as,

$$\frac{\dot{N}(\text{stressed})}{\dot{N}(\text{quiescent})} = \exp \left| \frac{K_Y^2 \gamma_e}{kT} \left(\frac{1}{(\Delta G_{\text{def}})^2} - \frac{1}{(\Delta G_V)^2} \right) \right| \quad (\text{II-5})$$

Equation II-5 provides a useful way of illustrating the stress enhancement of nucleation rates which does not require a knowledge of the mass transport term ΔF^* and the pre-exponential constant $\dot{N}_0$. However, a major problem in the evaluation of stress effects on nucleation rates (or $\frac{\dot{N}(\text{stressed})}{\dot{N}(\text{quiescent})}$) is the evaluation of the ΔG_{def} term.

a. Evaluation of ΔG_{def} . Here we present some of the basic ideas that have been used to evaluate ΔG_{def} in the literature.

Cross-Linked Samples

The best known and most thoroughly examined case from the standpoint of theory is that of cross-linked samples. The mechanisms of stress induced crystallization for cross-linked materials have been considered first by Flory (59), later by Krigbaum and Roe (140), Kim and Mandelkern (137) and Yamamoto and White (256). Flory (59) derived an equation for the equilibrium melting temperature of a permanently cross-linked polymer network subjected to a uniaxial deformation. It was assumed that this network is stretched to a fixed elongation α , before any crystallization takes place. Additional simplifying assumptions in Flory's analysis are that crystallization occurs under equilibrium conditions, crystallites are perfectly oriented in the stretch

direction, prior to crystallization all chains traverse through the crystallite in the same direction as their end-to-end vectors, and chain segments between the network junctions obey Gaussian statistics. Flory's equation relating the melting temperature (T_m^0) and elongation ratio (α) under affine deformation is (59) ,

$$\frac{1}{T_m^0} - \frac{1}{T_m} = \frac{k\hat{N}}{2\Delta H_f} \left[\left(\frac{24m}{\pi} \right) \frac{1}{2} \alpha - \left(\alpha^2 + \frac{2}{\alpha} \right) \right] \quad (\text{II-6})$$

where T_m^0 is the equilibrium melting temperature of the unoriented system, m is the number of statistically independent segments between cross-links, $\hat{N}$ equal to number of network chains/cm³, and ΔH_f is the heat of fusion per statistical segment.

Krigbaum and Roe (140) proposed a different equation for the equilibrium melting point of a uniaxially oriented polymer network. Their analysis was a largely macroscopic thermodynamic treatment for crystallization after attainment of a final level of strain. They assumed affine deformation, applicability of Gaussian statistics, and neglected the free energy change associated with the orientation of the crystallites. Their equation is (140)

$$\frac{1}{T_m^0} - \frac{1}{T_m} = \frac{k\hat{N}}{2\Delta H_f} \left[\alpha^2 + \frac{2}{\alpha} - 3 \right] \quad (\text{II-7})$$

Equations II-6 and II-7 correctly predict an increase in the equilibrium melting point with increasing α . Thus as α increases, the super cooling, ΔT , in these equations also increases, so that at a given crystallization temperature one can consider that he is at a greater super cooling if the sample is strained than if it is unstrained.

This would normally be expected to produce a large increase in nucleation rate.

Uncross-Linked Samples

The above treatment represents an upper limit of the effect for uncross-linked systems. For cross-linked samples, the end-to-end distances relax back towards the unstretched condition and the effective extension ratio must be much less than the usual draw down ratio. A steady state must be reached in which the chain extension and the orientation can be maintained provided there is flow with a velocity gradient parallel or perpendicular to the flow direction. The nature of this chain extension has, so far, proved very difficult to fully analyze theoretically. Pennings (188) has used an expression relating ΔG_{def} to the square of the shear rate (113,170) in dilute polymer solutions to interpret his experimental results;

$$G_{\text{def}} = \frac{1}{2} (P_{11} - P_{22}) = J_e \eta^2 \dot{\gamma}^2 \quad (\text{II-8})$$

where $P_{11} - P_{22}$ is the first normal stress difference, J_e is the equilibrium compliance factor.

McHugh (154) has given a free energy extension relationship of the form,

$$G_{\text{def}} = \frac{1}{c} \int_0^\alpha (P_{11} - P_{22}) \frac{d\alpha}{\alpha} \quad (\text{II-9})$$

where c is the polymer concentration in mass units.

Janssen and Janssen-Van Rosmalen (114) using Eq. II-8 and

under the assumption of a contravariant Maxwell model as a constitutive equation obtained

$$\Delta G_{\text{def}} = \frac{\tau n \dot{\gamma}^2}{c} \quad (\text{II-10})$$

where τ is a time constant. They developed a crude model for fiber growth from a flowing solution by combining the above expression with fluid mechanics, molecular structure of fluid and the crystal growth theory itself.

In the case of polymer melts, Haas and Maxwell (84) assumed that the stored energy in a shear experiment could be written as:

$$\int_0^{\gamma} P_{12} d\gamma \quad (\text{II-11})$$

where γ is the elastic or recoverable shear strain. Combining this with Krigbaum and Roe's analysis, and with the assumption of Hooke's law ($P = G$) they find,

$$\Delta T = \Delta T_i + \frac{T_m^0}{\Delta H_f} \left| \frac{P_{12}^2}{2G} \right| \quad (\text{II-12})$$

where ΔT is the effective supercooling of the system, ΔT_i is the initial supercooling due to temperature decrease only, G is the elastic shear modulus. The second term on the right-hand side of the above equation gives the additional supercooling, ΔT_a , due to stress. Ulrich and Price (233) evaluated ΔT_a using the relation $N_1 = \frac{2P_{12}^2}{G}$,

which gives,

$$\Delta T_a = \frac{T_m^0 N_1}{4 \Delta H_f} \quad (\text{II-13})$$

where N_1 is the first normal stress difference which they show to be equal to the reversible elastic energy of the system.

Kobayashi and Nagasawa (139) evaluated ΔG_{def} for a polymer melt assuming the effect of stress on ΔH_f to be zero, hence

$$\Delta G_{\text{def}} = -T \Delta S_{\text{def}} \quad (\text{II-14})$$

where ΔS_{def} is the reduction in melt entropy due to orientation.

Kobayashi et al. (139) have used the equations developed in rubber elasticity theory to evaluate ΔS_{def} from the molecular extension ratio,

α :

$$\Delta S_{\text{def}} = - \frac{kN}{2} \left| \alpha^2 + \frac{2}{\alpha} - 3 \right| \quad (\text{II-15})$$

where N equals number of network chains/cm³.

The main problem in using Eq. II-15 is that there is no a priori way to evaluate the microscopic deformation ratio, α . Kobayashi et al. (139) assume that affine deformation (as for a cross-linked system) applies in polymer melt, in which case α in Eq. II-15 can be equated to the macroscopic stretch ratio, λ . However, this analysis results in the overprediction of the value ΔS_{def} for a polymer melt. Ziabicki (265) further points out a numerical error in the evaluation of ΔS_{def} by Kobayashi et al. (139).

Yeh and Hong (259) recognized this problem and proposed an empirical relation patterned after Flory's equation. Their expression is,

$$\Delta S_{\text{def}} = - \frac{kN}{2} \left| \left(\frac{24m}{\pi} \right)^{1/2} (\alpha - 1) \right| \quad (\text{II-16})$$

where m is the number of statistical segments per network chain.

Although Eq. II-16 shows stronger dependency of ΔS_{def} on α , the basic problem of obtaining the microscopic deformation ratio (α) still exists.

Marrucci (170) and Jarecki (115) recently have developed expressions to evaluate ΔS_{def} from the measured stress in polymer melts and solutions. A detailed discussion of this will be postponed to a later chapter.

3. Nucleation Controlled Growth

Growth processes in polymers are usually described in terms of secondary nucleation on the surface of the growing crystal. The general formulation of the isothermal, steady state, linear growth rates ($\dot{G}$) are developed from Eq. II-1 with appropriate critical free energies (265).

A number of different theories have been proposed for coherent nucleation of macromolecules on the growth face of folded chain lamellae. Some of the more recent work on this problem has centered on the nature of the fold surface at the growing face of the lamellae. The earlier theories (see the review of Price (198) and the paper of Hoffman (98)) assumed that the chain folds were all of the same length. In more recent models (102) it is assumed that the molecules crystallize with an irregular fold period. That is, the thickness of the growth face fluctuates about a mean value equal to the lamellae thickness.

The first theories of Hoffman and co-workers (98,99,150) with regular chain folding (adjacent re-entry) and a smooth chain folded surface, led to the growth rate,

$$G = G_0 \exp\left| -\frac{\Delta E_a}{kT} \right| \exp\left| -\frac{4b_0 \gamma \gamma_e T_m^0}{\Delta H_f(\Delta T)kT} \right| \quad (\text{II-17})$$

where ΔE_a is the barrier that opposes the movement of particle to the interface where the growth is occurring and b_0 is the layer thickness. Hoffmann (98), Hoffmann and Weeks (100) have suggested that the barrier of interest is that associated with segmental mobility of polymer chain. According to Williams, Landel and Ferry (251) the effective barrier involving segmental motion may be expected to be temperature dependent. Thus

$$\Delta E_a = \Delta E_a^0 + \Delta E_a^{\text{WLF}}$$

where $\Delta E_a^{\text{WLF}} = \frac{BT}{T - (T_g - T_0)}$ (II-17a)

and ΔE^0 is the contribution to the activation energy barrier in the absence of WLF effect (251). B and T_0 are constants. The temperature dependent linear growth rate (assumed proportional to the rate of surface nucleation) is now given by

$$\dot{G} = G_0 \exp\left| -\frac{1}{kT} \left(\Delta E^0 + \frac{BT}{T - (T_g - T_0)} \right) \right| \exp\left| -\frac{4b_0 \gamma \gamma_e T_m^0}{kT \Delta H_f(\Delta T)} \right| \quad (\text{II-18})$$

Equation II-18 is applicable for growth rates from melt for both bundle type nuclei ($\gamma_e = \gamma_{e,\text{bundle}}$) and folded nuclei ($\gamma_e = \gamma_{e,\text{folded}}$).

B. OVERALL TRANSFORMATION KINETICS

The combined effect of nucleation and growth of crystalline entities from the amorphous melt results in the overall transformation kinetics of the polymer. The first treatment of this type appears to have been developed by Von Goler and Sachs (243). Avrami (15-17) derived relationships to describe the kinetics of phase change for inorganic materials.

The Avrami kinetic analysis is based on the following assumptions:

1. Nuclei are formed randomly throughout the melt at locations which are considered to be predetermined by so-called "germ" nuclei.
2. The nucleation may occur sporadically in time or instantaneously (i.e., in a very brief time interval compared to the total time required to complete crystallization).
3. The crystalline entities grow linearly with time in the radial direction, hence as spheres if growth is three dimensional.
4. The density of transformed phase is constant.

The Avrami (15-17) theory, under the conditions of isothermal crystallization, leads to the expression:

$$X = 1 - \exp(-Kt^n) \quad (\text{II-19})$$

where X is the fraction crystallized, t is the time of crystallization, n and K are constants whose values depend on the character of the nucleation and growth processes. Similar equations were derived by

Johnson and Mehl (118) and Evans (56). Mandelkern (160) subsequently modified Avrami's theory to describe the kinetics of polymer crystallization from amorphous to partly crystalline entities (spherulites). Modifications to Avrami theory were also made by Banks and co-workers (18,19) and Lacko (147). The value of K in Eq. II-19 for spherical growth with constant nucleation rate $\dot{N}$ and growth rate $\dot{G}$ is given by

$$K = \frac{\dot{N} \dot{G}^3 \pi \rho_c}{3 \rho_a} \quad (\text{II-20})$$

Here ρ_c and ρ_a are the densities of crystalline and amorphous phase, respectively.

Another important form of the Avrami rate constant K corresponds to the case that the nucleation rate quickly becomes zero, i.e., $\dot{N} = 0$ and there is a fixed nucleation density n_0 . For this case, assuming growth in three dimensions,

$$K = \frac{4\pi n_0}{3} \dot{G}^3 \quad (\text{II-21})$$

The usual method for treatment of experimental data in terms of the Avrami analysis is to plot (Eq. II-19) $\log - \ln (1 - X)$ as a function of $\log t$. This will produce a straight line with slope " n " and intercept " K ."

The Avrami treatment was formulated for an interface controlled process which requires only short-range diffusion of molecules. In this case only integer values of n are physically significant if it is assumed that the mechanism is the same throughout the crystallization

process. When the composition of the crystalline phase differs from that of the melt, long-range diffusion may become important in controlling the growth rate. The overall crystallization kinetics can then be described only in an approximate fashion by Eq. II-19 and the exponent is no longer an integer value. The values of n corresponding to specific models for the nucleation and growth processes are shown in Table II-1 (208).

TABLE II-1
AVRAMI COEFFICIENTS AND THE CORRESPONDING NUCLEATION/GROWTH PROCESSES

Coefficient, n	Nucleation	Growth Geometry	Growth Control
$1/2$	Instantaneous	Rod	Diffusion
1	Instantaneous	Rod	Interface
1	Instantaneous	Disc	Diffusion
$1-1/2$	Instantaneous	Sphere	Diffusion
$1-1/2$	Homogeneous	Rod	Diffusion
2	Instantaneous	Disc	Interface
2	Homogeneous	Disc	Diffusion
2	Homogeneous	Rod	Interface
$2-1/2$	Homogeneous	Sphere	Diffusion
3	Instantaneous	Sphere	Interface
3	Homogeneous	Disc	Interface
$3-1/2$	-	-	-
4	Homogeneous	Sphere	Interface

C. EXPERIMENTAL STUDIES OF QUIESCENT CRYSTALLIZATION

1. Kinetics of Crystallization of Polypropylene and Polyethylene

Overall transformation kinetics of the Avrami type have been successfully used in interpreting quiescent isothermal crystallization from the melt. Investigators have used several different techniques in following the crystallinity with time at a given temperature. These

include dilatometry (78,80,104), depolarization microscopy (34,104, 158), differential thermal analysis (25,53) and differential scanning calorimetry (DSC) (87,193).

Crystallization rate constants for isotactic polypropylene calculated from dilatometric and radial growth measurements in the temperature range 120-160°C have been reported by Marker et al. (168). Crystallization at higher temperatures appeared to proceed by spherical growth from a fixed number of nuclei ($n = 3$). It was assumed that the nuclei were formed heterogeneously due to interaction with foreign matter. The number of nuclei was found to increase with decreasing crystallization temperature.

Griffith and Ranby (80) studied the crystallization kinetics of polypropylene melts between 133°C and 155°C using the dilatometer technique. They obtained crystallization rate data for a commercial sample containing 9% extractable polymer (degree of polymerization, $DP = 10,000$), an experimentally extracted sample containing no stabilizer ($DP = 7,500$) and a thermally degraded, experimentally extracted sample ($DP = 1,200$). Their results indicate that crystallization rates are higher for low molecular weight (thermally degraded) samples and lower for samples with atactic content and stabilizer.

Homogeneous nucleation in molten isotactic polypropylene was investigated by Burns and Turnbull (39) using the droplet technique. It was found that minimum supercoolings of 100°C were required to initiate nucleation. A pre-exponential nucleation frequency factor and surface free energy were estimated.

Hoshino et al. (104) studied the crystallization kinetics of polypropylene fractions of varying tacticity using dilatometric

techniques. These results were supplemented with studies using the optical microscope and x-ray diffraction. Their results are consistent with a two-stage process of crystallization: (a) radial growth at the spherulitic interface described by an Avrami equation characterized by $n = 3.9$ in its earlier stages (primary crystallization) and (b) secondary crystallization within the spherulite described by an Avrami equation with an exponent of 1.8. Hoshino et al. (104) reported that for samples of very low tacticity spherulitic structures are "frustrated" in growth at very early stages of development, and a larger part of the crystallization is of the secondary type.

Pratt and Hobbs (193) from a comparative study of crystallization rates by DSC and depolarization microscopy report similar crystallization half times for polypropylene. They report Avrami index, $n = 3$, over a range of crystallization temperatures studied.

Ishizuka and Koyama (111) present a summary of the literature data on Avrami constant, k , and the growth rates for several polypropylenes.

Crystallization rate data for two molecular weight fractions of linear polyethylene were presented by Mandelkern (162). He found differences in the crystallization behavior with molecular weight fraction. The low molecular weight fraction crystallized with Avrami exponent, $n = 3.0$ while the higher molecular weight fraction showed essentially equal choice between $n = 2.0$ and 3.0 . Very similar observations have been reported by Banks and co-workers (20).

The crystallization rates in linear polyethylene were found to be extremely sensitive to the degree of supercooling (161). At 129°C

the appearance of crystallinity was not detected for 400 min. However, when the temperature is lowered by merely 4°C, crystallinity was observed in 6 min. Similar results were reported by Weeks and co-workers (248) for high density polyethylene. At constant crystallization temperature the spherulites showed constant growth rates. This behavior was observed over a wide range of crystallization temperatures.

Barrales-Rienda and Fatou (23) studied the effect of molecular weight on the rate of crystallization of polyethylene fractions at high undercoolings (109-123°C) using DSC. They reported that the crystallization rates increased with decreasing temperature for all the molecular weights. At lower crystallization temperature and higher molecular weights, crystallization rates were only slightly dependent on the molecular weight. Similar results were reported by Hser and Carr (106). Barrales-Rienda et al. (23) analyzed their crystallization data using classical nucleation theories. Taking into account the variation of x_e with molecular weight and assuming a constant x value, they calculated $\frac{\Delta G_i^*}{RT}$ from Turnbull and Fisher type equation. A plot of their nucleation results ($\ln 1/t_{0.1}$) vs $\frac{\Delta G_i^*}{RT}$ for all the molecular weights yielded a unique straight line with slope of -1, which is expected from the theoretical developments.

Hay, Fitzgerald and Wiles (87) studied crystallization kinetics of linear polyethylenes by DSC and dilatometry. Both techniques resulted in similar rate constants with the same temperature dependency. Crystallization rates increased with decreasing temperature. They also reported an Avrami index $n = 3$ for polyethylenes.

2. Nucleating Agents

Nucleating agents are important additives in crystallizable polymers as they promote the initiation of growth centers in the polymer melt, thereby increasing the overall rate of crystallization (33,34). Because of its finer spherulitic morphology a nucleated polymer has modified optical and mechanical properties (146). The effectiveness of the nucleating agents for modifying properties has been utilized by the commercial producers of polymers as evidenced by the patent literature (28-30,234,235).

Binsbergen (33) has carried out a detailed study of the chemical and physical nature of the nucleating agents. The effectiveness of a given substance depends both on the nature of the heterogeneous surface and its dispersion in the polymer melt. While many compounds can function as nucleating agents, a spectrum of nucleating activity exists. Among the more effective nucleating agents are alkali metals or aluminum salts of aromatic or alicyclic carboxylic acids. Inorganic compounds like silica, TiO_2 , CaO , carbon black, etc., though somewhat effective were poor as nucleating agents when compared to metal carboxylates (25,33). Besides nucleating agents, commercial polymers may contain dust and catalyst residue which can initiate heterogeneous nucleation (196).

Inoue (108) studied the effect of nucleating agents on the kinetics of isothermal crystallization of nylon-6 in the temperature range of 180-205°C. Inoue found an increase in the crystallization rates associated with a decrease of the induction period of crystallization. The spherulites are homogeneously distributed and are smaller in size.

Beck and Ledbetter (25) reported that in polypropylene the degree of supercooling, polymer morphology, clarity, tensile properties and density may be altered by the presence of deliberately added heterogeneous foreign agents. Increase in the concentration of nucleating agent increases the nucleation rate with greatest effects occurring at low concentration of nucleating agent (25).

Parrini and Corriari (187) reported that the presence of incompatible additives like CaCO_3 , SiO_2 and TiO_2 increased the crystallization rates in polypropylene and polyethylene. This increase was found to be a direct function of the additive concentration and an inverse function of particle size. Compatible substances like solvents decreased the crystallization rates of the pure polymer and this decrease was a function of their concentration in the mixture. Solid solvents at the melting temperatures of polymers showed similar results as the liquid solvents.

Binsbergen and De Lange (34) and Binsbergen (32) report studies of isothermal crystallization of nucleated polypropylene. The nucleation densities calculated from the Avrami constant K and the linear growth rates (with the assumption that the number of nuclei is constant) show a strong dependency on the temperature of crystallization as well as the amount of nucleating agent added.

Hobbs (96,97) studied the crystallization of polypropylene on carbon surfaces and demonstrated that the nucleating efficiency of a given surface depends not only on its chemical structure but also on its physical structure as well. In particular Hobbs (97) showed that

the orientation of graphite planes on carbon surfaces is important in determining the heterogeneous nucleation efficiency.

D. EXPERIMENTAL STUDIES OF STRESS-INDUCED CRYSTALLIZATION KINETICS

Polymers crystallized under stressed conditions exhibit different transformation kinetics and morphologies than those crystallized under quiescent conditions. Some of the studies found in the literature on stress-crystallized systems include stirred dilute solutions of crystallizing polymers, strained cross-linked materials, sheared non-cross-linked polymer melts and melts subjected to uniaxial stress fields. In addition, there are studies carried out under nonisothermal conditions as well. In general the nonisothermal studies relate directly to some polymer processing operation such as melt spinning while the isothermal studies are more fundamental in nature.

1. Dilute Solutions

The phenomena of stress-induced crystallization from polymer solutions have been well documented in the literature (61,155,157,188, 189,190). A fibrous structure termed "shish kebab" structure is produced if dilute solutions of polyethylene are stirred during crystallization. These structures were obtained by Keller (132) and Blackladder and Schleinitz (35) prior to their controlled production by Pennings and Keil (189). An important result of the studies of Pennings and co-workers (189) is that stirring solutions produced a strong accelerating effect on the crystallization rate. It was found that a critical stirrer speed or extensional flow rate is necessary to produce the shish kebab structure.

Pennings and co-workers (188,189) reported that in polyethylene solution the minimum supercooling at which crystallization is observed, decreased by as much as 20°C when the solution is subject to shear flow between coaxial cylinders. The maximum crystallization temperature was found to increase with increasing stirrer rpm. Pennings and co-workers (188,189) also found that the higher molecular weight polyethylene nucleates from solution at considerably higher temperatures compared to a lower molecular weight polymer. From this Pennings concludes that the pronounced reduction in the degree of supercooling for spontaneous nucleation in stirred polyethylene solution results from the effective coil stretching by small eddies combined with chain end anchoring by entanglement in an adsorbed layer on the rotor surface. The induction time measured from the time dependency of shear stress shows a linear relationship with the peripheral velocity of the surface of the inner cylinder and is independent of the annular gap.

Frank, Keller and Mackley (61) confirmed the importance of elongational flow in inducing crystallization by impinging together opposed jets of polyethylene solutions. Frank et al. (61) found that crystallization of fibrous crystals occurs in the plane of symmetry (where pure extensional flow exists) of the impinging jets.

Elongational flow experiments similar to Frank et al. (61) on dilute solutions of polyethylene in xylene were reported by Mackley and Keller (157). They found that the maximum crystallization temperature $T_{cr} \text{ (max)}$ is a function of both molecular weight and strain rate. For a given material $T_{cr} \text{ (max)}$ increases with strain rate to a limiting value.

2. Cross-Linked Polymers

The earliest quantitative studies on the crystallization kinetics of stressed rubber were carried out by Treloar (224). Treloar used the techniques of birefringence, x-ray diffraction and density measurements to follow the crystallization of stressed raw rubber at various extensions. With increasing extension ratios the crystallization rates and preferred orientation of polymer chains in the stretch direction was found to increase.

Gent (74) employed density measurements to follow the rapid crystallization of uniaxially stressed rubber vulcanizate samples. His results showed a wide deviation from theoretical Avrami kinetics. Gent (72) explained the enhanced crystallization rates in oriented samples on the basis of a rise in the melting temperature due to elongation of the macromolecules. Experimental studies of Gent (72,73) on crystallization kinetics of oriented trans polychloroprene and trans polyisoprene networks showed a correlation between the crystallization rates in elongated samples and the measured melting points. The Flory equation correctly predicted the enhanced supercooling at high elongations, whereas at small elongations, the supercooling calculated by the Flory equation exceeded the value needed to explain the enhanced crystallization rates. In a study with natural rubber and polychloroprene networks, Krigbaum and Roe (140) observed similar results. They also found that at low extensions the Krigbaum and Roe equation predicted better than the Flory equation.

Ashby (13) carried out crystallization studies on lightly cross-linked polyethylene melts. Using an Instron capillary rheometer,

he extruded oriented and unoriented samples. The extrudates were then sealed in a dilatometer and heated to 143°C for a period of time that he felt was sufficient to melt the material but not remove the orientation. The samples were then crystallized in the dilatometer at 125°C and the data were subjected to an Avrami type analysis. The Avrami plot showed different behavior for the oriented and unoriented materials. He found that the oriented material showed several definite changes in the slope of the Avrami plot due to selective growth directions in the oriented material.

Andrews (11,12) studied nucleation behavior during crystallization of thin films of natural rubber at fixed elongations. He found that the level of crystallinity and nucleation rate (not growth rate) increased very rapidly with strain.

T. Kawai, Iguchi and Tonami (122) studied the crystallization of stressed, cross-linked melts of polyethylene using dilatometry, TEM and x-ray analysis. Samples were stressed above the melting point and quickly brought to the desired crystallization temperature. An Avrami type analysis showed that the initial crystallization was enhanced by the stress with $n = 1$, but the later stages of the process were retarded. From these studies coupled with morphological studies, T. Kawai, Matsumoto, Kato and Maeda (124) concluded that the amount of macroscopic deformation is not important in determining kinetics (or morphology) but rather the degree of orientation of the molecular segments prior to crystallization.

Kim and Mandelkern (137) from their studies of crystallization kinetics of natural rubber reported that the crystallization rate was

not controlled exclusively by the degree of supercooling as was pointed out by Gent (72,73). When compared under the same supercooling conditions, slightly oriented networks crystallized faster than highly oriented networks. To explain this Kim and Mandelkern hypothesized that elongating a polymer network has two effects on the crystallization process. The dominant effect is the increase in supercooling which greatly speeds up crystallization and the secondary effect is a change in the mechanism of crystallization.

3. Polymer Melts

Between the extremes of dilute solutions and elastomers is the area of melts. Studies have shown that stressed melts will crystallize with kinetics and morphologies different from those for the quiescent case and rather similar to those seen for stress-crystallized elastomers (233). The development of molecular orientation and type of morphology differs for the polymer melts crystallized in shear and in elongation (179,261). As a result the enhancement of the rate of crystallization during these processes also differ. In the following section these two types of crystallization studies are treated separately as much as possible.

a. Crystallization kinetics under shear flow. The first experiments which demonstrated that shear flow can accelerate the crystallization rates were reported by Maxwell et al. (173) and Maxwell (172) on polybutene-1 and polypropylene. They reported that

the application of fixed shear strain to a supercooled melt significantly reduced the induction time* for crystallization.

Capillary viscometer investigations of polypropylene and unvulcanized cis 1,4-polybutadiene and cis 1,4-polyisoprene have been carried out by Van der Vegt and Smit (236). Their results showed that the apparent viscosity decreased with shear stress until a critical point is reached at which the viscosity suddenly increased. This behavior in the viscosity-shear stress curve was attributed to the crystallization of the melt even though they were working 10-30°C above the quiescent crystallization temperature. It was suggested that the onset of crystallization is governed by the elastic strain present and the minimum strain needed to cause crystallization. Similar results were reported by Sieglaff and O'Leary (210) on isotactic polypropylenes.

T. Kawai, Matsumoto, Kato and Maeda (124) measured viscosity changes during crystallization of supercooled polyethylene melts in a cone and plate device operated at one shear rate, 0.5 sec^{-1} . They observed greatly enhanced crystallization rates in the sheared case over the quiescent one.

Haas (83) and Haas and Maxwell (84) used a parallel plate shearing device attached to the stage of a polarizing microscope to study the crystallization kinetics of thin films of polyethylene and polybutene-1 at constant shear stress while following the rate of strain. Their results show that application of sufficiently high shear stress to an

*Induction times in the literature usually refer to the time from start of deformation to the point where a change in the viscosity is observed. The reciprocal of induction times are generally interpreted to be proportional to nucleation rates.

initially supercooled melt has substantial effect on the rates of crystallization. They attributed this effect to the localized supercooling caused by flow disturbances near heterogeneous particles in the melt. Haas and Maxwell interpreted this increased supercooling in terms of the decrease in the entropy in accord with the theories of Flory and Krigbaum and Roe. However, their calculations according to Eq. II-12 showed that the increased supercooling predicted by these theories is far too small to account for the greatly enhanced crystallization rates.

Kobayashi and Nagasawa (139) studied crystallization of high and low molecular weight polyethylenes under shear at slow cooling rates in a concentric cylinder viscometer. As the shear rate was increased, the induction time for crystallization decreased. The effect was more pronounced in high molecular weight material. The rate of crystallization, especially the rate of nucleation, increased rapidly with increased molecular orientation in the polymer melt. These results were interpreted on the basis of reduction in melt entropy (ΔS_{def}) due to orientation which in turn was calculated from the rubber elasticity theory. The direct application of rubber elasticity theory to flowing polymer melt violates all the key assumptions in the theory. Molecular relaxations were not taken into account and no justification was given for the particular type of nucleation used in the analysis. Despite these problems these authors have established a procedure by which theoretical curves relating both the nucleation and growth rates to the birefringence can be obtained.

Keaton (125) crystallized supercooled polypropylene melt during normal simple shear flow in a sliding plate rheometer. Induction times for crystallization were measured over a range of shear rates. At low shear rates the induction times were constant but eventually they began decreasing as the shear rate increased. The shear rate rather than the microscopic shear strain was considered to be the controlling factor in accelerating crystallization.

Wasiak (247) made a thorough study of crystallization using uncross-linked samples of amorphous polyethylene terephthalate (PET) with various degrees of initial orientation. The crystallization half times were reduced in the ratio 1:45 and the apparent Avrami exponent markedly reduced when an initially isotropic sample was replaced with one having a high amorphous orientation factor (of order $f_{am} = 0.6$).

T. Kawai, Kamoto, Ehara, Matsumoto and Maeda (123) studied isothermal shear crystallization of polyethylene terephthalate in a cone and plate shearing device. Kawai et al. (123) found that the induction time (as indicated by increasing shear stress) for crystallization decreased with the shear rate until the shear rate reaches a critical point. At this shear rate the induction period began to increase, reached a maximum and then decreased again.

Krueger and Yeh (143) measured induction times for crystallization of a supercooled polyethylene melt in a concentric cylinder rheometer-dilatometer. They reported a decrease in the induction times for crystallization with increasing shear rates.

Lagasse (148) and Lagasse and Maxwell (149) conducted a detailed experimental study of the effect of isothermal shear flow on

crystallization rates in polyethylenes of varying molecular weights and in one polypropylene. The results showed a strong accelerating effect on the crystallization rate with increasing shear flow when the deformation rates exceed a critical value. The high molecular weight polyethylene crystallized faster at a given shear rate and temperature. The induction time for crystallization was found to be independent of sample geometry.

Lagasse (148) and Lagasse and Maxwell (149) also studied the influence of a carbon black additive and heterogeneous nucleating agent in shear crystallization of polypropylene and ethylene-propylene co-polymer. They found that addition of a substantial number of heterogeneous carbon black particles had no effect on the crystallization kinetics of random co-polymer over the range of shear rates investigated ($\dot{\gamma}$, limited to 4 sec^{-1} due to slippage). The addition of nucleating agents also showed similar results. They report that even though the presence of heterogeneous nucleating agent has a strong accelerating effect on the crystallization of relaxed melts, it has no effect on the crystallization rate during flow. From this Lagasse (148) concludes that the initiation of crystal growth in sheared polymer melts is controlled by homogeneous nucleation. Lagasse (148) and Lagasse and Maxwell (149) suggest that the hydrodynamic origin of the shear-induced crystallization is elastic chain extension due to the entanglement couplings between molecules.

The crystallization behavior of samples of polyethylene oxide (PEO) of varying molecular weights and molecular weight distributions has been studied under varying conditions of shear rate and temperature by Fritzsche, Price and Ulrich (65). They used a concentric cylinder

dilatometer-rheometer and a parallel plate shearing device to study shear crystallization. The experimental results showed that increasing shear rate did not always increase the crystallization rate. They encountered conditions where a decrease in the rate of nucleation was observed with increasing shear rate. Break-up of crystalline nuclei and chain slippage were considered to be the cause of this phenomenon.

Ulrich and Price (233) using the polarizing microscope as a measuring technique studied the nucleation behavior of polyethylene oxide melt as it crystallized under well-defined temperature and shear conditions in a parallel plate rotary shearing device. They found a strong dependence of nucleation rate on supercooling and imposed stress. They concluded that the major effect of the relatively low stresses was to increase the nucleation rate of the system through elastic orientation of the molecular chains. The interpretation of the nucleation rate results through an additional supercooling term (ΔT_a) (see Eq. II-13) showed that the calculated and experimentally measured results are in the same order of magnitude.

Tan and Gogos (218,219) carried out flow-induced crystallization studies of polyethylene melts in a biconical rheometer with constant shear rates at temperatures above the normal melting point. Utilizing suspension theory to describe the increasing viscosity of the crystallizing melt, they have analyzed the stress data through an Avrami type analysis for crystallization. Tan and Gogos (218,219) interpreted the crystallization process as a two-stage process. Stage I is the nucleation of extended chain nuclei which act as substrate for overgrowth of bundle-like and folded lamellae. Stage II is the

growth process, which is found to follow the Avrami equation with $n = 3$. They also present a universal relationship for the induction time and the experimental parameters. The key to the expression developed from classical theory for polyethylene is the assumption that the true equilibrium melting temperature is 160°C , which seems unrealistically high.

Andersen (8) using a semiquantitative procedure, analyzed crystal nucleation in undercooled high density polyethylene sheared in a couette-type viscometer mounted on a Rheometrics mechanical spectrometer. The distribution function of chain extensions calculated from the theory was verified by testing against experimentally obtained values of melt birefringence. The entropy reduction calculated from rubber elasticity theory qualitatively explained the nucleation behavior observed by them.

Yeh, Hong and Krueger (260), interpreting induction times to be proportional to nucleation rate and with the help of Eq. II-16, analyzed shear flow crystallization data of Krueger and Yeh (143), Tan and Gogos (219) and Ulrich and Price (233). The analysis showed that the predicted "coil extension" in the melt prior to crystallization is small and ranges between 21 to 30%. The problem in this approach is obvious as these authors evaluate the microscopic deformation ratios from the induction times. Although this is of interest, there is no means available to reverse this procedure and evaluate the nucleation rates from experimentally measurable parameters. However, the analysis of induction times by Yeh et al. (260) proved an important point. In polymer melts the true microscopic deformation ratios of the polymer

chains are small compared to the macroscopic deformation ratios. Use of the macroscopic deformation ratios in lieu of microscopic deformation ratios would overpredict the nucleation rates in polymer melts.

b. Crystallization kinetics under elongational flow.

Isothermal

There are relatively fewer quantitative studies of the accelerating effect of extensional flow on crystallization rates because of the experimental difficulties involved in producing a pure extensional component in polymer melts.

Nadkarni and Schultz (181) reported studies of extensional flow induced crystallization in polyethylene by low speed spinning. The spinning process was carried out so that crystallization took place under approximately isothermal conditions. The spinline data showed an enhancement of crystallization rate in elongational flow. They also found that the temperature at the point of crystallization, T_{cr} , was much higher than that predicted from quiescent nonisothermal crystallization. The T_{cr} was not closely correlated to local values of stretch rate, cumulative draw or stress but did correlate with linear take up speed, which suggested that the time spent in the spinline itself is an important parameter.

Pucci and Carr (199) presented results of preliminary investigations on elongational flow induced crystallization of mono-disperse and commercial polyethylenes, using the mechanical spectrometer. Induction times were detected by monitoring the changes in melt viscosity brought about by the appearance of nuclei in the melt. Their results

showed a decrease in the induction times with increasing elongation rate at a constant temperature.

Nonisothermal

Katayama, Amano and Nakamura (120), Dees and Spruiell (50) and Nadella et al. (180) have made on-line studies of the development of crystallinity in the spinline for high density polyethylene and polypropylene fibers using on-line WAXS measurements. Their observations showed the important effect on crystallization kinetics of molecular orientation resulting from the elongational flow and draw down forces (stress). Spruiell and White (214) prepared continuous cooling transformation curves (CCT) to compare the kinetics of crystallization during melt spinning for polyethylene and polypropylene to those for quiescent melts of the same polymers. These results showed orders of magnitude increase in the crystallization rates for stressed samples compared to quiescent data for both polyethylene and polypropylene. They concluded that the stress and the accompanying molecular orientation decreases the free energy of formation of crystal nuclei, and it is primarily this fact which leads to the increased crystallization rates.

Ishizuka and Koyama (111) carried out a melt spinning experiment of polypropylene to investigate the crystallization behavior in a running filament using x-ray diffraction. Their results suggest that the crystallization orientation factor and the fraction of a^* oriented crystals are not changed throughout the process. They estimated the temperature and the orientation dependencies of nucleation and growth rates for polypropylene. Ishizuka and Koyama (111) also

speculate that crystallization during the melt spinning is governed mainly by the localized molecular orientation of the supercooled melt in the initial stages.

E. STUDIES OF STRUCTURE AND MORPHOLOGY DEVELOPMENT IN POLYPROPYLENE AND POLYETHYLENE DURING CRYSTALLIZATION

1. Morphology Under Quiescent Conditions

The gross morphology of polymers crystallized under quiescent conditions range from lamellar single crystals produced from dilute solutions to the spherulitic aggregates of bulk crystallized materials.

Growth and identification of single crystals of polyethylene from solution was reported independently by Till (220), Keller (133) and Fischer (58). It is this discovery that led to the interpretation of the morphology of polymers based on the idea of folded chain structure in which the crystallites were found to be lamellae of $100 \text{ \AA}$ in thickness.

Khoury (136) during crystallization studies of polypropylene in solution noted unusual dendritic precursor crystals from which spherulites evolve. These appeared to consist of lamellar branches which criss-crossed each other producing a basket-weave appearance.

Samuels (205) presented a photo-micrograph of a cross section cut through the center of a melt grown isotactic polypropylene spherulite. Radial fibrils can be seen emanating in all directions from the center of the spherulite. These radial fibrils extend out until they reach a boundary. The boundary is formed when the growing spherulite meets the outgrowing front of an adjacent spherulite.

Keith and Padden (126) made a survey of spherulites formed by the isothermal crystallization of polypropylene from the melt in the temperature range of 110-149°C. They distinguished four types of spherulites from the study of optical properties and conditions of growth. They also (127) obtained diffraction patterns of spherulites of type I and II and indexed them on the basis of the monoclinic α unit cell. Keith and Padden (127) and Von Haus (244) reported that the β -form results from the crystallization of rarer types of spherulites (type III and IV).

Both branched and linear polyethylene typically crystallizes from the melt in the form of banded spherulites composed of lamellae. The concentric band structure visible by transmitted light can also be seen on surface replicas examined by transmission electron microscopy. In linear polyethylene spherulites the bands which result from a double-armed spiral remain distinct to the boundary of the spherulite. In branched polyethylene spherulites these bands are narrower and usually become diffuse and disappear as growth progresses outward from the nucleus (70,71).

Keith and Padden (130) crystallized spherulites of linear polyethylene from molten thin films. Under crossed polarizers they observed nearly concentric extinction bands, zig-zag shape of the extinction cross and a number of radial faults. They also found that within each sector all structural units twist with same hand.

Spherulites with double-armed spirals nucleated on the bottom surface of the film were found in rapidly cooled thin films of linear polyethylene (71).

Banks and co-workers (21) observed that high molecular weight polyethylene shows banded or ring type spherulites and the low molecular weight (M_w -20,000) polyethylene shows very fibrous nonbanded spherulites.

2. Morphology Under Stressed Conditions

a. Dilute solutions. Pennings and Keil (189) discovered fibrillar polyethylene crystals in stirred dilute solutions and postulated that the fibers consist of extended chain crystal backbones with folded chain overgrowths. As mentioned already, these structures are generally referred to as shish-kebabs.

Morphological studies (134,253) of the shish-kebab structures indicate three levels of morphology. The first level consists of the kebab. These appear to be the usual chain folded lamellae which have nucleated on the fibrous backbone. The fibrous backbone appears to consist of two structures. There is a 200-300 Å periodicity along the central backbone which shows up as density differences in unshadowed transmission electron micrographs. These periodicities can be correlated to the appearance of the epitaxial shish-kebab by suitable treatment with nitric acid etch and/or ultrasonic degradation. Removal of these ordered platelets reveals the central thread or microfibril. The microfibrils were postulated to consist of highly extended polymer chains.

Studies of McHugh and Schultz (155) on crystallization in solution subjected to oscillatory uniaxial extension showed that the central nucleating fibrils have both folded and extended chain components.

Pennings (188) employing fibrillar polyethylene crystals as seeds studied their longitudinal growth from solutions. He reported a unique

process of longitudinal growth of linear polyethylene crystals from xylene solutions in couette flow when the seeds come in contact with the rotor surface. A growth rate at the rotor surface of 10 cm/min has been observed at a temperature of 123°C. Pennings (188) interprets this surface growth due to very effective stretching of coils that are attached with one end to the crystal faces and with the other end forming firm entanglements with polymer molecules adsorbed to the rotor surface.

b. Cross-Linked Polymers. Andrews (11,12) conducted one of the first studies of the morphology resulting from crystallization of an oriented polymer system. Thin films of natural rubber were crystallized at fixed elongations and were observed by transmission electron microscope (TEM). At moderate strains (up to 300%) the material crystallized in the form of lamellae oriented perpendicular to the stretch direction. As the strain was increased a fibrous morphology parallel to the stretch direction was observed. X-ray diffraction studies of the stress-crystallized samples revealed that the transition from lamellar to fibrillar structure is due to the rates of nucleation and lateral growth but not a reorientation of oriented lamellae.

TEM and x-ray studies by T. Kawai, Iquchi and Tonami (122) during the crystallization of stressed cross-linked melts of polyethylene showed that at low elongations (lower stresses) the morphology consists of stacks of folded-chain lamellae and higher elongations (higher stresses) yield c-axis orientation. Kawai et al. (122) concluded that the amount of macroscopic deformation is not important in determining

morphology but rather the degree of orientation of the molecular segments prior to crystallization.

Keller and Machin (134) studied the morphology of lightly cross-linked polyethylene. Their conclusion was that when stress or flow is imposed on crystallizing polymer melt, crystal nuclei are produced along lines parallel to the stress or flow direction. Chain folded lamellae grow on these nuclei. However, the nucleation density along the stress direction is so high that lamellar growth can only occur perpendicular to them. These lamellar overgrowths changed from twisted form to a flat blade-like form with increasing stress. This study demonstrated the relationship between stirred solution-grown shish-kebabs and row-nucleated lamellae, grown from stressed melts.

In a subsequent study, Hill and Keller (94) from the morphological changes observed during crystallization of lightly cross-linked polyethylenes, suggested a two-step process: formation of oriented fibers in the stress direction followed by transverse growth of chain folded lamellae on these fibers. This was confirmed in a later publication by Hill and Keller (95). In this paper (95) it was suggested that molecular elongation may actually inhibit the growth rate of the chain folded lamellae. However, this effect is overshadowed by the enhanced initiation of lamellar growth on the central fibers, so that at a given temperature the overall crystallization rate is increased by molecular orientation.

c. Polymer melts.

Elongational Flow

Here we mainly summarize the structure morphology studies under nonisothermal conditions during melt spinning.

Katayama, Amano and Nakamura (120) combined the measurements of filament surface temperature diameter, birefringence and both WAXS and SAXS to study structure formation in polyethylene, polypropylene and polybutene-1. Their results were interpreted to indicate a morphology consisting of lamellar and interlamellar regions stacked normal to the fiber axis. The SAXS especially indicated this morphology and pointed to similarities between polypropylene and polyethylene.

Based on their experimental studies and the row structure model of Keller and co-workers (94,95,134), Dees and Spruiell (50) proposed a detailed morphological model for melt spun linear polyethylene. This work together with other extensive experimental studies of structural development during the melt spinning of polyethylene (2,249), polyoxymethylene (135) and polypropylene fibers were reviewed by Spruiell and White (214). They concluded that the morphologies developed with increasing stress showed numerous similarities. At low spinline stress, the fibers have an unoriented lamellar super structure, probably a spherulitic structure which develops into a row nucleated structure at high spinline stresses.

Structure development during melt-spinning of polypropylene has been investigated by several investigators (9,66,138,179,180,214). Perhaps the major finding in the development of structure and morphology is that

presented by Nadella et al. (180). These authors from their experimental studies conclude that spinning variables such as polymer molecular weight, flow rate, melt temperature and take-up velocity all affect the morphology of the spun filaments, but the combination of these effects on morphology can be traced to their effect on the spinline stress.

Nadella et al. report that the birefringence, crystalline and amorphous orientation factors are a unique function of spinline stress for a broad range of polypropylenes over a range of spinning variables. Nadella (179) and Nadella et al. (180) also showed that both cooling rate and stress are important in developing a monoclinic or smectic structure during the melt spinning of polypropylene. A water quenched polypropylene fiber with a smectic structure can be transformed to monoclinic form by increasing the spinline stress.

Though there is a general similarity in the development of structure during melt spinning in polypropylene and polyethylene, the presence of bimodal distribution of unit cell orientations in polypropylene complicates the situation and makes polypropylene unique. Clark (44), Clark and Spruiell (46) and Andersen and Carr (9) have proposed morphological models for flow crystallized polypropylene. The interpretation of bimodal orientation by Clark (44) and Clark and Spruiell (46) consists of a row structure of planar lamellae interconnected by tie molecules, which gives rise to the c-axis oriented contribution. The a'-axis (a'-axis is perpendicular to b- and c-crystallographic axes) oriented contribution is suggested to arise from interlamellar crystals which grow with a special epitaxial relationship with the primary row structure.

Structural studies of Nadkarni and Schultz (181) during the isothermal slow spinning of polyethylene showed a b-axis radial orientation, the details of which changed with spinline parameters. They reported growth of lamellae crystals on extended chain fibrils (row structure), supporting the earlier models of Dees and Spruiell (50).

Shear Flow

The morphology developed during shear flow is similar to that in elongational flow. The row structure model (94,95,134) has found great utility in describing the morphology resulting from shear flow in polymer melts (45,67).

Kobayashi et al. (139) observed the morphological structure changes of polyethylene with shear rate. At low shear rates there is a lack of crystallite orientation (relative to shear strain direction), but as the shear rate is increased the orientation changes to a- and then to c-axis.

Observations (84) through a hot stage microscope during the crystallization of thin films of polyethylene and polybutene-1 at constant shear stress have shown that the application of shear stress to a polymer leads to large increases in number of crystalline structures formed and to the formation of oriented morphologies.

Keaton (125) from the crystallization studies of supercooled polypropylene melts during normal simple shear flow in a sliding plate rheometer concluded that "shear-induced crystallization results in simultaneous a- and c-axis crystalline orientation in the melt flow direction; both types of orientation increase with shear rate. Also, shear crystallization at 121°C produces thermally stable β -modification

crystals in addition to the usually observed α -modification (monoclinic) crystals."

T. Kawai et al. (123) from the analysis of DTA (differential thermal analysis), x-ray, etching and electron microscopy results for isothermal shear crystallization of PET concluded that the morphology changed from chain folded lamellae to bundle-like structure.

Ulrich and Price (233) studied the morphology development during shearing of PEO melts. The results showed crystalline aggregates with a sheaf-like morphology. The long axes of these sheaf-like structures oriented perpendicular to the flow direction when crystallized under shear.

CHAPTER III

THEORETICAL CONSIDERATIONS OF STRESS- INDUCED CRYSTALLIZATION KINETICS

In this chapter two alternate approaches used in the evaluation of stress induced crystallization kinetics will be discussed. A detailed development of the expression for nucleation rate from classical theories will be presented. Also presented is an approach relating the stress levels to dimensionless molecular orientation, which later will be used to interpret the nucleation rates.

A. NUCLEATION RATES FROM CONSIDERATIONS OF ORIENTATIONS

Before proceeding further it is important to consider molecular orientation and its relation to stresses in detail.

1. Molecular Orientation

Orientation in polymer systems is the preferential alignment of polymer chains with specific reference directions such as the axis of a fiber or the machine and transverse directions of a sheet. The development of methods for specification of uniaxial molecular orientation dates back to the studies of P. H. Hermans and co-workers (89,91-93). The approach of Hermans et al. was to specify the orientation in terms of the anisotropy of the polarizability tensor in a system with cylindrical fiber symmetry. This was initially described for a one-phase system (93) as,

$$f = \frac{\overline{\alpha_{11} - \alpha_{\perp}}}{\alpha_a - \alpha_b} = \frac{3 \overline{\cos^2 \phi} - 1}{2} \quad (\text{III-1})$$

where α_a and α_b are polarizabilities along and perpendicular to the polymer chain, $\overline{\alpha_{11} - \alpha_{\perp}}$ is the mean value of the difference between the axial and radial polarizability and ϕ is the angle between the chain axis and the fiber axis. Defined in this way the orientation factor, f , is a measure of the second moment of the orientation distribution.

The views of Hermans et al. for orientation specifications have been generalized by subsequent investigators. One direction has attempted to gain a more complete representation of the chain axis distribution function. Following the efforts of Muller (178) and Sack (203), Roe and Krigbaum (200,201) and McBrierty and Ward (153) represent orientation in terms of a series of spherical harmonics in which for the cases with fiber symmetry the Legendre addition theorem can be used. McBrierty and Ward (153) specifically derive and discuss higher order orientation factors involving $\overline{\cos^4 \phi}$, etc.

Stein (215) taking a different approach has generalized the Hermans et al. orientation factor to describe the orientation of three crystallographic axes for crystalline polymers as,

$$f_j = \frac{3 \overline{\cos^2 \phi_j} - 1}{2} \quad (\text{III-2})$$

where j can refer to the a , b or the c crystallographic axes. The orientations of the three axes are related through the geometry of the unit cell and only two are independent.

The birefringence Δn , describing the average molecular orientation, can be related to f through the Lorentz-Lorenz equation (1,11) as

$$\Delta n = \frac{2}{9} \pi \frac{\tilde{N}_0}{M} \left(\frac{(\bar{n}^2 + 2)^2}{\bar{n}} \right) (\alpha_{11} - \alpha_{\perp}) \quad (\text{III-3a})$$

$$= \Delta^0 f \quad (\text{III-3b})$$

where Δ^0 is the intrinsic birefringence of the system, $\bar{n}$ is the average refractive index parallel and perpendicular to the direction of deformation, $\tilde{N}$ is Avogadro's number and M the molecular weight per structural unit. It is important to note that the birefringence describes only the second moment of the orientation distribution, while the x-ray data can specify the complete distribution in crystalline materials.

2. Rheo-Optical Law

The rheo-optical law, first hypothesized by Clerk Maxwell (174) in 1853, states that the refractive index and stress ellipsoids are co-axial and that the difference in the principal refractive indices is proportional to the corresponding difference in the principal stresses, i.e.,

$$n_i - n_j = C(\sigma_i - \sigma_j) \quad (\text{III-4a})$$

or

$$\underline{n} - n_0 \underline{I} = C(\underline{\sigma} - \sigma_0 \underline{I}) \quad (\text{III-4b})$$

where

$$n_0 = \frac{1}{3} \text{tr } \underline{n}, \quad \sigma_0 = \frac{1}{3} \text{tr } \underline{\sigma}$$

in which $\underline{n}$ is the refractive index tensor, $\underline{\sigma}$ the stress tensor and C the stress optical coefficient.

Kuhn and Grun (145), Treloar (226) and Lodge (152) among others have derived an expression for the stress optical coefficient for cross-linked and entangled systems of flexible polymer chains of form,

$$C = \frac{2\pi}{45} \frac{1}{kT} \left(\frac{(\bar{n}^2 + 2)^2}{\bar{n}} \right) (\alpha_a - \alpha_b) . \quad (\text{III-5})$$

a. Elongational flow. For the case of elongational flow, the rheo-optical law (Eq. III-4) reduces to,

$$\Delta n_{12} = n_{11} - n_{22} = C(\sigma_{11} - \sigma_{22}) = C \sigma_{11} \quad (\text{III-6})$$

Where "1" is the direction of flow and "2" perpendicular to flow direction.

Combining Eq. III-6 with Eq. III-3b results in

$$f = \frac{C}{\Delta^0} \sigma_{11} . \quad (\text{III-7})$$

Equation III-7 relates f linearly to stress through the constant $\frac{C}{\Delta^0}$ (185).

b. Shear flow. For the case of shear flow, the rheo-optical law implies that the angle χ between the direction of flow and the principal axes of the stress tensor is the same as the optical extinction angle, χ_{opt} and

$$\begin{aligned} \Delta n_{12} &= C(\sigma_{11} - \sigma_{22}) / \cos 2\chi_{\text{opt}} \\ &= 2C \sigma_{12} / \sin \chi_{\text{opt}} \end{aligned} \quad (\text{III-8a})$$

$$\Delta n_{12} = C(\sigma_x - \sigma_y) \quad (\text{III-8b})$$

where

$$\sigma_x - \sigma_y = \left(4 + \left(\frac{N_1}{\sigma_{12}} \right)^2 \right)^{1/2} \sigma_{12} \quad (\text{III-9})$$

is the principal stress difference (185).

c. Verification of the rheo-optical law. The validity of rheo-optical law for unvulcanized rubber subjected to large homogeneous uniaxial and biaxial strains was shown by Treloar (227) and Saunders (207). Stein and Tobolsky (216) have shown that the rheo-optical law may be applied to follow stress relaxation in uncross-linked strained elastomer samples. Lodge (152) and Saunders (207) hypothesized that this was generally valid for flowing polymer solutions and melts and showed it to be consistent with existing data. This was subsequently verified by various investigators (4,36,85,113,192,246).

Oda, White and Clark (185) report a correlation between the principal stress differences in polystyrene melts and the birefringence of the vitrified amorphous samples prepared by either elongational or shear flow. They interpret this as the orientation frozen in from the melt. As suggested by Oda et al. (185), this result might be anticipated for amorphous vitrified polymers on the basis of the rheo-optical law. Matsumoto and Bogue (171) have provided a detailed experimental verification of the validity of the rheo-optical law in polystyrene under nonisothermal conditions and suggested its high stress level limitations.

3. Nucleation Rates-Orientation

The rheo-optical law cannot be directly applied to crystallizable polymers after crystallization since the final morphology and

orientation in this case is strongly affected by "oriented nucleation" and crystal growth. However, studies on melt spinning of polypropylene (180) showed that the morphology and orientation in spun fibers correlated with spinline stress independent of the molecular weight and spinline variables such as takeup velocity, mass flow rate and extrusion temperature. This finding was interpreted to mean that the morphology developed during spinning is controlled by the molecular orientation just prior to crystallization. This molecular orientation is in turn directly related to the uniaxial elongational stress applied to the spinning filament. Recent work by Choi, Spruiell and White (42) also suggests similar results in blown polyethylene films.

The above mentioned studies particularly for melt spun polypropylene suggest that in the uniaxial case, at least, a unique correlation exists between morphology and orientation and the state of stress existing during crystallization. This presents a possibility that crystal nucleation and growth rates (which affect morphology) can be related to the state of molecular orientation through measurements of stress (rheo-optical law). Based on the above considerations, we may speculate that there exists an expression relating $\dot{N}$ with orientation in the melt just prior to crystallization. Such a relation may be written intuitively as,

$$\dot{N} \propto f \quad \text{(III-10)}$$

where f is some appropriate measure of the orientation distribution (not necessarily the orientation factor defined above). If the orientation distribution is determined by the state of stress

we might expect that

$$\dot{N} = s(\sigma_i - \sigma_j) \quad (\text{III-11})$$

where s indicates a form of unknown functionality. For a given sample at a given crystallization temperature Eq. III-11, if applicable, should result in correlation of nucleation rates with the principal stress differences in the melt independent of mode of deformation.

B. NUCLEATION THEORIES

1. Development of Nucleation Rate Equation

a. Homogeneous nucleation-kinetics. Volmer and Weber (242) were the first to treat the formation of nuclei during condensation from vapor assuming that they form by a series of bimolecular reactions of the form:



and



where β_i represents a cluster containing i molecules and i^* is the number of molecules of the critical size cluster; i.e., a nucleus. They further assumed that the number of clusters of critical size always corresponds to the equilibrium number and the rate of reverse reaction in Eq. III-12c can be neglected. Under these assumptions, the rate of

nucleation per unit volume, $\dot{N}$ is given by

$$\dot{N} = Z S^* n_i^* \quad (\text{III-13})$$

where Z is the collision frequency of a single molecule with nuclei per unit area of the nuclei, S^* is the area of the critical nucleus, and n_i^* is the equilibrium concentration of critical size embryo. For the condensation of vapor the collision frequency is given by (76)

$$Z = P/(2\pi mkT)^{1/2} \quad (\text{III-14})$$

where P is the vapor pressure, m is the molecular mass, k is Boltzmann's constant.

Frenkel (62) presented a qualitative theory of heterophase fluctuations which he applied to condensation from the vapor, pre-melting and crystallization phenomena. Frenkel (62) viewed the microclusters as large molecules and wrote the Gibbs free energy of the system in the form

$$G = \sum n_i G_i - T S_{\text{mix}} \quad (\text{III-15})$$

where n_i is the actual number of atom clusters, S_{mix} is the configurational entropy changes arising from mixing the microclusters.

Von Smoluchowski (245) and Einstein (54) gave the probability of an isothermal fluctuation as

$$\omega \propto \exp\left(-\frac{\Delta A}{kT}\right) \quad (\text{III-16})$$

where ΔA is the Helmholtz free energy associated with formation of a fluctuation.

Combining Eqs. III-15 and III-16 and minimizing with respect to all possible n_i under the constraints of constant T , pressure and mass gives the equilibrium distribution of heterophase fluctuations in a condensed system as:

$$n_i^* = \sum n_i \exp\left(\frac{-\Delta G_i^*}{kT}\right) \quad (\text{III-17})$$

For $n \gg n_i$ ($i > 1$), then $\sum n_i = n$, number of atoms in the system, Eq. III-17 now becomes,

$$n_i^* = n \exp\left(\frac{-\Delta G_i^*}{kT}\right) \quad (\text{III-18})$$

By substituting Eqs. III-18 and III-14 into Eq. III-13, we obtain for $\dot{N}$,

$$\dot{N} = [nS^*P/(2\pi mkT)^{1/2}] \exp \frac{-\Delta G_i^*}{kT} \quad (\text{III-19})$$

Becker and Doring (27) improved the Volmer-Weber theory by allowing for reverse reaction in Eq. III-12c and by using a steady state number of critical size clusters rather than the equilibrium number. The expression for the nucleation rate has the form:

$$\dot{N} = \frac{B n_1 S^* P}{(2\pi mkT)^{1/2}} \exp\left(\frac{-\Delta G_i^*}{kT}\right) \quad (\text{III-20a})$$

where the Becker-Doring nonequilibrium factor, B is

$$B = \alpha_c \left(\frac{-v \Delta G_v}{2n_i^* kT} \right)^{1/2} \quad (\text{III-20b})$$

where α_c is a constant and is less than unity, v is the molecular volume in the embryo, i^* is the critical number of atoms in the cluster and ΔG_v is the value of the bulk free energy difference between gas and liquid phases per unit volume.

For nucleation in condensed phases, the free energy of activation for motion across the embryo-matrix interface must be included in the expression. This was done by Becker (26) and later more quantitatively by Turnbull and Fisher (230). The latter authors, combining the absolute reaction rate theory (77) with a Becker-Doring approach, derived an expression for the steady state nucleation rate of the form:

$$\dot{N} = N_0 \exp[-(\Delta F_i^* + \Delta G_i^*)/kT] \quad (\text{III-21})$$

where ΔF_i^* is the activation energy for motion across the embryo-matrix interface.

N_0 in Eq. III-21 for nonspherical multifaceted clusters is given by

$$N_0 = S^* n_s n_l v_0 \left(\frac{\sum_k a_k \gamma_k}{9\pi kT} \right)^{1/2} \quad (\text{III-22})$$

where n_l is the number of molecules per unit volume of α phase, and n_s is the number of molecules in the surface of the nucleus. The summation is over all the facets of the cluster, each being characterized by an interfacial energy γ and a geometrical factor a , and v_0 is a molecular frequency factor.

Several refinements could be made in the definition of N_0 such as consideration of crystal growth kinetics or time lag effects. These would have to change N_0 many magnitudes to alter appreciably the experimental conclusion, because of the exponential dependence of the nucleation rate on ΔG_i^* .

b. Homogeneous nucleation-thermodynamics. There are several recent papers (60,99,128,129,150,167,195,230,254) dealing with particular applications of classical nucleation theory to specific nucleus shapes and types. Adopting the formulation of Turnbull and Fisher (230), Mandelkern, Quinn and Flory (167) in 1954 described expressions for the spherical and disk-shaped nuclei. Hoffman and Lauritzen (99) in 1961 extended the Mandelkern et al. (167) approach to include the free energy of formation of folded chain crystals in dilute solution (150) and also the crystallization of bulk polymers in a bundle-like or chain folding fashion (99).

Consider the formation of a spherical embryo of phase β in a surrounding medium of phase α , the system maintained at constant temperature and pressure. The change in the free energy of this system due to a spherical embryo of radius r is

$$\Delta G_i = - \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (\text{III-23})$$

where ΔG_v is the difference between the volume free energy of the liquid and solid, γ is the specific surface free energy of the interface between embryo and matrix, and r is the radius of the particle.

The maximum value of ΔG_i , designated ΔG_i^* , occurs at a critical size r^* or a critical number of molecules i^* , and represents the

free energy of formation for the critical nucleus.

From Eq. III-23, setting $\frac{\partial \Delta G_i}{\partial r} = 0$ one obtains

$$r^* = - \frac{2\gamma}{\Delta G_v} \quad (\text{III-24})$$

and

$$\Delta G_i^* = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta G_v)^2} \quad (\text{III-25})$$

The spherical shape nucleus with isotropic γ may be a reasonable assumption in some cases. However, in polymeric systems this assumption is unreasonable as nonspherical geometries are more appropriate (39,47). Following Cormia, Price and Turnbull (47) and assuming the nucleus to be cylindrical in shape with surface energies γ for the side and γ_e for the end, we have

$$\Delta G_i = 2\pi r l \gamma + 2\pi r^2 \gamma_e - \pi r^2 l \Delta G_v \quad (\text{III-26})$$

and

$$\Delta G_i^* = \frac{8\pi \gamma^2 \gamma_e}{(\Delta G_v)^2} \quad (\text{III-27})$$

For a rectangular parallel piped case (39) we have:

$$\Delta G_i^* = \frac{32\pi \gamma^2 \gamma_e}{(\Delta G_v)^2} \quad (\text{III-28})$$

Substitution of Eq. III-28 for ΔG_i^* and Eq. III-22 for N_0 into the nucleation rate expression (Eq. III-21) gives the homogeneous nucleation

rate as

$$\dot{N} = S^* n_s n_l v_0 \left[\frac{\sum_k a_k \gamma_k}{9\pi kT} \right]^{1/2} \exp \left[-\frac{\Delta F_i^*}{kT} - \frac{32\pi \gamma^2 \gamma_e}{(\Delta G_v)^2 kT} \right] \quad (\text{III-29})$$

The above expression is applicable for both folded chain and bundle-like nucleus when used with the appropriate surface free energy terms.

c. Heterogeneous nucleation-kinetics. Consider the nucleation of β phase from α phase under conditions where there is heterogeneous nucleation at an interface between α and another phase θ . By arguments similar to those used for homogeneous nucleation, Turnbull (229), ignoring strain, obtained an expression for the heterogeneous nucleation rate in condensed phases as:

$$\dot{N} = S^* n_s N_s v_0 \exp \left[-\left(\frac{\Delta F_i^* + \Delta G_i^*}{kT} \right) \right] \quad (\text{III-30})$$

where S^* is area of a critical cluster which is in contact with the phase θ , n_s is the number of α atoms across from the cluster per unit area of cluster and N_s is the number of α atoms in contact with surface or are effectively adsorbed on θ . N_s as defined here is proportional to the surface area of the θ phase. This results in a nucleation rate proportional to the surface area of phase for a heterogeneous system.

d. Heterogeneous nucleation-thermodynamics. Using the classical approach which assumes that the surface energy required to form a nucleus is reduced by the catalyst, Price (197) derived an expression for the critical free energy (ΔG_i^*) for heterogeneous nucleation of

polymer from solution or melt with folded chain nuclei as

$$\Delta G_i^* = \frac{16\gamma\gamma_e(\Delta\gamma)}{\Delta G_v^2} \quad (\text{III-31})$$

where $\Delta\gamma = \gamma_{os} - \gamma_s$ (63) and γ_{os} and γ_s are interfacial energies of the catalyst in contact with the polymer crystal and the melt or solution, respectively. When the substrate is absent, $\gamma_s = 0$, $\gamma = \gamma_{os}$ hence $\Delta\gamma = 2\gamma$ and Eq. III-31 reduces to Eq. III-28 for the homogeneous case. However, as long as $\Delta\gamma < 2\gamma$, the heterogeneous process will dominate. This will happen when polymer crystal and catalyst interaction is strong (γ_{os} small).

Substitution of Eq. III-31 into Eq. III-30 gives the heterogeneous nucleation rate as,

$$\dot{N} = S^* n_s N_s v_0 \exp\left[-\frac{\Delta F_i^*}{kT} - \frac{16\gamma\gamma_e(\Delta\gamma)}{kT(\Delta G_v)^2}\right] \quad (\text{III-32})$$

2. Temperature Dependency of the Nucleation Rates

The exponential terms containing ΔF_i^* and ΔG_v in Eq. III-21 have opposite temperature dependencies. At very high degrees of supercooling the term containing ΔF_i^* (the energy barrier effecting the transport of the material across the liquid crystal interface) in Eq. III-21 begins to override the second exponential, causing the nucleation rate to drop. As described earlier, according to Williams, Landel and Ferry (251), the effective barrier involving segment motion may be expected to be temperature dependent. This leads to

$$\Delta F_i^* = \Delta F_{WLF}^* = BT/(T_0 + T - T_g) \quad (\text{III-33})$$

where T_g is the glass transition temperature of the polymer, B and T_0 are constants.

At low to moderate supercoolings, the ΔF_i^* is approximately independent of temperature and ΔG_v in the second exponent in Eq. III-21 is a strong function of temperature.

At the equilibrium melting temperature, T_m^0 , $\Delta G_v = 0$ and hence the nucleation rate is zero. We may write the volume free energy change as:

$$\Delta G_v = \Delta H_f - T\Delta S_f \quad (\text{III-34})$$

and

$$\Delta S_f = \frac{\Delta H_f}{T_m^0} \quad (\text{III-35})$$

Assuming the variation in ΔS_f and ΔH_f to be independent of temperature, the free energy change between the solid and the liquid phase is given by (160):

$$\Delta G_v = \frac{\Delta H_f(\Delta T)}{T_m^0} \quad (\text{III-36})$$

where $\Delta T = T_m^0 - T$, is the supercooling. Substitution of Eq. III-36 in Eq. III-32 results in the quiescent, heterogeneous nucleation rate as

$$\ln \dot{N} = A - \frac{B}{T} \left[\frac{T_m^0}{\Delta H \Delta T} \right]^2 \quad (\text{III-37})$$

where

$$A = \ln(S^* n_s N_s v_0) - \frac{\Delta F_i^*}{kT} \quad (\text{III-38})$$

and

$$B = \frac{16\gamma\gamma_e(\Delta\gamma)}{k} \quad (\text{III-39})$$

When supercooling is not too great and the second exponential term is in control, Eq. III-37 predicts an approximately linear relationship between $\ln \dot{N}$ and $T_m^{02}/T\Delta T^2$ with slope equal to $B/\Delta H^2$ and intercept, A . This, of course, further assumes that the pre-exponential factor in Eq. III-32 is not a strong function of temperature in the range plotted. Such results were first presented by Frenkel (63) and then by Mandelkern et al. (167).

3. Stress Induced Nucleation Rates

The form of expression derived for nucleation rate in the quiescent case has generally been assumed applicable for the stressed case with appropriate modification of certain parameters (139,188,259). There are two differences which stress is assumed to cause. First, the mass transport term, ΔF^* may be affected slightly by the existence of a flow field. However, this effect is small compared to the effect of stress on the bulk free energy, ΔG_v . In general, one can write (188):

$$\Delta G_v(\text{stressed}) = \Delta G_v(\text{quiescent}) + \Delta G_{\text{def}}$$

where $\Delta G_v(\text{quiescent})$ is the usual difference in the bulk free energy between the liquid and solid under quiescent conditions. ΔG_{def} represents

the elastically stored free energy resulting from the deformation of the polymer chains by flowing solution or melt. Substitution of the above expression into Eq. III-32 results in a nucleation rate equation for the stressed melt (139);

$$\dot{N} = S^* n_s N_s v_0 \exp\left[\frac{-\Delta F_i^*}{kT} - \frac{16\pi\gamma e(\Delta\gamma)}{kT(\Delta G_v + \Delta G_{\text{def}})^2}\right] \quad (\text{III-40})$$

In the above expression, deformation or flow will effect the pre-exponential term as the heterogenities present in the melt provide more effective surface area, S^* . However, this would have to change many orders of magnitude to have any significant influence on the nucleation rates due to the exponential dependency of the nucleation rate on ΔG_v . Under these assumptions, the nucleation rate for a stressed case can be written as

$$\ln \dot{N} = A - \frac{B}{T} \left[\frac{1}{(\Delta G_v + \Delta G_{\text{def}})^2} \right] \quad (\text{III-40a})$$

where A and B are constants given in Eqs. III-38 and III-39. Eq. III-40a shows that the stress induced nucleation rates can be predicted from the knowledge of A and B from quiescent crystallization results and the ΔG_{def} .

In a sample containing purposefully added nucleating agent, a nucleating agent, under quiescent conditions can affect both A (by increasing the available surface area S^* for nucleation) and B (by changing the $\Delta\gamma$ term in Eq. III-39). In the presence of stress or

flow a nucleating agent can conceivably affect both A and B, in a manner different from the quiescent case. An affect on A may result from the fact that particles in motion may come into contact with a larger number of polymer molecules, thus in effect offering a greater effective surface area than stationary particles. Stress may affect B if the catalytic effect of the nucleating agent is sensitive to the local molecular orientation in the vicinity of the particles.

a. Evaluation of ΔG_{def} . As described in the literature review, an expression for ΔG_{def} for a cross linked polymer has been derived (170). In this expression ΔG_{def} has been related to macroscopic stretch ratio. As previously discussed, such a relation between ΔG_{def} and macroscopic stretch ratio is of little value in a polymer melt or solution because of the violation of several of the basic assumptions involved in the derivation. In a polymer melt or solution the molecular chains relax and ΔG_{def} would depend on a true molecular chain deformation ratio, α . It is not possible to independently obtain the value of α . This lack in the adequate treatment to predict the ΔG_{def} in polymer melts from externally controlled variables make the quantitative prediction of $\dot{N}$ difficult. A preferable way is to relate the ΔG_{def} to the state of the stress in the melt. Since the free energy of deformation is a scalar and the stress is a tensor, the only way to relate ΔG_{def} to the stress levels is through their invariants (117), i.e.,

$$\Delta G_{\text{def}} = f(I_{\text{C}-1}, II_{\text{C}-1}, III_{\text{C}-1}) = f(\text{tr } \underline{P}, \text{tr } \underline{P}^2, \text{tr } \underline{P}^3) . \quad (\text{III-41})$$

Evaluation of the above form has been suggested by Jarecki and Zialicki (117). This equation can be expanded in a series form as

$$\Delta G_{\text{def}} = a_{11} \text{tr } \underline{P} + a_{21} \text{tr } \underline{P}^2 + a_{22} (\text{tr } \underline{P})^2 + a_{31} \text{tr } \underline{P}^3 + \dots \quad (\text{III-42})$$

Equation III-42 is general and requires the knowledge of several constants. In the following section we could consider the derivation of a simpler expression relating ΔG_{def} to the stress field in the system (170). Cross-linked system is considered first, followed by polymer melts and dilute solutions.

Cross-Linked System

Entropy in a polymer network:

For the case where rotation about the bonds in the molecular chain (freely jointed) can be considered to be unrestricted, the internal energy of the molecule will be the same for all conformations and the Helmholtz free energy, A , is given by

$$\Delta A = -T\Delta S \quad (\text{constant } T) \quad (\text{III-43})$$

According to the general principles of statistical thermodynamics as developed by Boltzmann, the entropy is given by

$$S = k \ln \Omega \quad (\text{III-44})$$

where Ω is the number of conformations available to the system.

In a network the cross-linkage points restrict the motion of the chains which in turn restricts the number of configurations

available to the system. Here one can assume that one end of the chain is fixed (origin) while the other end is confined to a small volume element dv at a distance r from the origin. In the presence of this restriction and for constant volume element, the number of conformations available to the chain is proportional to the product of Gaussian probability density and the volume agent.

The entropy S of the chain is

$$S = k \ln \left[\frac{b_n^3}{\pi^{1/2}} \exp(-b_n^2 r^2) \right] \quad (\text{III-45})$$

which can be rewritten as

$$S = C - k b_n^2 r^2 \quad (\text{III-46})$$

where k is the Boltzmann constant and $b_n = \frac{3}{2n \ell^2}$ in which n is number of bonds of length ℓ .

The entropy per unit volume of a permanently cross-linked network is given by

$$S = C - kN \sum_i b_{n,i}^2 r_i^2 \quad (\text{III-47})$$

where N is the number of chains/unit volume, r is the end-to-end vector of each network strand, b_n depends on the n and ℓ constituting the chain, and the summation i is over all the network strands.

The arbitrary constant in Eq. III-45 may be chosen so that ΔS represents the excess with respect to conditions of rest (3,170):

$$\Delta S = - kN \sum_i b_{n,i} (r_i^2 - \langle r^2 \rangle_0) \quad (\text{III-48})$$

where $\langle r^2 \rangle_0$ is the equilibrium value of r^2 for strands containing n segments.

The elastic force and local stress tensor:

As a result of molecular deformation, an elastic force $\vec{F}$ directed along the end-to-end vector $\vec{r}$ arises between the ends of the molecule. For chains obeying Gaussian statistics with neglected intra-molecular interactions the elastic force can be expressed as a linear function of the end-to-end vector (223,239):

$$\vec{F} = 2 kT b_n^2 \vec{r} \quad (\text{III-49})$$

This force is responsible for a local stress in the vicinity of the chain. This local or the extra stress tensor can be written as (170),

$$\vec{P} = 2 kT N \sum_i b_{n,i} (\vec{r}_i \vec{r}_i - \frac{1}{3} \langle r_0^2 \rangle \vec{1}) \quad (\text{III-50})$$

and

$$\text{tr } \vec{P} = 2 kT N \sum_i b_{n,i} (r_i^2 - \langle r_0^2 \rangle) . \quad (\text{III-51})$$

Comparison of Eqs. III-49 and III-46, recalling $\Delta G_{\text{def}} = -T\Delta S_{\text{def}}$, gives

$$\Delta G_{\text{def}} = -T\Delta S_{\text{def}} = \frac{1}{2} \text{tr } \underline{P} \quad (\text{III-52a})$$

Dilute Solutions and Polymer Melts

In a polymer melt or solution there are temporary networks due to entanglements. Hence Eq. III-46 derived for a network system is applicable for the present case also. Further, the dumbbell model proposed by Marrucci (170) substitutes for the real molecule two friction centers located at the ends connected by a spring, i.e.,

$$\underline{F}(\text{network}) = \underline{F}(\text{dil. sol. and melts}) = 2 kT \frac{b^2}{n} \underline{r} \quad (\text{III-53})$$

Now by following an analysis similar to that given for the network system, one can arrive at an equation similar to Eq. III-50a:

$$\Delta G_{\text{def}} = \frac{1}{2} \text{tr } \underline{P} \quad (\text{III-52b})$$

Equation III-50b (and also Eq. III-50a) relates free energy due to deformation to the extra stress tensor for an arbitrary flow field under isothermal conditions and it allows one to calculate the ΔG_{def} from corresponding stress levels, $\underline{P}$.

Recently Jarecki (115) developed an expression relating the free energy of a deformed chain to the conformational entropy, entropy of mixing and the internal energy. The effects of internal energy and the

entropy of mixing cancel out each other for the Gaussian approximation. Using this approximation, Jarecki (115) derived a general formula relating ΔG_{def} and the local stress tensor. His result is equivalent to that of Marrucci and co-workers (3,170).

Bernstein, Kearsley and Zapas (31) (BKZ) proposed an expression relating the conformational entropy, $\mathcal{E}$, to the net rate of entropy production, S . This is written as,

$$\mathcal{E} = \int_{-\infty}^t S dt' \quad (\text{III-54})$$

In order to calculate $\mathcal{E}$, one must assume a function for the S . One of these proposed S functions may be written as,

$$S = \frac{1}{2} \sum_n \frac{G_n}{\rho T} \frac{e^{\frac{(t-t')}{\tau_n}}}{\tau_n} [I_{C-1} - 3] \quad (\text{III-55})$$

where t and t' are the present and past times and I_{C-1} is the first invariant of the finger strain tensor. Appendix I shows the analyses for simple shear and uniaxial extensional flows for both the Marrucci (3,170) and BKZ theories (31). Comparison of the two analyses indicates similar relationships.

The simpler equation (Eq. III-50b) is a direct result of the linearity assumption in Eq. III-51 which can break down when the molecule is very much extended. In spite of these considerations, the results obtained above provide at least an approximate means by which the state of stress in the melt can be related to ΔG_{def} .

For steady elongational flow Eq. III-50b can be written as,

$$\begin{aligned}
 \Delta G_{\text{def}} &= \frac{1}{2} (P_{11} + P_{22} + P_{33}) \\
 &= \frac{1}{2} (P_{11} - P_{22} + 2P_{22} + P_{33})
 \end{aligned}
 \tag{III-56}$$

By symmetry $P_{22} = P_{33}$

and as

$$\sigma_{11} = -p + P_{11}, \quad \sigma_{22} = -p + P_{22} = 0$$

$$\sigma_{11} = P_{11} - P_{22}$$

$$\begin{aligned}
 \Delta G_{\text{def}} &= \frac{1}{2} (\sigma_{11} + 3P_{22}) \\
 &\approx \frac{1}{2} \sigma_{11}
 \end{aligned}
 \tag{III-57}$$

Since P_{22} is much smaller compared to σ_{11} , the tensile stress.

For simple shear flow Eq. III-50b can be written as,

$$\begin{aligned}
 \Delta G_{\text{def}} &= \frac{1}{2} (P_{11} + P_{22} + P_{33}) \\
 &= \frac{1}{2} (P_{11} - P_{22} + 2P_{22} + P_{33}) \\
 &= \frac{1}{2} (N_1 + 2P_{22} + P_{33})
 \end{aligned}
 \tag{III-58}$$

For elastic solid model and integral type models with memory function $m_2 = 0$,

$$P_{22} = P_{33} = 0$$

$$\Delta G_{\text{def}} \approx \frac{1}{2} N_1$$

(III-59)

CHAPTER IV

MATERIALS AND EXPERIMENTAL PROCEDURES

A. MATERIALS

The materials used in the present research include high density polyethylene, nonnucleated polypropylenes and nucleated polypropylenes. The nonnucleated polypropylene used as a control in the studies is a commercial polypropylene of the same type as the nucleated samples. The nonnucleated polypropylenes may contain certain heterogeneities that induce nucleation, but they do not contain purposely added nucleating agents or fillers. Table IV-1 gives a detailed description of the polymers including the code names used in the present work.

B. EXPERIMENTAL PROCEDURES

1. Isothermal Quiescent Crystallization Kinetics

A Perkin-Elmer Differential Scanning Calorimeter (DSC) Model 1B was used in these studies. This instrument has the capability for rapid, precise temperature change as well as the ability to maintain constant isothermal temperature. Both these capabilities are essential for isothermal crystallization studies. The procedure requires the fusion of roughly 15 mg of polymer in the instrument at a temperature and time period sufficient to eliminate unwanted melt memory effects. This for PP was 226°C and for PE, 200°C for a period of 5 minutes. The melt is then allowed to cool rapidly in the instrument to an appropriate precalibrated temperature where isothermal crystallization of the

TABLE IV-1
DETAILS OF EXPERIMENTAL POLYMERS

Manufacturer and Commercial Code	Melt Index	Our Code Name	Nucleating Agent	Weight Percent of Addition	[η](4)	GPC Results		
						$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w/\bar{M}_n^{(3)}$
Hercules Profax® 6623	2.50	PP025	None	--	3.05	4.03×10^5	6.05×10^5	$4.90^{(1)}$ 4.0
Hercules Profax® 6323	12.0	PP120	None	--	2.05	2.45×10^5	2.55×10^5	$5.60^{(1)}$ 8.0
Hercules Profax® 6501	4.0	PP040	None	--	2.35	2.91×10^5	--	--
Hercules Profax® 6501	4.0	PPS850	Sodium Benzoate	0.50	--	--	--	--
Hercules Profax® 6501	4.0	PPS810	Sodium Benzoate	0.10	--	--	--	--
Hercules Profax® 6501	4.0	PPT05	Sodium Benzoate	0.05	--	--	--	--
Hercules Profax® 6501	4.0	PPT50	Talc	0.50	--	--	--	--
Phillips Marlex® 6050	5.0	PE	None	--	--	--	$1.14 \times 10^5^{(2)}$	8.08 --

¹Dr. H. Stryker, Gulf Oil Chemicals, Orange, Tex., GPC results.

²Chemplex, Chicago, Ill., GPC results.

³Estimated from rheological properties.

⁴Dilute solution viscosity at 135°C in decalol measured at Esso Chimie, NDG, France.

⁵ $\bar{M}_w$ estimated from [η] results.

polymer occurs. A time base recorder traces the polymer's exothermic crystallization peak. The procedure described in the instrument manual was followed in both temperature calibration and in the actual experiments. For all the polymer samples, the crystallization experiments have been carried out from minimum possible temperature (crystallization starts before temperature equilibration) to a maximum possible temperature (no detectable exothermic peak). Within this range measurements were made at regular intervals of 3°C in PP and 2°C in PE.

The DSC crystallization curves were integrated using the trapezoidal rule. The integration is carried out by first digitizing the DSC trace with a Tektronix tablet reader connected to an IBM computer. The weight fraction of the material crystallized at time t was calculated from the equation

$$x_t = \int_0^t \frac{dA_t}{dt} dt / \int_0^{\infty} \frac{dA_t}{dt} dt, \quad (\text{IV-1})$$

where A_t represents the area under the crystallization peak.

The data were plotted and analyzed according to Avrami theory.

2. Stress Induced Crystallization Studies

A Rheometrics Mechanical Spectrometer was used to study the stress induced crystallization kinetics in both shear and elongational flows. The changes in viscosity as detected by stress measurements were used to follow crystallization. The Mechanical Spectrometer provides an isothermal chamber with good temperature control, steady deformation rate and an accurate load cell to measure the stress levels

in the system. The main reason behind using the same apparatus for both the shear and elongational flow was to utilize the same force sensing system as well as equivalent heating controls. In the following sections a more detailed description of the experimental procedures are given.

a. Isothermal shear flow. Studies of crystallization kinetics under the influence of shear stress were carried out on the Mechanical Spectrometer manufactured by Rheometrics Inc., Union, NJ. A cone-and-plate set-up was used in the experiments. The cone has 25 mm diameter with 0.1 radian cone angle. Compression molded samples (mold temperature 190°C, PP and 170°C, PE) were used in the experiments. The samples were first preheated to 226°C in the case of PP and 212°C for PE. The cone-plate gap was set at 50 μ and the residual stresses in the sample were allowed to decay. The total time that the samples were preheated at 226°C was approximately 7 minutes. At the end of this period, the temperature of the isothermal chamber was changed to the crystallization temperature and 6 minutes period of time was allowed for the sample to reach the isothermal crystallization temperature (T_{Cr}) and stabilize as indicated by the temperature recorded by the thermocouple in the cone. Obviously, this means that measurements could only be carried out at temperatures sufficiently high so that the incubation time for quiescent crystallization is much greater than the stabilization period (2 min). The sample was then sheared while torque and normal forces were recorded as a function of time. Figure IV-1 shows a general scheme for the experiment where both the cooling and force curves are shown.

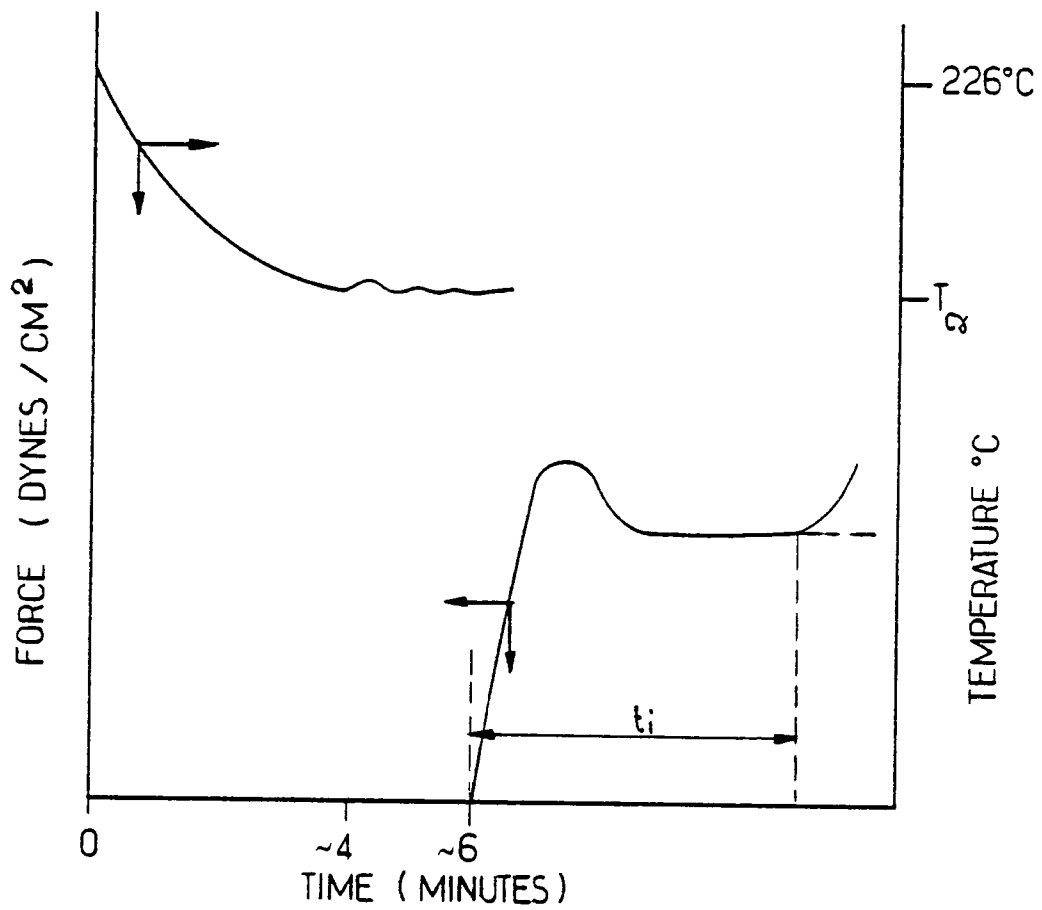


Figure IV-1 : Experimental scheme showing both the temperature and stress traces from the mechanical spectrometer.

To obtain the shear stress and the first normal stress difference the following equations were used:

$$\sigma_{12} = \frac{3M}{2\pi R^3}, \quad (\text{IV-2})$$

$$N_1 = \sigma_{11} - \sigma_{22} = \frac{2F_z}{\pi R^2}. \quad (\text{IV-3})$$

The shear rate is:

$$\dot{\gamma} = \Omega/\alpha, \quad (\text{IV-4})$$

and

$$\eta = 3M\alpha/2\pi R^3\Omega \quad (\text{IV-5})$$

where M is the torque, F_z is the normal force, R is the radius of the cone, Ω the angular velocity, α the cone angle and η the shear viscosity.

b. Isothermal elongational flow. Pucci and Carr (199) have shown that crystallization under elongational flow can be carried out on a Mechanical Spectrometer. In the present studies the Mechanical Spectrometer was used with special sample clamps. These special clamps are off-centered so as to give sample spacing L_0 (see Figure IV-2). One of these sample clamps is connected to a load cell while the other acts as a winder as shown in Figure IV-2.

Strips of approximately 20 mm length, 8 mm width and 1.4 mm thickness are mounted in the sample clamps. These strips were cut from the compression molded sheets prepared for the shear flow experiments. The sample,

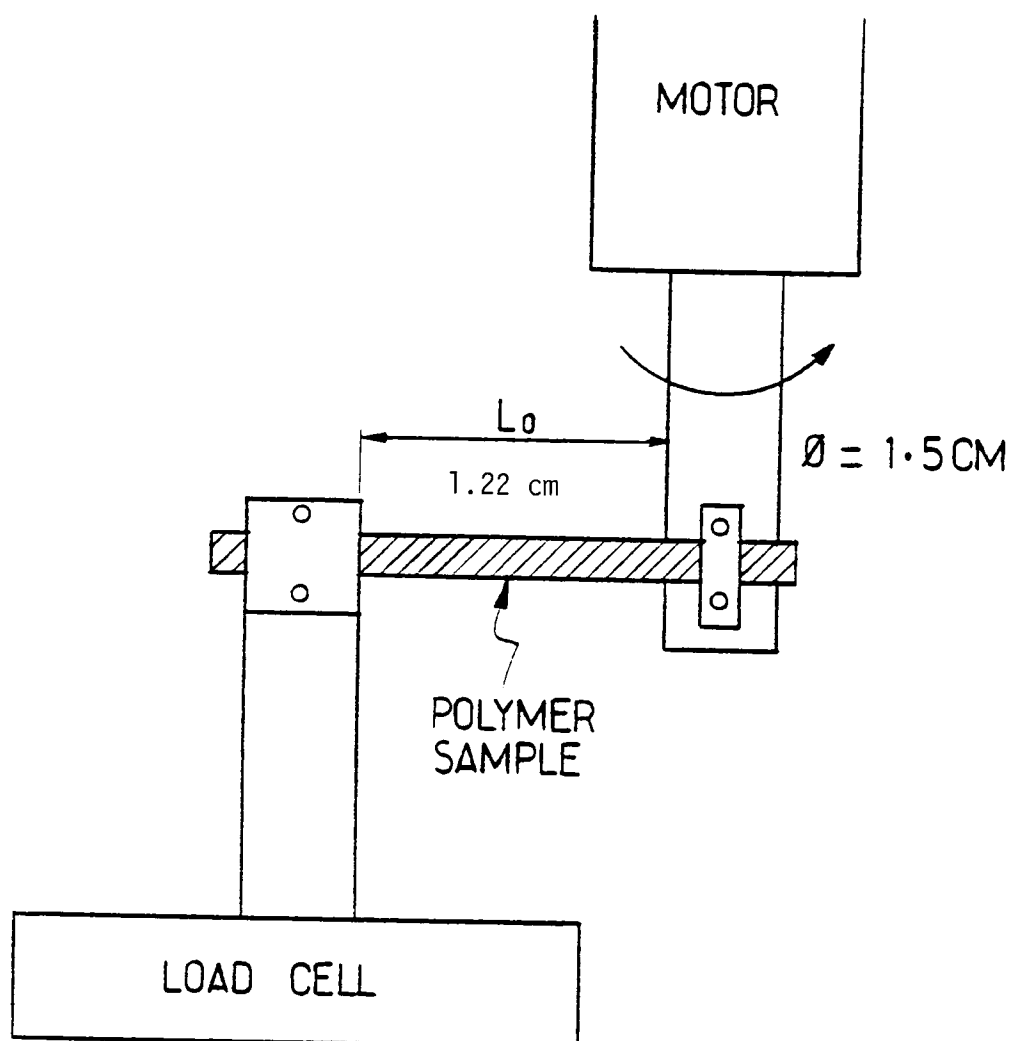


Figure IV-2 : Sample holders set up for elongational flow experiments on the mechanical spectrometer.

after melting at 200°C (for a period of 4 min in the case of PP, and 170°C for about 2-1/2 min in the case of polyethylene) is then allowed to cool by changing the temperature of the isothermal chamber to T_{cr} . An additional 5 minutes period of time was allowed in order to reach equilibrium in PP and 4-1/2 minutes in the case of PE. The sample was then stretched by rotating the spindle at a constant velocity.

The elongational rate $\dot{\epsilon}$ is determined from

$$\dot{\epsilon} = \frac{1}{L_0} \frac{dL}{dt} = \frac{V_L}{L_0} = \frac{R\Omega}{L_0} \quad (IV-6)$$

where Ω is angular velocity, R the radius of the spindle.

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

$$\sigma_{11}(t) = \frac{4F(t)}{A_0} e^{\dot{\epsilon}t} \quad (IV-7)$$

where $F(t)$ is the total force and A_0 is the cross sectional area before stretching. A_0 has been corrected for the expected increase in A_0 at the temperature of crystallization.

CHAPTER V

QUIESCENT AND FLOW/STRESS-INDUCED CRYSTALLIZATION OF POLYETHYLENE AND POLYPROPYLENE MELTS WITHOUT NUCLEATING AGENTS

In this chapter the results of both quiescent crystallization studies and stress induced crystallization (SIC) studies are presented. Results on Phillips Marlex® 6050 (PE) and Hercules Profax® 6623 (PP025), 6323 (PP120), 6523 (PP040) are reported here. The presentation of the quiescent crystallization results is limited to the extent required for comparison with the SIC studies. Further analysis of the quiescent crystallization data and comparison to samples containing nucleating agents is discussed in Chapter VI.

A. QUIESCENT STUDIES

1. Results

Figures V-1 and V-2 show the differential scanning calorimetry (DSC) exotherms for PP025 and PE respectively at different isothermal crystallization temperatures. The ordinates of these figures represent the rate of enthalpy change due to crystallization. Thus the peak represents the point of maximum crystallization rate at a given temperature and the height indicates the relative maximum crystallization rates for the different samples.

The basic results presented in Figures V-1 and V-2 show the simple and effective use of DSC in the study of quiescent

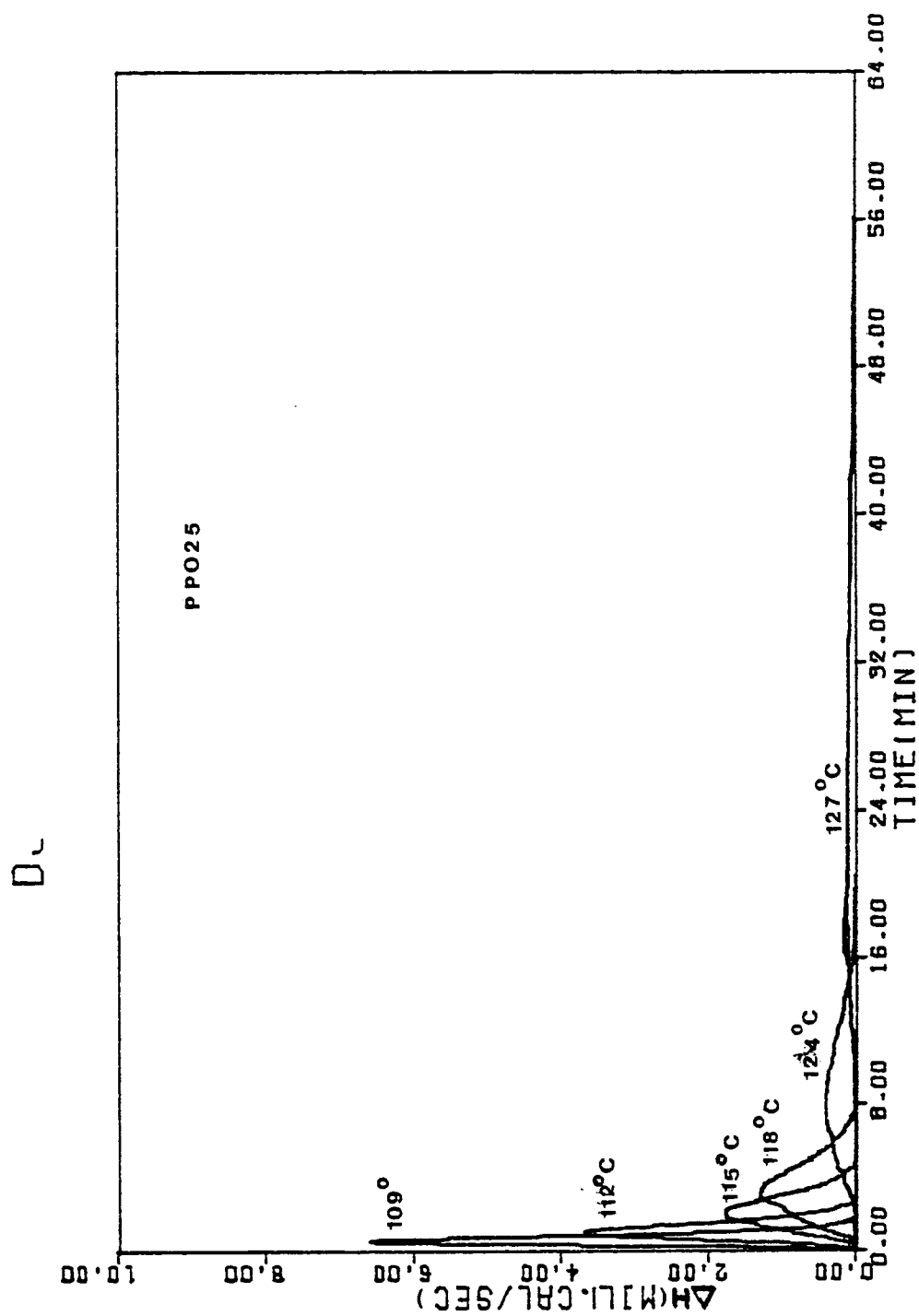


Figure V-1 : DSC crystallization traces of PP025 at different isothermal crystallization temperatures.

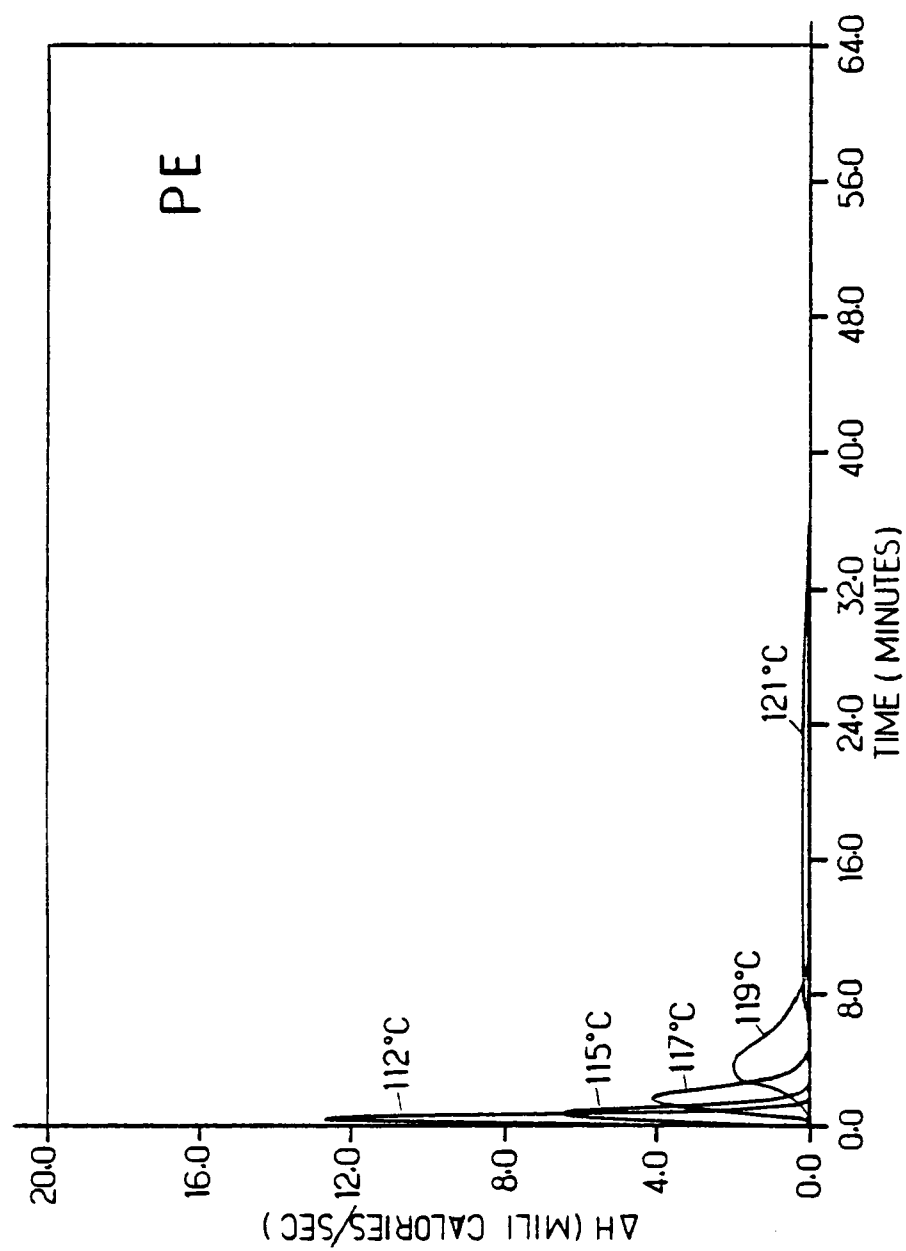


Figure V-2 : DSC crystallization traces of PE at different isothermal crystallization temperatures.

crystallization. DSC provides a fast temperature equilibration, good temperature control and a sensitive thermal response to the variations in the sample during crystallization. However the DSC is limited to studies of crystallization kinetics of polymers with rapid crystallization rates ($t_{0.5} < 60$ min) with relatively high enthalpy of fusion. In the present experimental studies, the experimentally accessible temperature ranges for PP and PE were 109-130°C and 112-121°C, respectively. Figures V-1 and V-2 show the sensitivity (peak heights) of DSC to crystallization rates within these temperature ranges.

Figure V-3 is a plot of reciprocal of crystallization half times ($t = t_{0.5}$ at $X = 0.5 X_f$) versus isothermal crystallization temperature, T_{cr} , for PP025, PP120, PP040 and PE. The reciprocal half time ($1/t_{0.5}$) is used here as a measure of the crystallization rate. Figure V-3 shows that $1/t_{0.5}$ in both PP and PE decreases with increasing T_{cr} . The PE exhibits a stronger temperature dependency of $1/t_{0.5}$ compared to the polypropylenes. PP040 shows faster crystallization rates compared to PP025 and PP120, which exhibit similar crystallization rates.

Figure V-4 is a plot of reciprocal of induction time ($1/t_i$) versus T_{cr} . The induction time is defined here as the time at 1% of final crystallinity. The explanation and interpretation of this induction time will be discussed in detail in the next section where the results from Figure V-4 will be used to make direct comparisons with SIC studies.

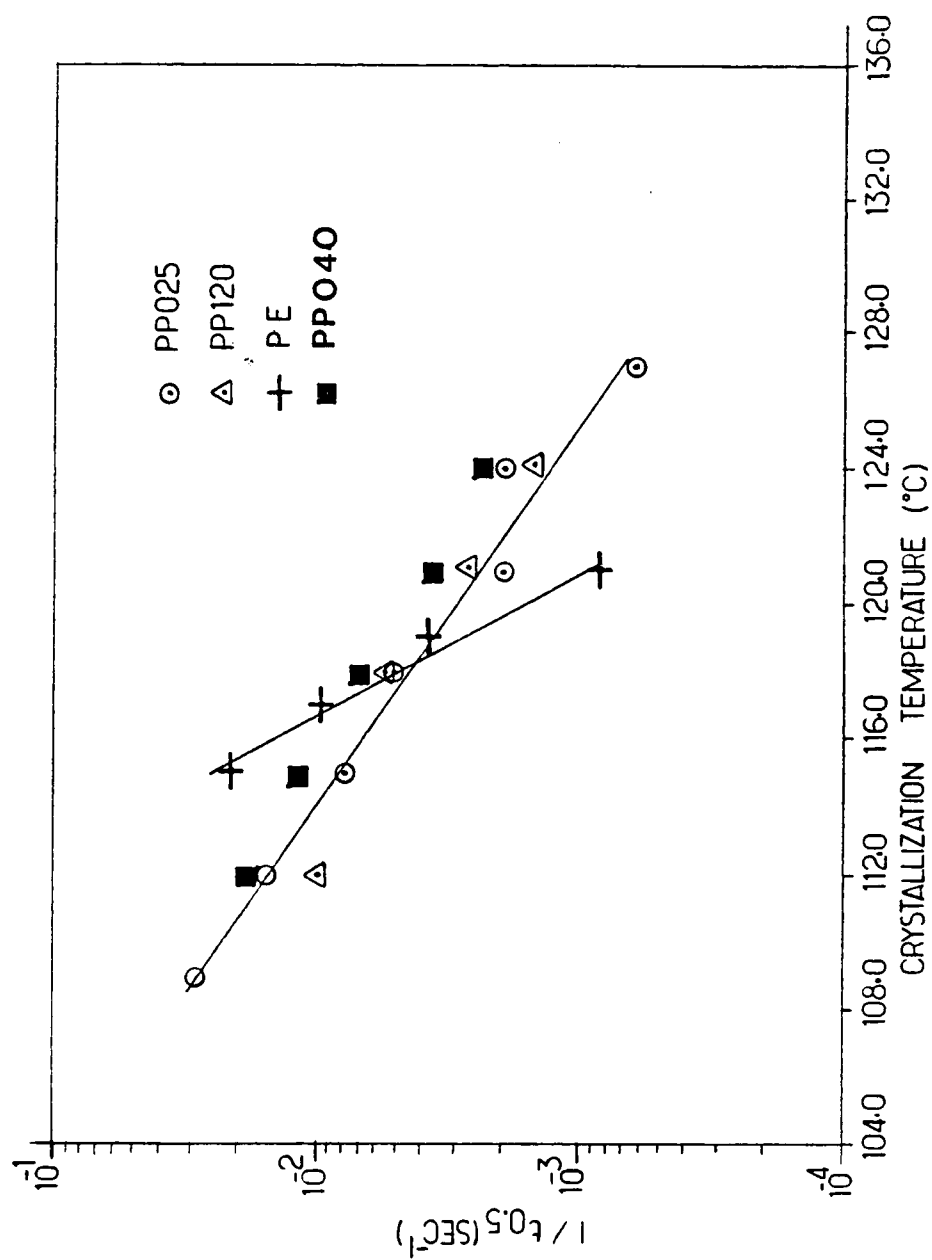


Figure V-3 : Reciprocal crystallization half times versus isothermal crystallization temperatures for PP025, PP120 and PE.

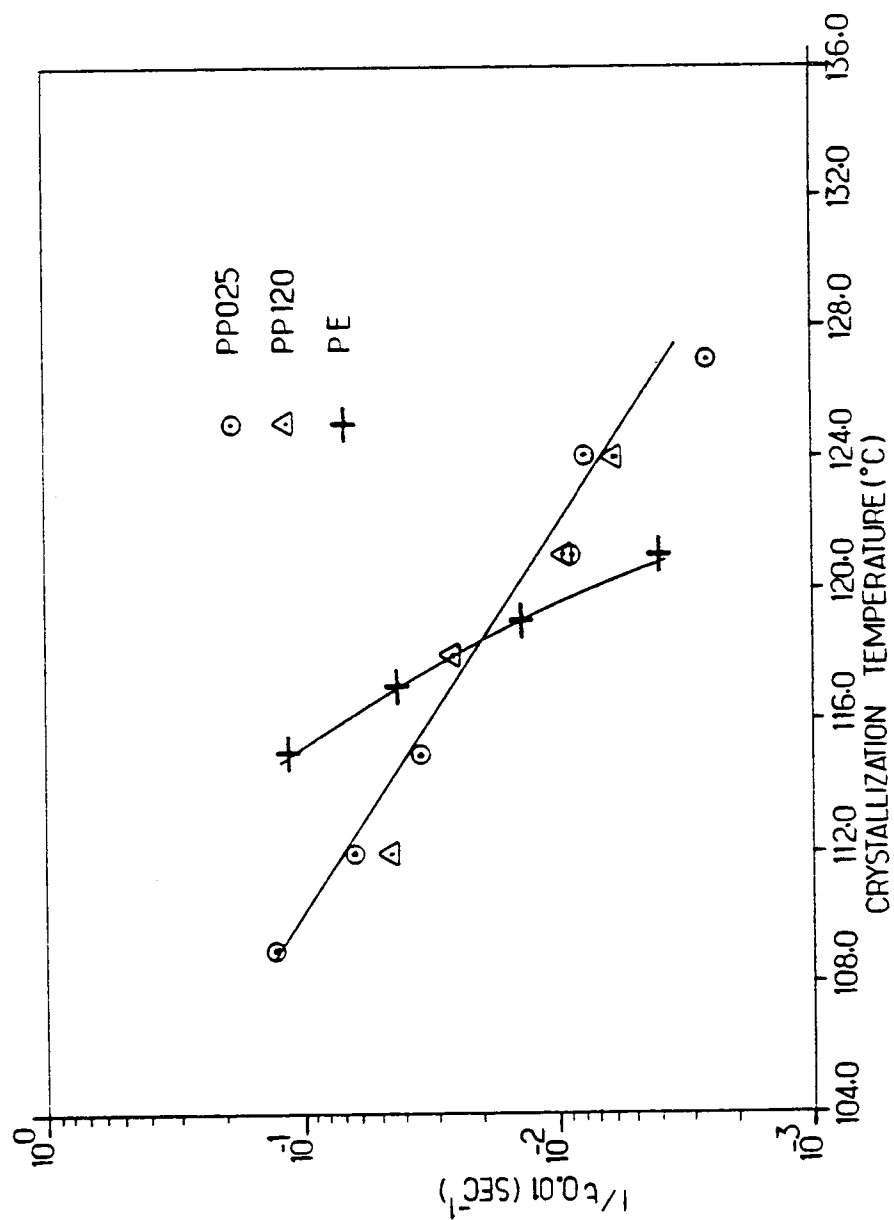


Figure V-4 : Reciprocal induction time versus isothermal crystallization temperature for PP025, PP120 and PE.

Both Figures V-3 and V-4 show that polypropylenes, PP025 and PP120 have similar crystallization half times and induction times within the range of variables investigated.

2. Discussion

A detailed analysis of the crystallization data presented in Figures V-1 and V-2 (pp. 73 and 75) includes fitting the data to the Avrami kinetic equation and determination of the rate constant K and Avrami exponent n . This analysis has been carried out but its presentation will be postponed to a later section (Chapter VI) where it is compared to the results of a similar analysis for samples containing purposely added nucleating agents. The present discussion is restricted to those kinetic features that can be directly compared to the stress induced crystallization results presented in the next section. The technique used for SIC measurements does not give the complete transformation isotherm, but only a measure of the induction time.

According to the Avrami analysis of the overall crystallization kinetics, the reciprocal of crystallization half times are proportional to the Avrami rate constant K ($K = \frac{\ln 2}{t_{0.5}^n}$). It is adequate to interpret the $1/t_{0.5}$ as the rate parameter in the present section. A comparison of $1/t_{0.5}$ from the present study with those from the literature (80,168,193) for polypropylenes are shown in Figure V-5. Figure V-5 shows that at a given temperature the rate parameter ($1/t_{0.5}$) from the present measurements is lower than comparable results from the literature. The observed differences in the rate parameters between the investigations for different polypropylenes with different experimental systems is not unexpected because the crystallization

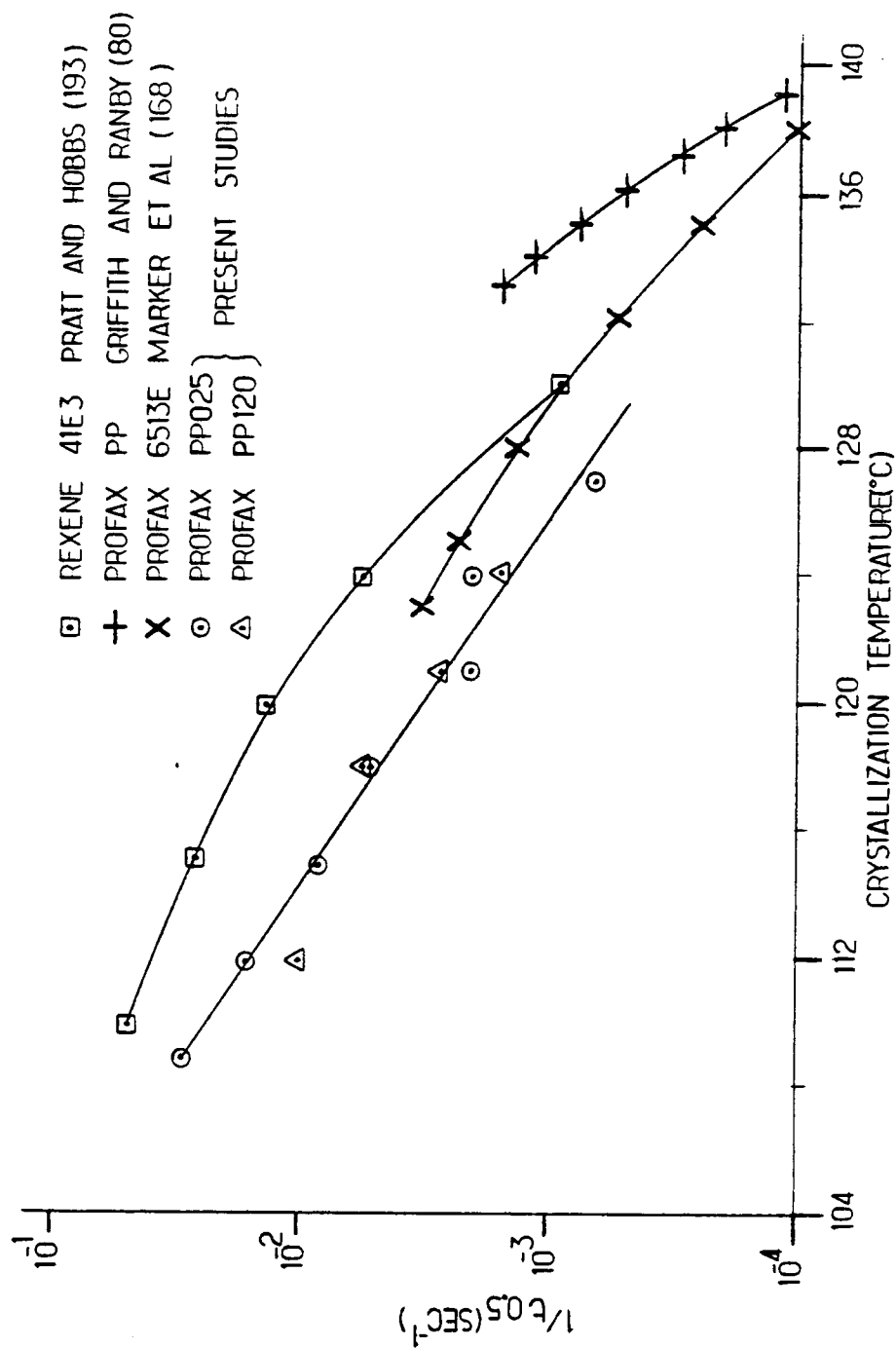


Figure V-5 : Comparison of reciprocal crystallization half time versus isothermal crystallization temperature results from the present studies with those from literature for polypropylene.

process is likely to be sensitive to variations in heterogeneities such as catalyst residues, and may also be affected by molecular weight and its distribution, the degree of tacticity and other variables. It is for this reason that it was deemed necessary to measure the quiescent crystallization kinetics in order to have a direct comparison with the measurements of SIC kinetics.

B. STRESS-INDUCED CRYSTALLIZATION

1. Shear Flow Results

a. General stress response. The stress response from the Mechanical Spectrometer at constant shear rate and temperature is shown in Figure V-6. The stress response as shown in this figure can be broken up into 4 regions. The first region is associated with the stress overshoot phenomenon which is observed with all polymeric melts at intermediate and high shear rates. The second region represents the steady flow response of the melt. The third region involves a steady stress increment without slippage. The fourth region exhibits stress changes due to considerable slippage.

The stress overshoot does not concern us here because our sole interest is in the flow induced crystallization process. The second region of the stress-time curve with zero slope represents the steady state melt viscosity and the magnitude of stress in this region is a function of the isothermal melt temperature and the nature of the polymeric sample itself (e.g., molecular weight, poly dispersity, etc.). The increase of stress (at inflection point) following the zero slope

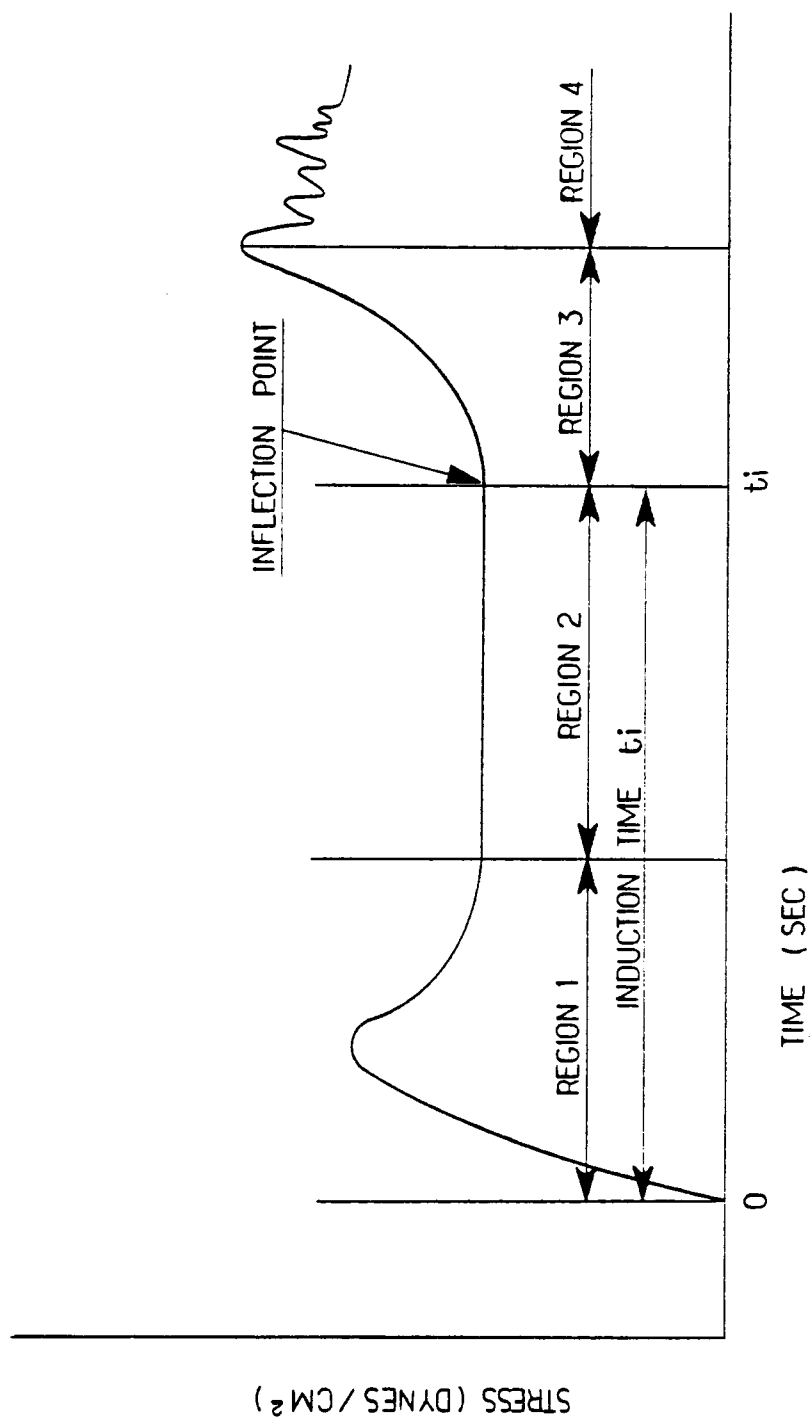


Figure V-6 : Typical stress response from mechanical spectrometer at constant shear rate and temperature.

steady state condition is due to the onset of crystallization. In the present experimental study, it is this transition zone from region 2 to region 3 that is of primary importance. The behavior in region 4 is due to the viscosity of the melt being very high (due to partial phase transformation) which results in high shear stresses that overcome the cohesive forces between the sample and the cone and plate surfaces. This results in slippage as indicated by the abrupt changes in the shear stress value.

The majority of the experiments on PP were carried out in the temperature range of 120-130°C at shear rates ranging from 0.01-16.0 sec^{-1} . At shear rates higher than 16.0 sec^{-1} , problems with edge failure of the PP sample prevented us from making measurements. Polyethylene, on the other hand, can be studied at higher shear rates ($\dot{\gamma} \sim 40.0 \text{ sec}^{-1}$) but within a smaller range of temperatures compared to polypropylene. Above the equilibrium melt temperatures, shear flow in a cone-plate geometry is unstable for $\dot{\gamma} \geq 10 \text{ sec}^{-1}$. The experimental studies in the present research were conducted at temperatures far below their equilibrium melting temperature and the test results at shear rates greater than 10 sec^{-1} are thought to be valid.

b. Induction time. The only parameter related to crystallization kinetics that can be experimentally measured from stress versus time data such as that shown in Figure V-6 is the "induction time." It is defined as the time interval between the beginning of shear and the start of crystallization. The start of crystallization is assumed to

correspond with the onset of region 3 in Figure V-6. This point of inflection is specified by the point where the deviation of the stress trace is observed from the extrapolated line for the zero slope, steady stress trace. This induction time is proportional to reciprocal of nucleation rate and will be discussed in more detail later.

c. Rheological properties

Shear Viscosity

In Figure V-7 the steady state shear viscosity is presented as a function of shear rate for PP025, PP040 and PP120. The viscosity results are calculated according to Eq. IV-5 (p. 74), just prior to crystallization, at the isothermal crystallization temperature. The data show a strong dependency on the molecular weight and/or molecular weight distribution (MWD). Included in this same figure are the viscosity results on PP040 at 180°C obtained by J. Roman et al. (202).

Following Vinogradov and Malkin (238) and others (43,176,217), Figure V-8 shows the relative shear viscosity (η/η_0) as a function of relative shear stress ($\eta_0\dot{\gamma}$) for the experimental data from Figure V-7. The zero shear viscosity (η_0) used in these calculations is an extrapolated value (to zero slope) of the curves in Figure V-7. Minoshima, White and Spruiell (176) showed plots of relative shear viscosity versus $\eta_0\dot{\gamma}$ where the curves indicated the differences in molecular weight distributions between the samples, independent of their molecular weight and the temperature of measurements. Their results also show that in polypropylene at any fixed $\eta_0\dot{\gamma}$, smaller η/η_0 indicates a broader MWD in the sample. Figure V-8 shows that at

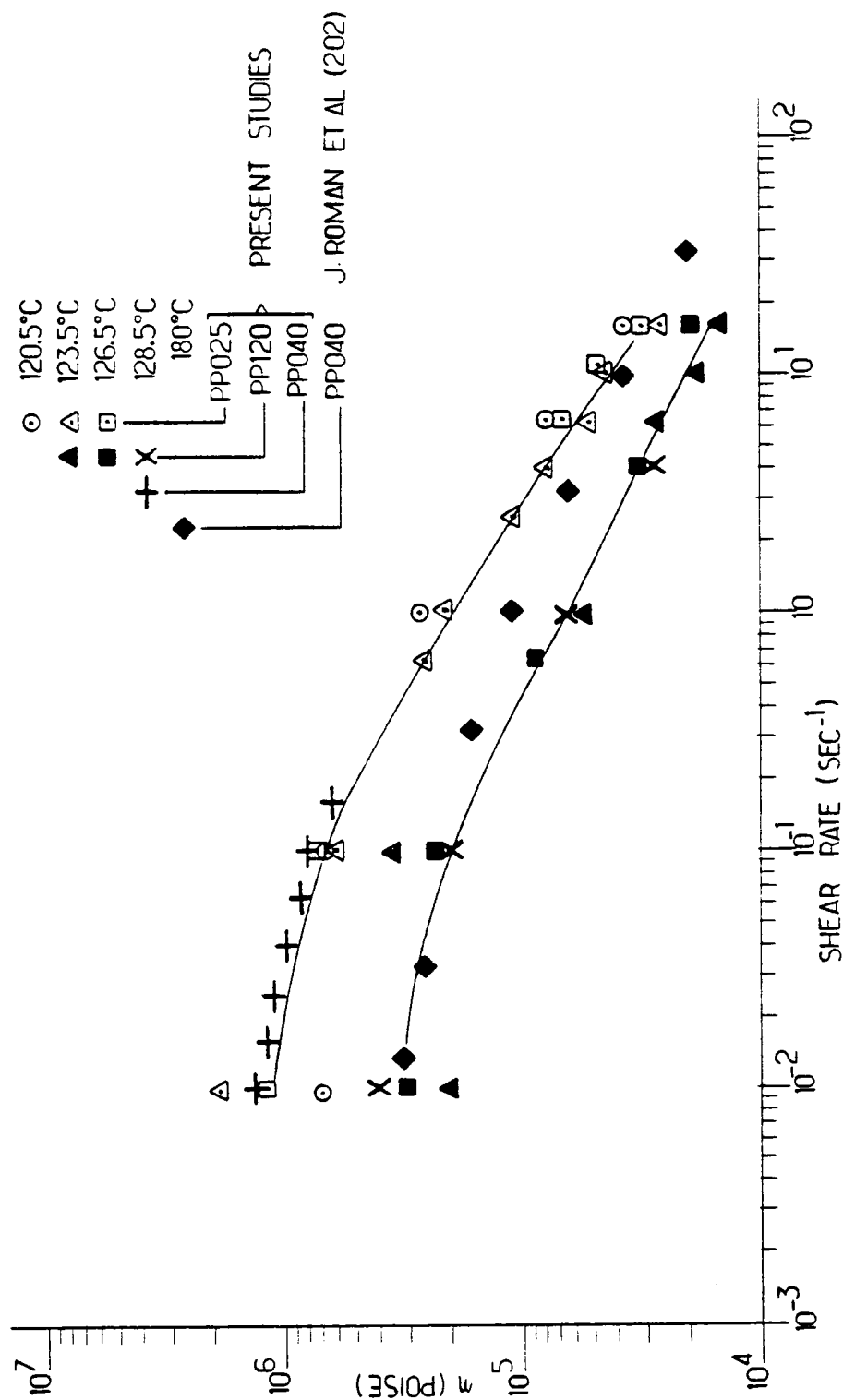


Figure V-7 : Comparison of polypropylenes steady state shear viscosity results at different isothermal crystallization temperatures from the present studies with those from literature.

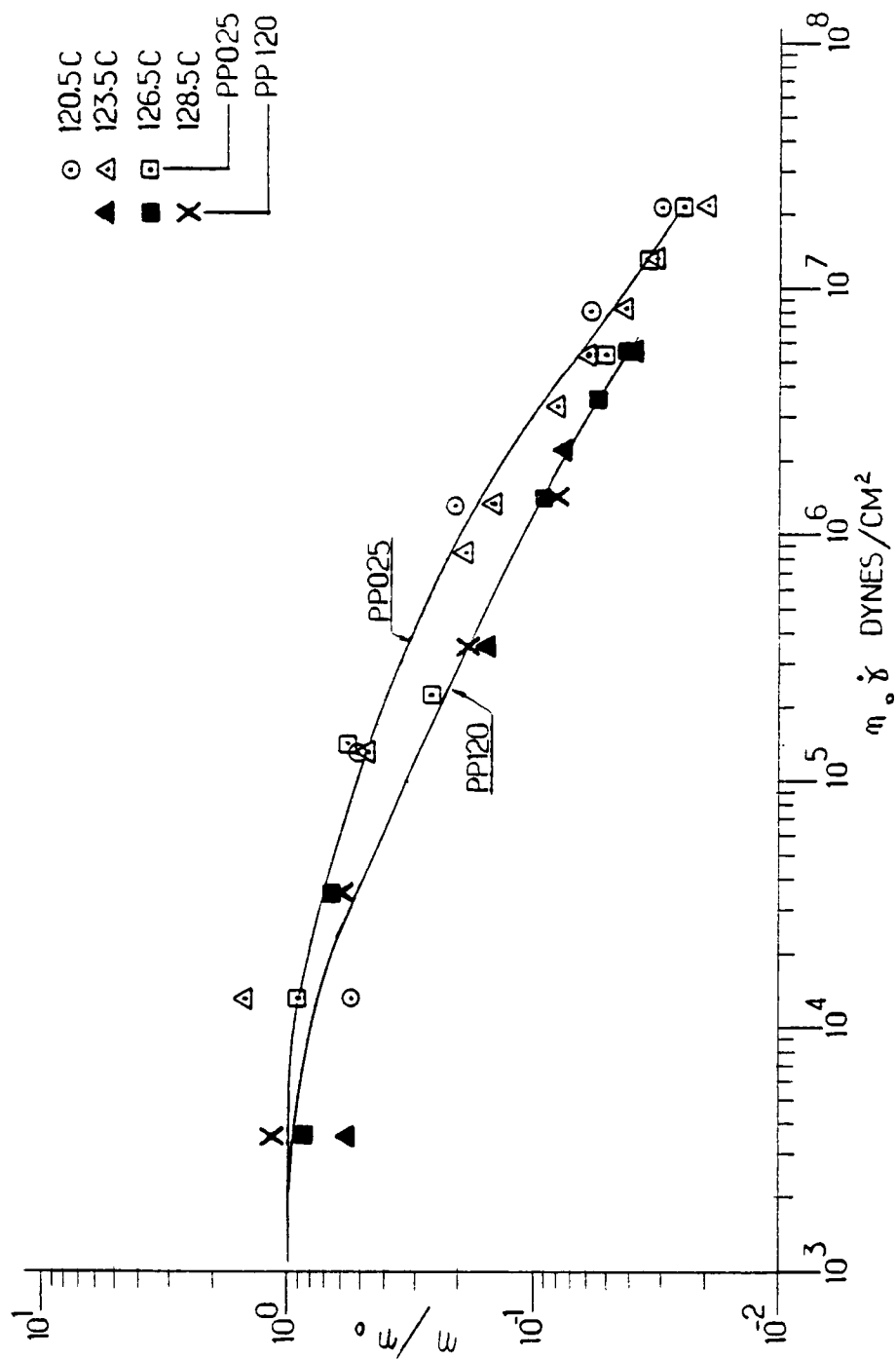


Figure V-8 : Relative shear viscosity versus relative shear stress for PP025 and PP120.

any fixed $\eta_0 \dot{\gamma}$, PP120 has smaller η/η_0 compared to PP025. This indicates that PP120 has a broader MWD compared to PP025.

First Normal Stress Differences

Minoshima et al. (176) show that the first normal stress difference may be expressed explicitly as a function of σ_{12} and MWD, not molecular weight or temperature. These authors also showed that (1) the broader the MWD the higher the value of N_1 , (2) the broader the MWD the smaller the gradient $\frac{d \log N_1}{d \log \sigma_{12}}$. Figure V-9 shows the N_1 vs. σ_{12} from Minoshima et al. together with the data from the present experimental studies. Also shown in this figure are the results for PP040 by J. Roman (202). The N_1 data for the present experimental polymers shown in Figure V-9 were calculated from Eq. IV-3 (p. 74), just prior to crystallization. Because of the lower temperature the shear stresses, σ_{12} , and the normal stress differences, N_1 , are in a higher range for the present results than for those of Minoshima et al. For the present experimental polypropylenes the linear least squares fit of the data results in equations:

$$N_1 = 0.0093 \sigma_{12}^{1.5} \text{ (for PP120) ,}$$

and

(V-1)

$$N_1 = 0.00041 \sigma_{12}^{1.71} \text{ (for PP025, PP040) .}$$

These results again confirm that PP120 has a broader MWD (8.0) compared to PP025 and PP040 (4.0) as shown by rough estimates presented in Appendix 2.

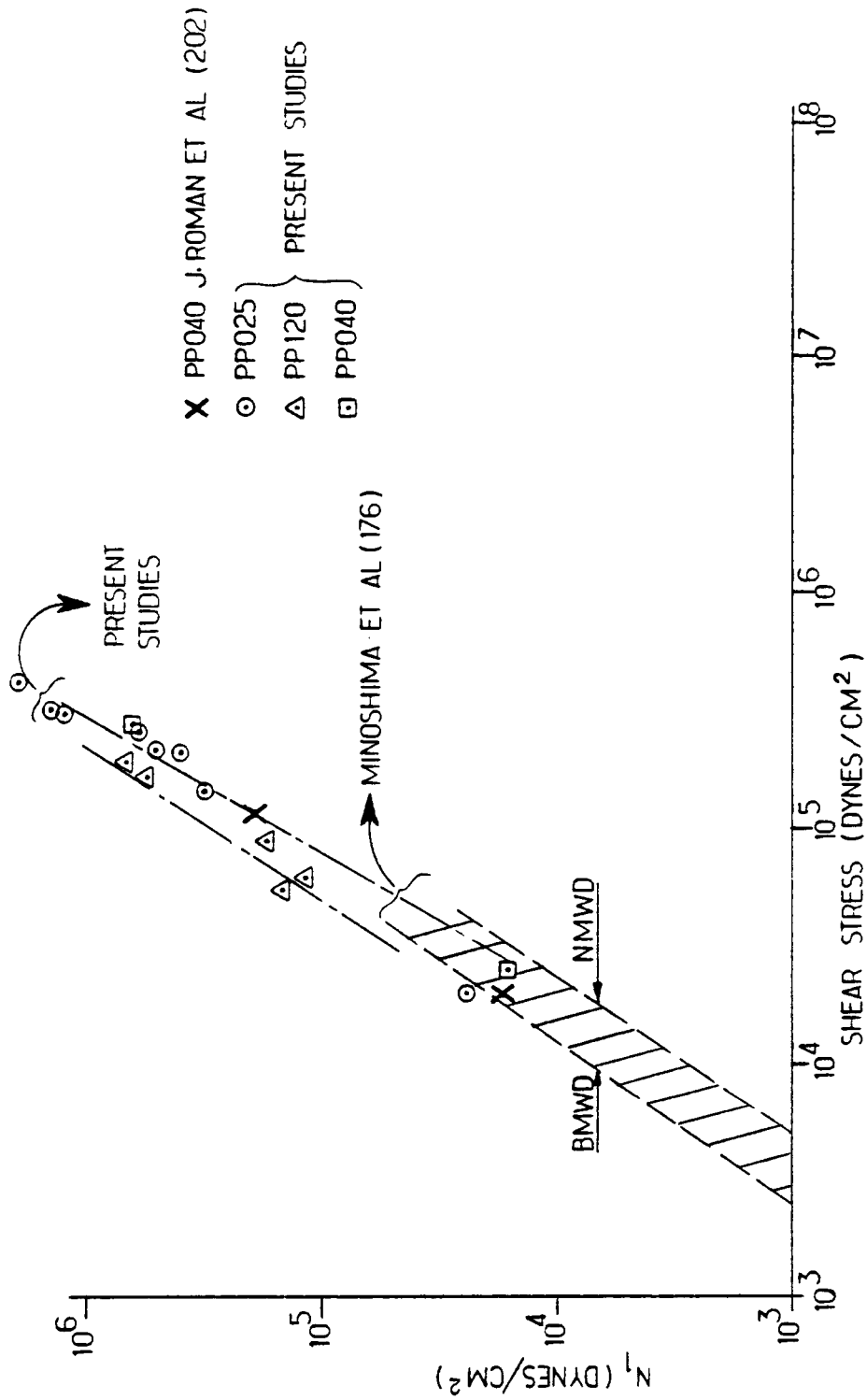


Figure V-9 : Comparison of first normal stress difference versus shear stress results from the present studies with those from literature.

d. Reciprocal induction time versus shear rate results. The effect of the shear rate and of the crystallization temperature on the reciprocal of induction time ($\frac{1}{t_i}$) are shown in Figures V-10 and V-11 for polypropylenes PP025 and PP120, respectively. Figures V-10 and V-11 show an increase in $1/t_i$ with increasing shear rate and decreasing crystallization temperature. The dotted line on the ordinate in these and the following figures indicate the reciprocal induction times for the quiescent case and correspond to the time for 1% conversion measured by the DSC at the temperatures indicated in the legend. At low shear rates ($\dot{\gamma} = 0.01 \text{ sec}^{-1}$) the $1/t_i$ values for stressed case are close but slightly greater than those for the quiescent case. The difference between the low shear rate values and the quiescent values appear to be a function of temperature.

Figure V-12 shows the effect of crystallization temperature at constant shear rates on $1/t_i$ for PP025. This figure also shows the quiescent $1/t_i$ results on PP025. The $1/t_i$ in both the quiescent and the stress induced case are decreasing with increasing temperature. At any given temperature the sheared samples have higher $1/t_i$ values than the quiescent results and the $1/t_i$ values of the sheared samples increase with increasing shear rate. Difference between $1/t_i$ for quiescent samples and those crystallized under low shear rate ($\dot{\gamma} \leq 0.1 \text{ sec}^{-1}$) appears to narrow with increases in crystallization temperature. This indicates a decreasing sensitivity of crystallization rates as temperature increases at low shear rate. This would seem to be consistent with more rapid molecular relaxations at higher temperature resulting in lower molecular orientation at a given shear rate.

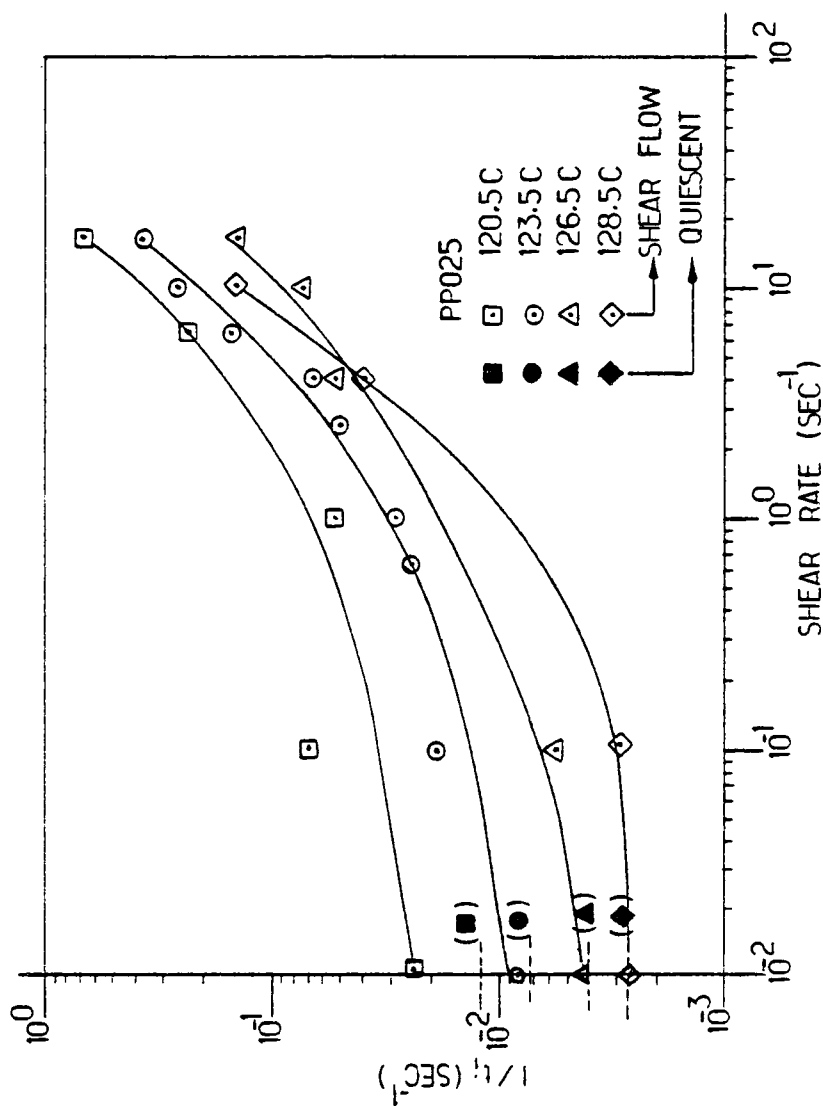


Figure V-10 : Reciprocal induction time versus shear rate for PP025 at different isothermal crystallization temperatures.

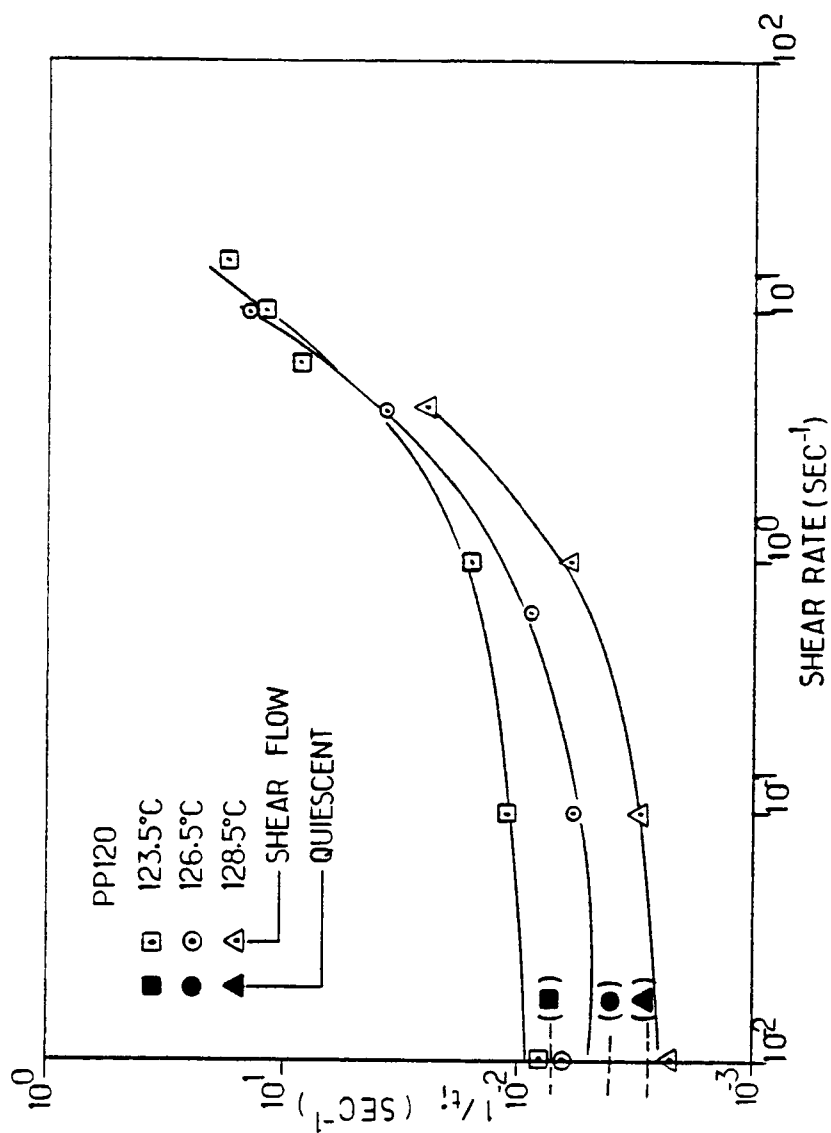


Figure V-11 : Reciprocal induction time versus shear rate for PP120 at different isothermal crystallization temperatures.

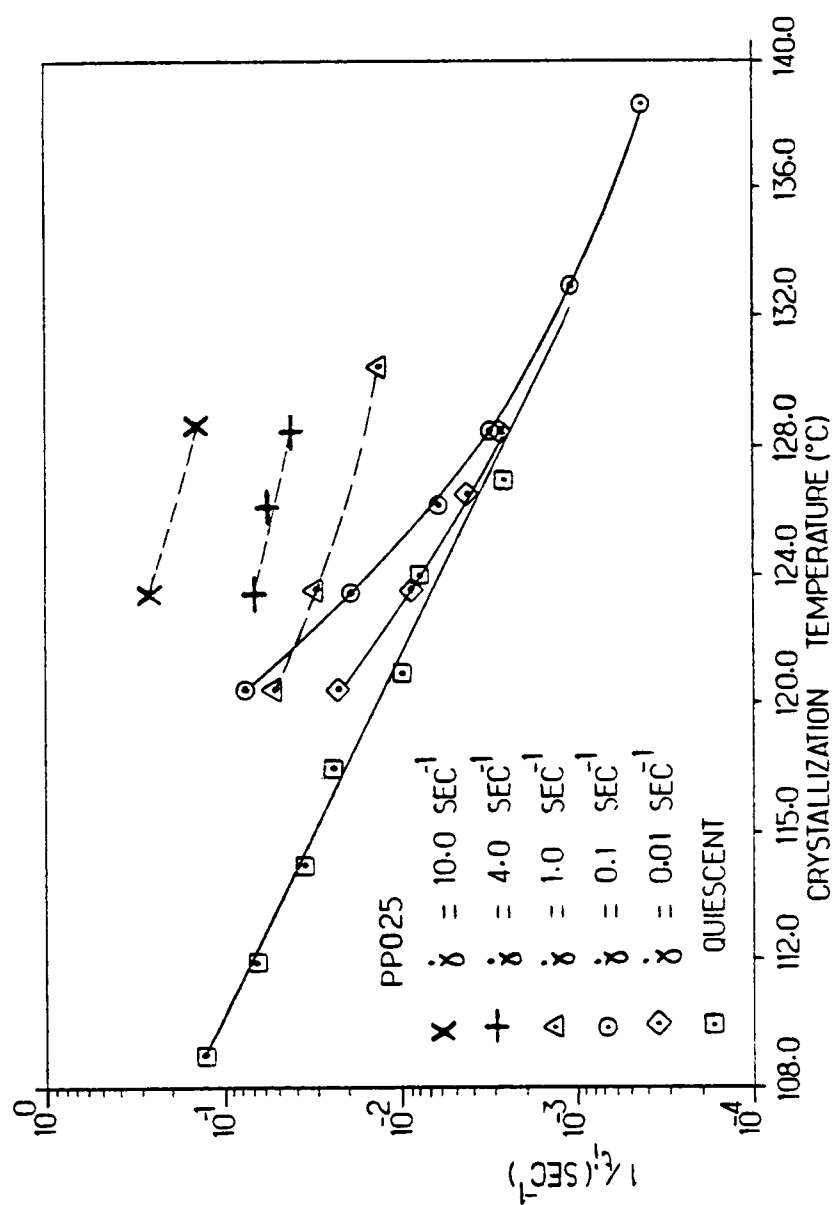


Figure V-12 : Reciprocal induction time versus isothermal crystallization temperature for flow induced and quiescently crystallized PP025.

Figure V-13 shows the $1/t_i$ results for PE at 123.5°C. In PE as in PP, the $1/t_i$ increases with increasing shear rates. The $1/t_i$ at low shear rate ($\dot{\gamma} = 0.01 \text{ sec}^{-1}$) is about an order of magnitude higher than the quiescent $1/t_i$. Apparently PE is much more sensitive to shear in the very low shear rate range than polypropylene.

e. Further analysis of induction time results. Figures V-14 and V-15 show again the $1/t_i$ data as a function of shear rate for PP025 and PP120 at 123.5°C and 128.5°C, respectively. These data are replotted here in order to facilitate a direct comparison of the results for the two different polypropylenes. PP025 with higher molecular weight and narrower molecular weight distribution shows greater $1/t_i$ compared to PP120 at any given shear rate. Replots of these and other shear flow results are shown as a function of shear stress in Figure V-16. These results indicate that for a given polymer, the temperature dependency of the nucleation rate is greatly reduced at high stresses. This is possibly due to the fact that at higher stresses the variation of $1/t_i$ with σ_{12} become so great that they dominate the temperature effect. The plot further indicates that the effect of the sample on $1/t_i$ is large at higher stresses and it decreases with decreasing shear stress. The reciprocal induction times when plotted against shear stress, follow the order PP120 > PP025 $\geq$ P040 indicating no systematic correlation with respect to molecular weight. Sample PP120 with lower molecular weight and broader molecular weight distribution ($\bar{M}_w = 2.45 \times 10^5$, $\bar{M}_w/\bar{M}_n$) show much higher $1/t_i$ values compared to PP025 ($\bar{M}_w = 4.03 \times 10^5$, $\bar{M}_w/\bar{M}_n$

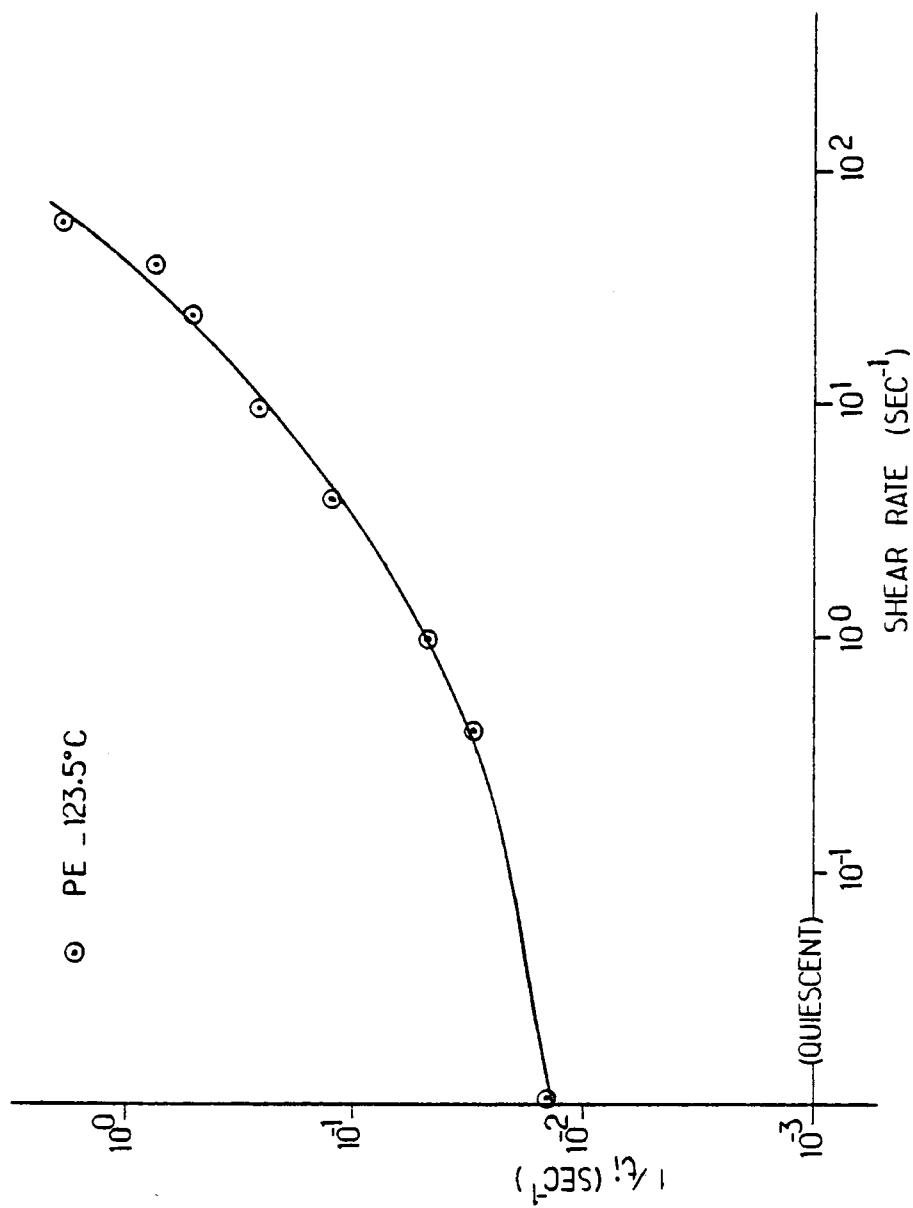


Figure V-13 : Reciprocal induction time versus shear rate for PE at 123.5°C.

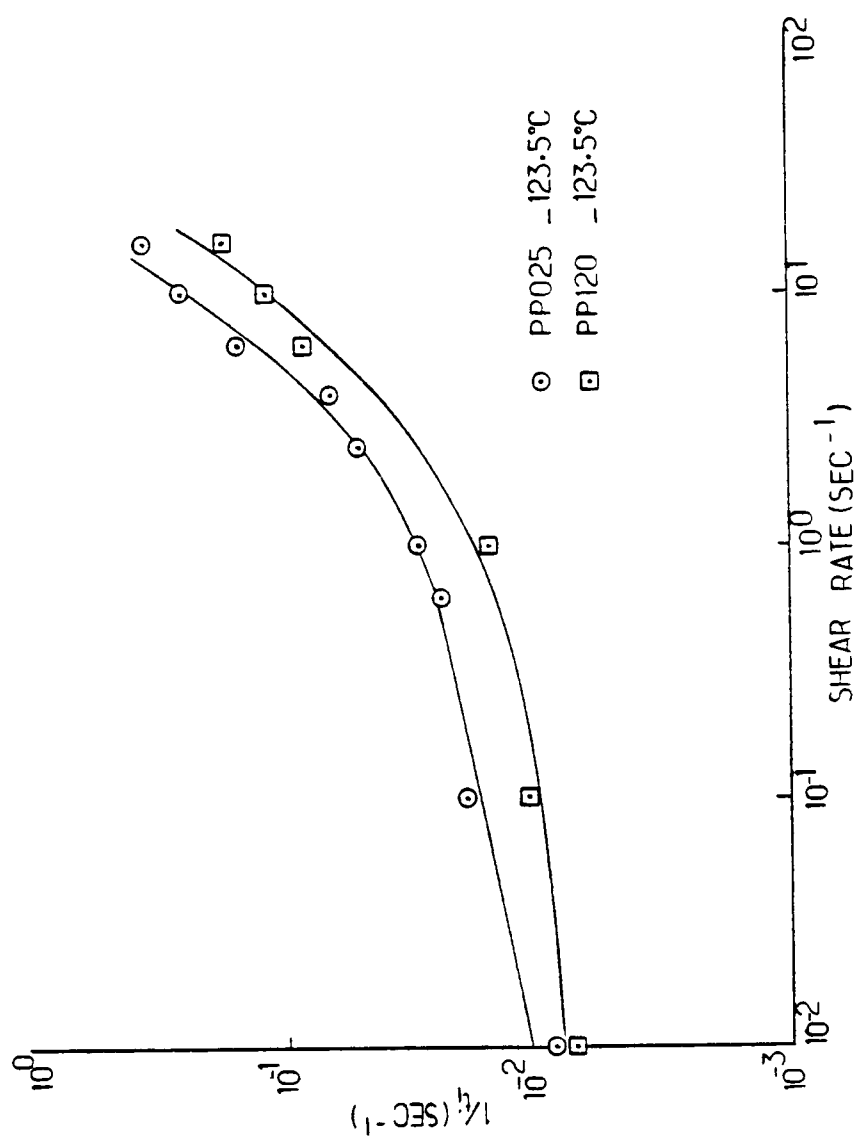


Figure V-14 : Reciprocal induction time versus shear rate for PP025 and PP120 at 123.5°C.

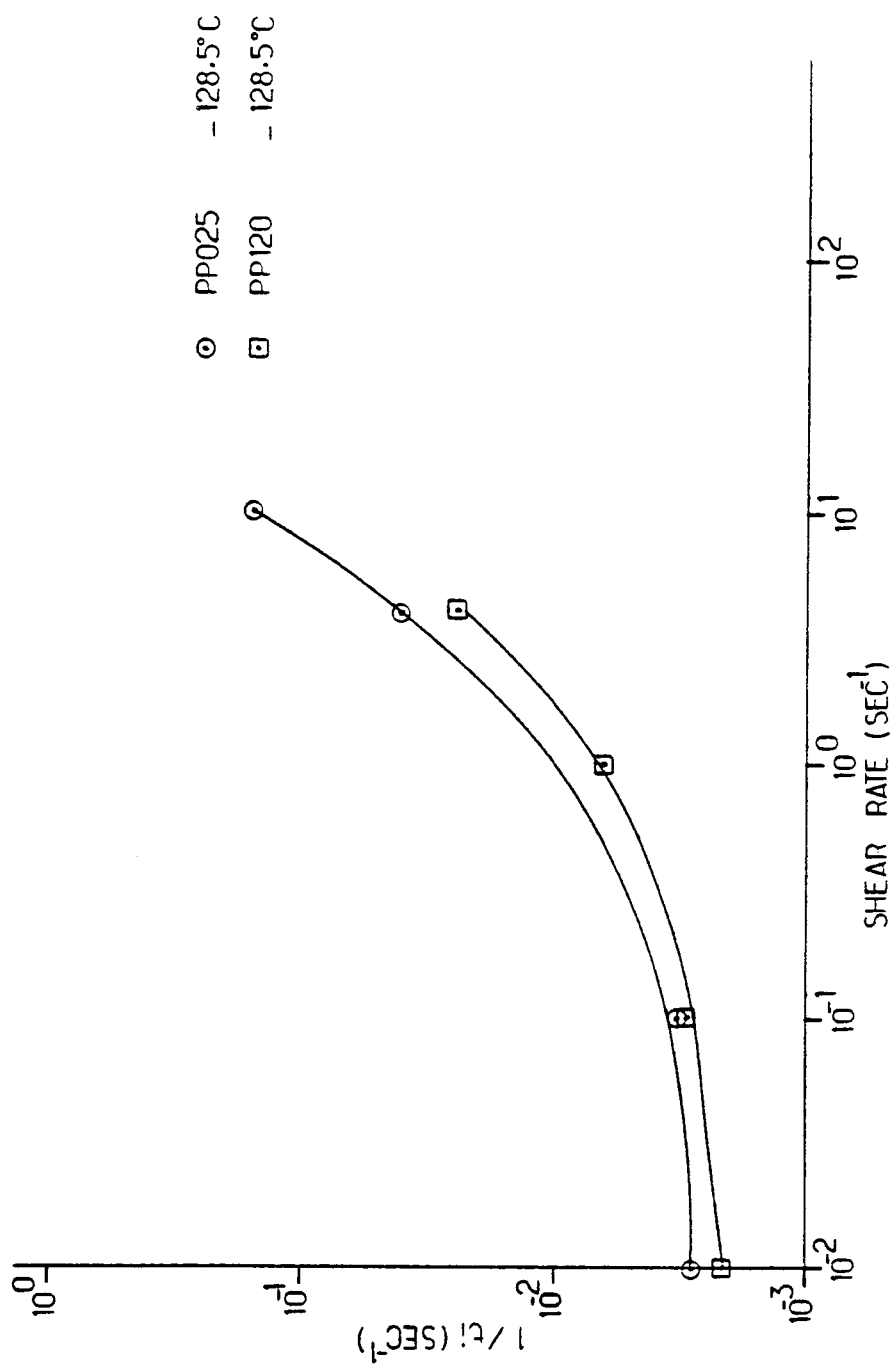


Figure V-15 : Reciprocal induction time versus shear rate for PP025 and PP120 at 128.5°C.

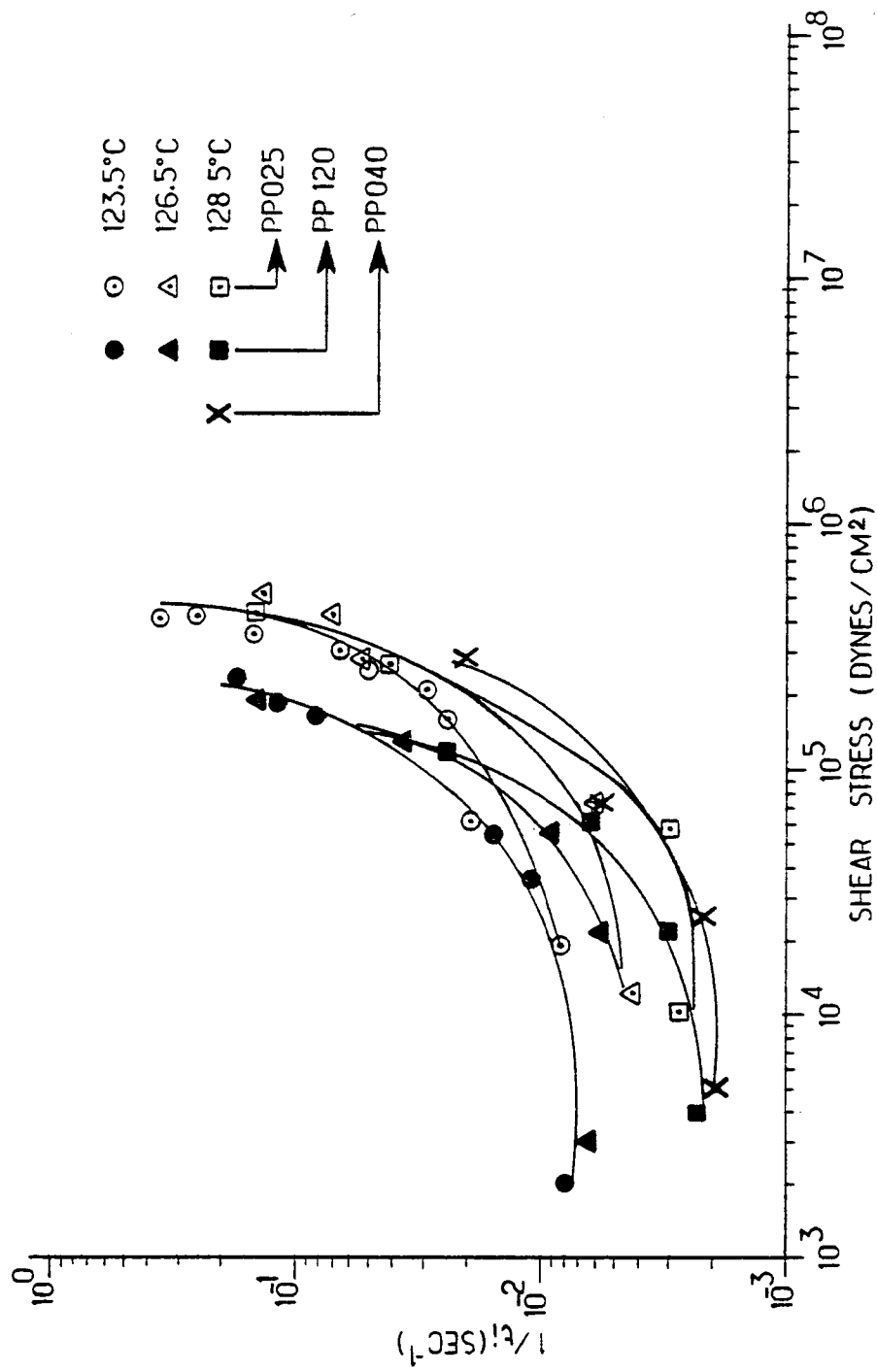


Figure V-16 : Reciprocal induction time versus shear stress for PP025, PP120 and PP040 at different crystallization temperatures.

= 4.0) and PP040 ($\overline{M}_w = 2.9 \times 10^5$, $\overline{M}_w/\overline{M}_n = 4.0$. This is opposite to the behavior shown in Figures V-14 and V-15 where for a given shear rate PP025 showed higher $1/t_i$. Under flow conditions, PP025 with higher molecular weight (lower melt index) and presumably similar molecular weight distribution compared to PP040, show slightly higher $1/t_i$. The above results suggest that sample molecular weight distribution plays an important role in determining the kinetics of crystallization under shear flow. The sample molecular weight effect on $1/t_i$ appears to be secondary compared to the molecular weight distribution effect.

2. Elongational Flow Results

a. General stress response. Figure V-17 shows typical tensile force curves recorded during steady elongational deformation of polypropylene. A transient period can be seen in the tensile force in both the curves in the initial stages of deformation. Curve 1 or curve 2 is observed depending on the experimental conditions such as elongational rate $\dot{E}$, the crystallization temperature and the sample type. The force trace of form shown in curve 1 results for the experiments in which (a) the elongation rate is very small and the sample crystallizes before failure (e.g., PP, $\dot{E} < 0.0062 \text{ sec}^{-1}$, and $T_{cr} = 120.5\text{--}126.5^\circ\text{C}$), (b) the crystallization rates are very fast which result in phase transformation before failure even at higher elongation rates (e.g., PE, $\dot{E} \leq 0.25 \text{ sec}^{-1}$ and $T_{cr} = 123.5^\circ\text{C}$). Traces of type 2 were obtained for polypropylenes at higher elongational rates ($0.25 \text{ sec}^{-1} \geq \dot{E} \geq 0.039 \text{ sec}^{-1}$) where the decrease in the sample

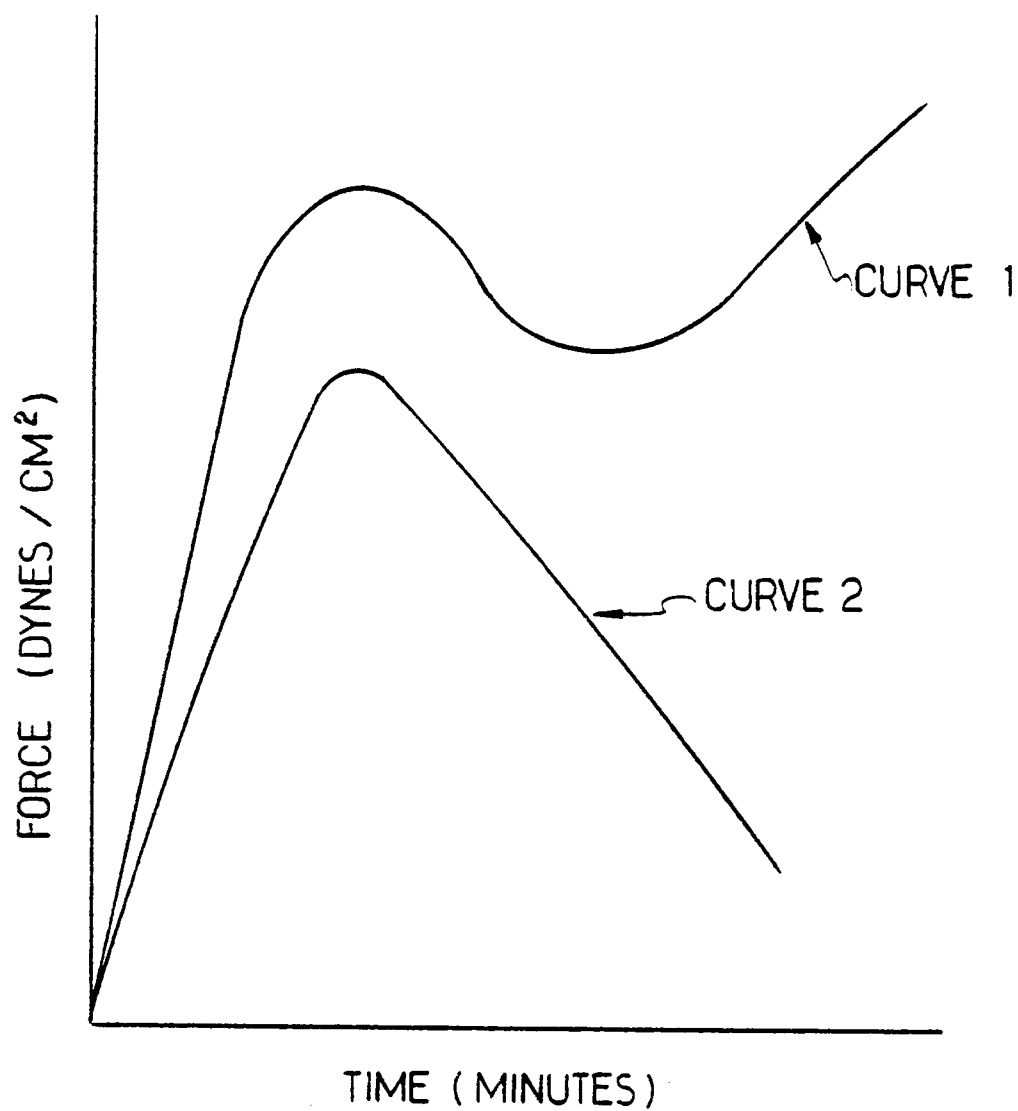


Figure V-17 : Typical tensile force response during steady elongational deformation.

dimensions are rapid. This results in a continuous decrease in the force with time. This on the surface appears to be for the case where there is no crystallization. However a plot of true tensile stress versus time for some curves of this general shape are shown in Figure V-18. In this figure the experimentally measured tensile force is converted to tensile stress by assuming a uniform extension. This assumption enables us to calculate the cross sectional area of the sample as a function of time according to the equation,

$$A(t) = A_0 e^{-\dot{\epsilon} t} \quad (V-3)$$

where A_0 is the area before deformation and t is the time.

The results presented in Figure V-18 show an increase in the tensile stress from a steady state value. This increase in the stress (or viscosity) in the shear flow case was interpreted earlier as due to crystallization. However this interpretation in the case of elongational flow is somewhat complicated. Minoshima et al. (176) studying the elongational viscosity of PP at higher temperatures (180°C) showed sudden increases in the elongational viscosity with time at a given $\dot{\epsilon}$ for broader molecular weight distribution higher molecular weight samples. However these increases are not as dramatic as that shown in Figure V-18 for PP025. They interpret this increase in elongational viscosity as due to some viscoelastic and/or deformation effects which are unrelated to crystallization. Minoshima et al. (176) report that for narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 6.37$), high molecular weight ($M.I. \leq 11.6$) polypropylenes, there is no strain

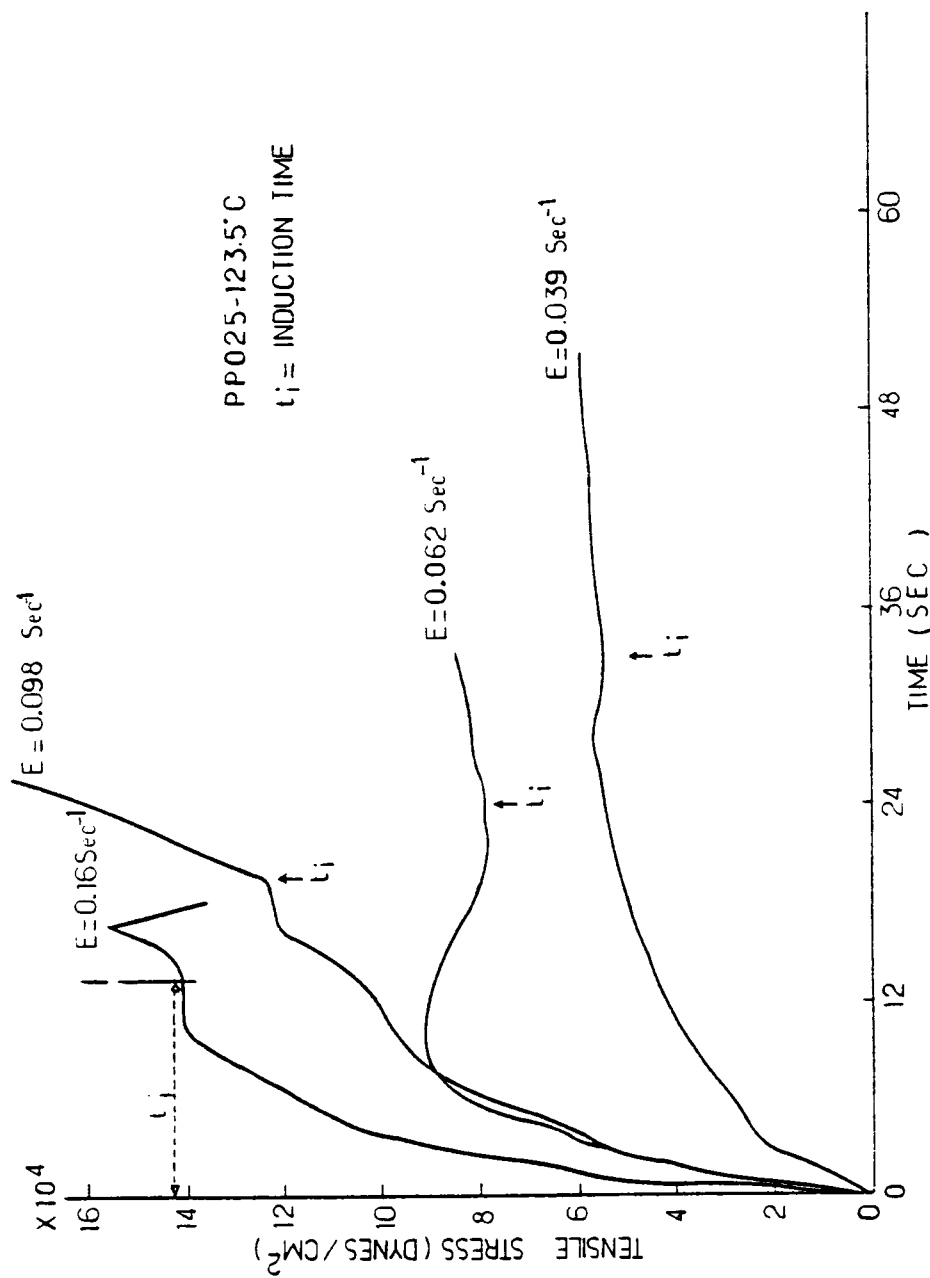


Figure V-18 : True tensile stress versus time for PP025 at 123.5°C and different elongation rates.

hardening effect (see Appendix 3). Ide and White (107) conclude that in elongational flow in PP and PE, the stress varies linearly with time. In the present studies the PP sample under investigation has narrower molecular weight distribution (estimated $\overline{M}_w/\overline{M}_n = 4.0$) and higher molecular weight (M.I = 2.5). Also both stress and temperature (120.5-126.5°C) conditions favor phase transformation. At low $\dot{\epsilon}$ it has been possible to confirm that the stress (or viscosity) increase corresponds to crystallization by observing simultaneous changes in the optical characteristics of the sample. Further, as will be shown later, the crystallization rates obtained from these experiments at low elongation rates are consistent with DSC-quiescent crystallization studies. These above arguments reasonably justify our interpretation of change in tensile stress from a steady state value as due to crystallization.

The experimentally accessible range of variables of different samples during the crystallization under elongational flow are limited compared with the shear flow experiments. This is because of the discontinuous nature of the sample in elongation which limits the time of deformation at higher $\dot{\epsilon}$ ($\dot{\epsilon} > 0.25 \text{ sec}^{-1}$) and higher crystallization temperatures ($T_{cr} > 126.5^\circ\text{C}$). Further, samples with low molecular weights sag between the grips during the melting and equilibrium period which interferes with the elongational flow crystallization studies as they deform non uniformly.

In the present experimental studies crystallization kinetics under elongational flow were investigated for PP025 in the range of crystallization temperatures 120.5-126.5°C and for elongation rates

$0.0015\text{--}0.25\text{ sec}^{-1}$. The other polypropylenes, PP120 and PP040, either crystallized prior to the application of stress in the temperature range of interest ($120.5\text{--}126.5^\circ\text{C}$) or deformed nonuniformly.

The PE sample sagged considerably and showed a smaller temperature range in which it can be crystallized than did PP.

b. Reciprocal Induction Time Versus Tensile Stress

The effect of the tensile stress and of the crystallization temperature on the reciprocal of induction time are shown in Figure V-19 for polypropylene PP025. The induction times here also are measured from the start of deformation to the point where the stress increased from a steady state value. Figure V-19 exhibits trends similar to the shear flow results shown earlier (Figure V-13, p. 98). Figure V-19 indicates an increase in $1/t_i$ with increasing tensile stress and decreasing crystallization temperatures. In the low range of stresses, $1/t_i$ shows a reciprocal temperature dependency. This temperature dependency of $1/t_i$ is greatly decreased at higher stresses. These temperature effects are not quite as clear in PE as can be seen in Figure V-20 because of limited results. The reciprocal induction times in polypropylene extrapolate to values near the quiescent induction times at low stresses whereas in PE they are much higher than the quiescent ones.

3. Interpretation of Results

Before proceeding to the interpretation of the stress induced crystallization results, a detailed discussion and interpretation of the reciprocal induction time, $1/t_i$, is needed. In this section we

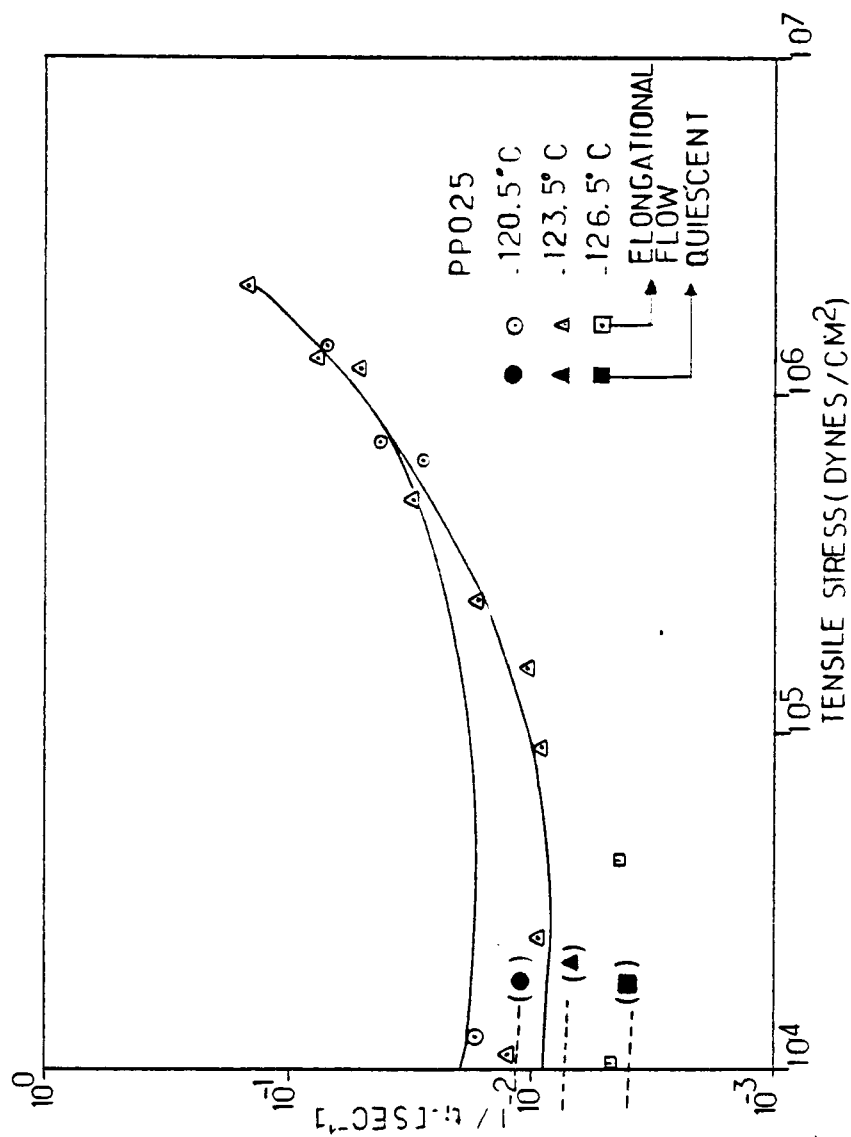


Figure V-19 : Reciprocal induction time versus tensile stress for PP025 at different crystallization temperatures.

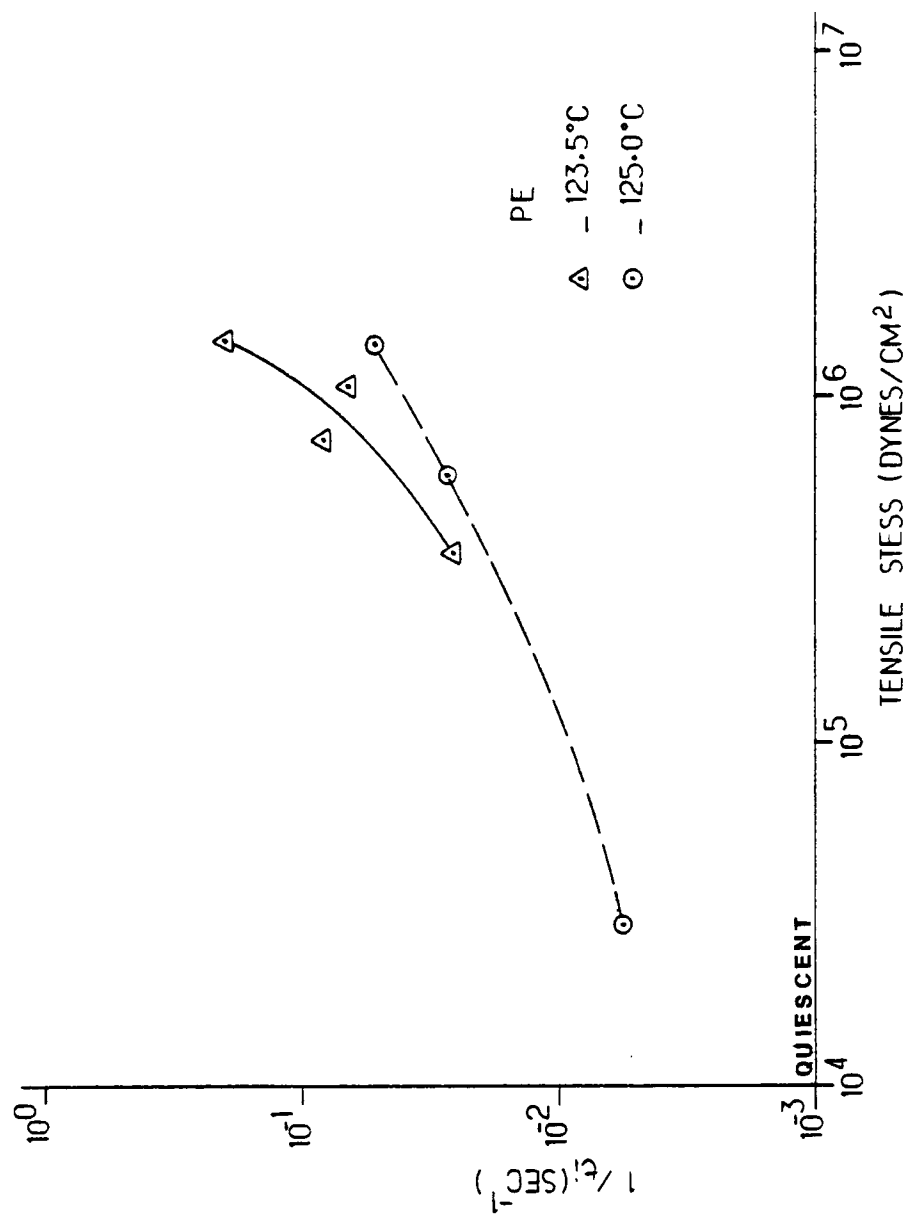


Figure V-20 : Reciprocal induction time versus tensile stress for PE at different crystallization temperatures.

will first present the interpretation of $1/t_i$ which will be used in the analysis of the stress induced crystallization results.

a. Interpretation of reciprocal induction times. Several investigators (219,260) in their studies of SIC have used a parameter "induction time, t_i ," which is related to the crystallization kinetics. These investigators in their studies of SIC have interpreted the reciprocal induction time to be proportional to the nucleation rate. This interpretation is reasonable and appropriate, but strictly speaking depends on an assumption of constant nucleation rate during the induction time period and on a critical nucleation density, n_0^* , needed to produce a detectable change in sample viscosity. This is illustrated in Figure V-21. In reality, the nucleation rate may be a function of time, particularly in the very early stages of crystallization. One such possibility is shown by the curve in Figure V-21a, where the nucleation density is plotted as a function of time. The assumption of constant nucleation rate approximates this situation by a straight line with an average nucleation rate,

$$\dot{N} = \frac{n_0^*}{t_i} \propto \frac{1}{t_i} . \quad (V-4)$$

As described earlier, the induction times in the present experimental studies are measured from the start of the shear to the inflection point on the stress-time curve. This means that the nucleation density is assumed to be equal to zero at t to equal zero (just prior to shearing the sample) with no delayed nucleation.

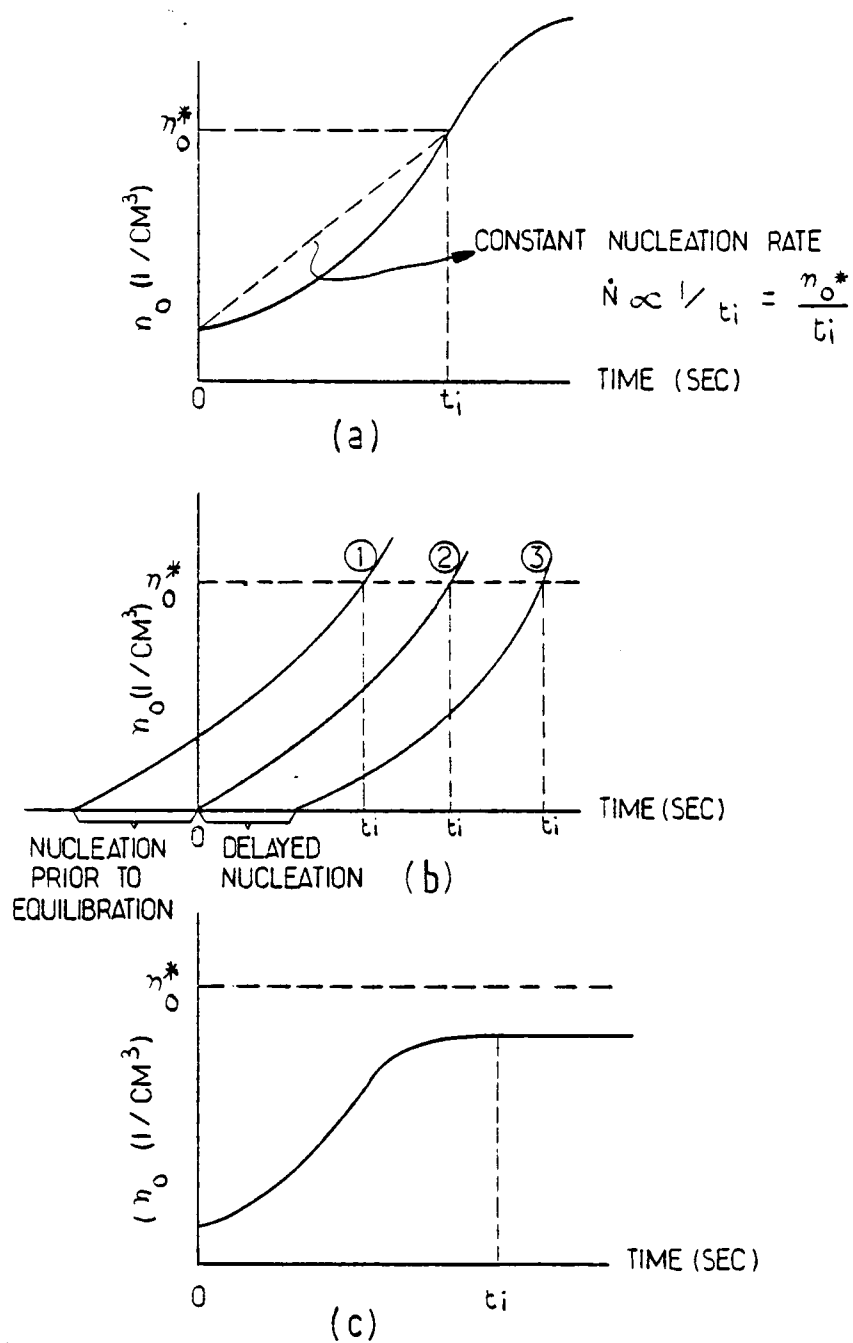


Figure V-21 : Qualitative curves showing nucleation densities versus time.

Curve 2 in Figure V-21b describes this situation while curves 1 and 3 describe two other possibilities which are likely to occur at the crystallization temperature extremes. Another possible complication occurs if the number density of nuclei saturates before the critical number of nuclei needed to produce a detectable increase in viscosity is reached (Figure V-21c). For this, the apparent value of $1/t_i$ includes contributions from both nucleation and growth. In this case $1/t_i$ still indicates some approximate measure of the nucleation rate.

While the above complications exist in the interpretation of induction time, there is little else reasonable that can be done to directly measure the nucleation rates under deformation. Like other researchers (219,260) we will use the above approach to interpret $1/t_i$ results and the reader should keep the limitations of this approach firmly in mind while examining the results.

b. Interpretation of stress induced crystallization results.

In Chapter III, two different approaches have been presented to facilitate the analysis for the nucleation rates under deformation or flow. The first approach is an intuitive proposal which relates the nucleation rates to a molecular orientation distribution which is determined by the state of the stress in the melt. In the second approach, nucleation rate expressions were developed from the theoretical considerations. The theoretical analysis showed that the nucleation rates are basically related to the ΔG_{def} , which can be evaluated from the state of stress in the melt. The expressions for ΔG_{def} have been presented in Chapter III specifically for simple

shear and steady elongational flows. In the following paragraphs we present an analysis of our induction time results based on the above two considerations. As per our earlier discussion on induction time, in the following discussion we will interpret $1/t_i$ as proportional to the nucleation rate.

Correlation of nucleation rates with principal stress differences:

Based on the discussion leading up to Eq. III-11 (p. 50) we would expect to see a correlation between the nucleation rates and the principal stress differences independent of mode of deformation and sample type at any given crystallization temperature. We will test this proposal with our elongational and shear flow crystallization results.

Figures V-22 and V-23 show the comparison of nucleation rates in shear and in elongational flow for PP025 at 120.5°C and 123.5°C. The independent variable for shear flow is shear stress and for the elongational flow it is the tensile stress. A strong dependency of the nucleation rates on the mode of deformation can be seen in this figure. The differences in the nucleation rates between the two deformation modes is decreasing with decreasing σ_{12} or σ_{11} .

Figures V-24 and V-25 show the nucleation rate results from Figures V-22 and V-23, replotted as a function of the principal stress difference, $\sigma_x - \sigma_y$. The $\sigma_x - \sigma_y$ presented here are computed from the normal stress data according to Eq. III-9 (p. 48). These figures show that the nucleation rates in PP025 at crystallization

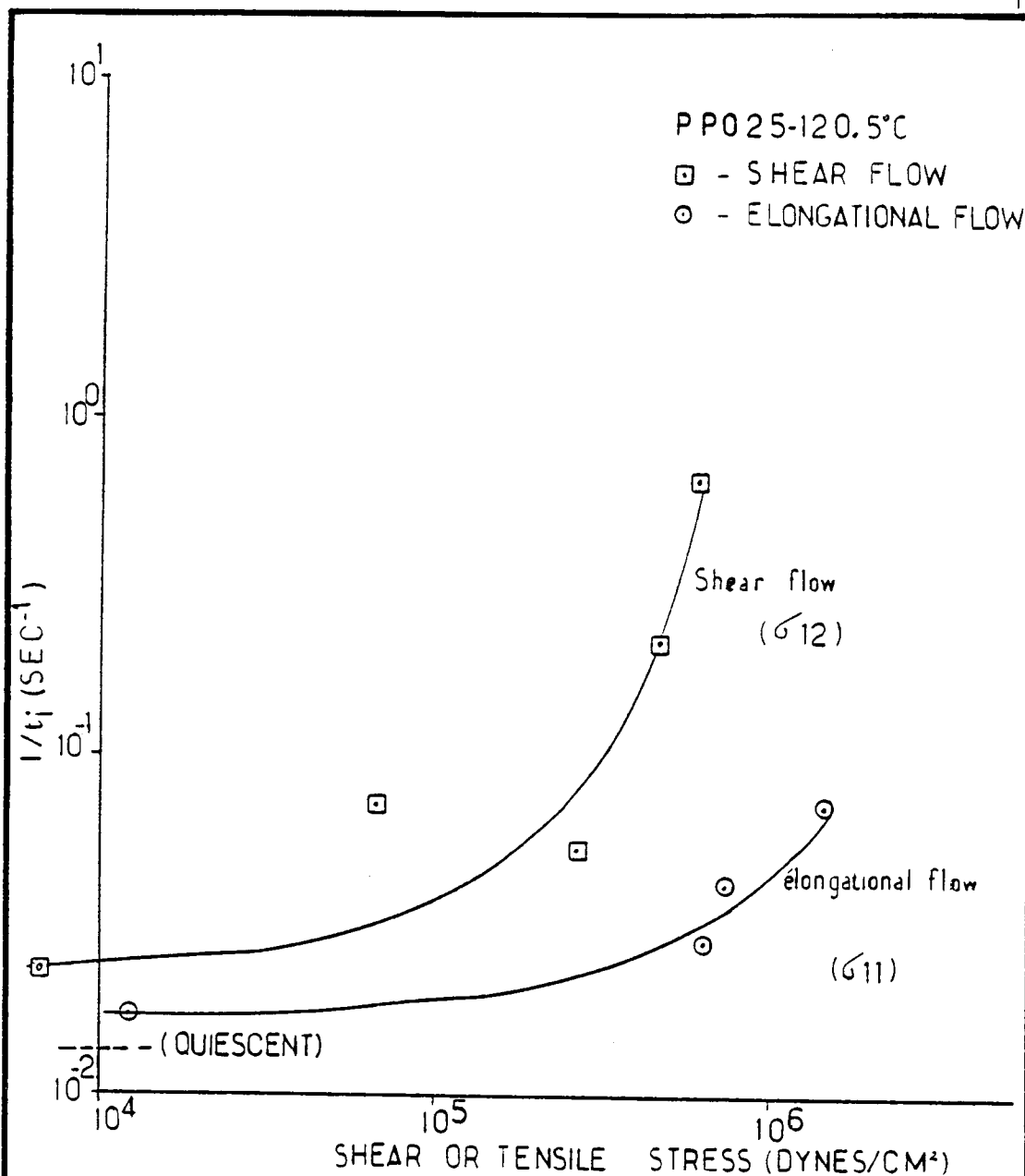


Figure V-22 : Reciprocal induction time (nucleation rate) versus stress for PP025 in shear and elongational flow at 120.5°C.

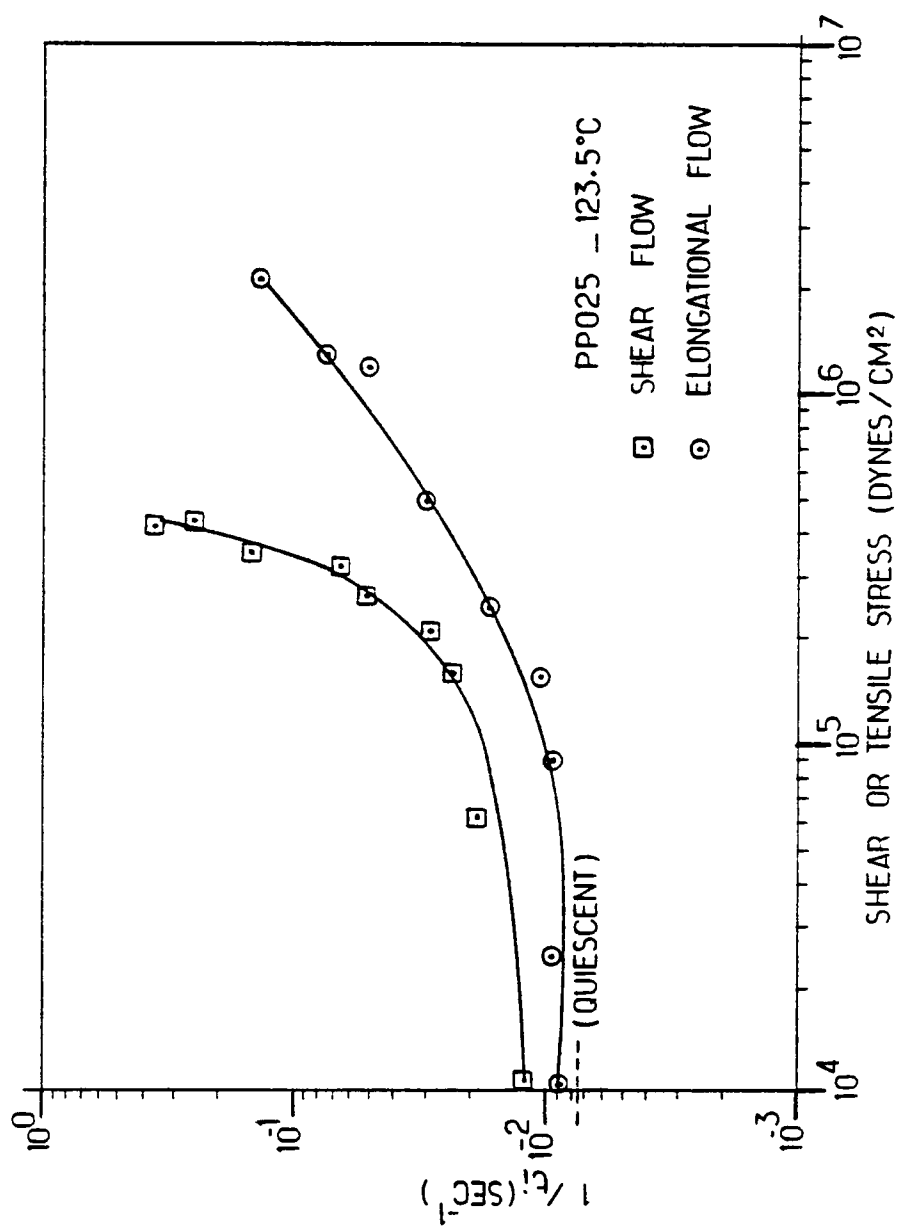


Figure V-23 : Reciprocal induction time (nucleation rate) versus stress for PP025 in shear and elongational flow at 123.5°C.

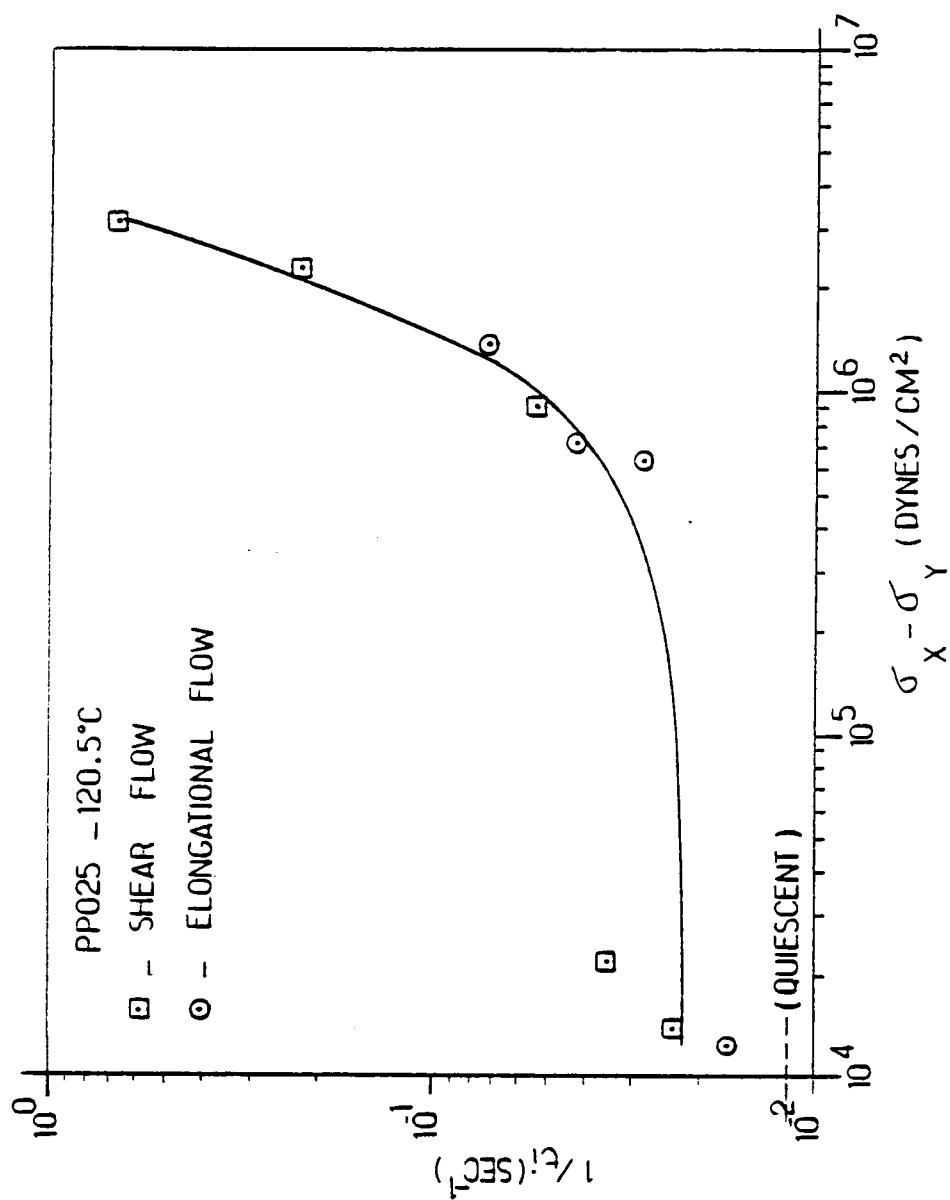


Figure V-24 : Reciprocal induction time versus principal stress differences in PP025 at 120.5°C.

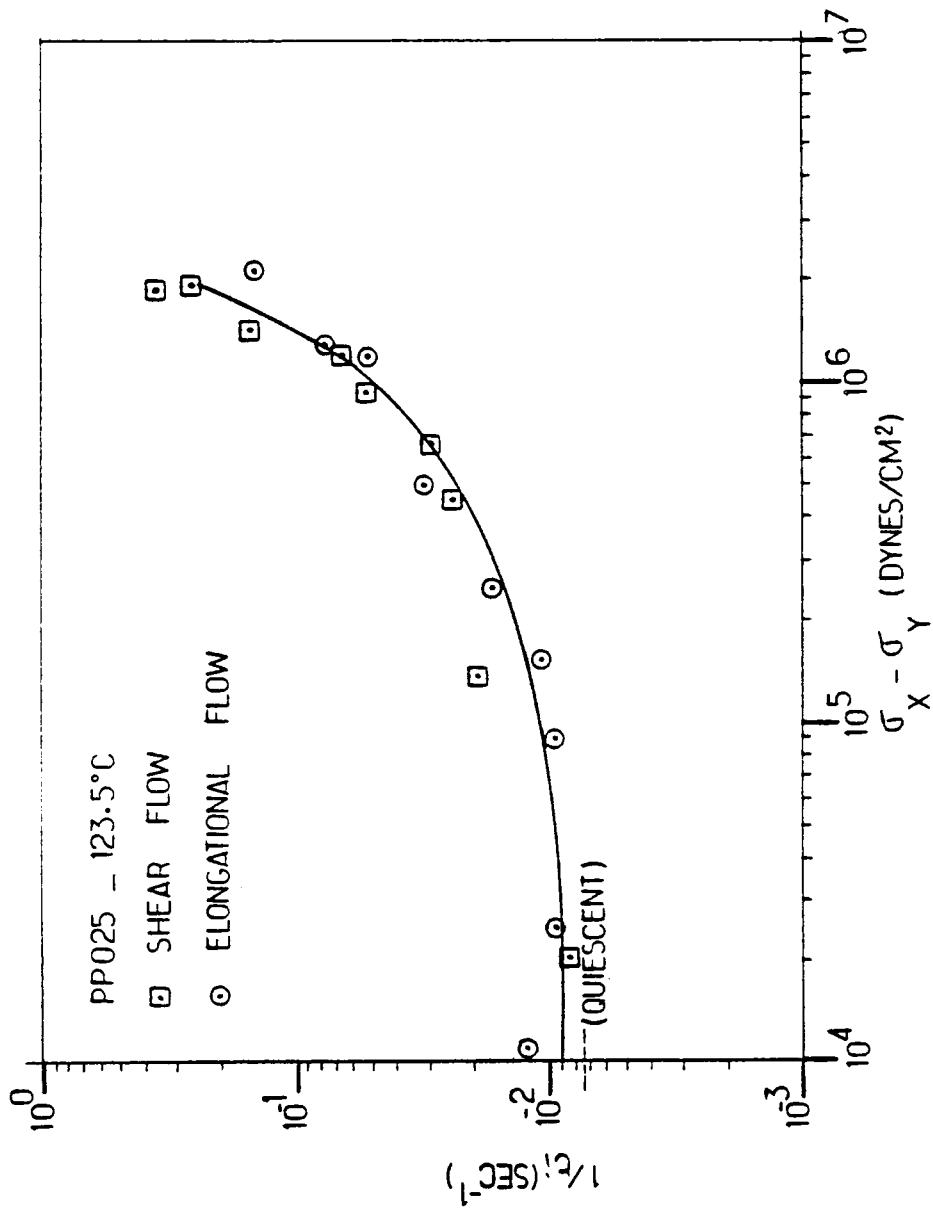


Figure V-25 : Reciprocal induction time versus principal stress differences in PP025 at 123.5°C.

temperatures of 120.5°C and 123.5°C correlate with $\sigma_x - \sigma_y$, independent of mode of deformation.

In PE, as in PP, the reciprocal induction times correlate with $\sigma_x - \sigma_y$ independent of the deformation mode, as shown by the results in Figures V-26 and V-27 at 123.5°C (compare Figure V-26 with V-27). However, the experimentally accessible principal stress range in elongational flow is unfortunately too small to be very convincing. The $\sigma_x - \sigma_y$ values for the shear flow case in PE are calculated from the experimental normal stress results.

Figures V-28 and V-29 are plots of $1/t_i$ as a function of $\sigma_x - \sigma_y$ for PP120 and PP025 at 123.5°C and for PP120, PP025 and PP040 at 128.5°C, respectively. Figures V-28 and V-29 facilitate a direct comparison of the results for the different polypropylenes. These figures exhibit no systematic correlation of nucleation rates with respect to the molecular weights. PP120, with broader molecular weight distribution still shows faster nucleation rates compared to PP025 and PP040, particularly at higher $\sigma_x - \sigma_y$.

A comparison of nucleation rates of PE with PP120 and PP025 at 123.5°C is shown in Figure V-30. As expected, PE exhibits faster nucleation rates compared to the polypropylenes at any given $\sigma_x - \sigma_y$ value.

Correlation of nucleation rates with ΔG_{def} :

In this section the nucleation results will be interpreted based on the rate expressions developed in Chapter III from the classical theories. If Eq. III-40a (p. 60) is at all valid, there should exist a correlation between the nucleation rate and ΔG_{def} for samples

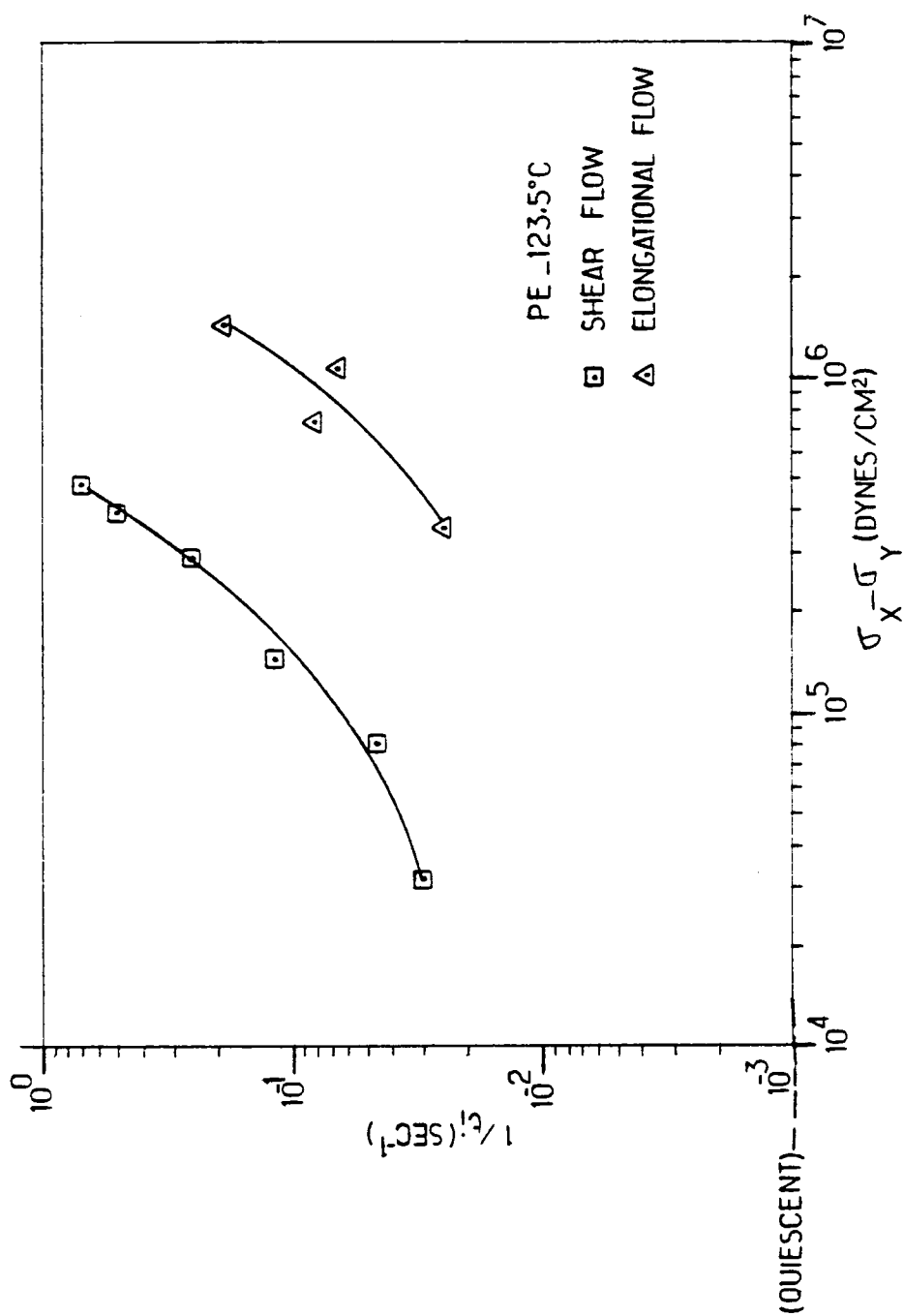


Figure V-26 : Reciprocal induction time versus stress in shear and elongational flow for PE at 123.5°C.

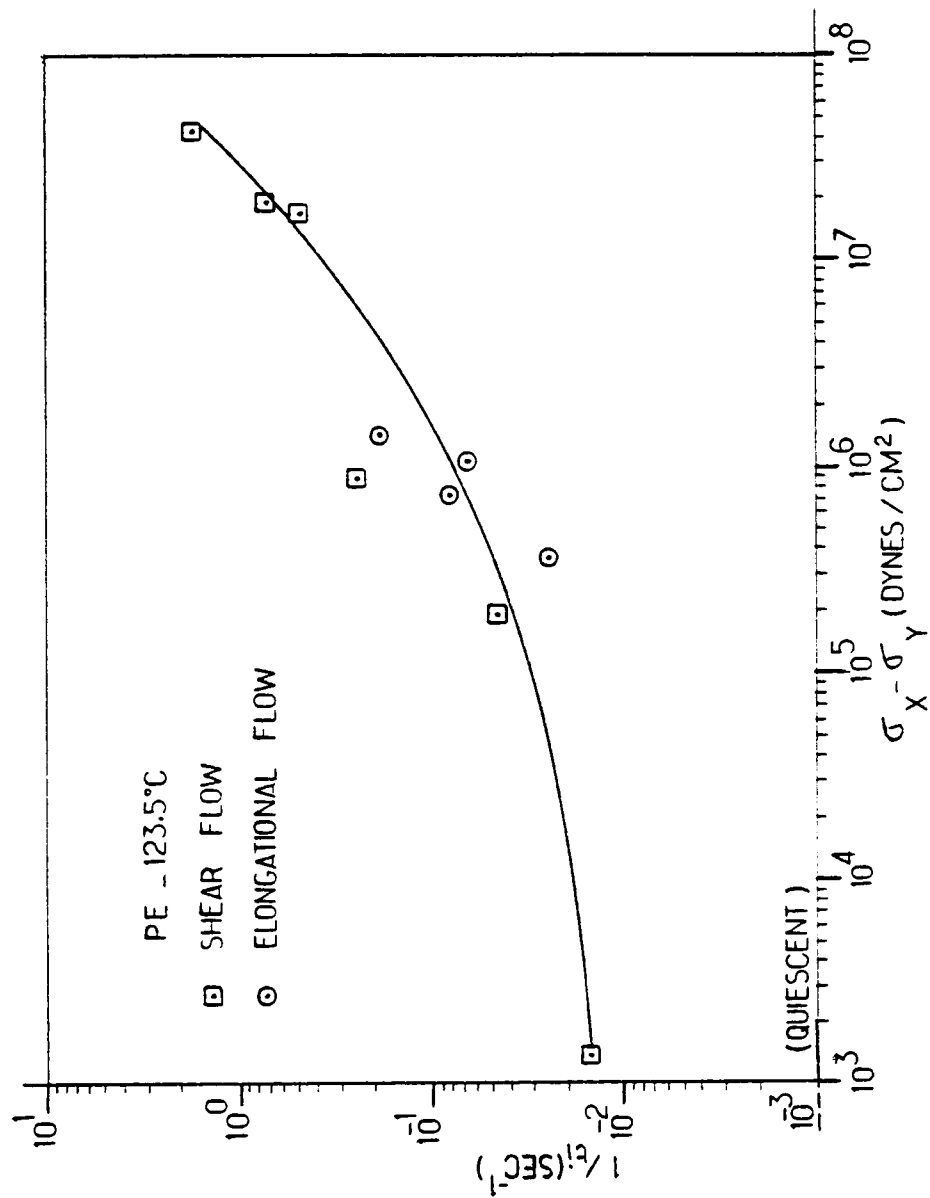


Figure V-27 : Reciprocal induction time versus principal stress difference for PE at 123.5°C.

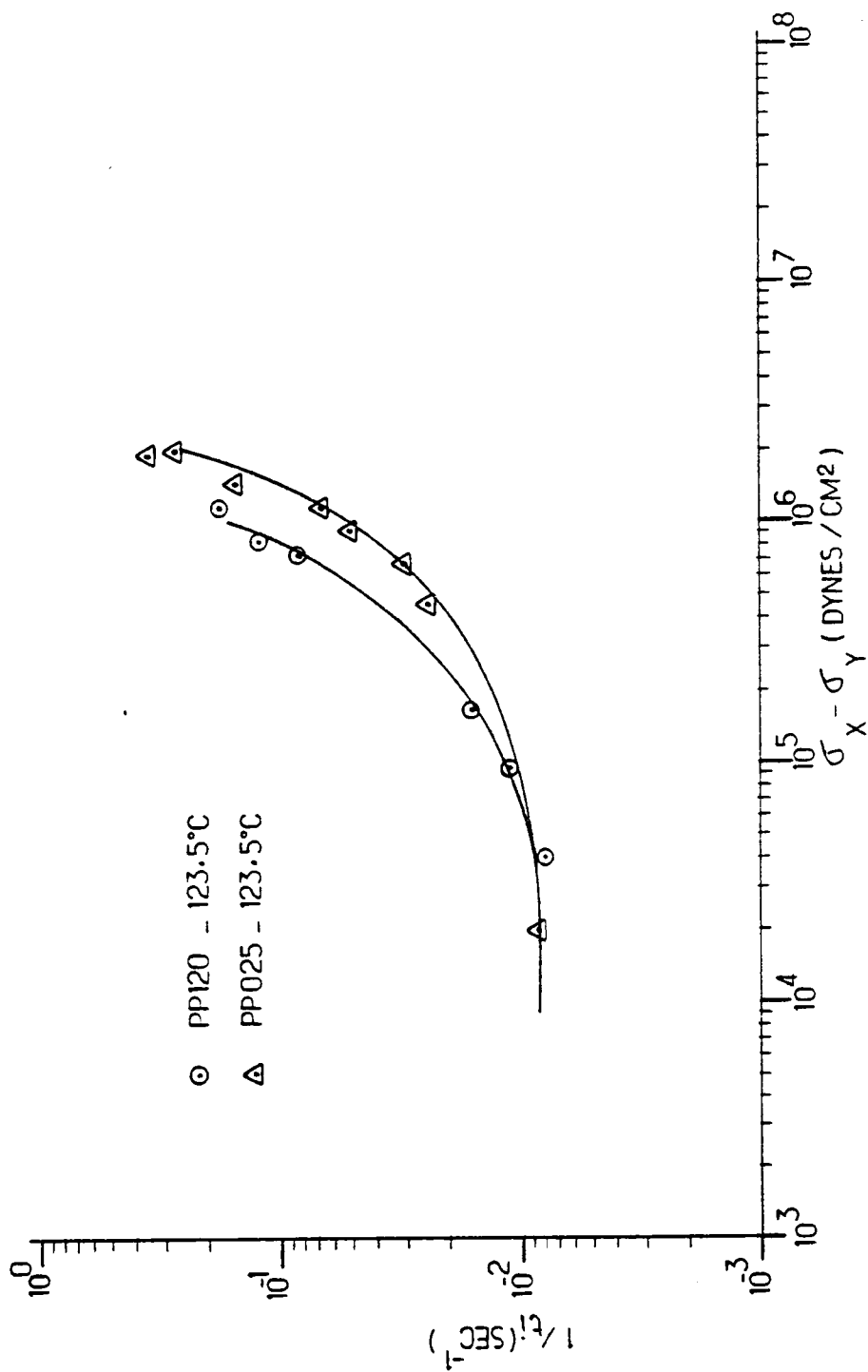


Figure V-28 : Reciprocal induction time versus principal stress difference at 123.5°C for PP120 and PP025.

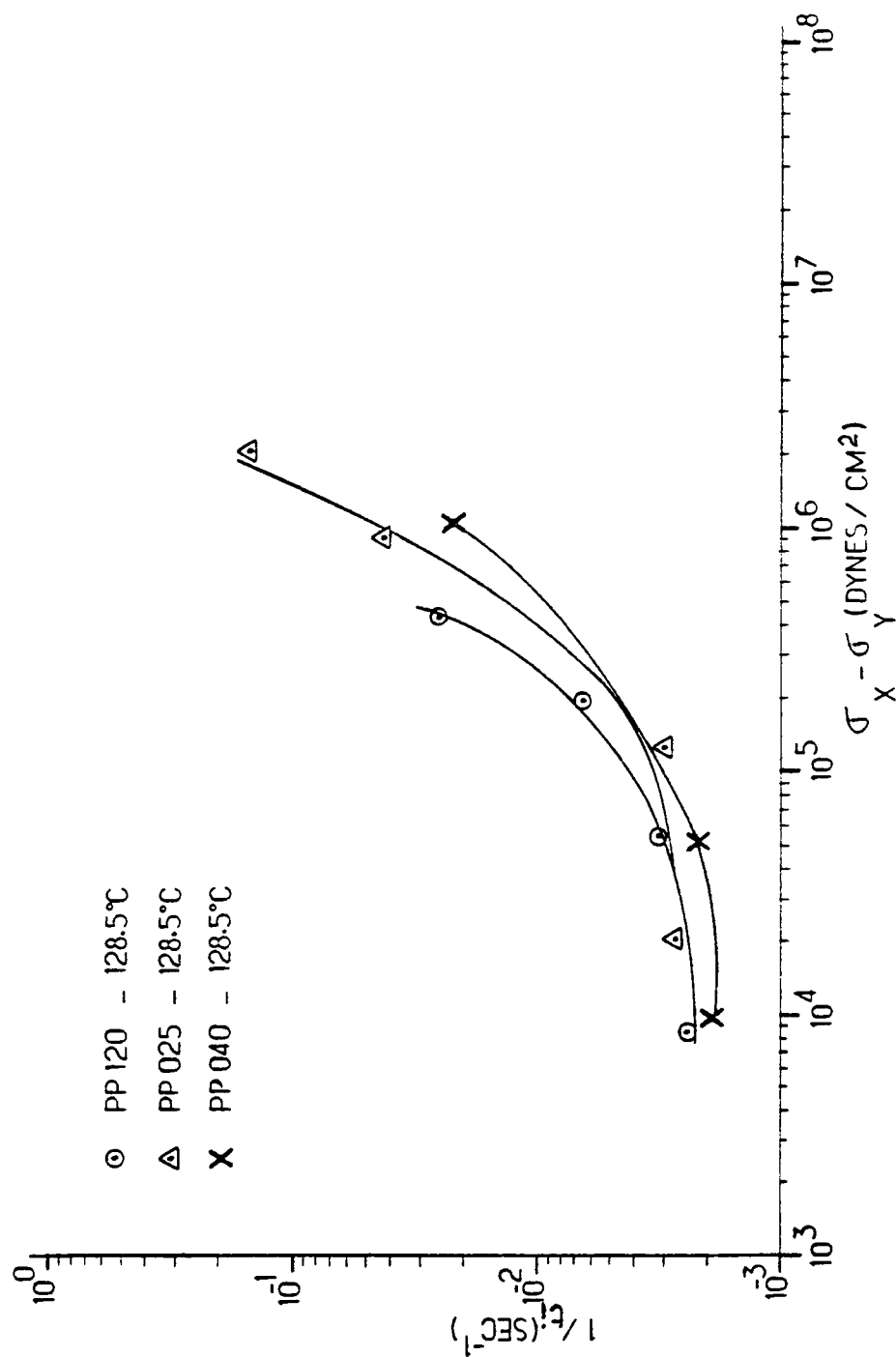


Figure V-29 : Reciprocal induction time versus principal stress difference at 128.5°C for PP120 and PP025.

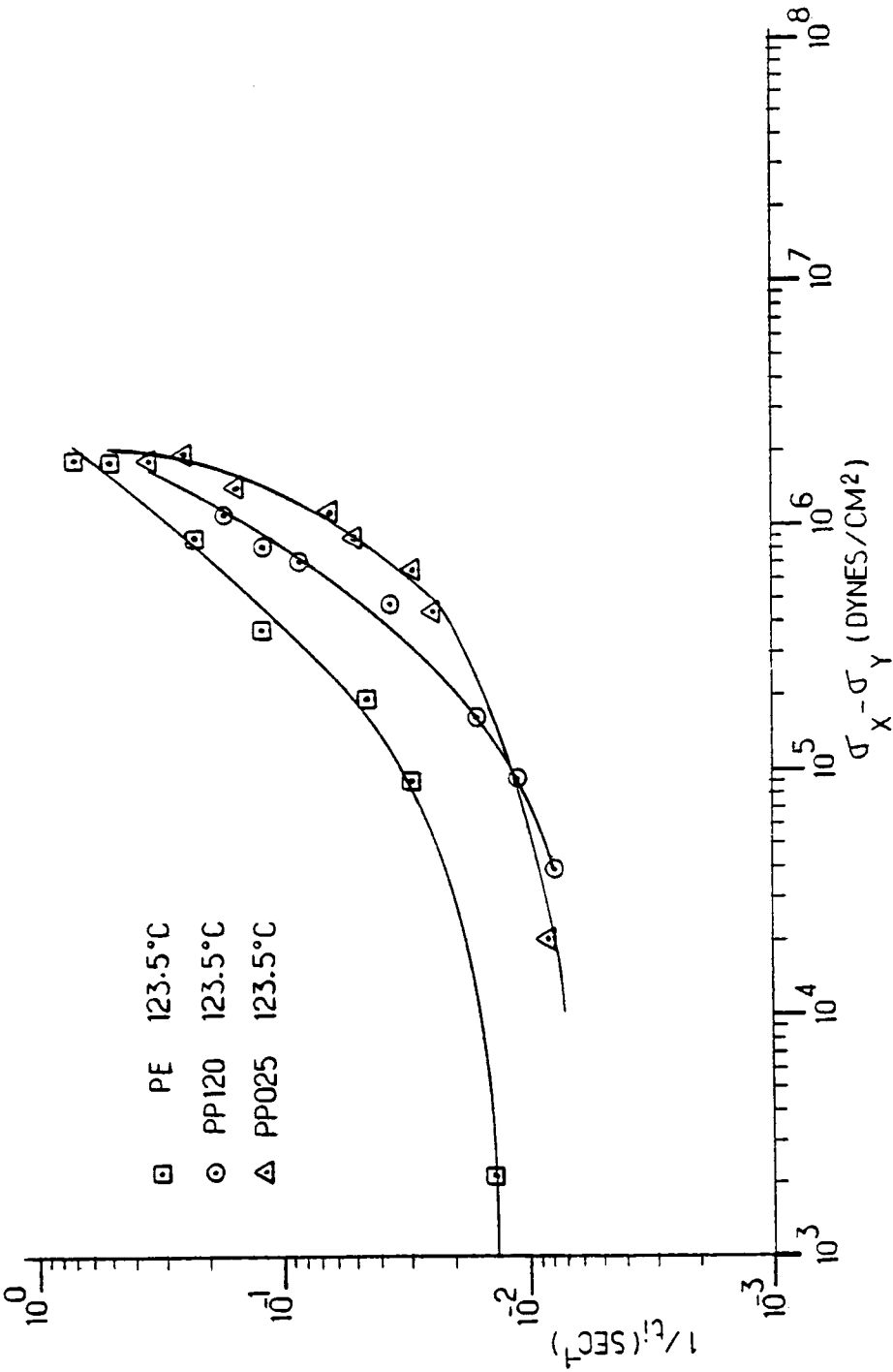


Figure V-30 : Reciprocal induction time versus principal stress for PE, PP120 and PP025 at 123.5°C.

crystallized at the same temperature but under different stress states. This assumes that the quantities A and B in Eq. III-40a, p. 60, are unaffected by a change in the mode of deformation. Based on our earlier discussion in Chapter III, this seems to be a reasonable assumption. Earlier ΔG_{def} has been shown to be proportional to the $\text{Tr}P_{\lambda}$ (see Eq. III-50b, p. 64). In the following figures, we use $\text{Tr}P_{\lambda}$ values computed from Eq. III-57 and III-59 (pp. 67,68) for the elongational and shear flow cases, respectively.

Figure V-31 shows the shear and elongational flow $1/t_i$ data presented earlier in Figures V-22 and V-23, replotted as a function of $\text{Tr}P_{\lambda}$. Figure V-31 shows that there is a correlation in PP025 between the nucleation rates ($1/t_i$) and the $\text{Tr}P_{\lambda}$ independent of mode of deformation at 120.5°C and 123.5°C, respectively. Similar conclusions can be drawn for PE at 123.5°C as indicated by the results in Figure V-32 which is a replot of Figure V-26, as a function of $\text{Tr}P_{\lambda}$. These results suggest that the theory resulting in Eq. III-40a (p. 60) should be examined more thoroughly in an effort to establish whether it accurately describes the effect of stress on nucleation rate. See Figure V-33.

In order to predict the nucleation rates from Eq. III-40a, prior knowledge of the constants A and B is required. Both A and B contain parameters (see Eqs. III-38 and III-39 (p. 59)) which cannot be readily evaluated for a given polymer in a manner that is completely independent of nucleation rate measurements. The most feasible approach is to assume that A and B are independent of stress (see discussion of this point in Chapter III). With this assumption, A

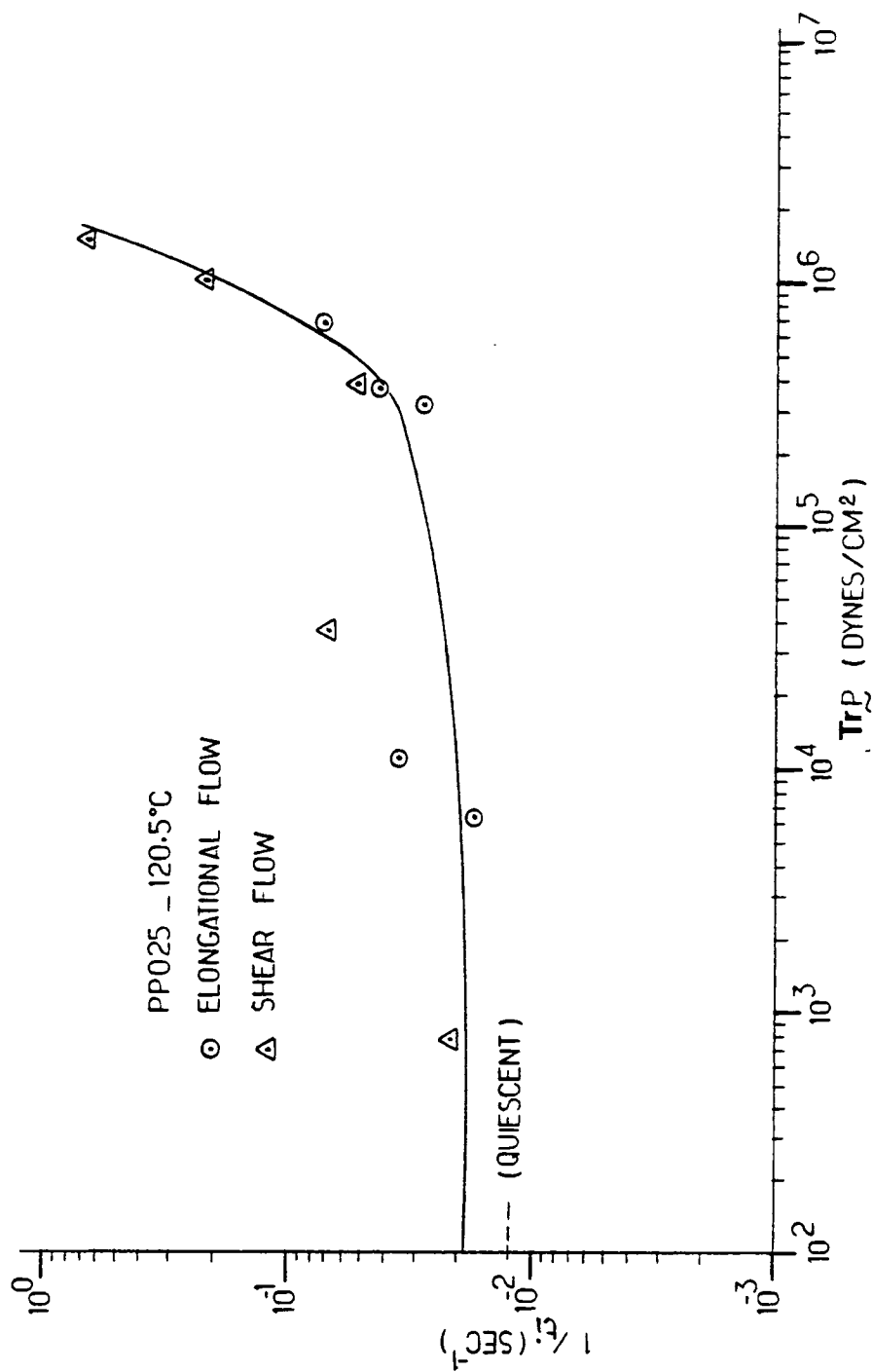


Figure V-31 : Reciprocal induction time versus Tr_P for PP025 in shear and elongational flow at 120.5°C.

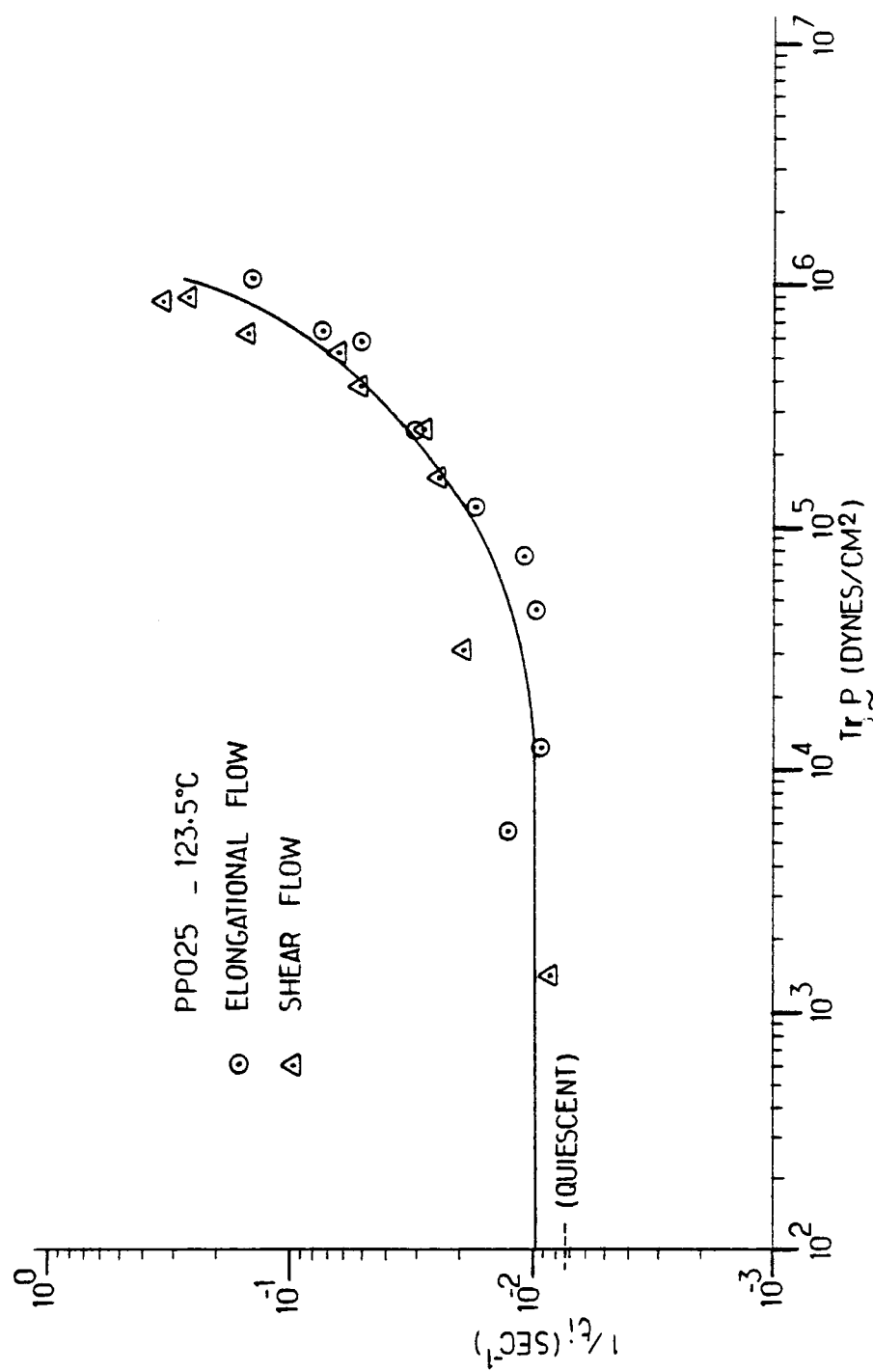


Figure V-32 : Reciprocal induction time versus Tr_p for PP025 in shear and elongational flow at 123.5°C.

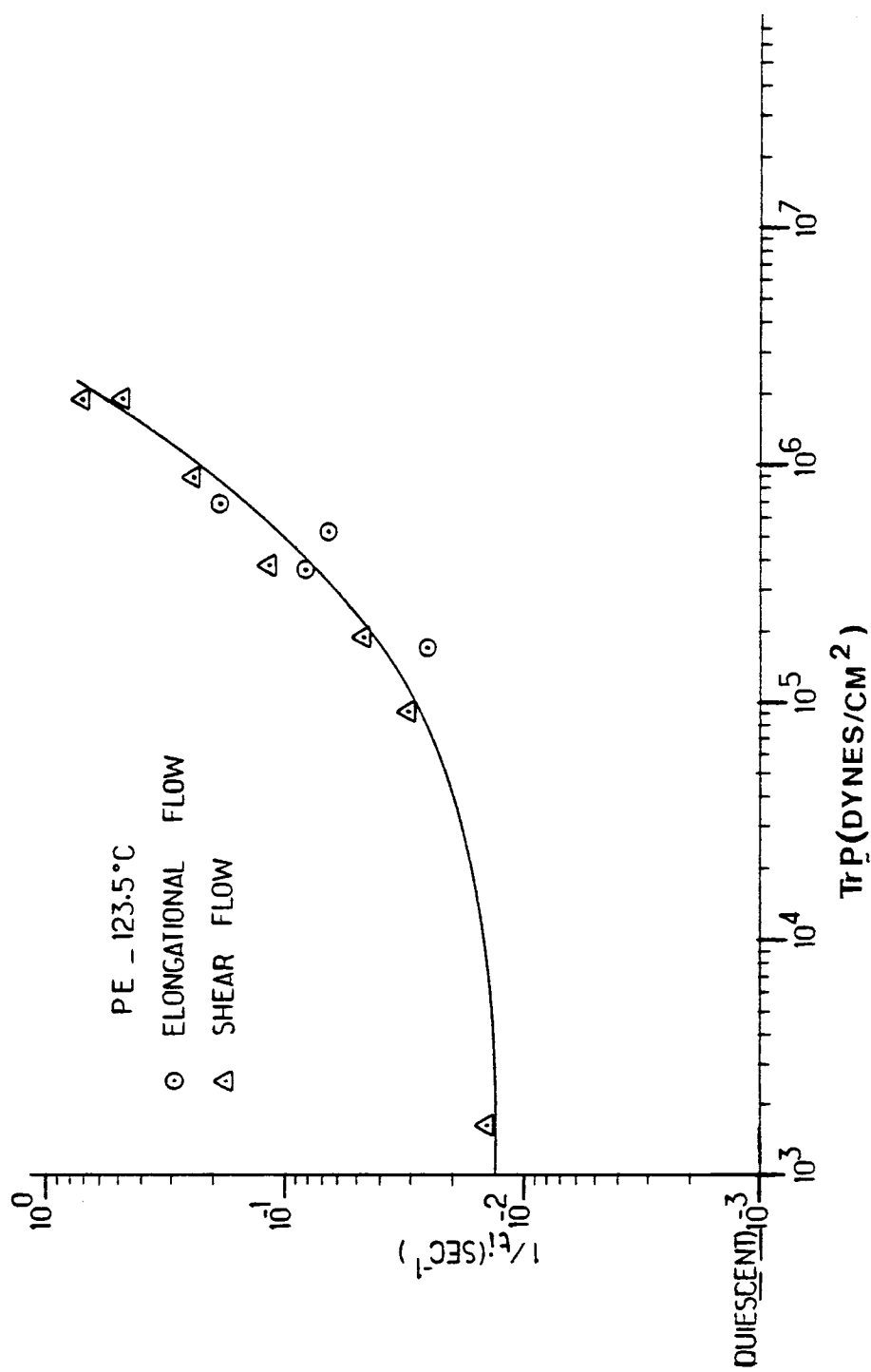


Figure V-33 : Reciprocal induction time versus TRP_{∞} for PE in shear and elongational flow at 123.5°C.

and B can be evaluated from the quiescent crystallization data. If the nucleation rates are assumed to be proportional to the reciprocal of induction times (Eq. V-40, p. 60, Eq. III-37, p. 58) describing the quiescent nucleation rate can be written as

$$\ln \frac{1}{t_i} = A' - \frac{B}{\Delta H^2} \left[\frac{T_m^0}{T \Delta T} \right]^2 \quad (V-5)$$

where A' is proportional to A and the proportionality constant which relates $\dot{N}$ to $1/t_i$ also relates A to A'.

Figure V-34 is a plot of $\ln 1/t_i$ vs. $t_m^0/T \Delta T^2$ for PP025 and PP120 under quiescent conditions. As expected from Eq. V-5, Figure V-34 shows a linear relationship between $\ln 1/t_i$ and $T_m^0/T \Delta T^2$ with $A' = 3.102$ and $\frac{B}{\Delta H^2} = +56$.

The stress induced nucleation rate (Eq. III-40a, with $\dot{N} \propto \frac{1}{t_i}$) with A' and B evaluated from quiescent results can be written as

$$\ln \frac{1}{t_i} = 3.102 - \frac{56 \times \Delta H^2}{T \left[\frac{\Delta T \Delta H}{T_m^0} + \Delta G_{\text{def}} \right]^2} \quad (V-6)$$

Figure V-35 shows a comparison between experimental data and the theoretical predictions of $\ln(1/t_i)$ according to Eq. V-6 plotted as a function of tr_L^P at different crystallization temperatures. In the computation of $1/t_i$ values from Eq. V-6, ΔH and T_m were taken as $1.96 \times 10^9 \text{ erg/cm}^3$ and 457 °K, respectively. Figure V-35 shows that both the experimental and theoretical nucleation rates have similar general shape with the effect of temperature becoming less noticeable

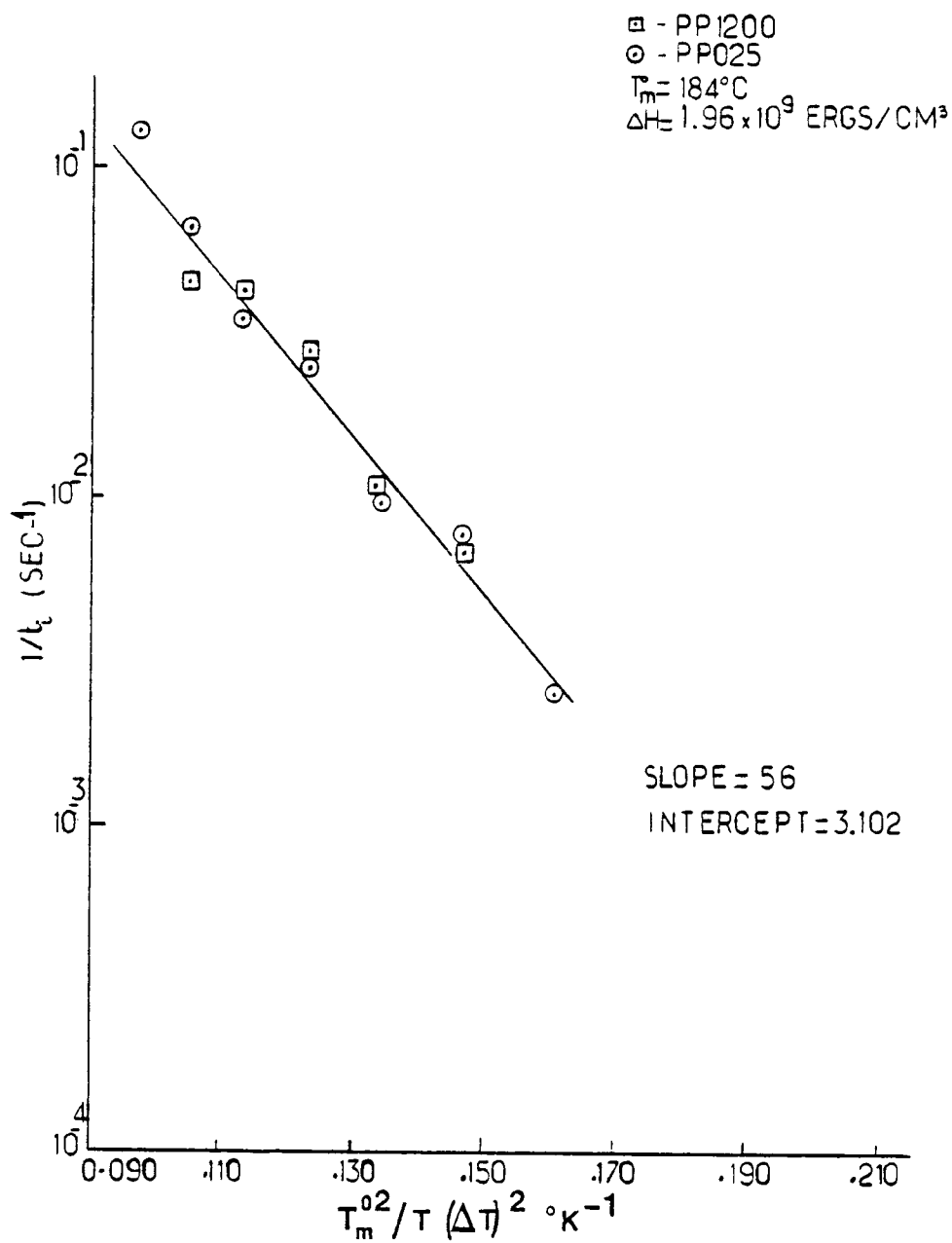


Figure V-34 : Reciprocal induction time versus
 $T_m^{0.2} / T (\Delta T)^2$ for PP120 and PP025.

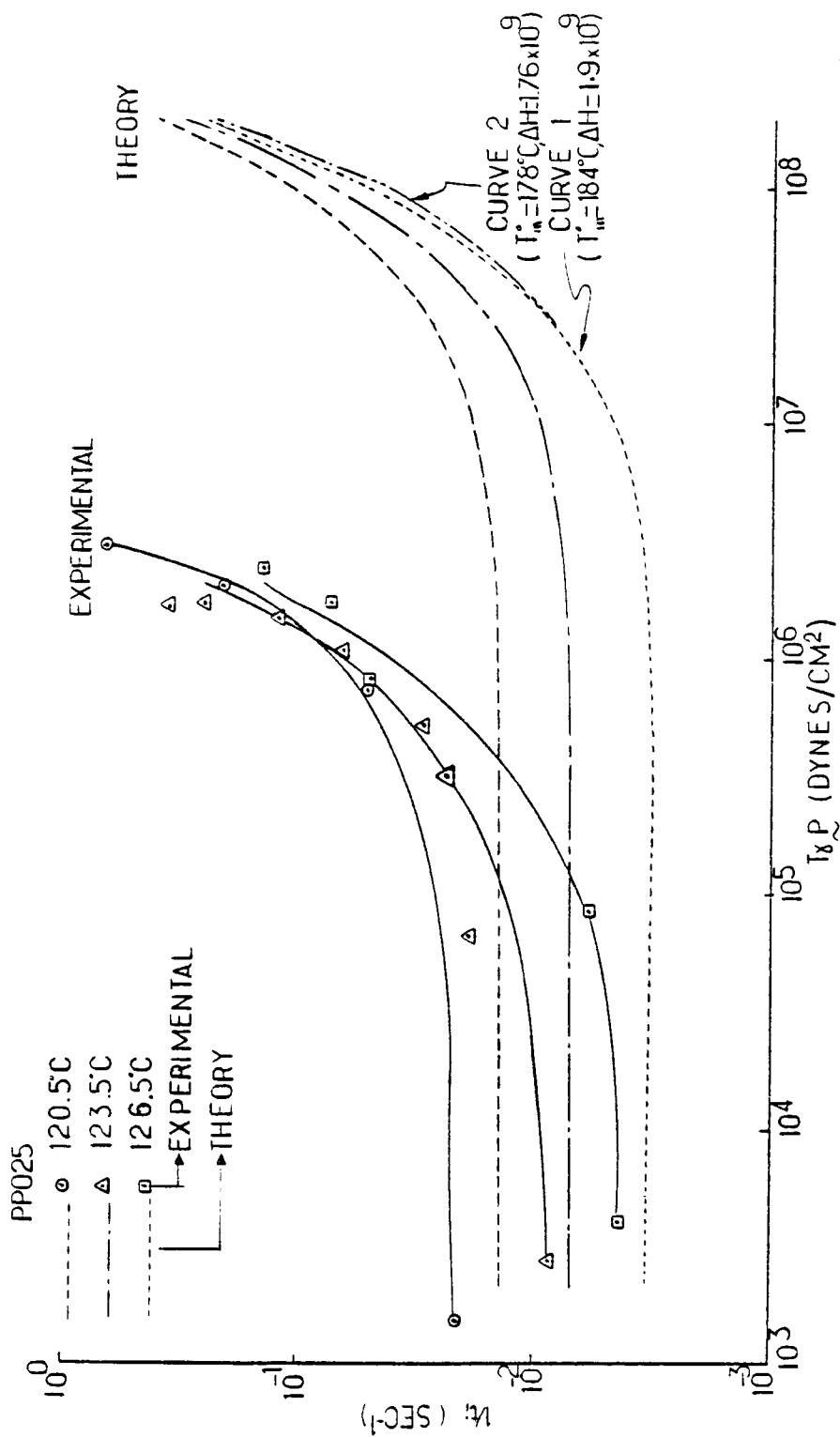


Figure V-35 : Comparison of theoretical and experimental reciprocal induction times (nucleation rates) versus Tr_0 results for PP025 at 120.5°C, 123.5°C and 126.5°C respectively.

at higher tr_λ^P values. However, the theory grossly underpredicts the sensitivity of nucleation rates on the magnitude tr_λ^P . No appreciable differences in the calculations of $1/t_i$ resulted when a different set of T_m and ΔH were used (compare curve I with curve II in Figure V-35). This leads to the conclusion that either the Marrucci expression underpredicts ΔG_{def} , which in turn results in the underprediction of $1/t_i$ in a polymer melt, or that ΔG_{def} does not have the effect on nucleation rate indicated by Eq. III-40, p. 60. In the present work we consider it is the inadequacy in Marrucci's analysis to be the cause for the lower predicted $\dot{N}$ values.

It is possible to treat ΔG_{def} as an adjustable parameter and determine a value for it which forces Eq. V-6 to give the best fit to the experimental data. The results of this approach are shown in Figures V-36, V-37, and V-38. The reasonably good fit to the experimental data shown in these figures was accomplished by considering only the first term in the general expression (Eq. III-42, p. 62).

$$\Delta G_{\text{def}} = a_{11} \text{Tr}_\lambda^P \quad (\text{V-7})$$

The constant a_{11} is dimensionless and is simply adjusted to give a good fit to the experimental data. In the case shown, $a_{11} = 50$ and the values of A' , B , ΔH and T_m are the same as those used for the calculations plotted in Figure V-35. Also note here that for $a_{11} = 1/2$, Eq. V-7 reduces to Marrucci's equation (Eq. III-50b, p. 64).

Figures V-37 and V-38 are plots of $1/t_i$ as a function of Tr_λ^P for PP120 and PP025 at 123.5°C and for PP025, PP040 and PP120 at 128.5°C. The solid curves are the predicted nucleation rates with

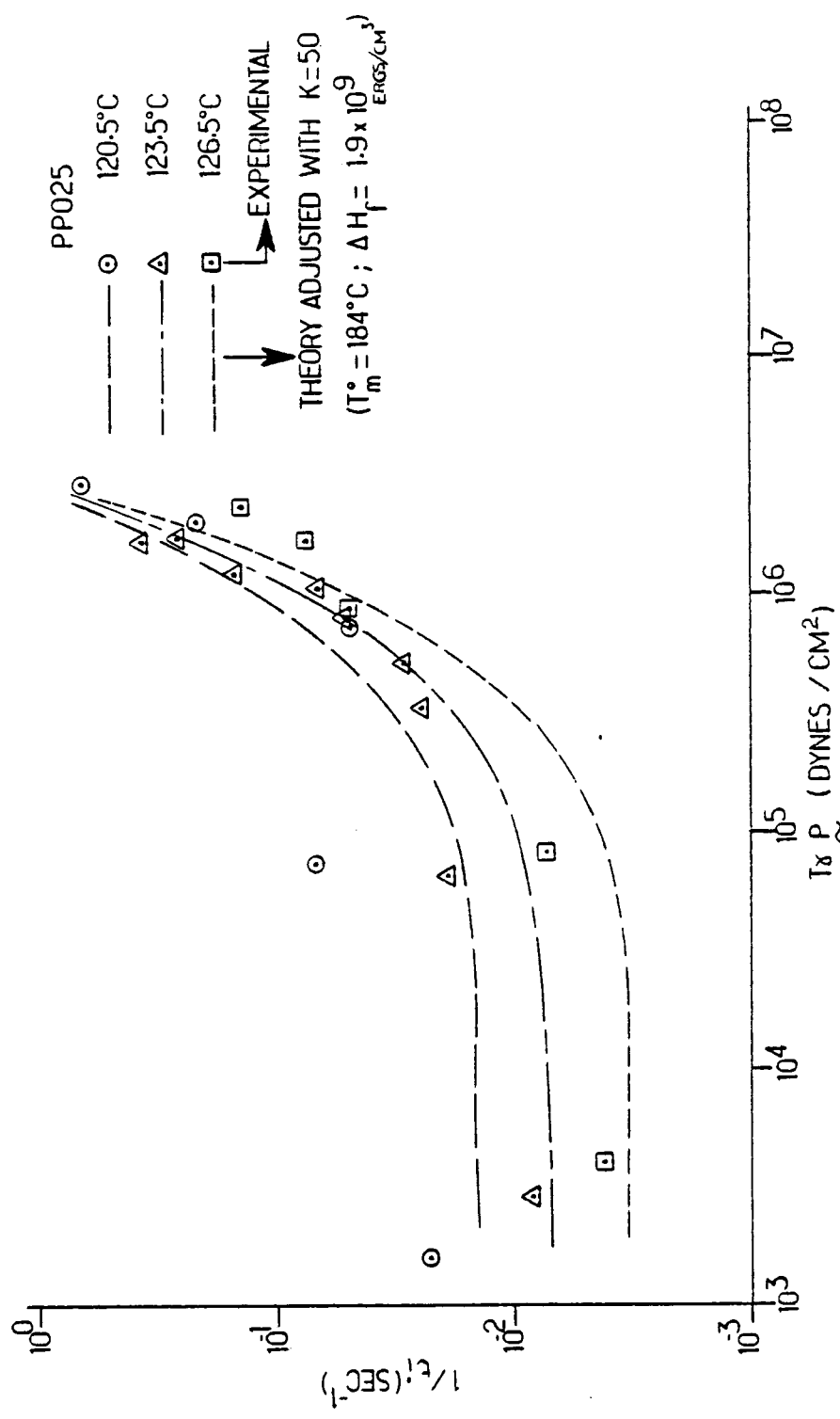


Figure V-36 : Comparison of adjusted theoretical and experimental reciprocal induction times (nucleation rates) versus γ_s results for PP025 at 120.5°C, 123.5°C and 126.5°C respectively.

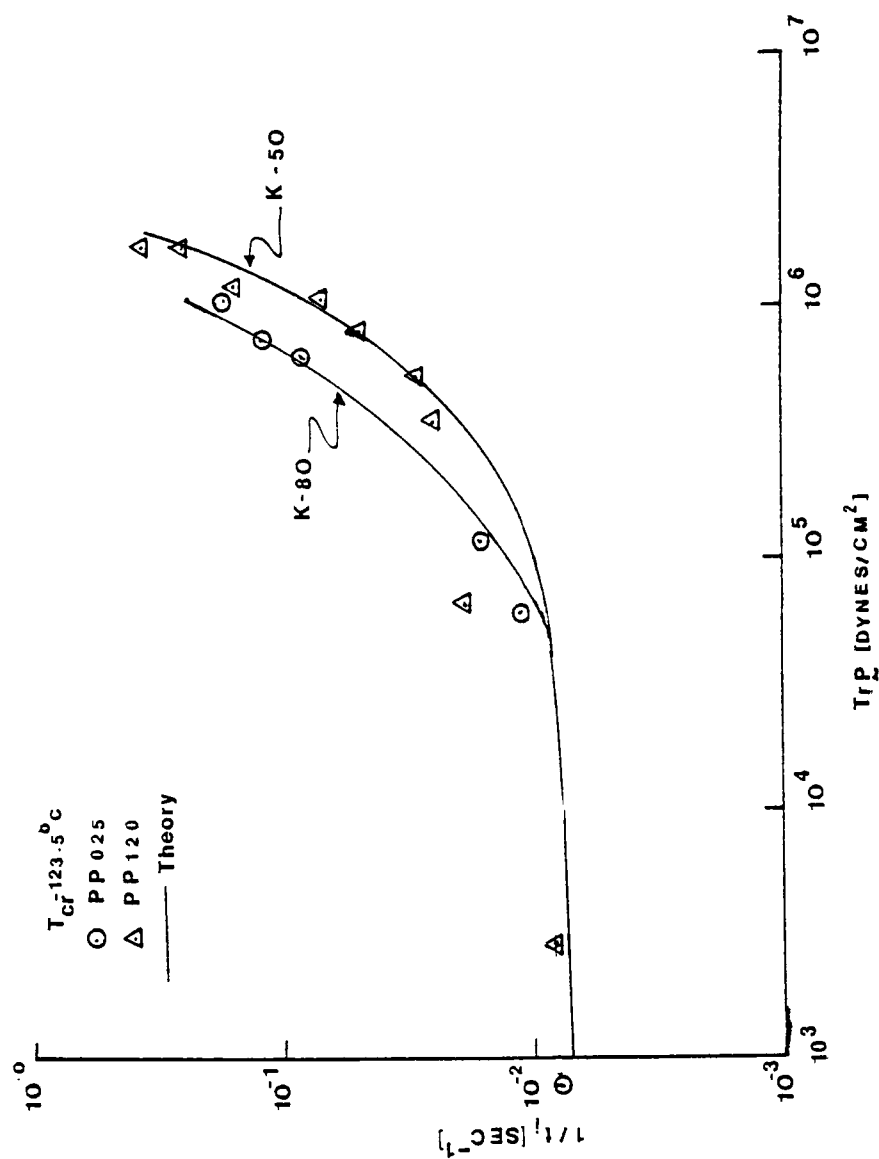


Figure V-37 : Comparison of adjusted theoretical and experimental reciprocal induction times (nucleation rates) versus TrP results for PP025 and PP120 at 123.5°C .

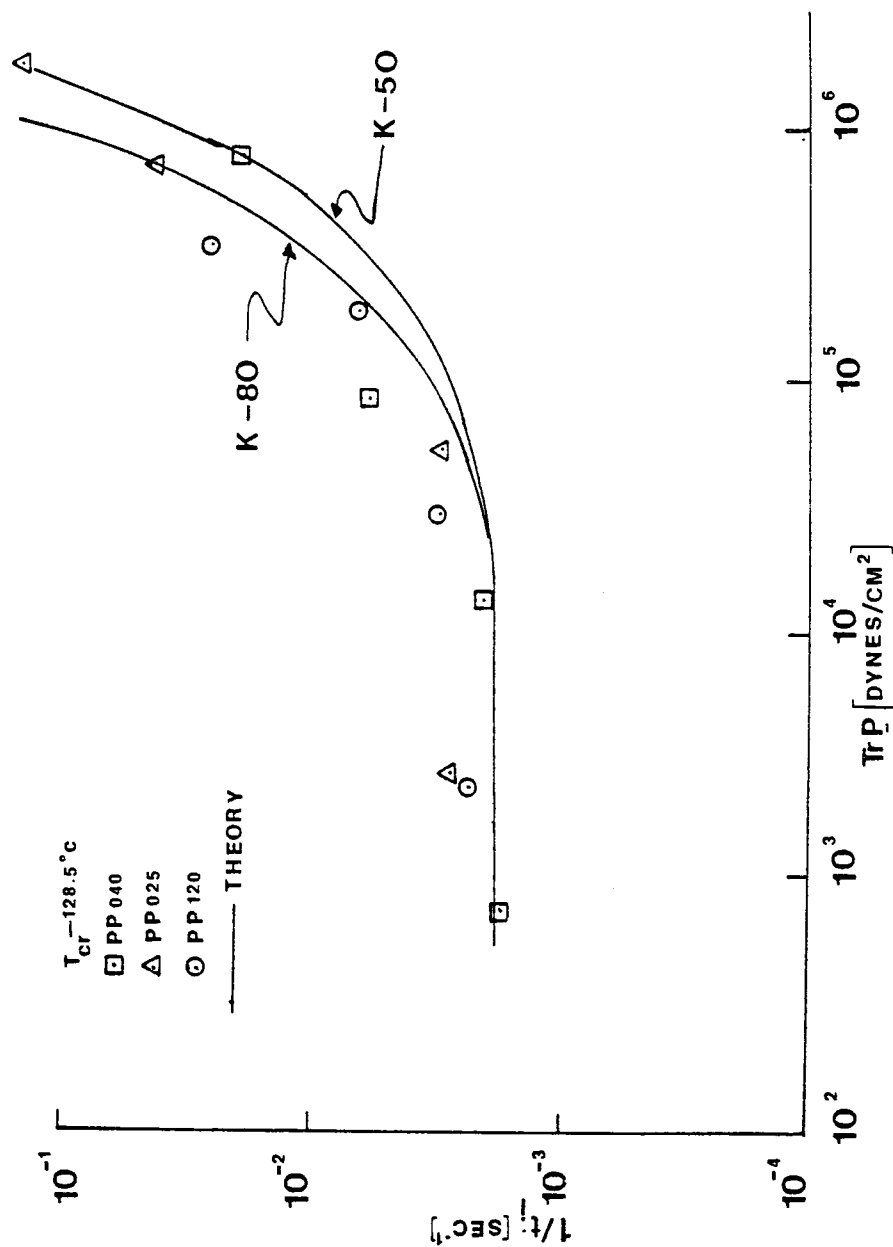


Figure V-38 : Comparison of adjusted theoretical and experimental reciprocal induction times (nucleation rates) versus TrP results for PP025, PP120 and PP040 at 128.5°C .

different a_{11} values. The experimental results show that PP120 still shows faster nucleation rates compared to PP025 and PP040, particularly at higher tr_P . The calculated values show that the constant a_{11} (estimated from curve fitting the results in Figure V-37) is higher for PP120 ($a_{11} = 80$) compared to the other polypropylenes ($a_{11} = 50$).

4. Discussion

Commercially available polypropylenes were used in the present studies. Some of these samples have been used extensively in earlier melt spinning (88,180) and rheological studies (107,202) at The University of Tennessee. Continuation of studies with these samples furthered the understanding of crystallization behavior under both quiescent and stressed conditions. However in the current studies the separation of effect of molecular weight and molecular weight distribution on the nucleation rates became complicated.

Undoubtedly, an important drawback of the current studies is that there is no direct observation of crystallization process under flow conditions particularly in elongational flow. Such observations would have given more direct evidence of the start of crystallization. However, because of the anticipated experimental difficulties we decided to follow the changes in viscosities due to crystallization. Such procedures may have caused some errors in the measurement of induction times particularly in elongational flow.

Figures V-39 and V-40 show the comparison of the $1/t_i$ from the present work with those found in the literature (125,148) on polypropylenes in shear flow at 121°C and 128.5°C, respectively. Both

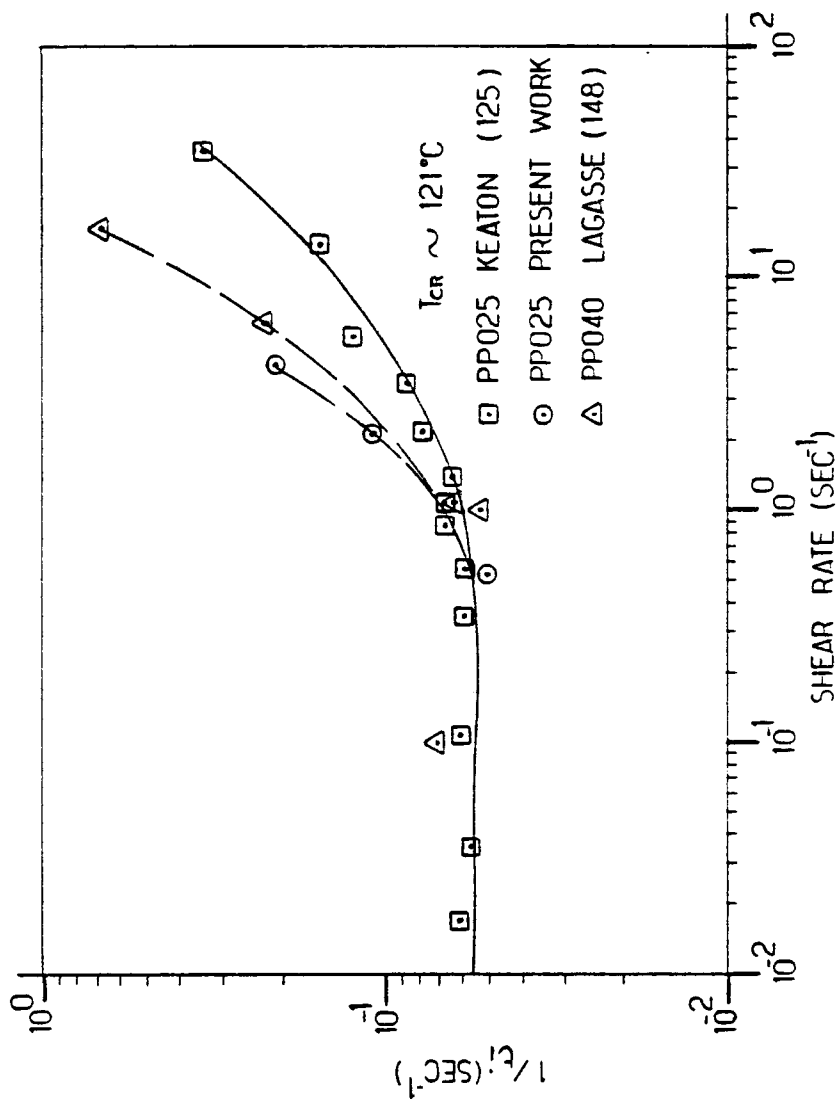


Figure V-39 : Comparison of reciprocal induction time as a function of shear rate results for polypropylenes from the present studies with those from literature at 120.5°C.

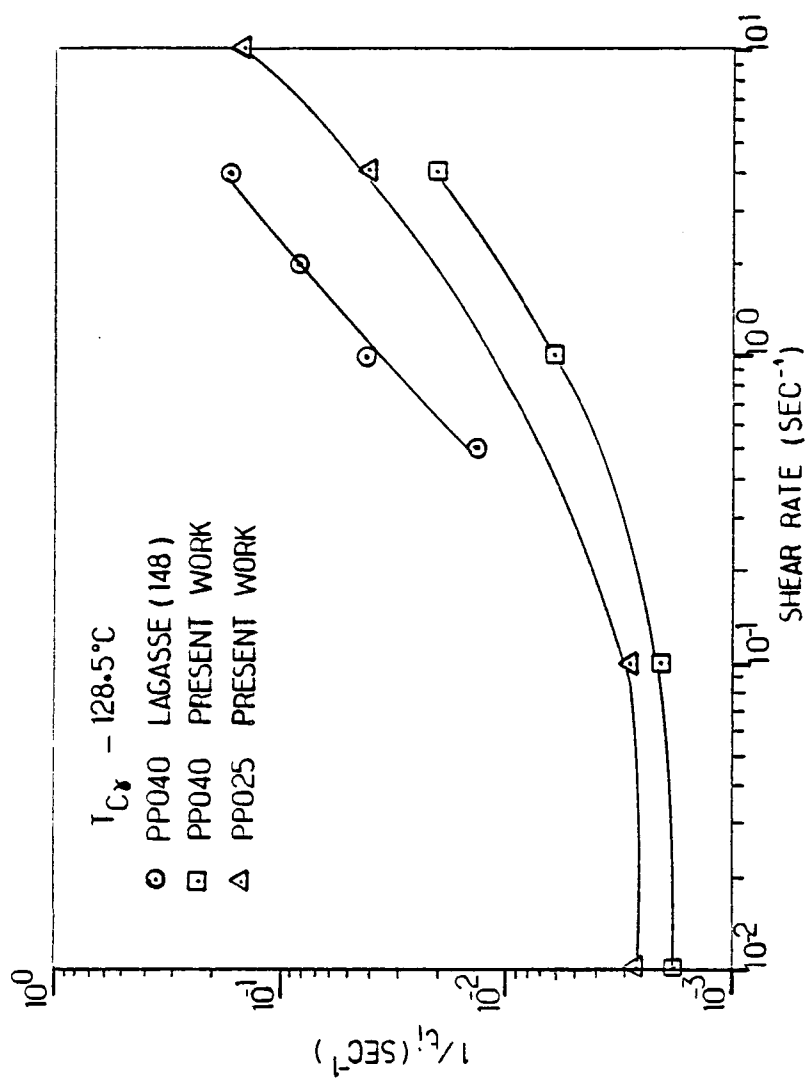


Figure V-40 : Comparison of reciprocal induction time as a function of shear rate results for polypropylenes from the present studies with those from literature at 128.5°C.

these figures show similar trends in the variation of $1/t_i$ as a function of shear rates for the present and the literature results. There are some differences in $1/t_i$ values between the investigators which do not appear to be unreasonable considering the fact that the polymers and the experimental systems and procedures are different in each case.

Direct comparison of induction times under isothermal elongational flow with literature values is not possible, since there exists no other such data for commercial polypropylenes and polyethylenes.

Samples crystallized at lower stresses (Figure V-16, p. 101) showed a strong effect of crystallization temperature but a small effect of the differences in samples on the nucleation rates. This is consistent with the nucleation behavior observed in quiescently crystallized samples (Figure V-4, p. 82). At higher stresses, the crystallization temperature effect on nucleation rate seems to decrease due to the dominant effect of stress on $1/t_i$.

In the literature several investigators presented nucleation rate results as a function of $\dot{\gamma}$. In the present studies the nucleation rate results under shear flow conditions were presented as a function of $\dot{\gamma}$ (Figures V-14 and V-15, pp. 99 and 100). The conclusion with respect to the sample effect reversed when the same results were plotted as a function of σ_{12} . This suggests that σ_{12} (which is a measured response from the sample to the imposed deformation or $\dot{\gamma}$) measurements are important in interpreting the nucleation rates.

Nucleation rates when plotted as a function of σ_{12} showed that PP040 with lower molecular weight ($\bar{M}_w = 2.91 \times 10^5$) and presumably

similar molecular weight distribution as PP025 ($\overline{M}_w/\overline{M}_n = 4.0$, $\overline{M}_w = 4.03 \times 10^5$) crystallized at a slower rate. This suggests that under stressed conditions higher molecular weight samples crystallize faster. However, under isothermal quiescent conditions (Figure V-3, p. 81) PP040 crystallized faster than PP025. This is reasonable if we consider that under quiescent conditions low molecular weight samples with higher chain mobility would have higher nucleation rates. However under flow conditions, at moderate super coolings ($T_{cr} \gg T_g$), the differences in chain mobility is overshadowed by the stress effects on ΔG_{def} . Higher molecular weight samples with higher entanglement between molecules are subjected to greater chain extension during flow and hence give rise to faster nucleation rates.

The results in Figure V-16, p. 101, also showed that PP120 with a lower molecular weight ($\overline{M}_w = 2.45 \times 10^5$) but a broader molecular weight distribution ($\overline{M}_w/\overline{M}_n = 8.0$) compared to PP025 ($\overline{M}_w = 4.03 \times 10^5$, $\overline{M}_w/\overline{M}_n = 4.0$) and PP040 ($\overline{M}_w = 2.91 \times 10^5$, $\overline{M}_w/\overline{M}_n = 4.0$) crystallizes faster. One explanation justifying the above result comes from the conclusion that the high molecular weight tail in the broader molecular weight distribution in PP120 contributes strongly to the entanglements causing the nucleation rates to be faster.

In all of the above discussion on sample effects on nucleation results one must keep in mind that differences in the presence of adventitious species in different samples could cause the nucleation states to be different under both quiescent and stress induced cases.

The results presented in the previous section showed correlation between the nucleation rates and the principal stress differences

independent of the mode of deformation (shear or elongational) at any given crystallization temperature for both PP025 and PE. A similar correlation between the nucleation rates and $\text{Tr}P_{\lambda}$ (or ΔG_{def}) was also observed. The correlation between the nucleation rate and molecular orientation is a result of the postulation from intuitive arguments whereas the relation between the nucleation rate and ΔG_{def} originates from the classical theories. As the results in the previous sections indicated, both the above approaches seem to give equally good correlation independent of mode of deformation. The reason for this is our inability in distinguishing between the experimentally measured values of $\sigma_x - \sigma_y$ and the $\text{Tr}P_{\lambda}$. Both the principal stress differences and $\text{Tr}P_{\lambda}$ are proportional to the first normal stress differences as per Eqs. III-9 and III-59, pp. 48 and 68.

According to the "Rheo-optical law," $\sigma_x - \sigma_y$ is a measure of the average molecular orientation in the melt. This molecular orientation is independent of mode of deformation and also the molecular weight and weight distribution. From this one would expect a correlation between the nucleation rates and $\sigma_x - \sigma_y$ (or orientation) to be independent of the molecular parameters of the samples. However, nucleation rates of different PP samples showed a strong sample effect when plotted as a function of $\sigma_x - \sigma_y$ (see Figures V-28 and V-29, pp. 121 and 122). At a given principal stress difference, PP samples with broad molecular weight distribution showed faster nucleation rates compared to the narrower molecular weight distribution samples. The probable reason for this may simply be that the

nucleation rate is more sensitive to the molecular weight distribution, particularly the presence of high molecular weight species which could cause significantly higher localized orientations due to increased entanglements. If this is the case samples containing high molecular weight species should exhibit higher nucleation rates at a given average orientation, than samples that do not. The experimental results confirmed this. A second possible explanation for the observed sample effect could be due to the differences in the hydrodynamic interactions during flow between the polymer molecules and any adventitious species. These differences in interaction may cause the observed differences in the nucleation rates.

Linear relationship between $\ln 1/t_i$ and $T_m^{02}/T_m^0 \Delta T^2$ shown in Figure V-34 (p. 129) are anticipated for the quiescent crystallization case from the classical nucleation theories. Theoretical predictions of stress induced nucleation rates (which utilize the quiescent results) showed a similar temperature dependency and general shape as the experimental results. However as shown in Figure V-35, p. 130, these values are lower than the experimental $1/t_i$ results due to the underprediction in ΔG_{def} (or ΔS_{def}) by Marrucci analysis (Eq. III-50b, p. 64). A comparison of estimates of ΔS_{def} as a function of macroscopic deformation ratio, λ , using Marrucci (170) (ΔS_{def} estimated from the stress values, λ from the stretch ratio), Yeh and Hong (259) and Krigbaum and Roe (140) type analyses is shown in Figure V-41. Also shown in this figure are the ΔS_{def} values calculated using Eq. III-40b, p. 60, and the elongational flow experimental

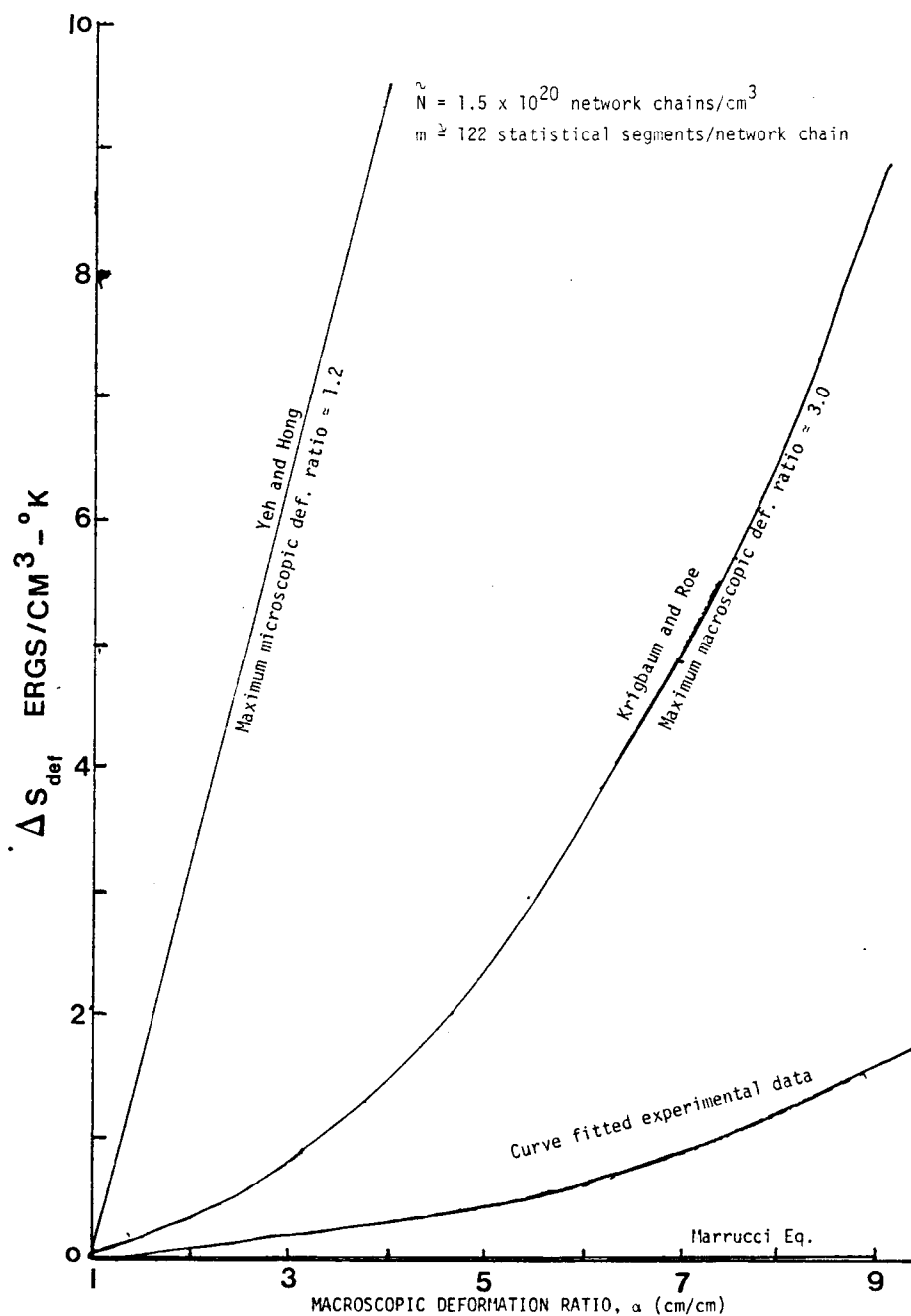


Figure V-41 : ΔS_{def} versus macroscopic deformation rates.
 Comparison of experimental results with several
 available theoretical estimates.

$1/t_i$ results. These results show that Yeh and Hong and Krigbaum and Roe's expression greatly overpredicts the ΔS_{def} while Marrucci's approach underpredicts the ΔS_{def} . This again confirmed that the use of affine deformation model from rubber elasticity theory overpredicts the ΔS_{def} (and hence the corresponding $1/t_i$ results) in a polymer melt under deformation. On the other hand Marrucci's approach which to some degree takes into account the molecular relaxations occurring during flow, underpredicted the ΔS_{def} . While there appears to be no preference to the above two approaches, we feel that relating ΔS_{def} to the stress state in the melt (Jarecki and Ziabicki (272), Marrucci et al. (170) type approach) is the direction to follow. The general expression for ΔG_{def} (or ΔS_{def}) such as the one described by Jarecki and Ziabicki (272) involving multiple constants and higher order $\text{tr} P_{\nu}$ terms should be considered carefully in light of our experimental results. Curve fitting of our experimental results with a simplified Jarecki and Zwabicki expression (Eq. V-7, p. 131) showed that the constant a_{11} can be a function of sample (see Figures V-37 and V-38, pp. 133 and 134), and that this value is quite high (nearly 2 orders of magnitude) compared to the constant ($a_{11} = 1/2$) in Marrucci's analysis.

The constant a_{11} needed to make the theoretical nucleation rate values compare with experiment ($\Delta G = a_{11} \text{tr} P_{\nu}$) might conceivably be interpreted as measuring the effect of the average stress on the high molecular weight tails. That is, in enhancing the nucleation rate. If this is the case then a_{11} should be sensitive (vary) with M_w

distribution. This was shown to be the case in Figures V-37 and V-38 (pp. 133 and 134).

CHAPTER VI

QUIESCENT AND STRESS-INDUCED CRYSTALLIZATION KINETICS OF NUCLEATED AND NONNUCLEATED POLYPROPYLENES

A. QUIESCENT STUDIES

1. Results

Figure VI-1 shows traces of crystallization exotherms for polypropylenes at 124°C. The traces include both nucleated and non-nucleated control polypropylenes. This figure is very similar to Figure V-1 (p. 78). Figure VI-1 indicates that nucleated polypropylenes crystallize faster than the control. This figure further indicates that sodium benzoate is more effective as a nucleating agent at 124°C than talc (compare samples PPSB10 and PPT50). The talc nucleated sample (PPT50) crystallizes only slightly more rapidly than the control (PP040).

Figure VI-2 is a plot of reciprocal crystallization half time as a function of crystallization temperature (T_{cr}) for the control and the nucleated polypropylenes. This figure shows that $1/t_{0.5}$ decreases with increasing T_{cr} for all the samples in the temperature range investigated. Sodium benzoate nucleated PP (PPSB50) crystallizes at rates about 1.5 orders of magnitude higher than the control sample at any given T_{cr} . Another way of looking at this is that at constant crystallization rate ($1/t_{0.5}$) PPSB50 crystallizes about 20°C higher than the control. The talc nucleated sample, PPT50, has crystallization rates slightly higher than the control. There is also a nonlinear effect of amount of nucleating

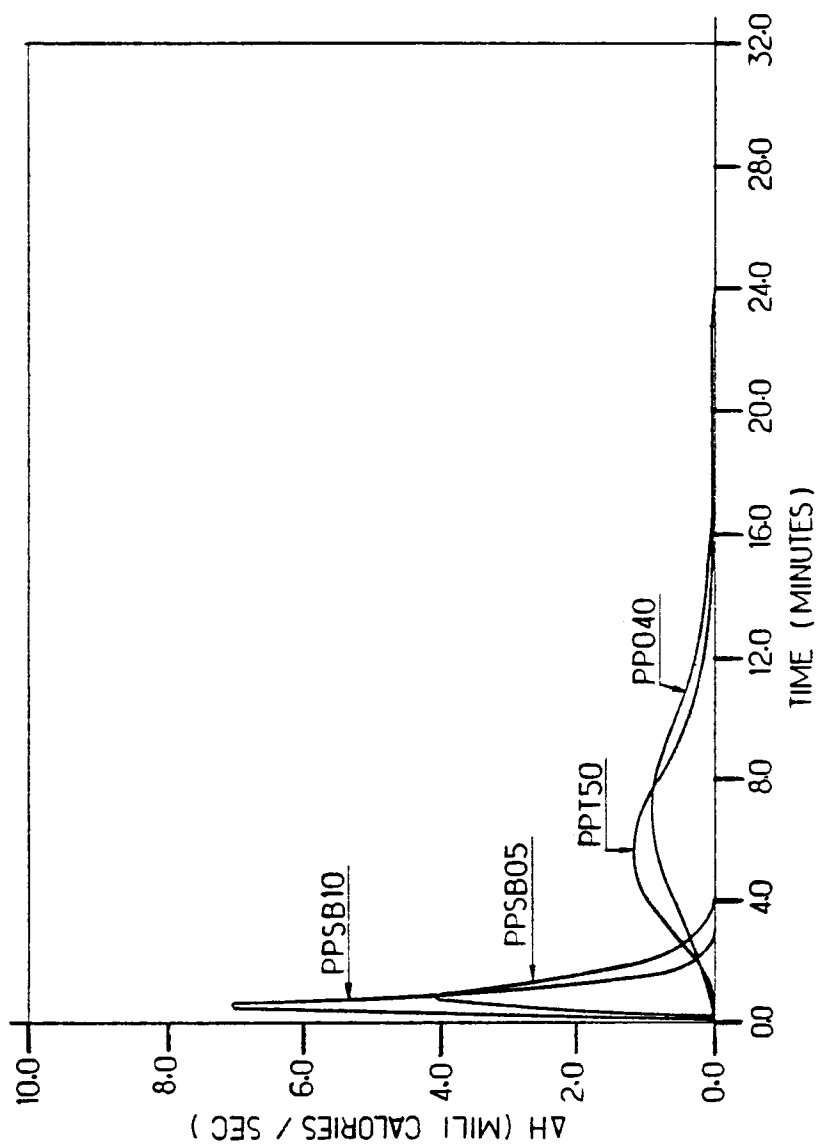


Figure VI-1 : DSC crystallization traces of control and nucleated polypropylenes at 124°C.

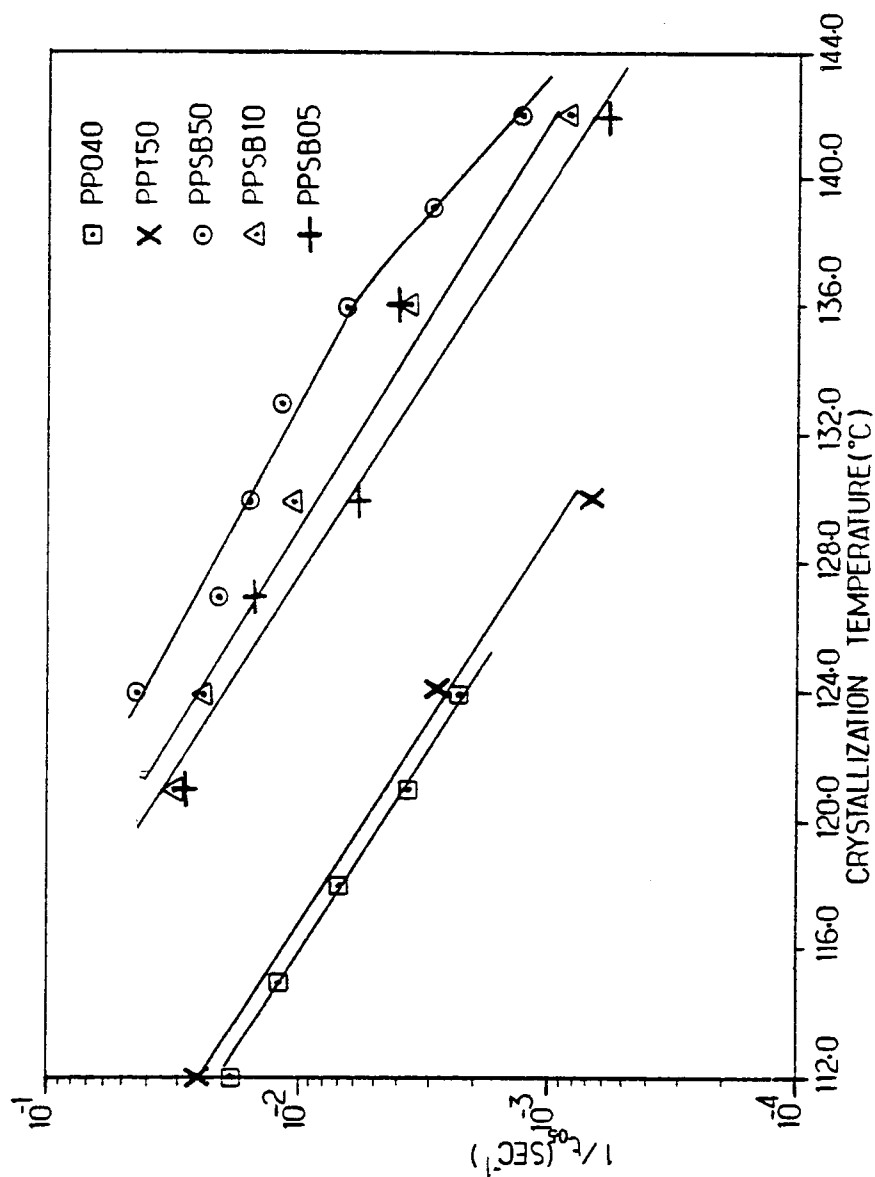


Figure VI-2 : Reciprocal crystallization half times versus isothermal crystallization temperature results for control and nucleated polypropylenes.

agent, sodium benzoate, on the crystallization rates. The addition of 0.5% sodium benzoate is only slightly more effective than 0.05% sodium benzoate.

2. Interpretation of Results

a. Avrami analysis. The kinetic data were analyzed by means of the Avrami equation (22,78). Typical Avrami plots ($\text{Log-ln} (1 - \frac{X}{X_f})$ vs. time)) obtained by DSC for PP040 and PPSB50 are shown in Figures VI-3 and VI-4. The crystallization temperature and the corresponding slope values, n , for these and other experimental polymers are listed in Table VI-1. These slopes were determined over the range of $X = 0.1-0.87$, to avoid difficulties associated with errors in the small enthalpy variations during the early stages of crystallization and the truncation and secondary crystallization effects near the end of crystallization. Table VI-1 shows that there is no systematic variation in the Avrami n with crystallization temperature and it is approximately equal to the integer 3 for all types of samples. The Avrami index $n = 3$ can be interpreted to be a result of heterogeneous, predetermined nucleation with 3-dimensional growth and constant growth rate. Similar findings and interpretations on polypropylenes have been reported by several investigators (168,110,104,112,80,111).

b. Nucleation density. The Avrami index $n = 3$ means that the nucleation density quickly reaches a constant value. The time

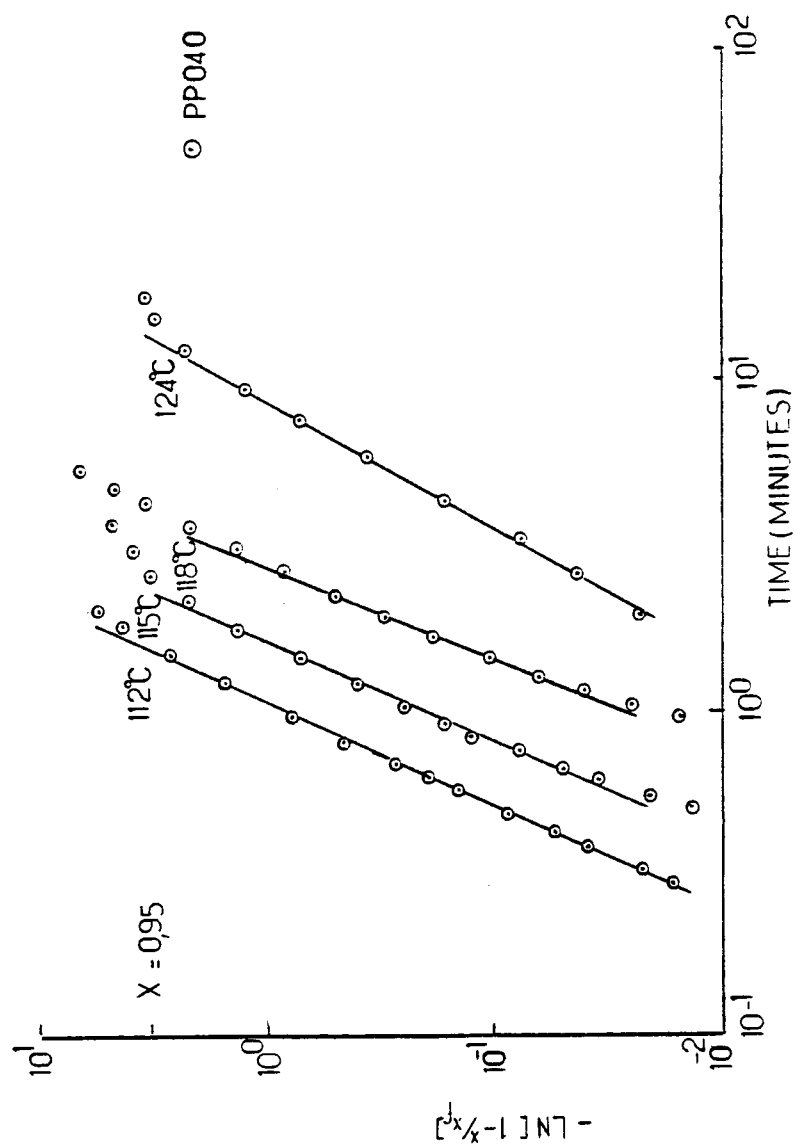


Figure VI-3 : Avrami plot for PP040 at different crystallization temperatures.

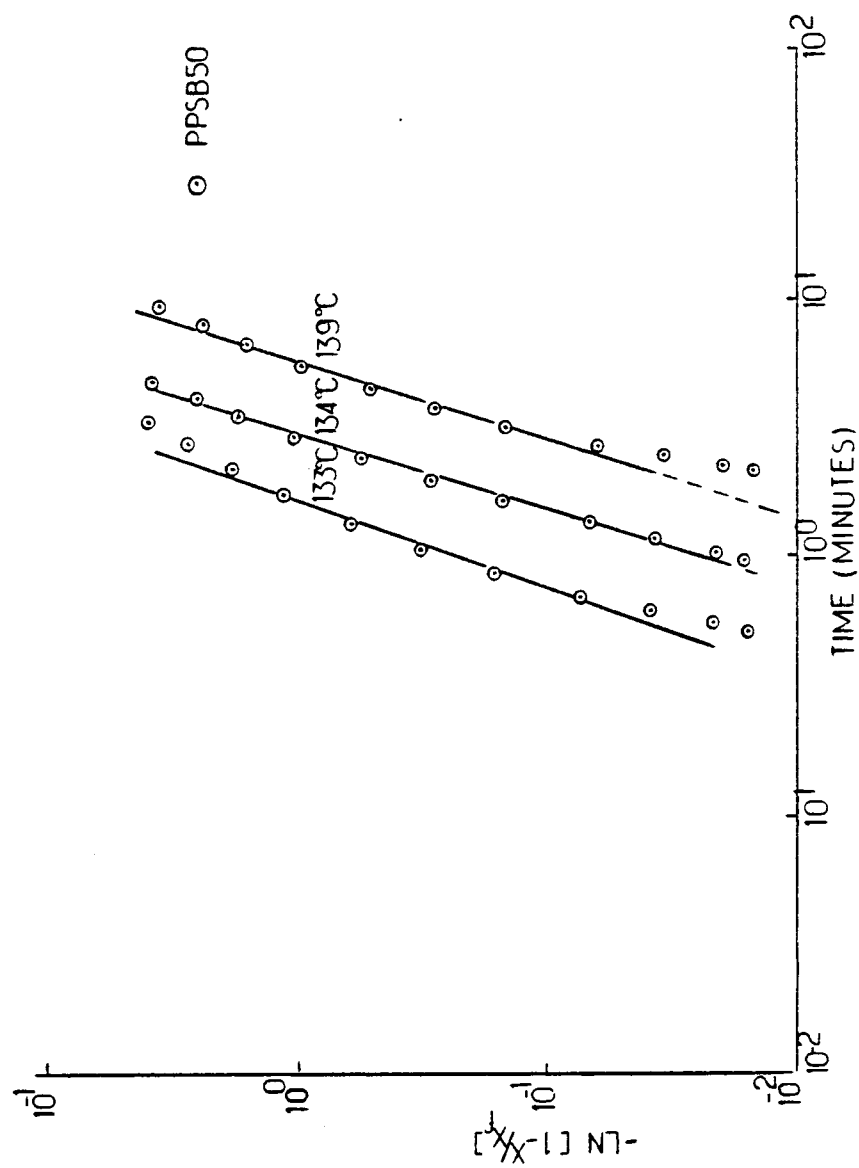


Figure VI-4 : Avrami plot for PPSB50 at different crystallization temperatures.

TABLE VI-1

VALUES FOR AVRAMI INDEX, n FOR NUCLEATED AND CONTROL PP
AT DIFFERENT CRYSTALLIZATION TEMPERATURES

Sample	Cryst. Temp ($^{\circ}\text{C}$)	Avrami n
Control PP040	112	3.22
	115	3.25
	118	3.25
	121	2.93
	124	2.60
PPT50	112	2.61
	124	3.00
	130	2.96
PPSB50	127	2.98
	130	2.88
	133	2.67
	136	3.25
	139	3.25
	142	2.67
PPSB10	124	3.05
	130	2.82
	136	2.54
	142	3.16

required to reach this constant value, t_i , is small compared to the crystallization half times, $t_{0.5}$. The constant nucleation density, n_0 , as a function of temperature for a given polymer sample can be calculated at $t = t_{0.5}$ according to the equation,

$$n_0 = \frac{3}{4\pi} \frac{K}{G^3} \quad (\text{VI-1})$$

where G is the constant growth rate, K the Avrami rate constant at $t = t_{0.5}$ calculated with $n = 3$.

Table VI-2 shows the n_0 results for the control and nucleated polypropylenes calculated with the growth rate data from Binsbergen et al. and Ishizuka et al. (34,111). The effect of nucleating agent, sodium benzoate, on n_0 is shown clearly in Table VI-2. These nucleated samples show about four orders of magnitude higher nucleation density compared to the control and talc nucleated samples. The value of n_0 for the control and talc nucleated polypropylenes decrease with increasing crystallization temperature. Both K and $\dot{G}$ values used in the n_0 calculations are extremely small, and small errors could lead to large effects on n_0 . However, the values of n_0 appear to be almost independent of temperature in the range investigated for the sodium benzoate nucleated samples.

The effect of the amount of the nucleating agent on the number of growth centers (n_0) is shown in Figure VI-5. These results indicate an increase in the nucleation density with increasing amount of nucleating agent. The heterogeneous nucleation theory (Eq. III-32) predicts a

TABLE VI-2

NUCLEATION DENSITY RESULTS FOR BOTH NUCLEATED AND CONTROL PP
AT DIFFERENT CRYSTALLIZATION TEMPERATURES

Sample	Temp. (°C)	K (sec ⁻³)	G ³ (*) cm ³ /sec ³	n ₀ (1/cm ³)
PP040	112	4.4 x 10 ⁻⁶	1 x 10 ⁻¹¹	1.0 x 10 ⁵
	115	1.2 x 10 ⁻⁶	4 x 10 ⁻¹²	6.8 x 10 ⁴
	118	2.2 x 10 ⁻⁷	8 x 10 ⁻¹³	6.3 x 10 ⁴
	121	3.1 x 10 ⁻⁸	5.1 x 10 ⁻¹³	1.3 x 10 ⁴
	124	8.0 x 10 ⁻⁹	8 x 10 ⁻¹⁴	2.4 x 10 ⁴
PPSR50	127	5.9 x 10 ⁻⁶	5.9 x 10 ⁻¹⁵	2.4 x 10 ⁸
	130	2.5 x 10 ⁻⁶	6.6 x 10 ⁻¹⁶	9.1 x 10 ⁸
	133	1.1 x 10 ⁻⁶	2.7 x 10 ⁻¹⁶	9.7 x 10 ⁸
	136	1.8 x 10 ⁻⁷	3.6 x 10 ⁻¹⁷	1.2 x 10 ⁹
	139	1.7 x 10 ⁻⁸	4.8 x 10 ⁻¹⁸	8.5 x 10 ⁸
	142	1.5 x 10 ⁻⁹	6.4 x 10 ⁻¹⁹	5.6 x 10 ⁸
PPSR10	124	8.7 x 10 ⁻⁶	8 x 10 ⁻¹⁴	2.6 x 10 ⁷
	130	7.1 x 10 ⁻⁷	6.6 x 10 ⁻¹⁶	2.6 x 10 ⁸
	136	2.9 x 10 ⁻⁸	3.6 x 10 ⁻¹⁷	2.0 x 10 ⁸
	142	3.7 x 10 ⁻¹⁰	6.4 x 10 ⁻¹⁹	1.5 x 10 ⁸
PPT50	112	1.2 x 10 ⁻⁵	1 x 10 ⁻¹¹	2.8 x 10 ⁵
	124	1.3 x 10 ⁻⁸	8 x 10 ⁻¹⁴	3.9 x 10 ⁴
	130	2.0 x 10 ⁻¹⁰	6.6 x 10 ⁻¹⁶	2.5 x 10 ⁴
PPSR05	121	1.7 x 10 ⁻⁵		6.9 x 10 ⁶
	127	2.2 x 10 ⁻⁶	5.9 x 10 ⁻¹⁵	9.1 x 10 ⁷
	130	1.3 x 10 ⁻⁷	6.6 x 10 ⁻¹⁶	4.7 x 10 ⁷
	136	3.1 x 10 ⁻⁸	3.6 x 10 ⁻¹⁷	2.1 x 10 ⁸
	142	1.0 x 10 ⁻¹⁰	6.4 x 10 ⁻¹⁹	3.9 x 10 ⁷

(*) G³ results from Binsbergen (34) for 127-142°C temperature range,
from Ishizuka (111) for 109-124°C range.

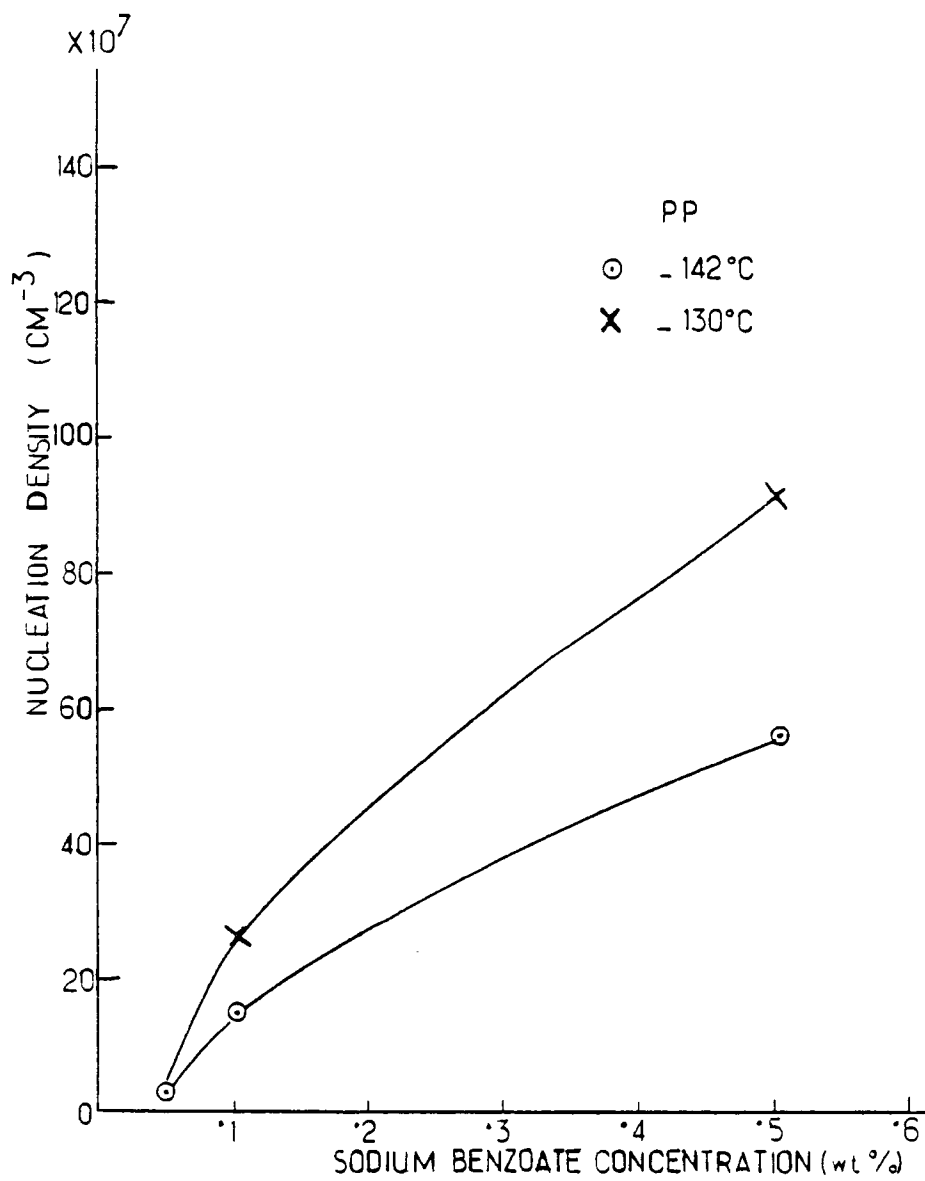


Figure VI-5 : Nucleation density versus sodium benzoate concentration in PP040.

linear relationship between the amount of nucleating agent and the nucleation rate. In the present case the limited data with different nucleating agent concentrations (.05-.5 wt %) seems to indicate a nonlinear relation between the nucleation density and the nucleating agent concentration.

c. Nucleation rates. Figure VI-6, similar to Figure V-34, p. 129, is a plot of $\ln 1/t_i$ vs. $T_m^{02}/T\Delta T^2$ for nucleated and control polypropylenes. The selection of equilibrium melting temperature (T_m^0) is important as it affects not only the slope but also the goodness of fit (160). Values of T_m^0 for PP are given in the literature (47,141) ranging from 174°C to 184°C. Ishizuka and Koyama (111) used $T_m^0 = 184^\circ\text{C}$. Recent work of Krigbaum et al. (141) supports this high T_m^0 value in PP. The calculations presented in Figure VI-5 are based on $T_m^0 = 184^\circ\text{C}$. This figure shows a linear relationship according to Eq. V-5, p. 128. Use of other T_m^0 values resulted in different slopes with no clear choice for the goodness of fit. Figure VI-6 shows that at any given undercooling, the $1/t_i$ in the talc nucleated PP is slightly higher than that for the control sample but considerably lower than the $1/t_i$ for the sodium benzoate nucleated samples. Figure VI-6 also indicates nonlinear, increasing effect of the concentration of sodium benzoate on $1/t_i$.

Table VI-3 shows the slopes and intercepts for all the control and nucleated polypropylenes from Figure VI-6 and also from Figure V-33, p. 127. The slopes and intercepts of these curves are described by

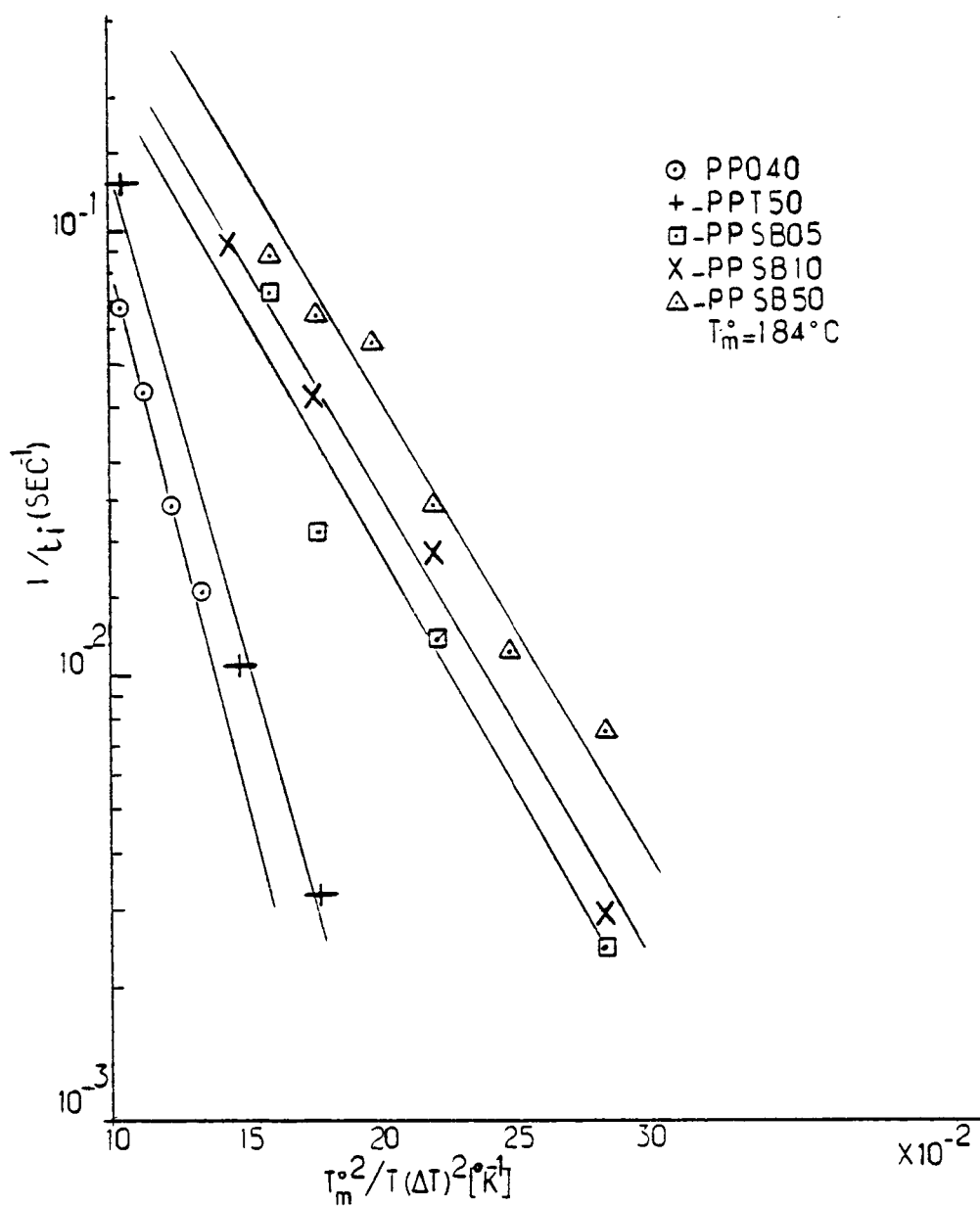


Figure VI-6 : Reciprocal induction time versus $T_m^{02}/T(\Delta T)^2$ for control and nucleated propylenes.

TABLE VI-3

CALCULATED INTERFACIAL ENERGY PARAMETERS FOR CONTROL AND
NUCLEATED PP UNDER QUIESCENT CONDITIONS

Sample	Slope $B/\Delta H^2$	Intercept A'	$\gamma\gamma_e\Delta\gamma$ erg^5/cm	$\Delta\gamma = \gamma + \gamma_{OS} - \gamma_S$ erg/cm^2	$\gamma_{OS} - \gamma_S$ Assume $\gamma = 12.1$ erg/cm^2
PP025	56.0	3.1	4273	6.0	6.1
PP120	56.0	3.1	4273	6.0	6.1
PP040	55.5	3.1	4235	5.9	6.2
PPT50	55.5	3.4	4235	5.9	6.2
PPSB50	23.8	1.6	1816	2.5	9.6
PPSB10	23.8	1.1	1816	2.5	9.6
PPSB05	23.8	0.8	1816	2.5	9.6

$$\text{Slope } \frac{B}{\Delta H^2} = \frac{16\gamma\gamma_e\Delta\gamma}{2.303 k \Delta H^2}$$

$$A' = \ln S^* n_S N_S v_0 - \frac{\Delta F_i^*}{kT}$$

$$\gamma\gamma_e = 714 \text{ erg}^2/\text{cm}^4 \text{ and } \gamma = 12.1 \text{ erg}/\text{cm}^2 \text{ (39)}$$

$$\Delta H = 1.96 \times 10^9 \text{ erg}/\text{cm}^2$$

$$K = 1.38 \times 10^{-16} \text{ erg}/^\circ\text{K}$$

Eqs. III-38 and III-39, p. 59, respectively. Also shown in this table are the interfacial energy parameters. The value of $\Delta\gamma$ was obtained by dividing $\gamma\gamma_e\Delta\gamma$ with a literature value of $\gamma\gamma_e$ (30). The quantity $\gamma_{OS} - \gamma_S$ in Table VI-3 is a measure of the nucleating ability of the nucleating agents. A higher value of $\gamma_{OS} - \gamma_S$ indicates a better heterogeneous nucleating agent since, relative to the melt, less energy is expended in creating a unit area of substrate-crystal interface (41). Table VI-3 shows that the adventitious nucleant in the control and the nucleant in the talc containing samples have practically the same nucleating ability while the sodium benzoate addition produces a much greater nucleating ability which results in higher nucleation rates at any given undercooling. Table VI-3 also shows that the increase in the amount of nucleating agent (sodium benzoate) increases its intercept value as more and more surface area (S^*) becomes available for the formation of nucleus. This results in higher nucleation rates for samples with higher nucleating agent concentration. However, this effect is nonlinear in concentration, as shown in Figure VI-6. The intercept value is lower for nucleated samples compared to the nonnucleated samples. This perhaps is due to the greater increase in $-\Delta F_i^*$ term (see Eq. III-33, p. 58) due to generally higher crystallization temperature range compared to the nonexponential increase in s^* due to the additional nucleating surface.

3. Discussion

There are several problems in the evaluation of kinetics of crystallization according to the Avrami equation. The Avrami plots

do not describe the entire crystallization process. Even if the data are well preserved over the major portion of the crystallization process, no account is taken of the secondary crystallization, which can cause deviations from the theory. Besides this, there are problems associated with the experimental difficulties such as nonuniform thermal history of the sample, uncertainty about the starting time of crystallization, etc. In spite of all these problems, Avrami analysis is still useful, particularly in comparing the crystallization rates of different samples.

Figure VI-7 shows the rate constant (K) data of the present research as well as the data from the literature on PP (compiled by Ishizuka and Koyama (111)) as a function of $T_m^0/T\Delta T$. This figure indicates that rate constants for control polypropylenes and the talc nucleated polypropylene of the present research have similar temperature dependency but are lower compared to the rate constants for commercial polypropylenes in the literature. It is also important to note that the slopes of the plot in Figure VI-7 for the present and literature samples are approximately the same but the intercept values are lower for the present samples. This may be because the results from the literature are about 20 years old and the commercial polypropylenes manufactured now may be cleaner with less residual heterogeneities, hence lower rate constants. The sodium benzoate nucleated samples shown in this figure have much higher rate constants compared to both the literature and the present study control samples.

In analyzing the quiescent crystallization data we have used two different approaches. In one case we calculated the nucleation

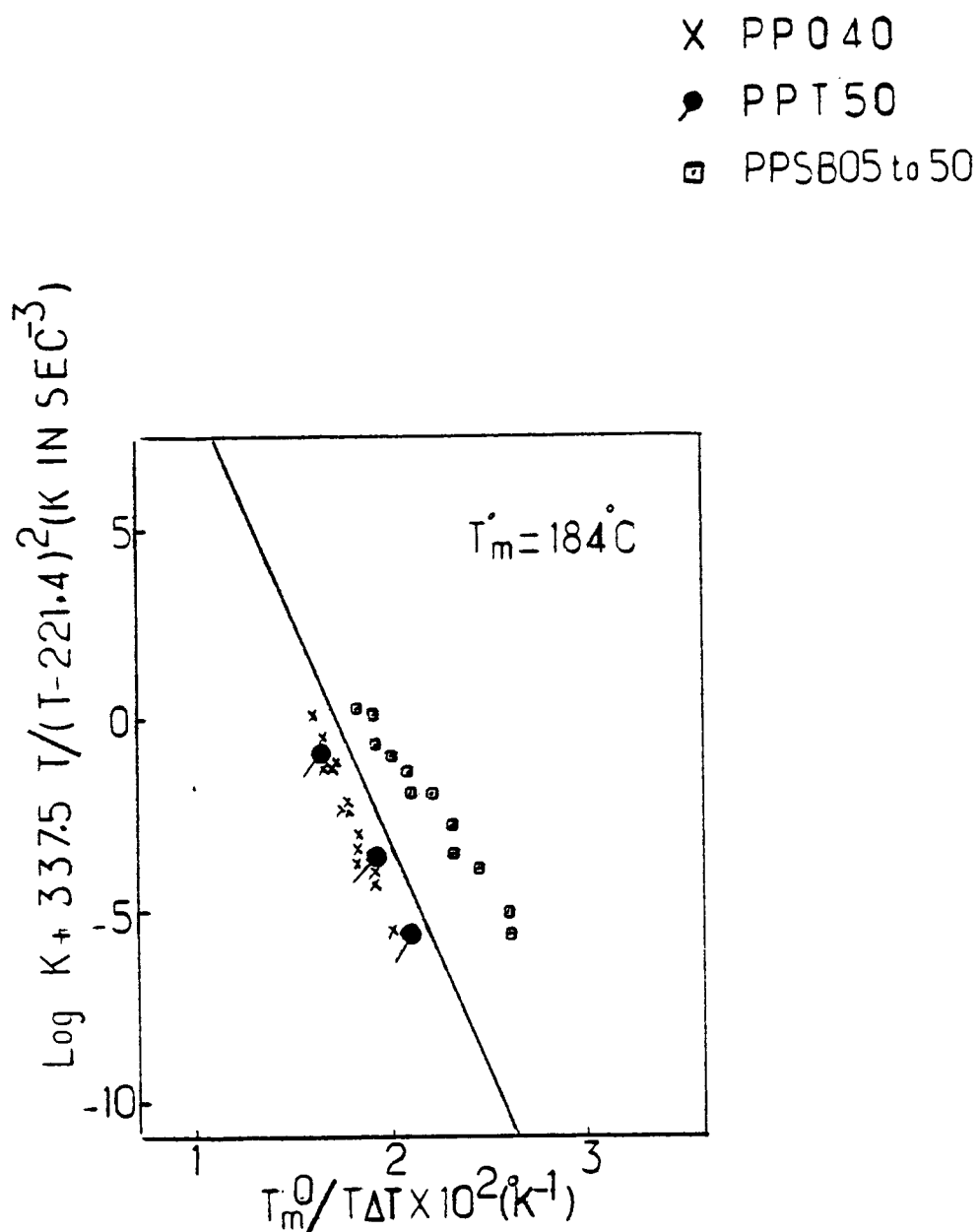


Figure VI-7 : Comparison of Avrami constant, K, results from the present studies with those compiled by Ishizuka et al. (111).

density (n_0) by assuming that the nucleation rate quickly becomes zero. In the second case, the results were analyzed using the nucleation rate equation. It is very important to clarify the differences between these two approaches. The assumption that nucleation rate quickly becomes zero means that the time t_S is much lower than $t_{0.5}$ (see Figure VI-8). It is possible to calculate n_0 at any point during crystallization by using the proper time and the corresponding K . However, by selecting $t_{0.5}$ (with $K = K_{0.5}$) we are certain that $dn/dt = 0$. In the second approach, the nucleation rate expression was used in the very early parts of the crystallization ($t \leq t_S$) where the nucleation rate is not equal to zero.

Within the limited number of nucleating agent concentrations studied, a nonlinear increase of the nucleation density with increasing nucleating agent concentration was observed. Similar results were reported by Binsbergen et al. (34) and Beck and Ledbetter (25).

B. STRESS-INDUCED CRYSTALLIZATION STUDIES

1. Results

The general stress response of nucleated samples in shear flow is similar to the stress response shown in Chapter V for the control samples. The measurements and interpretations of the induction times described earlier for control samples are applicable for the nucleated samples.

The range of shear rates experimentally accessible in the nucleated samples is less ($\dot{\gamma}_{\max} \leq 1.6 \text{ sec}^{-1}$) compared to the control

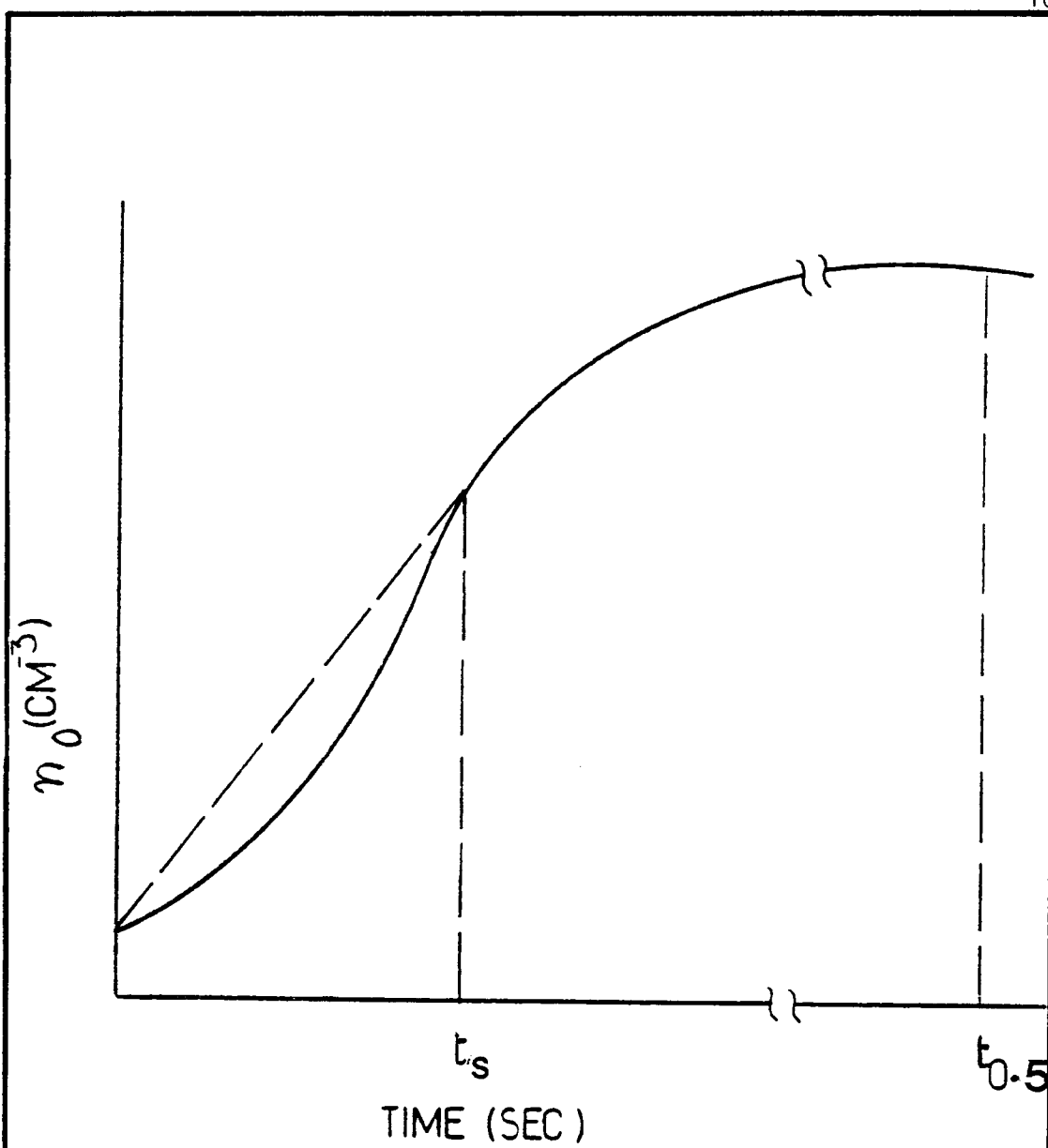


Figure VI-8 : Qualitative curve showing nucleating density versus time.

samples ($\dot{\gamma}_{\max} \leq 16.0 \text{ sec}^{-1}$). The accessible range of crystallization temperatures for sodium benzoate nucleated samples is high (142.5-152.5°C) compared to the control (121.0-138.5°C). This difference in the crystallization temperature makes direct comparison between the control and nucleated SIC results difficult. Figure VI-9 shows the reciprocal induction times versus shear stress for the control at 128.5°C and sodium benzoate nucleated PP at 146.5°C. This figure shows that at any given stress the $1/t_i$ in PPSB50 and PPSB05 are high (even at a crystallization temperature 20°C higher) compared to the control sample. PPSB50 with 0.5 wt % of sodium benzoate nucleating agent shows an order of magnitude higher $1/t_i$ compared to PPSB05 with 0.05 wt % of nucleating agent.

An effective comparison of quiescent and stress induced crystallization kinetics of nucleated and control samples is shown in Figure VI-10 where the $1/t_i$ are plotted as a function of crystallization temperature. The stress induced crystallization results shown in Figure VI-10 correspond to a relatively low shear rate of 0.1 sec^{-1} . This figure shows that the quiescent nucleation rates in the control and talc nucleated polypropylenes are similar but are significantly lower than the quiescent results for sodium benzoate nucleated (0.5 wt %) polypropylene. The stress crystallized control samples show a small but noticeable influence of shear on $1/t_i$. The influence of shear appears to be strongly temperature dependent. At the highest accessible crystallization temperatures the nucleation rates for the sheared control samples appear to be an extension of the quiescent results at the modest shear rate presented

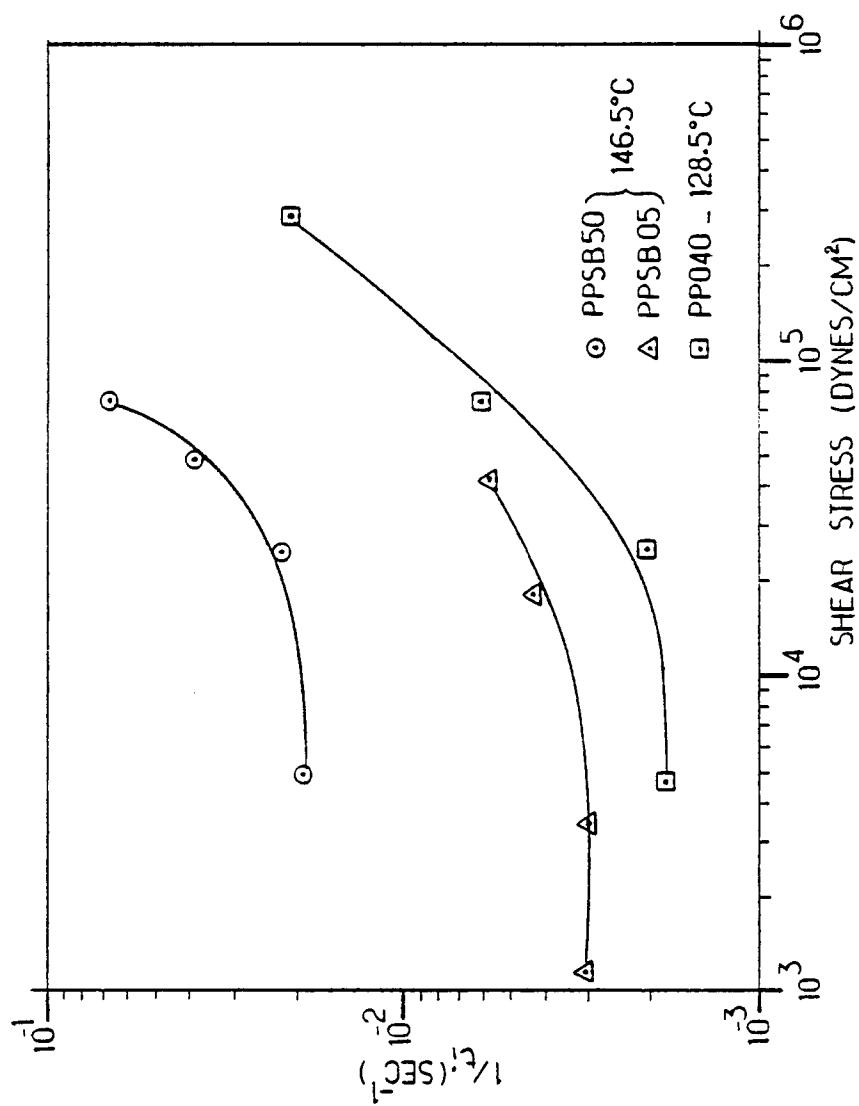


Figure VI-9 : Reciprocal induction time versus shear stress for control and nucleated polypropylenes at 128.5°C and 146.5°C.

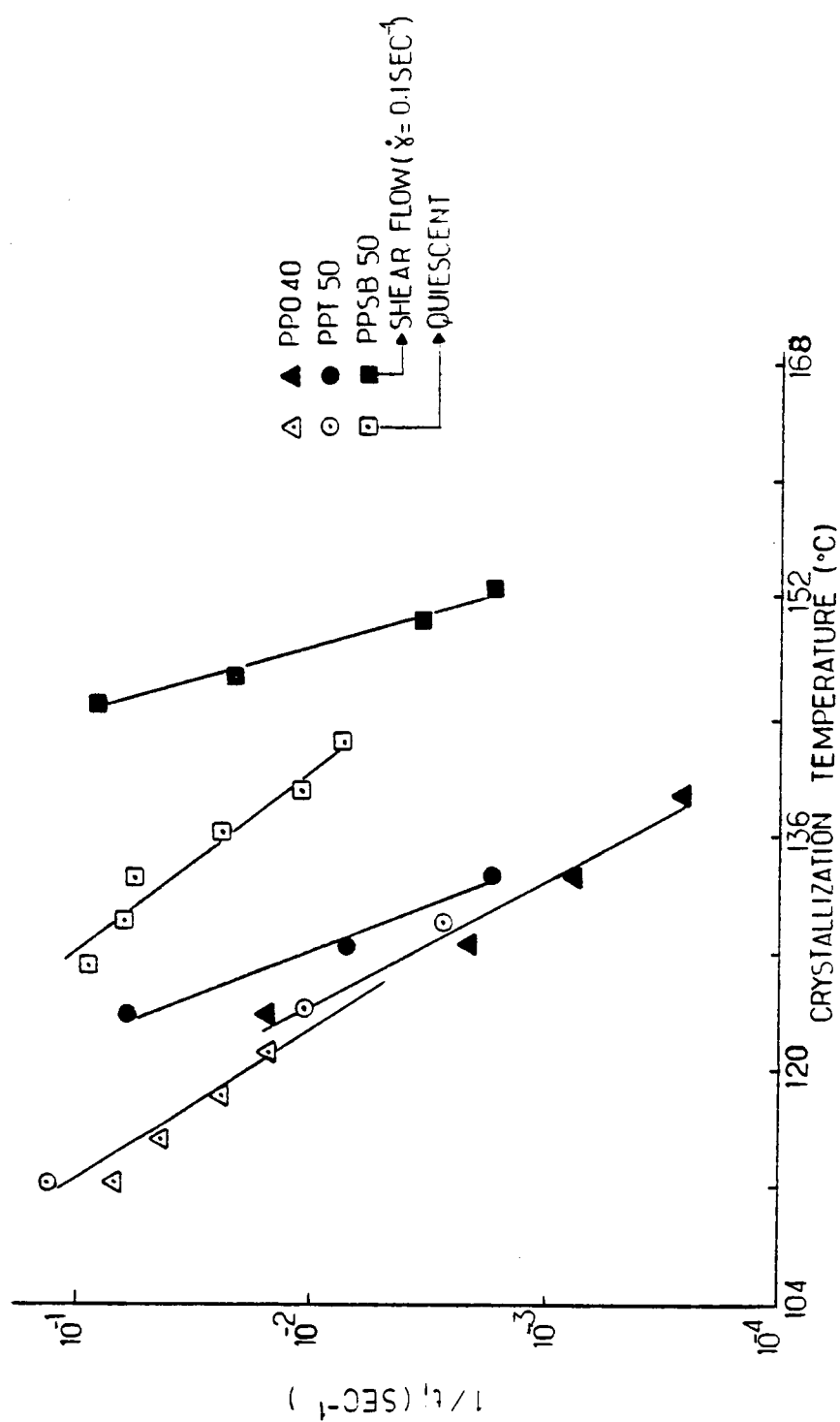


Figure VI-10 : Comparison of plots of quiescent and stress induced reciprocal induction times versus isothermal crystallization temperature for both control and nucleated polypropylenes.

in Figure VI-10. However, talc and sodium benzoate nucleated polypropylenes showed significant stress enhancement effect on $1/t_i$ at any given crystallization temperature in the accessible range. Note, however, that the temperature dependence for these sheared samples is clearly greater than for the quiescent samples.

a. Further analysis of reciprocal induction time results.

It is of interest to see how the predicted values (as per the procedure developed in Chapter V) of nucleation rates ($1/t_i$) compare with the experimental results. Figure VI-11 shows such comparison, where the drawn curves are predicted values and the points are the experimental measurements. The predicted values are from Eq. V-5, p. 128, with $\frac{B}{\Delta H^2}$ and A' values from the quiescent results given in Table VI-3. Like in the earlier chapter, the predicted values with the constant $a_{11} = 50$ fits the data for control (PP040) sample. However, for the sodium benzoate nucleated PP, the predicted values are much lower than the experimental results. The probable reason for this is the use of A' from the quiescent results. For a nucleated sample under flow, the A' can be much higher than for the quiescent case. This is because of the nucleating agents in motion offer a larger effective nucleating surface area which could depend on the concentration of the nucleating agent. The A' used in $1/t_i$ calculations is proportional to the nucleating surface area (S^*). Accepting these arguments and making A' as an adjustable parameter, the experimental results in Figure VI-11 can be curve fitted. Figure VI-12 shows such results where the predicted values fit the

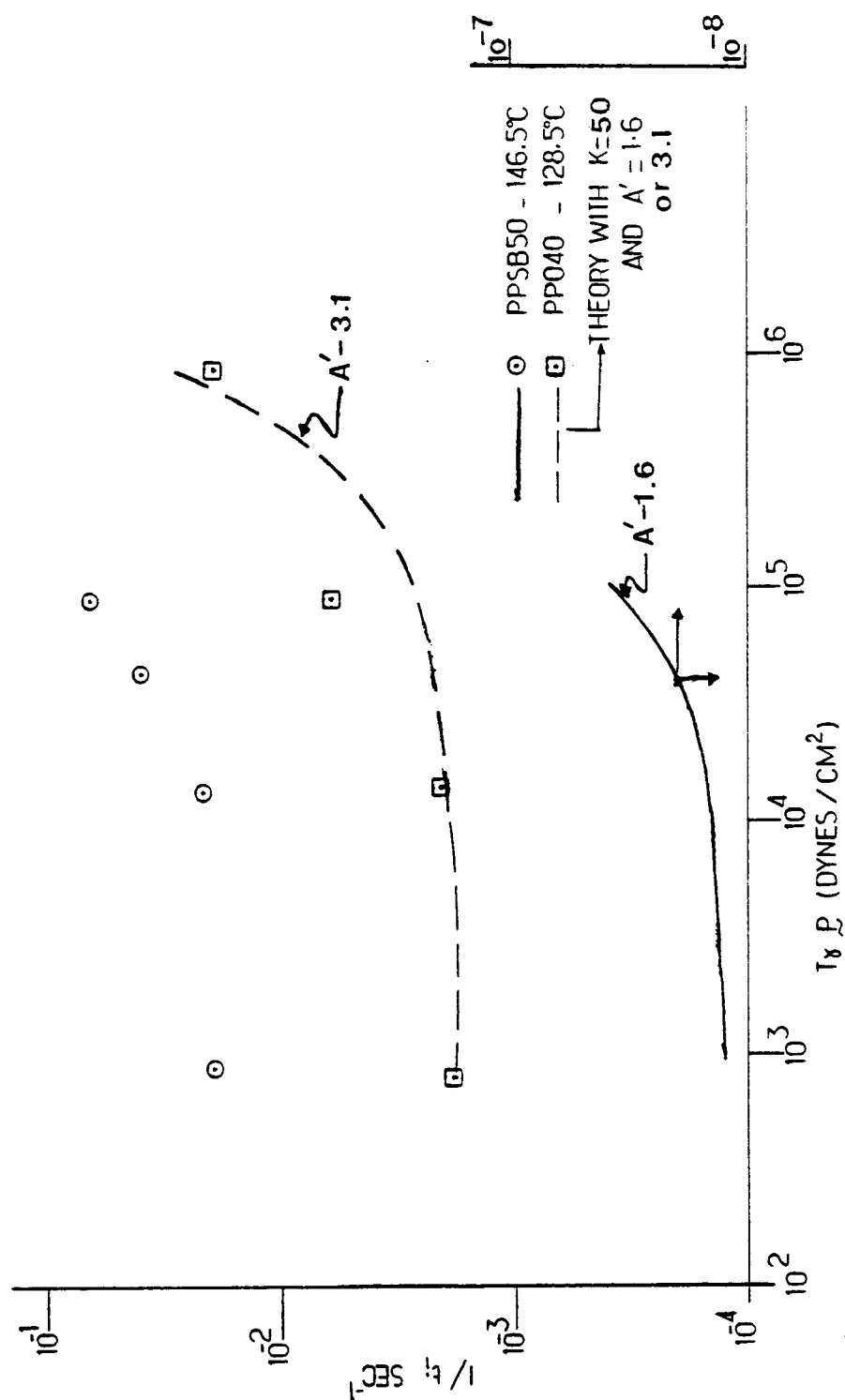


Figure VI-11 : Comparison of calculated and experimental reciprocal induction times (nucleation rates) as a function of γ_s for PP040 at 128.5°C and for PPSB50 at 146.5°C.

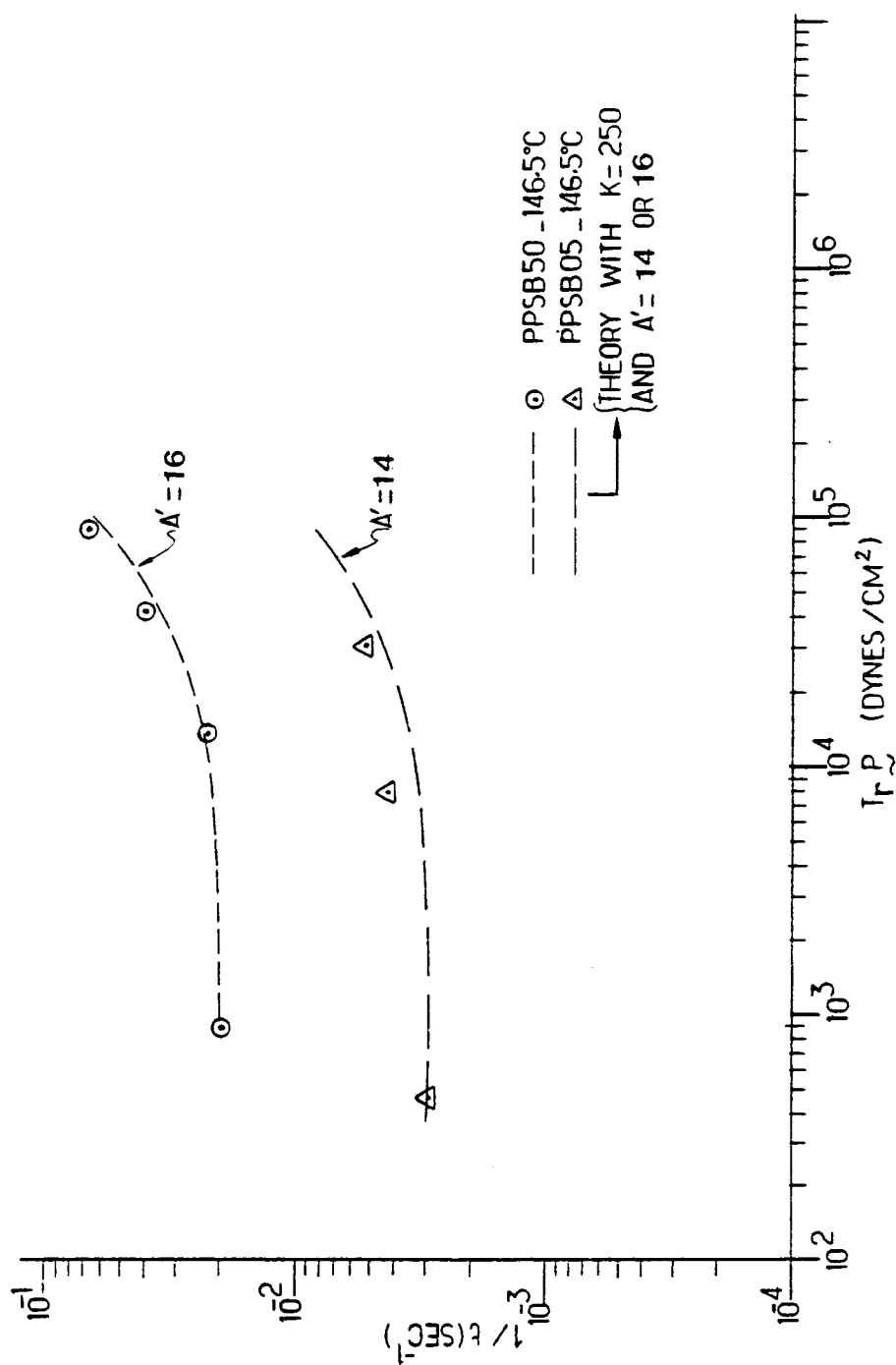


Figure VI-12 : Comparison of calculated (adjusted) and experimental reciprocal induction times (nucleation rates) as a function of γ_s for PP040 at 128.5°C and for PPSB50 at 146.5°C .

experimental results with $a_{11} = 50$, $A' = 16$ for PPSB50 and $a_{11} = 50$, $A' = 14$ for PPSB05.

The value of the above analysis for nucleated samples is reduced due to the fact that adjustments have to be made (2 parameters) each time the concentration of the nucleating agent or type of polymer or possibly mode of deformation is changed. However, this two adjustable parameter equation is consistent and can be justified from the arguments of classical nucleation theories. Clearly, this analysis is questionable at best. Considerably more experimental data is needed to sort out the details of the behavior of nucleated samples subjected to deformation.

2. Discussion

In the open literature quiescent crystallization studies of nucleated polypropylenes are very limited and the detailed studies involving the stress induced crystallization of nucleated samples are nonexistent.

Figure VI-9, p. 164, showed that at any given reciprocal induction time addition of sodium benzoate increases the phase transformation temperature by about 15°C while subjecting the same sample to stress further increases this temperature by 7-19°C depending on the temperature at which the sample is being stressed. Although addition of talc (0.5 wt %) to polypropylene showed very little effect on the crystallization temperature, subjecting it to stress field raised this phase transformation temperature by 3-9°C depending on temperature of crystallization under shear flow. Thus stress (or strain) is even more

effective in enhancing the nucleation rates of nucleated samples than it is for samples that do not contain nucleating agents. 0.5 wt % sodium benzoate nucleating agent under 0.1 sec^{-1} shear rate increased the crystallization temperature in PP040 to a maximum value of 44°C .

Two possible explanations for the high stress enhancement effect on the nucleation rates for nucleated samples include: (1) stress concentration effects of the nucleating agents (82,105,211); and (2) increase in the specific activity of the nucleating agent as it moves in the polymer melt subjected to deformation. The motion of the nucleating particle may increase its effective area available for nucleation and promote better epitaxial relationship with the partially oriented melt.

For the case where the additives levels of talc and sodium benzoate are the same at 0.5 wt %, the nucleation rates for sodium benzoate containing PP is much higher. Since average particle size of both these nucleants are similar (10-15 μm), the stress concentration effects should be similar for the PP containing these nucleating agents. This suggests that the difference in nucleation rates between PPSB50 and PPT50 is mainly due to the differences in their nucleating abilities. The local stress concentration effects of the talc particles ($\sim$ factor of 3) may be adequate to account for the weak enhancement of nucleation rate during shearing in PPT50.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

1. Nucleated and Nonnucleated Quiescent Crystallization

a. Nonnucleated isothermal quiescent crystallization results from the present studies showed lower $1/t_{0.5}$ and K values than comparable literature results (80,168,111). These differences are reasonable considering differences in heterogeneities such as catalyst residues (present day polymers are much cleaner compared to 20 years ago), molecular weights and weight distributions, the degree of tacticity and other variables.

b. Quiescent crystallization results showed minor differences in the crystallization behavior between the control polypropylenes due to the differences in the heterogeneities or due to the differences in their molecular weight and molecular weight distribution. Crystallization rates in PE showed a much stronger temperature dependency compared to PP. All the results indicated a decrease in crystallization rates with increases in crystallization temperature.

c. Addition of 0.5 wt % of sodium benzoate nucleating agent enhanced the crystallization rates ($1/t_{0.5}$) by about 1.5 orders of magnitude over the control PP. Another way of looking at this is that at constant crystallization rate ($1/t_{0.5}$) PPSB50 crystallizes at about 20°C higher than the control. The talc nucleated sample, PPT50,

has crystallization rates slightly higher than the control. There is also a nonlinear effect of amount of nucleating agent, sodium benzoate, on the crystallization rates. As nucleating agent concentration is increased its effectiveness tends to saturate. The nucleation density, n_0 , calculations with literature $\bar{G}^3$ data) also showed 4 orders of magnitude higher n_0 for sodium benzoate nucleated samples compared to talc nucleated and control PP.

d. Avrami analysis of the quiescent kinetic data resulted in an approximate Avrami index, n , of 3 for both control and nucleated PP over the accessible isothermal crystallization temperature range. This $n = 3$ can be interpreted to be a result of heterogeneous, pre-determined nucleation with 3-dimensional constant growth rate. Similar findings and interpretation on PP were reported by several investigators (38,80,111).

e. As expected from the classical nucleation theories, $\ln 1/t_i$ ($1/t_i$ interpreted as nucleation rate) vs. $T_m^{02}/T\Delta T^2$ plots showed a linear relationship for both control and nucleated polypropylenes for the results obtained under quiescent conditions.

The conclusions on the effectiveness of nucleating agent were reconfirmed in this analysis according to heterogeneous nucleation theory. The slope of the straight line from the above plot is proportional to the product of interfacial energy parameters ($\gamma\gamma_e\Delta\gamma$) and the intercept is approximately proportional to the available nucleating surface area (S^*). The calculations of $\Delta\gamma$ (interpreted as a measure of nucleating ability of the nucleating agents) showed that the adventitious nucleant in the control and the nucleant in the talc

containing samples have practically the same nucleating ability, while the sodium benzoate addition produced a much greater nucleating ability which results in higher nucleation rates at any given under-cooling. The results also showed that the increase in the amount of nucleating agent (sodium benzoate) increases its intercept value as more and more surface area (S^*) becomes available for the formation of nuclei. This resulted in higher nucleation rates for samples with higher nucleating agent concentration.

2. Nucleated and Nonnucleated SIC

a. Analyses of rheological data (η and N_1) obtained during the stress induced crystallization studies resulted in the conclusion that PP120 has lower melt viscosity and broader molecular weight distribution (~ 8) compared to PP025 and PP040 (~ 4). These conclusions combined with dilute solution viscosity results have been successfully used in explaining sample effects on nucleation behavior during SIC studies.

b. The SIC results in control PP and PE ($1/t_i$ vs. $\dot{\gamma}$) showed an increase in the nucleation rate, $1/t_i$, with increasing $\dot{\gamma}$ in the accessible range of crystallization temperatures investigated. For a given shear rate, the nucleation rates decreased with increases in the isothermal crystallization temperature. Similar trends were reported in the literature (71,74). In control PP the difference between $1/t_i$ for quiescent samples and those crystallized under low shear rate ($\dot{\gamma} \leq 0.1 \text{ sec}^{-1}$) decreased with increases in crystallization

temperatures. However, in PE this difference remained high (1 order of magnitude) at $\dot{\gamma} = 0.01 \text{ sec}^{-1}$ and $T_{cr} = 123.5^\circ\text{C}$.

c. Nucleation rates in control PP when plotted against shear stress or tensile stress showed similar general trends. At low stresses the nucleation rates were close to the quiescent values. The effect of crystallization temperature was significant and clear at any given stress (higher crystallization temperature, lower nucleation rates). At higher stresses the differences in nucleation rates due to temperature differences are low perhaps due to the dominating effect of stress.

d. The shear flow results showed that the effect of sample on $1/t_i$ which was large at higher stresses decreased with decreasing shear stresses. PP with lower molecular weight and broader molecular weight distribution showed faster nucleation rates. Polypropylenes with approximately similar molecular weight distributions but different molecular weights showed much lower differences in their nucleation rates. This suggests that the high molecular weight tail in the broader distribution plays an important role in determining the kinetics of crystallization under shear. A second possible explanation for the sample effects could be the differences in the presence of adventitious species which could cause different nucleation and stress concentration effects.

e. Two different approaches were presented to interpret the nucleation rate results under shear and elongational flow. The first approach, which is an intuitive proposal, related the nucleation rates to a molecular orientation distribution which can be determined

by the state of the stress in the melt. In the second approach, expressions relating nucleation rates to ΔG_{def} were developed from theoretical considerations. These above approaches were tested by the experimental results.

Comparison of nucleation rates at a given temperature in PP under shear and elongational flow showed significant differences. However, the same results when plotted as a function of principal stress differences (or melt orientation) indicated a unique correlation between the nucleation rates and the difference of principal stresses or melt orientation independent of mode of deformation. Similar conclusions were obtained from the limited PE results.

Nucleation rates in PP and PE for a given crystallization temperature also correlated with the ΔG_{def} term (evaluated as a function of stress state in $\text{Tr}P_{\text{L}}$) independent of mode of deformation as per the nucleation theories.

Both the above approaches resulted in equally good correlation which probably is due to our inability in distinguishing between the experimental measurements of $\sigma_x - \sigma_y$ and the $\text{Tr}P_{\text{L}}$ as they both are related to N_1 .

f. Nucleation rates calculated from the classical theories with the use of quiescent crystallization results and Marrucci's analysis (to estimate ΔG_{def}) showed similar general shape and temperature sensitivity as the experimental results. However, the predicted values are much lower than the experimental values at any given ΔG_{def} . The reason for the under prediction in the nucleation rates is presumably because of the low ΔG_{def} values.

Comparison of estimates of ΔS_{def} ($\Delta G_{\text{def}} = T\Delta S_{\text{def}}$) by Marrucci, Krigbaum and Roe and Yeh and Hong analyses with experimental ΔS_{def} results showed that Yeh and Hong and Krigbaum and Roe's analyses greatly overpredict ΔS_{def} and hence $1/t_i$ results, while Marrucci's approach underpredicts ΔS_{def} and the corresponding $1/t_i$ values. Curve fitting of the experimental results showed that the constant a_{11} (in a simplified Jarecki and Ziabicki equation) is in the 50-80 range. This compares to $a_{11} = 0.5$ for Marrucci's analysis. The constant a_{11} appeared to be a function of the molecular weight distribution where it is high for broader molecular weight distribution samples which suggests that the high molecular weight ends play an important role in the development of enhanced nucleation rates.

g. In a nucleated sample, stress (or shear flow) increases the nucleation rates to a greater extent compared to the nonnucleated sheared sample. For similar particle sizes, the sodium benzoate nucleated PP showed greater increases in $1/t_i$ compared to talc nucleated PP. This is due to the better nucleating ability of the sodium benzoate. The local stress concentration effects of the talc particles may be adequate to account for the weak enhancement of nucleation rate during shearing in the talc nucleated sample.

Sodium benzoate nucleated PP samples under shear flow ($\dot{\gamma} = 0.1 \text{ sec}^{-1}$) showed an increase of 44°C in its maximum crystallization temperature compared to the control quiescent case.

h. For sodium benzoate nucleated PP, the predicted $1/t_i$ results (with previously determined constant, a_{11} , for the control PP) are much lower than the experimentally obtained values. The results can be curve fitted by adjusting the intercept value (A') in the nucleation rate equation. The probable need for this adjustment is due to the use of A' values from quiescent results which could be much lower. The nucleating agents in motion provide more effective surface area and hence higher A' .

B. RECOMMENDATIONS

1. Quiescent and SIC studies using well characterized polymer samples (molecular weights, molecular weight distributions, etc.) would be useful. Samples should be selected in a way to separate the effects of the molecular parameters on $1/t_i$.

2. More results need to be obtained both with nucleated and nonnucleated SIC experiments to further verify the theoretical predictions. Use of an optical system to independently follow the crystallization is essential, especially in elongational flow studies.

3. Nucleating agents seem to be very useful in increasing the maximum crystallization temperature. It would be of interest to establish in a nucleated sample the interaction between the structure, morphology and processing variables and their affect on the physical properties.

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APPENDICES

APPENDIX 1

COMPARISON OF MARRUCCI AND BKZ ANALYSES FOR ΔG_{def}

From Marrucci (170) type analysis:

$$\begin{aligned} S &= -\frac{1}{2T} \text{tr } \underline{P} \\ &= -\frac{1}{2T} (P_{11} + P_{22} + P_{33}) . \end{aligned}$$

BKZ proposal for conformational entropy, Σ , is,

$$\Sigma = \int_{-\infty}^t S dt' ,$$

where S = net rate of entropy production. One of the arbitrary choices for the S function is,

$$S = \frac{1}{2} \sum \frac{G_n}{\rho T} e^{-\frac{z}{\tau_n}} [I_{C-1} - 3]$$

where $z = t - t'$ in the elapsed time.

For simple shear flow case:

Kinematics

$$x_1 = x_1 - \dot{\gamma} x_2 z$$

$$x_2 = x_2$$

$$x_3 = x_3$$

and for model

$$P_{ij} = \frac{G}{\tau} \int_0^\infty e^{-\frac{z}{\tau}} (C_{ij}^{-1} - \delta_{ij}) dz$$

where

$$C_{ij}^{-1} - \delta_{ij} = \begin{vmatrix} \dot{\gamma}^2 z^2 & \dot{\gamma} z & 0 \\ \dot{\gamma} z & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

For Marrucci's analysis,

$$\begin{aligned} S &= -\frac{1}{2T} (P_{11} + P_{22} + P_{33}) \\ &= -\frac{G}{2T\tau} \left[\int_0^\infty e^{-\frac{z}{\tau}} \dot{\gamma}^2 z^2 dz \right] \end{aligned} \quad (A)$$

For BKZ Analysis:

$$\begin{aligned} I_{C-1}^{-3} &= \dot{\gamma}^2 z^2 \\ \Sigma &= \frac{G}{2\rho T} \int_0^\infty e^{-\frac{z}{\tau}} \dot{\gamma}^2 z^2 dz \end{aligned} \quad (B)$$

Equations A and B are the same.

For uniaxial extension:

Kinematics:

$$x_1 = x_1 \exp[\dot{\gamma} z]$$

$$x_2 = x_2 \exp -[\dot{\gamma} z/2]$$

$$x_3 = x_3 \exp -[\dot{\gamma} z/2]$$

$$(C_{ij} - \delta_{ij}) = \begin{vmatrix} e^{2\dot{\gamma}z} & 0 & 0 \\ 0 & e^{-\dot{\gamma}z} & 0 \\ 0 & 0 & e^{-\dot{\gamma}z} \end{vmatrix}$$

For models

$$\sigma_{ij} = -p\delta_{ij} + \frac{G}{\tau} \int_0^\infty e^{-\frac{z}{\tau}} C_{ij}^{-1} dz .$$

For Marrucci analysis:

$$S = -\frac{G}{2T\tau} \left[\int_0^\infty e^{-\frac{z}{\tau}} (e^{2\dot{\gamma}z} + 2e^{-\dot{\gamma}z}) \right] \quad (C)$$

For BKZ

$$I_{C-1} - 3 = e^{2\dot{\gamma}z} + 2e^{-\dot{\gamma}z} - 3$$

and

$$\Sigma = \frac{G}{2\rho T\tau} \int_0^\infty e^{-\frac{z}{\tau}} (e^{2\dot{\gamma}z} + 2e^{-\dot{\gamma}z} - 3) dz . \quad (D)$$

Equations C and D are the same.

APPENDIX 2

ESTIMATES OF MOLECULAR WEIGHT DISTRIBUTION

Molecular weight distributions for the present experimental polypropylenes were estimated using η/η_0 vs. $\eta_0\dot{\gamma}$ and N_1 vs. σ_{12} correlations. In the literature (176) such correlations have been presented for samples with known $\bar{M}_w/\bar{M}_n$ values. Recently Yamane et al.* successfully used such literature results to estimate $\bar{M}_w/\bar{M}_n$. Following we present the original results of Minoshima et al. (176). Comparison of components A and b and η/η_0 from the present experimental studies with mainly Minoshima et al. give $\bar{M}_w/\bar{M}_n \sim 8.0$ for PP120 and $\bar{M}_w/\bar{M}_n \sim 4.0$ for PP025 and PP040. An estimate of $\bar{M}_z/\bar{M}_w$ from a plot of J_e vs. $\bar{M}_z/\bar{M}_w$ (176) showed that at 10^5 dynes/cm² $\bar{M}_z/\bar{M}_w$ is 1.9 and 2.6 for PP025 and PP120, respectively. See Tables II-1 and II-2.

*Yamane, H., J. L. White, Patra Report No. 185, The University of Tennessee, Knoxville, May 1982.

TABLE 2-1
COEFFICIENTS OF $N_1 = A\sigma_{12}^b$ RELATIONSHIP

Sample	$A \times 10^4$	Exponent b	$N_1 \times 10^{-3}$ (dyne/cm ²) ($\sigma_{12} = 10^4$ dyne/cm ²)	M_w/M_n (Value from η/η_0)
PP no treatment	26	1.6	4.05	(8.0~9.0)
PP 260/0.5	11	1.6	3.50	(6.5~7.0)
PP 260/1.0	7.1	1.7	3.15	(6.5~7.0)
PP 260/1.5	2.2	1.8	2.75	(4.5~5.0)
PP 280/0.5	5.2	1.7	2.90	(4.0~5.0)
PP 280/1.0	3.2	1.7	2.57	(3.5~4.0)
PB-1 no treatment	75	1.5	5.90	(>17.01)
PB-1 240/1.0	50	1.5	5.45	(10.0~15.0)
PB-1 260/1.0	27	1.6	4.75	(7.0~8.0)
PB-1 280/1.0	5.9	1.7	3.82	(4.5~6.5)
PP-B	150	1.4	7.20	9.0
	26	1.6		8-9
PP-D	15	1.6	2.72	4.6
Commercial PS	2.1-33	1.5~1.7	1.68~4.55	2.4-3.0
Monodisperse PS	0.23	2.0	0.299	1.06

Yamane
et al.Minoshima
et al.
(176)

Source: Ref. 176.

For present studies at ~125°C

 M_w/M_n estimate

~8.0

~4.0

PP120 93 1.5

PP025 4.1 1.71

PP040

TABLE 2-2

η/η_0 RESULTS FOR POLYMERS WITH KNOWN MOLECULAR WEIGHT DISTRIBUTIONS AT 180°C

Sample	M_w/M_n	$\eta/\eta_0 (\eta_0 \dot{\gamma} = 10^6 \text{ dyne/cm}^2)$
1. Monodisperse PS	1.06	0.515
2. Commercial PS	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	17.0	0.173

Source: Ref. 176

η/η_0 RESULTS FOR EXPERIMENTAL POLYPROPYLENES
AT AROUND 125°C

PP120	0.11
PP025	0.18

For a difference in η/η_0 of 0.7, the molecular weight distributions ($\bar{M}_w/\bar{M}_n$) in PP120 can be higher than the PP025 by about 4.0 depending on the base M_w/M_n value.

Estimates of $\bar{M}_z/\bar{M}_w$:

$$J_e = \frac{N_1}{2\sigma_{12}^2}$$

For PP025, $N_1 = 4.1 \times 10^{-4} (\sigma_{12})^{1.71}$

For PP120, $N_1 = 93 \times 10^{-4} (\sigma_{12})^{1.5}$

At $\sigma_{12} = 10^5 \text{ dynes/cm}^2$

$$J_e = 7.3 \times 10^{-6} \text{ for PP025}$$

$$J_e = 1.5 \times 10^{-5} \text{ for PP120}$$

$\overline{M}_Z/\overline{M}_W$ from Minoshima et al. (176) for the above J_e are

$$\overline{M}_Z/\overline{M}_W = 1.9 \text{ for PP025}$$

and

$$\overline{M}_Z/\overline{M}_W = 2.6 \text{ for PP120.}$$

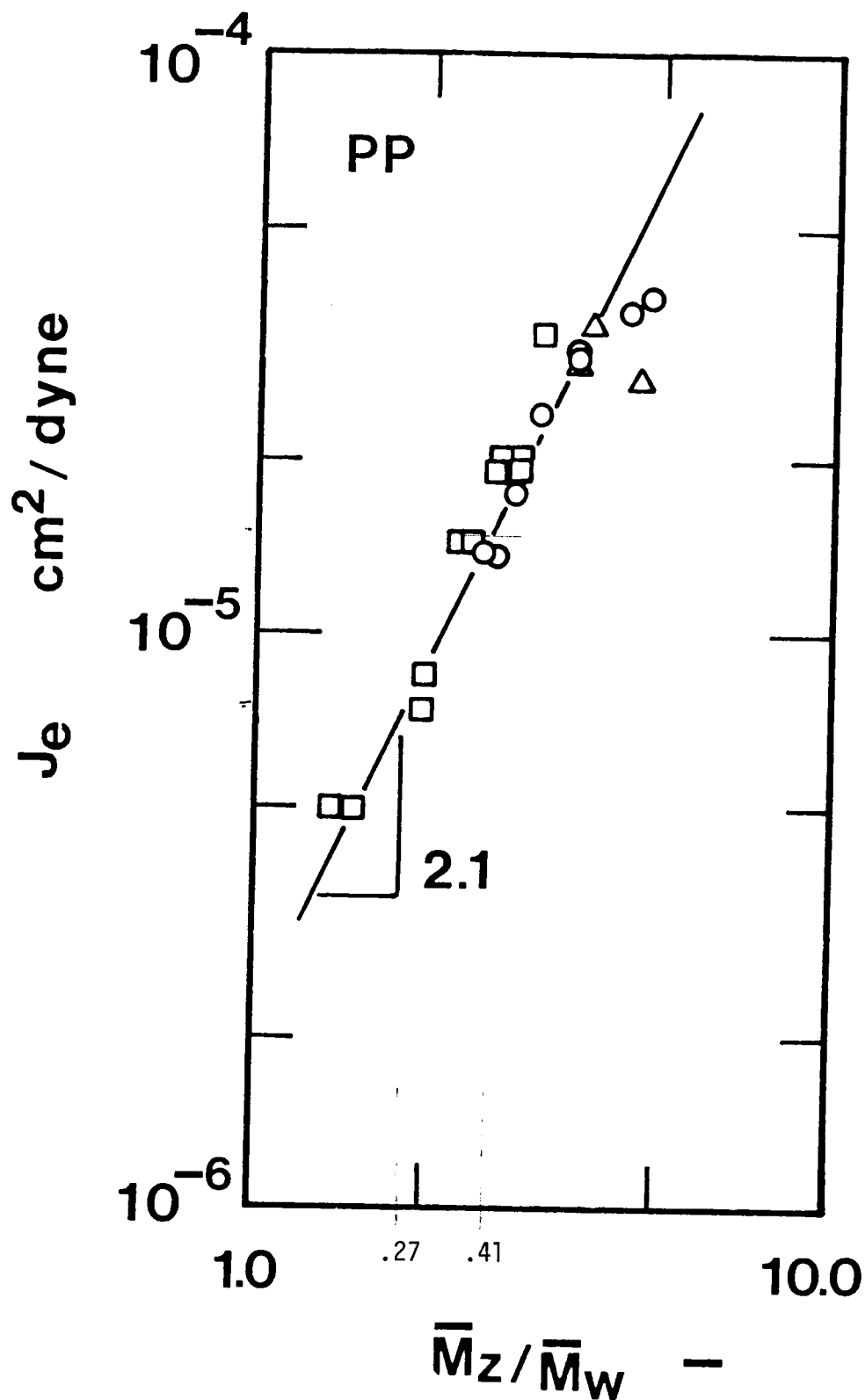


Figure 2-1 : Steady state compliance (J_e) as a function of $\bar{M}_z/\bar{M}_w$ for polypropylene melts.

Source: Ref. 176.

APPENDIX 3

ELONGATIONAL VISCOSITY RESULTS IN PP AT 180°C

FROM LITERATURE

Following elongational viscosity results at 180°C for polypropylene show that for a narrower and moderate molecular weight distribution polypropylene there is no strain hardening effect. For the present experimental polypropylene

$$\overline{M}_w/\overline{M}_n = 4.0 \text{ and } \overline{M}_z/\overline{M}_w = 1.9$$

and

$$\overline{M}_w = 4.03 \times 10^5 .$$

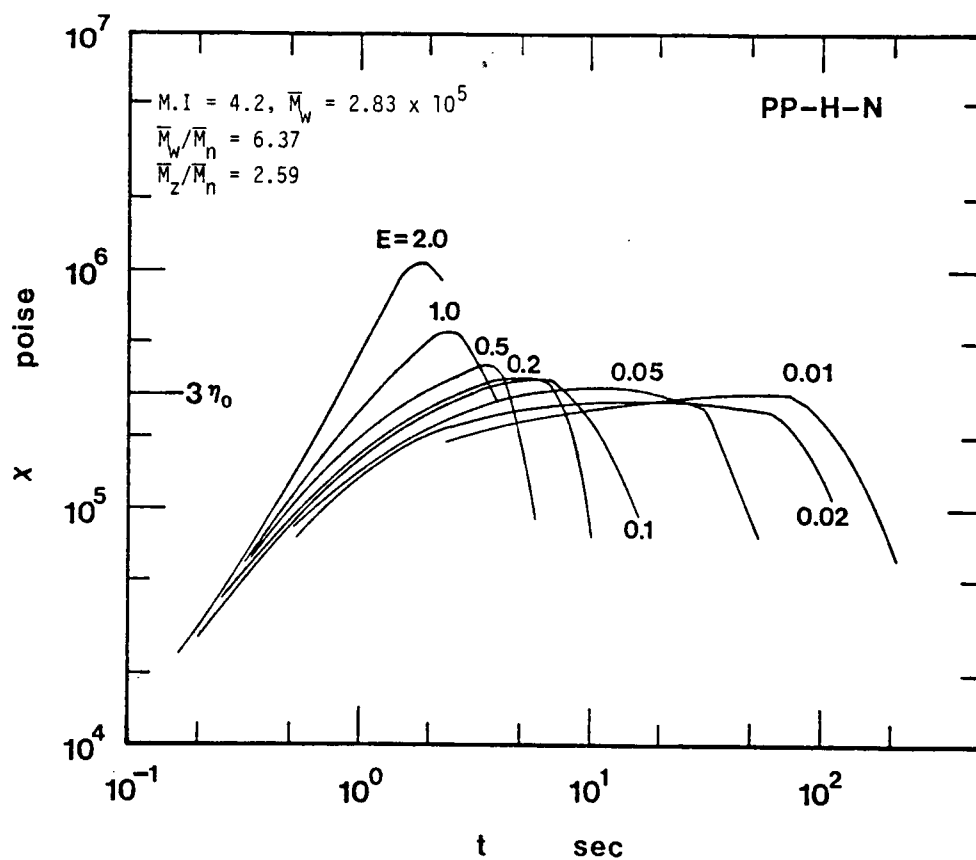


Figure 3-1 : Elongational viscosity (x) as a function of elongational rate (E) and time (t) for PP-H-N at 180°C. (From Minoshima et al. (176).)

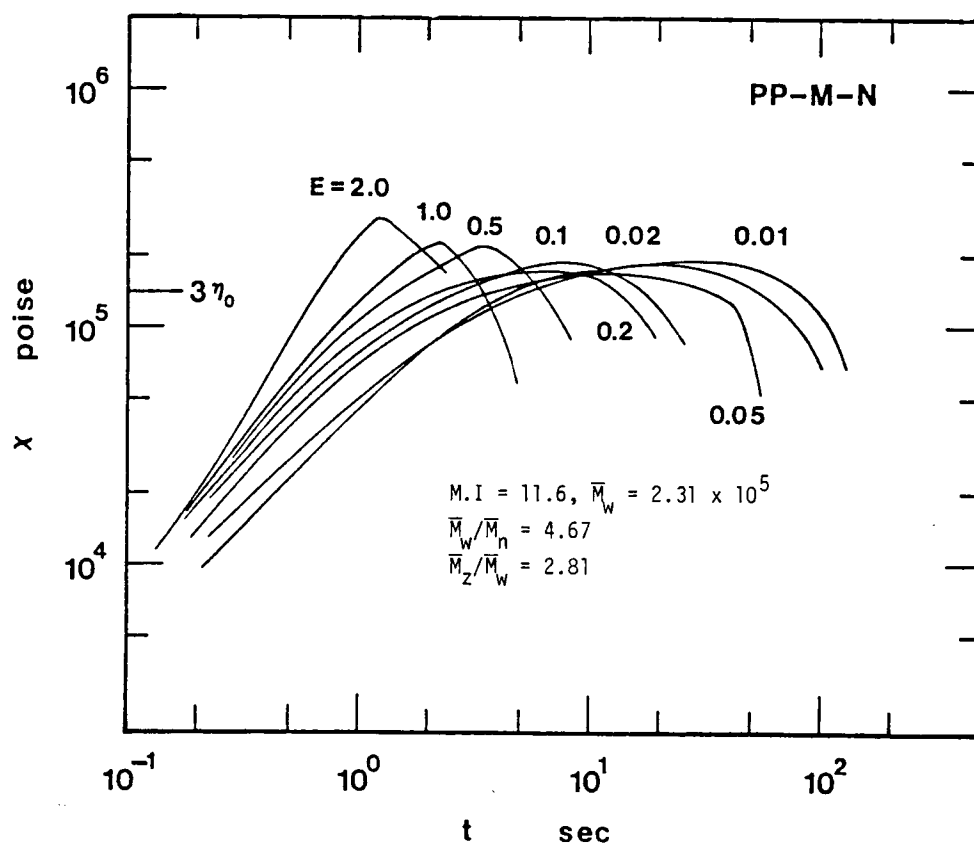


Figure 3-2 : Elongational viscosity (χ) as a function of elongational rate (E) and time (t) for PP-M-N at 180°C. (From Minoshima et al. (176).)

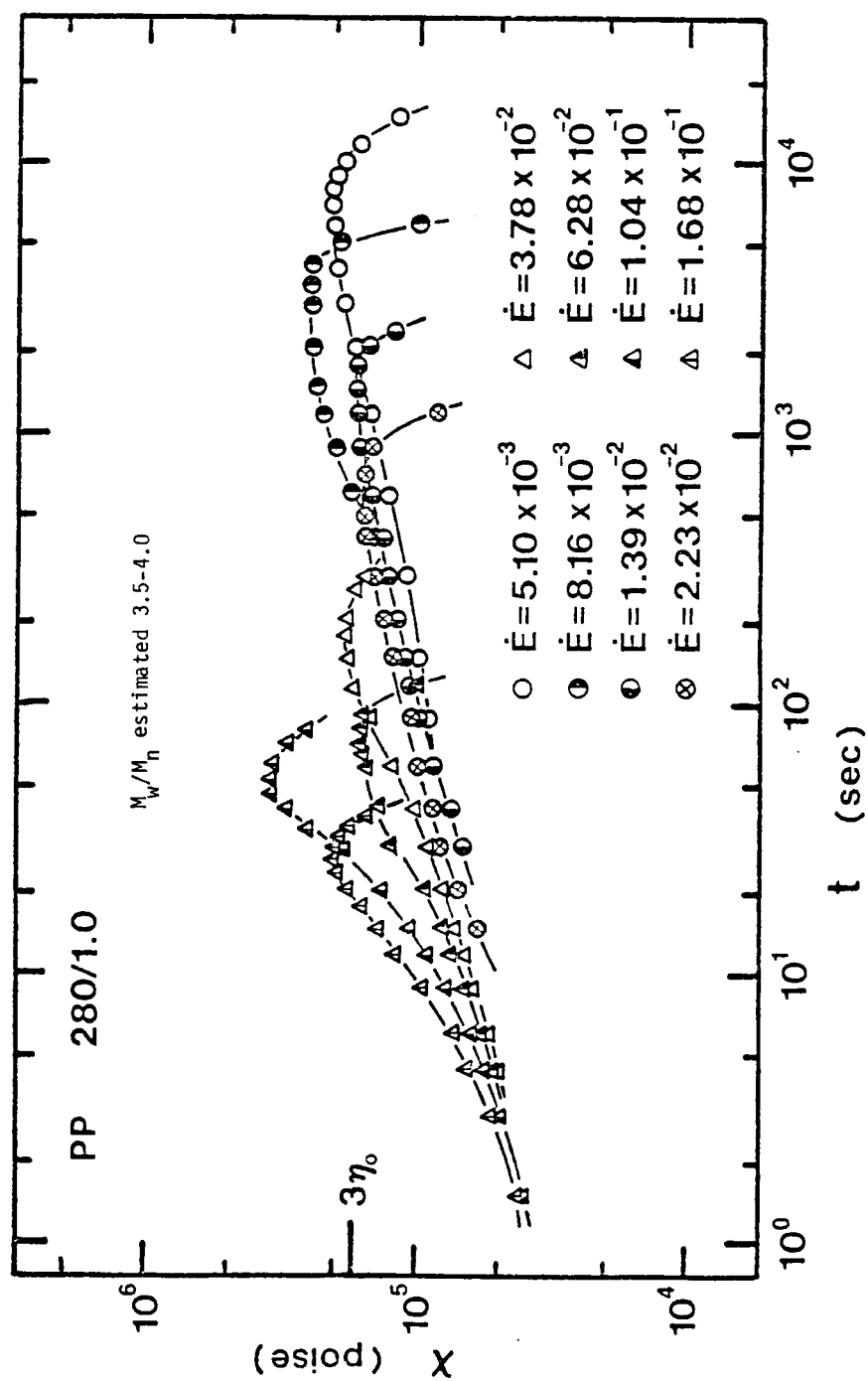


Figure 3-3 : Transient elongational viscosity versus time of degraded PP samples. (From Yamani et al.)

VITA

The author, Hari P. Nadella, was born in Guntur, India, on July 1, 1950. After completing high school studies in Repalle, India, he entered the Bachelor of Science program at Jagtial in 1967. After completion of first year, he was selected to specialize in chemistry at Osmania University, where he obtained his Bachelor's degree in chemistry in 1970. He came to the United States in 1971 and entered in a chemical engineering program at the University of Akron, Ohio. After completing a Bachelor of Science at Akron, he entered The University of Tennessee, Knoxville, in 1973 to study polymer engineering. There he obtained his Master's degree in 1976 and Ph.D. in 1983.

The author is married and has two children. He is currently employed by Exxon Chemical Company, Linden, New Jersey.