

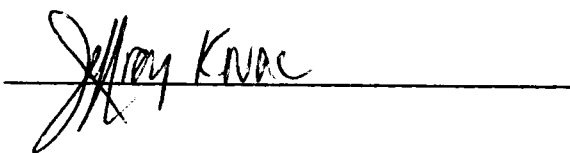
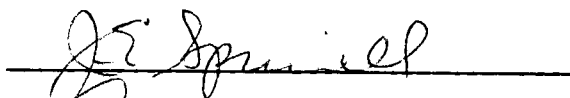
To the Graduate Council:

I am submitting herewith a dissertation written by Deepak R. Parikh entitled "The Mechanism of Orientation of Aromatic Solutes in Oriented Polyethylenes." 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.



Paul J. Phillips, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Vice Provost
and Dean of The Graduate School

THE MECHANISM OF ORIENTATION OF AROMATIC
SOLUTES IN ORIENTED POLYETHYLENES

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Deepak R. Parikh

December 1986

DEDICATION

This dissertation is dedicated to my parents,

Rasiklal and Snehlatta Parikh.

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ABSTRACT

Oriented linear low-density polyethylene (LLDPE) has the ability to orient many fused ring aromatic compounds. Dielectric relaxation studies of polar aromatic molecules in oriented LLDPE confirm orientability but only a fraction of the molecules are active. These immobilized molecules are located on the lateral surfaces of the polyethylene crystals through orientation mechanisms such as surface adsorption or surface crystallization. Spectroscopic and thermal analysis studies suggest specific surface adsorption on the surfaces of polyethylene crystals related to the epitaxial growth of solute microcrystals on polyethylene crystals as the major orientation mechanism. The mechanism of orientation for many of the fused ring aromatic compounds is epitaxial crystallization on the (110) and/or (100) crystal planes exposed by drawing. In order to obtain a better understanding of the fundamental interactions occurring in the systems of polyethylene and fused ring aromatic compounds, phase diagrams have been constructed using differential scanning calorimetry and X-ray diffractometry. The systems LLDPE/acridine and HDPE/phenazine exhibit formation of compound crystals.

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CHAPTER 1

INTRODUCTION

It has been known for many years that aromatic molecules introduced into oriented polyethylene have a preferred orientation. The extent of orientation of aromatic molecules in oriented polyethylene is determined by their shapes. Polyethylene has been used by organic spectroscopists as a substrate to orient aromatic molecules but the mechanism of orientation of aromatic molecules in oriented polyethylene is not known. Some experimentation has been carried out in this area but no direct studies have been attempted. A detailed study of the orientation mechanism has been conducted here.

Oriented polyethylene contains oriented and unoriented amorphous phases and oriented crystalline phases, hence, it is likely that both unoriented and oriented populations of solute molecules will be present. The unoriented populations are undoubtedly present in the amorphous phase, however, the location of the oriented fraction is a matter of controversy. The orientation mechanism should involve the polyethylene crystals and some mechanisms have been proposed. Yogev and co-workers (1969, 1973, 1978) suggested that the aromatic molecules are present in the polyethylene crystals. The study carried out by Jang et al. (1982) demonstrated that the solute molecules are not present inside the polyethylene crystals. A surface adsorption mechanism was proposed earlier by

Konwerska-Hrabowska and others (1973, 1978, 1981) based on far-infrared study. Dielectric relaxation studies of polar aromatic molecules in oriented polyethylene have demonstrated orientation but only a fraction of the molecules participate in the relaxation processes. The undetected molecules may be oriented such that they cannot reorient or they may be immobilized. Studies have been carried out with the aim of identifying the orientation mechanism which was presumed to be related to the 'lost' molecular fraction. It is demonstrated that these molecules are located on the lateral surfaces of the polyethylene crystals through surface crystallization.

With the help of spectroscopic and thermal analytical techniques it is demonstrated that the guest molecules are present in the form of microcrystals of solute which have grown epitaxially on the surfaces of the crystalline microfibrils. Studies carried out to explore the epitaxial crystallization process have demonstrated that epitaxy can occur on both the (110) and (100) planes (slip planes) of polyethylene. A method has been devised to estimate the relative areas of (110) and (100) exposed planes. Phase diagrams of aromatic compounds and polyethylene have been constructed to investigate the thermodynamic interactions of polyethylene chains with aromatic molecules. They have detected the existence of co-crystallization of both the components resulting in compound formation. Such a compound introduces a totally new class of polymer composite which could have potential applications in many

areas because of the oriented crystallization and preferential molecular organization within the compound crystals.

CHAPTER 2

LITERATURE REVIEW

Oriented polyethylene has been used by organic spectroscopists for many years as a means of orienting anisotropically shaped aromatic molecules for ultraviolet, visible and infrared dichroism studies (Thulstrup et al., 1968, 1970, 1974, 1975, 1976a, 1976b, 1977; Michl et al., 1970, 1974, 1977). Different aromatic molecules are oriented to different extents by polyethylene depending on the aspect ratio (length/width) of the molecules. The orientation phenomenon was initially developed for the elucidation of electronic structure through the use of ultraviolet spectroscopy but recently was extended for use with Fourier-transform infrared spectroscopy (Mitchell et al., 1983; Radziszewski and Michl, 1981) and polarized fluorescence spectroscopy (Langkilde et al., 1983).

2.1 Spectral Shift

Study of the orientation of aromatic solute molecules in polymers started as early as 1934 when Jablonski (1934) found that dye molecules orient in cellophane film during stretching. He noticed that the orientation effect varied from one dye molecule to another. Spectral shifts of some ultraviolet transitions of aromatic polar and non-polar molecules in a series of paraffin hydrocarbons were observed by Weigang (1960). These shifts were attributed to differences in the energy of interaction with the

surrounding solvent molecules between the excited state and the ground state. Such shifts have been observed by many scientists (Bayliss, 1950; Longuet-Higgins and Pople, 1957; McRae, 1957; Robertson et al., 1957). This effect suggested that strong interactions existed between aromatic molecules and paraffin hydrocarbons. Spectral shifts could be interpreted as due to a difference in perturbation of a light absorber in its ground and its excited states when surrounded by a particular configuration of solvent molecules. McRae (1957) analyzed theoretically the effect of electric dipole interactions on electronic band frequencies in spectra and derived a general expression for the frequency shift using perturbation theory, which was widely applicable.

Lamotte et al., (1972) showed that correlations of molecular orientation with n-alkane structure could be deduced from spectral shifts of the bands of aromatic hydrocarbons dissolved in n-alkane solvents. They noticed distinct spectral shifts of the bands of aromatic hydrocarbons dissolved in linear and branched alkanes of the same number of carbon atoms. Lamotte and co-workers in 1974 made the hypothesis that the difference was due to orientational order which becomes important when n-alkanes are in contact with flat molecules but not with spherical ones. Further they suggested that the correlation of molecular orientation is based on the occurrence of a crude anisotropic interaction potential between n-alkane and aromatic molecules. The spectral shifts can be explained by means of the potential interaction energy. Lamotte and

co-workers paid special attention to the specific interaction of the aromatic hydrocarbons with the extended zig-zag chains of the n-alkane. For the case of naphthalene interacting with n-pentane or n-octane in the trans configurations, the equilibrium energy is obtained when the aromatic plane is parallel to the plane of the paraffinic chain and separated by a distance of 3.6 Å. The minimum energy configuration for naphthalene and n-octane is shown in Figure 2.1. In a thorough study of the adsorption of hydrocarbons on graphite, Groszek (1970) was able to explain satisfactorily the features of adsorption by noting that a zig-zag hydrocarbon chain fits well on the basal plane of the graphite crystal. The results of Lamotte agree very well with the model proposed by Groszek for the adsorption of hydrocarbons on graphite. Groszek suggested that the longer the chain the more contacts it can form with the graphite surface and the more strongly it is adsorbed. This model of an n-paraffin adsorbed on the basal plane of graphite is shown in Figure 2.2.

2.2 Effect of Dye Molecules on Polymers

To measure the orientation in fibers and stretched films, aromatics, especially dyes, have been used. The measurement of orientation in fibers is complicated by the fact that they do not consist of only crystalline material, but also contain a considerable amount of amorphous (non-crystalline) material. Patterson et al., (1957) prepared fibers of polymers by melt

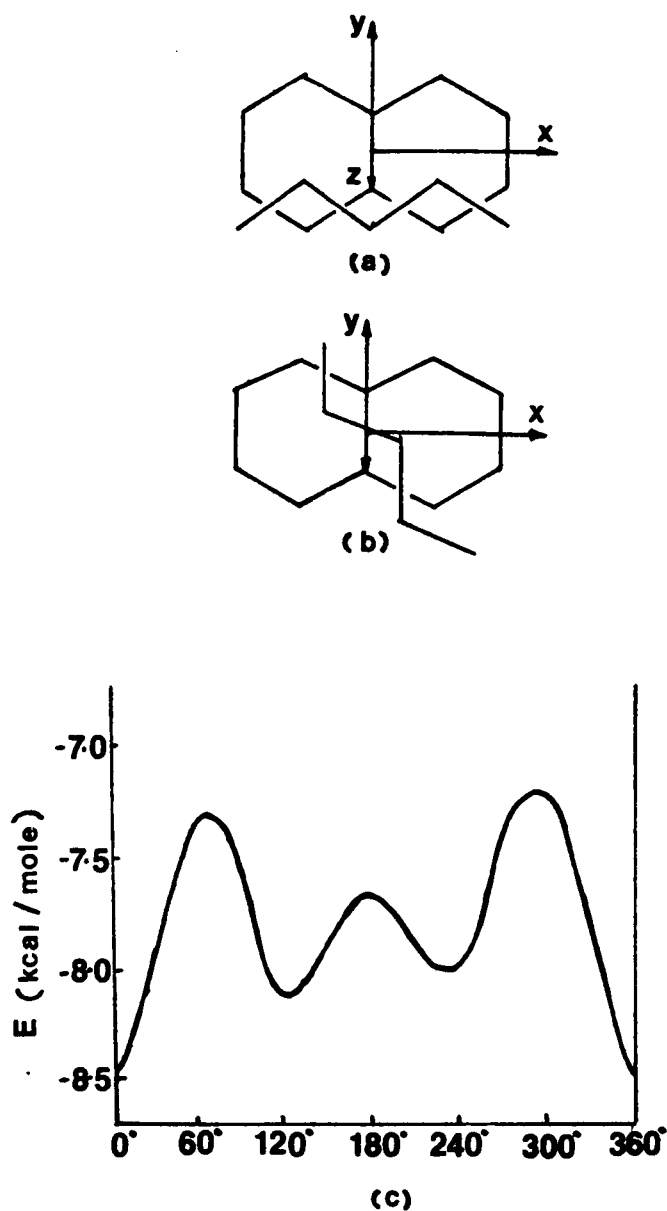


Figure 2.1. Minimum Energy Configurations and Variations of the Total Interaction Energy Between Naphthalene and n-Octane. (a) Trans Chain Axis Lying Parallel to the Longer Axis of the Naphthalene Molecule. (b) Trans Chain Axis Lying at an Angle to the Longer Axis of the Naphthalene Molecule. (c) Variation of the Total Interaction Energy Between Naphthalene and n-Octane According to the Rotation of the Alkane Chain in a Plane Parallel to the Aromatic Plane.

Source: Lamotte, M., Jousset-Dubien, J., Mantione, M. J. and Claverie, P., Chem. Phys. Lett., 27, 515 (1974).

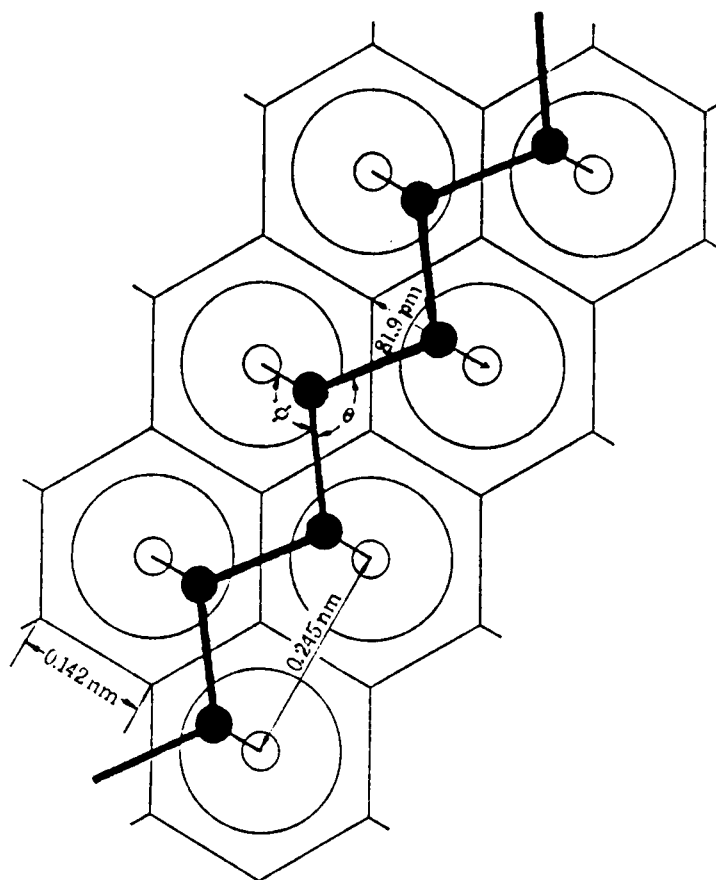


Figure 2.2. n-Paraffin Adsorbed on the Basal Plane of Graphite.

Source: Groszek, A. J., Proc. Roy. Soc. London, Part A, 314, 473 (1970).

spinning followed by drawing. It was possible to mix a small amount of dichroic dye in the molten polymer and to follow the changes in the orientation of the dye molecules using optical dichroism. They noticed that when the polymer molecules became oriented in a drawing process a similar orientation of the dye molecules took place. In a semi-crystalline fiber, they expected that the dye molecules would reflect the orientation of the amorphous regions. In an independent study of dynamic dichroism of the dyed polymers, poly (vinyl alcohol) and nylon-6, Yamada et al., (1964) observed that the dichroism does not vary with time and elongation in the same way as birefringence suggesting that different portions of the polymer structure contribute to these experiments.

Konwerska-Hrabowska et al., (1973, 1977, 1978, 1981) showed that aromatic molecules can pass from the vapor phase into stretched polyethylene film and are bonded inside the film producing orientational dichroism. They studied the interaction between aromatic compounds and polyethylene using ultraviolet-visible spectroscopy for solute molecules including anthracene, pentacene, pyrene, stilbene and diphenyl-octatetralene. These molecules were introduced into the stretched film of polyethylene from the vapor phase. They found that the aromatic molecules in stretched polyethylene films could be classed as two groups when related to the two phases of the semi-crystalline polymer. On the basis of their experimental results it was proposed that the less oriented molecules are surrounded by an amorphous medium, whereas the better

oriented ones are subjected to stronger interactions and may be located on the crystalline surfaces of polyethylene. Information on differences in interaction energy in relation to both the polymer regions was obtained from the spectral shift of the absorption bands.

These above-mentioned reports show that efforts have been made at understanding the interaction between aromatic molecules and polymers. Since most of the earlier research in this area has been concentrated on studies of the solute molecules themselves the interaction with the polymeric substrate was either ignored or regarded as being of lesser importance. All work in this area considered the interpretation of the results of spectroscopic experiments and involved an analysis of the orientation of solute molecules using dichroism. In the analysis of the results of linear dichroism measurements, there are several models involved each of which involves major assumptions. Many aspects have been oversimplified leading to controversial conclusions. The models are discussed in this chapter with emphasis being placed on the assumptions made, their effects on the structure of aromatic molecules, their limitations and their special features.

2.3 Models used in Analysis of Linear Dichroism

The procedures for analysis of linear dichroism of solute molecules contained in saturated polymers were developed by Fraser (1953, 1956) and Beer (1956), by Tanizaki et al., (1967) and

Hiratsuka et al., (1972), by Popov (1975) and by Thulstrup et al., (1968, 1970) and Michl et al., (1970).

2.3.1 The Fraser-Beer Model

This is one of the earliest models and has been used often in the quantitative interpretation of infrared dichroism. Fraser (1953, 1956) and Beer (1956) assumed that all angles of backbone rotation along the polymer chain were equally probable. This assumption was used in the interpretation of results of work carried out on solutes contained in stretched polymers by Moore et al., (1971, 1974, 1977) and Yogev et al., (1969, 1970, 1971a, 1971b, 1973, 1975). The assumption was also made that all angles of rotation of the solute molecule around its own long axis are equally probable. This assumption is reasonable for molecules which have cylindrical symmetry and for molecules, of any shape, which happen to have their z-axes nearly perfectly aligned in the stretching direction.

The Fraser-Beer Model was developed for the interpretation of infrared dichroism measurements used in the study of the molecular structure of organic compounds. It also defines the relationship between the transition moment direction and the dichroic ratio. This model was one of the earliest attempts at obtaining quantitative structural information from the dichroic ratios of partially oriented samples. One assumption amounts to a postulate that two of the molecular axes are equivalent. It was explained clearly by Thulstrup and Michl (1980) that there is no obvious physical reason

why the Fraser-Beer assumption should be generally valid for solutes other than those which are rod shaped or disk shaped. The problem illustrated in Figure 2.3 in which the two orientations shown have the same values of α and β but are physically inequivalent since they differ in their γ angles. f is a hypothetical totally oriented fraction of molecules (which can be located on Figure 2.4 at $[(K_z, K_y) = (1, 0)]$, where K is orientation factor) and $1-f$ is the totally random fraction of molecules (denoted at $[K_z, K_y) = (1/3, 1/3)]$. Variation of f from 0 to 1 produces all (K_z, K_y) pairs lying on the bottom side of the orientation triangle (TEM triangle) as shown in Figure 2.4. The applications of the formulation to some low symmetry molecules like biliverdin (Chae et al., 1975), peptides (Ingwell et al., 1975), and dimedone (Yogev et al., 1971a) appear questionable because of the shapes of the molecules.

Most of the molecules for which Popov and Smirnov (1970) used this model were not close to rod shaped and the results are also of questionable value. Thus, the Fraser-Beer assumption of two equivalent short axes cannot be used in general.

2.3.2 The Tanizaki Model

This is a quantitative model used by Tanizaki et al., (1967) and Hiratsuka et al., (1972) in the evaluation of the linear dichroism of solutes in stretched poly (vinyl alcohol). The basic assumption in this model is that at infinite stretching ratios all molecules would be aligned alike. One particular direction in the molecular framework, referred to as the orientation axis, would be

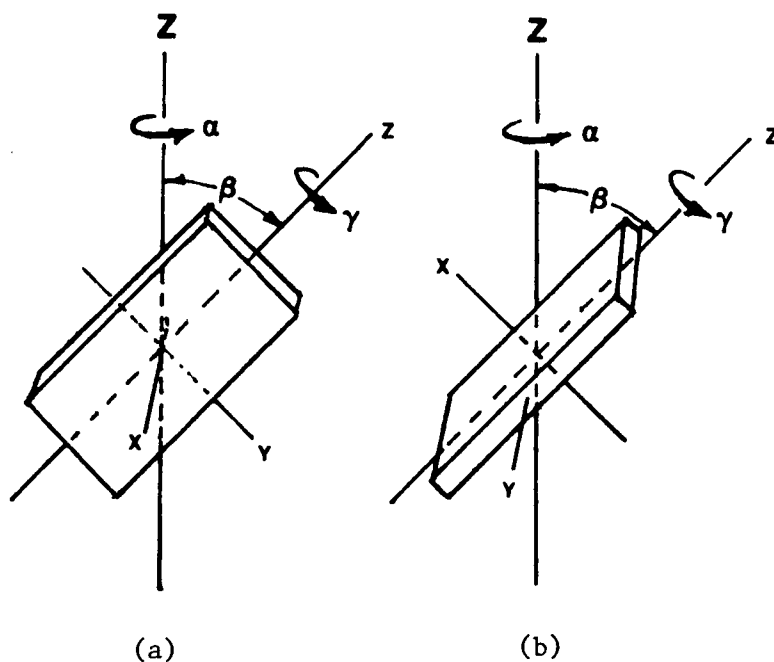


Figure 2.3. Description of Molecular Orientation by the Euler Angles α , β and γ . The Unique Sample Axis is Z . The Molecular Axes are X , Y and Z . $\gamma = 0$ for Figure (a) and $\gamma = -90$ for Figure (b).

Source: Thulstrup, E. W. and Michl, J., J. Phys. Chem., 84, 82 (1980).

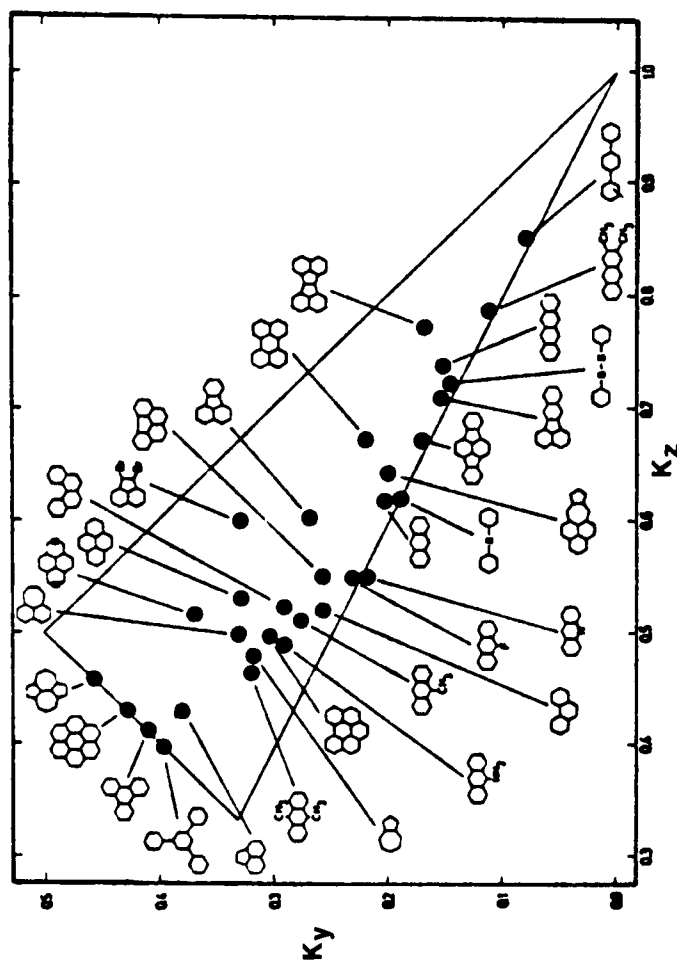


Figure 2.4. The Orientation Triangle from UV-Visible Spectra Including a Number of Experimental Values. K_z and K_y are the In-Plane Hosemann Orientation Functions for the Major and Minor Molecular Axes. The Lower Side of the Triangle Describes Rod-Like Orientation Distributions ($K_x = K_z$); the Upper Left Side Disc-Like Orientation ($K_z = K_y$), and the Upper Right Side Corresponds to Perfect Alignment of the Molecular Plane with the Stretching Direction ($K_z + K_y = 1, K_x = 0$). The K_x Value for any Point (K_z, K_y) may be Found as the Vertical Distance Between the Point and the Upper Right Side of the Triangle.

Source: Michl, J. and Thulstrup, E. W., Spectrosc. Lett., 10, 401 (1977).

aligned exactly along the stretching direction. One of the problems connected with the use of Tanizaki's model for unsymmetrical molecules is the uniqueness of the orientation axis. According to Fucaloro and Forster (1971, 1974) this assumption cannot always be made for strongly non-polar molecules. This assumption implies the existence of a definite relation between K_z and K_y for any given stretch ratio. According to this model, if the dichroic ratio of two or more electronic bands were determined, the angle between the transition moments could be evaluated by analyzing the dichroic behaviour. For a symmetric planar molecule, the pure absorption curves from dichroic spectra can be derived along the two principal (orthogonal) axes of the molecular plane, if the orientation axis of the molecule is known. One of the problems in the Tanizaki model is that the direction of the orientation axis is difficult to estimate from the molecular structure. In a perfectly aligned polymer there will be undoubtedly a continuous distribution of orientation of guest molecules around their most probable positions of alignment, and, most importantly, the molecular planes will not be perfectly parallel to the stretching direction. Yogeve et al., (1971a, 1971b) claimed in their critical discussions that Tanizaki's model leads to the same orientation for all molecules. The different positions of the orientation axis in different molecules should be taken into account before such a comment can be made.

2.3.3 The TEM Model

Thulstrup et al., (1968, 1970a, 1970b) and Michl et al., (1970) described a general procedure for quantitative analysis of linear dichroism of solutes contained in stretched polymers which is free of assumptions concerning the nature of the solute orientation, now known as the TEM model. This model has been applied to a large number of aromatic solutes by many organic spectroscopists. According to the TEM model two independent parameters are needed to describe adequately the orientation distribution for a symmetrical solute, rather than just one independent parameter. This reflects the average alignment of the three molecular axes with the stretching direction. There are assumptions involved in the TEM evaluation procedure and they are:

1. There is an equivalence of all directions perpendicular to the polymer stretching direction, (i.e., uniaxial stretching direction). The validity of this assumption was confirmed even in thin polymer sheets by Michl et al., (1970).
2. The spectrum contains at least some recognizable spectral features which are purely polarized. The measurements of at least two such features polarized in different directions are sufficient for the TEM model, which is a two-parameter model.
3. The effect of solvent on transition energies and intensities is independent of molecular orientation. For

this third assumption, Thulstrup and Michl (1980) mentioned that this is not rigorously correct and that small differences in the peak positions in $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ are most likely responsible for some of the 'fine structure' in the derived purely polarized spectra.

The TEM model in its most general form, for symmetrical molecules, makes no assumptions beyond these three.

The orientation factor K can be defined as

$$K = \frac{D}{D+2} = \langle \cos^2 u \rangle \quad (2.1)$$

where D = Dichroic Ratio

$$\text{and } D = \frac{\text{Absorbance}_{\parallel}(\lambda)}{\text{Absorbance}_{\perp}(\lambda)} \quad (2.2)$$

and $\langle \cos^2 u \rangle$ is the average of the square of the projection of a unit vector along the u th axis ($u = x, y, z$) in the stretching direction. The orientation factor K is defined for each axis.

For highly symmetrical molecules, the axes are labeled such that $K_z \gg K_y \gg K_x$. From the properties of directional cosines, $K_z + K_y + K_x = 1$. In the TEM model, the values of K_z and K_y are taken as the two independent orientation parameters and K_x is determined as $1 - (K_z + K_y)$. A TEM procedure for low symmetry molecules was introduced by Michl et al., (1970). The principal difficulty not present in the case of highly symmetrical molecules is ambiguity in the choice of molecular axes. Generally the z axis lines up best with the polymer stretching direction, so that the

square of its direction cosine has the largest average value among all possible molecular axes. It is the molecular orientation axis. The y axis is the one perpendicular to z which aligns best with the stretching direction. Obviously the x axis will be the molecular axis which has the lowest average value for the cosine square of its angle with the polymer stretching direction.

To use the TEM model, the values for two of the K 's and the direction for the molecular orientation axis are required. From this information, it is still only possible to derive absolute values of the cosines. A reasonable determination of angles will only be possible if the molecules orient like a rod ($K_x = K_y$) or the molecules orient like a disk ($K_z = K_y$), or if the molecule has a plane of symmetry.

Since the values of orientation factors satisfy the relation $K_y \leq K_z$, $(1 - K_z)/2 \leq K_y \leq 1 - K_z$, they can be conveniently represented as points in the orientation triangle (Figure 2.4) in which each orientation distribution is represented by a point with coordinates K_z, K_y . The vertical distance of this point from the line $K_z + K_y = 1$ is equal to the value of K_x . A totally random distribution is represented by the point $K_z = K_y = K_x = 1/3$ in the orientation triangle. Perfect alignment of the yz planes of all molecules with the stretching direction, with total equivalence in the distribution of the directions of the y and z axes, is represented by the point $K_z = K_y = 1/2$ ($K_x = 0$). Perfect alignment of the z axes of all molecules with the stretching direction is

represented by the point $K_z = 1$, $K_y = K_x = 0$, being the only point in the triangle that corresponds uniquely to a single orientation distribution. The location of the points inside the triangle in Figure 2.4 is related to the molecular shape. The models of Fraser-Beer and Tanizaki can be viewed as special cases of the TEM model.

2.3.4 The Popov Model

This model is an elaboration of the TEM model proposed by Popov (1975). He introduced a third parameter which characterizes the uniaxially stretched polymer by $A = \langle \cos^2 \theta \rangle$, where θ is the angle between the direction of a polymer chain and the macroscopic stretching direction. The value of A is independent of the solute used and depends only on the nature of the polymer and the degree of stretching.

Analysis of the Popov model generates the 'transformed orientation triangle' which contains points for all possible orientations with respect to the polymer chain, having an assumed cylindrical symmetry around the polymer chain. Of course this model makes the calculation more complicated than the TEM model but there is an advantage to the Popov model. In the TEM procedure, there is an orientation triangle not only for each polymer but also for each degree of stretching whereas in the Popov model the position of a point for a solute in the transformed orientation triangle is independent of the degree of stretching so that there is only one such diagram for each polymer. This model has been used by Dekkers

et al., (1978) for analysis of the polarized emission of molecules contained in a stretched polymer.

2.4 Role of Polymer Scientists

All these models involve assumptions regarding the orientation mechanism of solute aromatic molecules in stretched polymers. Solute-polymer interactions are bound to exist and need to be explored. Oriented polymers containing aromatic solute molecules need to be studied in detail with the objective of understanding the mechanisms of orientation. This research work is aimed at answering such questions. During polymer processing organic molecules are added to increase the life span of polymer products influencing the properties and characteristics of the material. Hence in order to understand this subject in detail organic chemists and polymer scientists have started working together--amongst the first ones are Michl, Thulstrup and Phillips.

2.5 Polymer Morphology

Before trying to understand the interaction of organic molecules with polymer morphology it is necessary first to understand polymer morphology. There are questions to be answered such as: Where do the molecules go? How does the presence of organic molecules affect relaxation processes? How does the structure of polyethylene affect the location of organic molecules? What could be the operating mechanism of orientation? These questions can be

considered more effectively if one has a clear picture of the polymer morphology.

2.5.1 Semi-Crystalline Polymers

The characteristic of crystalline polymers that distinguishes them from most other solids is that they are normally semi-crystalline. This is evident from the fact that the density of a crystalline polymer is normally between that expected for a fully crystalline polymer and that of the amorphous polymer. The degree of crystallinity and the size and arrangement of the crystallites in a semi-crystalline polymer have a profound effect on its physical and mechanical properties. In order to understand these properties fully it is necessary to have a clear understanding of the nature of these crystalline and amorphous regions.

Many thermoplastic polymers, including polyethylene, will crystallize when the molten polymer is cooled below the melting point of the crystalline phase. Variables such as the rate of cooling, the presence of orientation in the melt, the melt temperature, the amount of chain branching, the tacticity, the presence of additives such as nucleating agents can affect the rate of and extent to which crystallization can occur. But the basic question is why and how do polymer molecules crystallize? The answer to this question can be obtained through the thermodynamics of the crystallization process. The free energy G of any system is represented by the relation

$$G = H - TS \quad (2.3)$$

where H is the enthalpy, S is the entropy, and T is the thermodynamic temperature. Whenever G is a minimum the system is in equilibrium.

In the melt, the polymer consists of entangled random coils which have very high entropy, leading to a lower value of G . When a polymer melt is cooled below the melting temperature crystallization will occur, ordering chains and thereby reducing the entropy. This reduction in entropy is offset by a large reduction in enthalpy during crystallization. If the magnitude of the change in enthalpy (ΔH) is greater than the magnitude of the product of melting temperature and entropy change ($T_m \Delta S$), crystallization will occur since a lower value of G will result. For an idealized linear polyethylene the first requirement for crystallization is that ample mobility is provided in the crystallizing melt for the molecules to arrange themselves. The second requirement is a unit cell. The third requirement is a degree of regularity in the folding of the chain molecules leading to specific morphology.

2.5.2 Crystal Structure

Most crystalline solids consist of three-dimensional arrays of atoms or molecules whereas in polymers the atoms are joined together as chains prior to crystallization. These chains pack side-by-side

and lie along a particular direction in the crystals. By defining a regular pattern of segments of the polymer chain which is repeated, the structure of a polymer crystal can be defined. This repeating unit is the unit cell, crystals being made up of stacks of these unit cells. There can be several segments of a number of polymer chains in a unit cell resulting in many atoms being present in the unit cell of a polymer crystal. In general, polymer crystals have very anisotropic properties because the chains lying along a particular direction have atoms connected by covalent bonds. There are relatively weak secondary bonds between the molecules. The chains pack into the crystals so as to fill space as efficiently as possible. The crystal structures of several hundred polymers have been determined. Polyethylene has $(\text{CH}_2 - \text{CH}_2)_n$ as a repeat unit and a linear zig-zag chain conformation. The polyethylene unit cell is orthorhombic having $a = 7.42 \text{ \AA}$, $b = 4.94 \text{ \AA}$ and c (chain axis) $= 2.56 \text{ \AA}$ (Brandrup and Immergut, 1975). Orthorhombic polyethylene is the most stable crystal structure but a monoclinic modification can be formed by mechanical deformation as observed by Young et al., (1973, 1974). The molecules in the monoclinic form are still in the form of a planar zig-zag. The chain direction repeat distance and crystal density are virtually unchanged. These two crystal structures of polyethylene differ only in the way the molecules are packed in the unit cell. Bassett and Turner (1972) proposed the existence of a new phase in the crystallization of linear

polyethylene at high pressures and it was demonstrated to occur in a hexagonal form by Bassett et al., (1974).

The crystal structure of PE and its correspondence to the interplanar distances of the organic molecule's crystal structure is an important subject to this research and will be discussed here.

Because of frequent perturbations in a real crystal, such as side groups, kinks and jogs in the conformation, long range thermal motions, problems in chain folding, etc., considerable irregularities can be found in lateral packing (Clark, 1973). This type of disorder is found to a higher degree than in metals and has been treated in terms of the "paracrystallinity" concepts described by Hoseman (1962, 1963). This concept of paracrystallinity was used by Yogeve and co-workers (1969, 1970, 1971a, 1971b, 1973, 1975) for the discussion of orientation mechanisms. But it is a concept not generally acceptable for low density polyethylene because of the large amorphous fraction present.

2.5.3 The Nature of Chain Folding

The possibility of crystallization with a folded conformation was first proposed by Storks (1938). By examining thin films (~270 Å) of gutta percha evaporated from a dilute solution in chloroform, he concluded:

Films of gutta percha are found to be composed of relatively large crystallites which are precisely oriented with their fiber axis direction normal to the film surface. It is presumed that the macromolecules are folded back and forth upon themselves in such a way that adjacent sections remain parallel.

Evidence of a chain-folded conformation in single crystals was first presented by Keller (1957), Till (1957) and Fischer (1957); however, the idea of adjacently reentered folded chains was proposed by Keller alone. In his paper he considered chain folding in a polyethylene single crystal. Before the discovery of chain folding it was believed that the principal reason for not finding 100% crystallinity in polymer molecules was a lack of mobility, the chains being frozen into non-equilibrium positions. The nature of polymer morphology was thought to be of the simple form shown in Figure 2.5 and known as the fringed micelle model (Bryant, 1947). In this model, segments cluster together to form small crystallites interconnected by entangled amorphous regions. A single chain passes through a crystallite, moves through an amorphous region and enters another crystallite. This model was logical, explained mechanical properties but could not explain spherulitic structures when they were observed at a later date.

The single crystals of polyethylene were grown by precipitation from dilute solution. In general, solution grown crystals have a thickness of the order of $100 - 200 \text{ \AA}$ and a width of up to a few microns. These crystals are too small for X-ray studies and can only be studied using electron diffraction and microscopy. Since the thickness of the lamellae ($\sim 100 - 200 \text{ \AA}$) is very small compared to the length of the chain, some form of chain folding is essential to create the regular lateral packing of the chains in the unit cell. Density measurement of solution grown crystals shows that

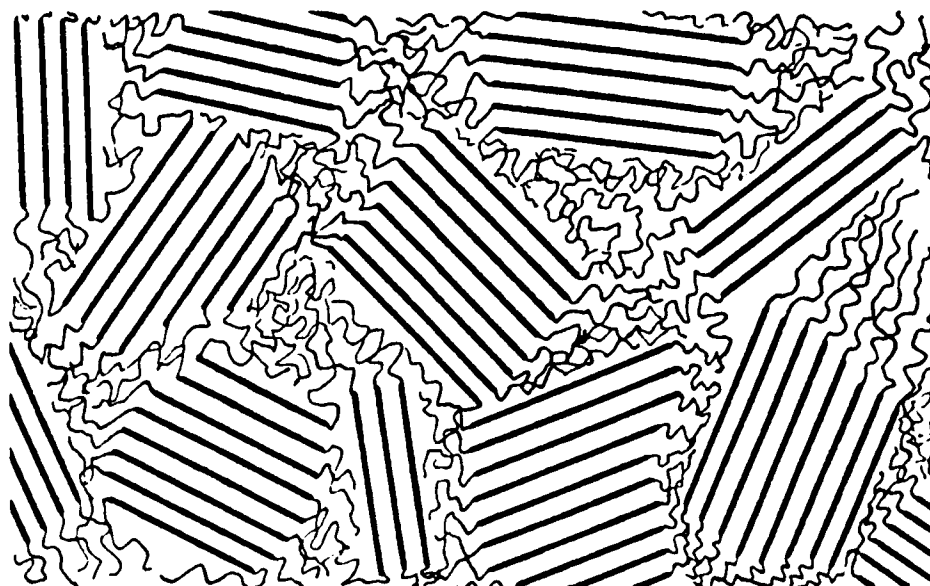


Figure 2.5. Fringed Micelle Model.

Source: Bryant, W. M. D., J. Polym. Sci., 6, 547 (1947).

they are not perfect single crystals. The density tends to be less than theoretical, implying that non-crystalline material must be present. The possible site is the fold surfaces of the single crystals. It appears that chain-folding can be described by three models. These are shown in Figure 2.6 (a), 2.6 (b) and 2.6 (c), of which 2.6 (a) and 2.6 (b) are adjacent re-entry and 2.6 (c) is random re-entry or 'switchboard'. Figure 2.6 (a) (regular adjacent re-entry model) shows perfect regularity in folding with periodic placement of the chain folds on the crystal surface. Figure 2.6 (b) (irregular adjacent re-entry model) lacks regularity in chain folding resulting in variable lengths of chain in a fold, with the presence of loose chain ends on the surface. The regular adjacent re-entry model is a limiting case and can be obtained in practice only under very carefully controlled crystallization conditions. In spite of the fact that the regular adjacent re-entry model represents the model of lowest free energy in a folded lamellar crystal, achieving this perfection may be difficult because of the restricted mobility of chains in a condensed system.

In a melt-crystallized system, where one crystal lamella is growing in very close proximity to another, it is easy for a fraction of the chain to traverse more than one lamella, providing the 'tie chains' which are responsible for elasticity. This kind of structure with 'amorphous' regions of loose chain ends, chain loops and tie chains leads to a more realistic model known as the irregular adjacent re-entry model. This model can be used to

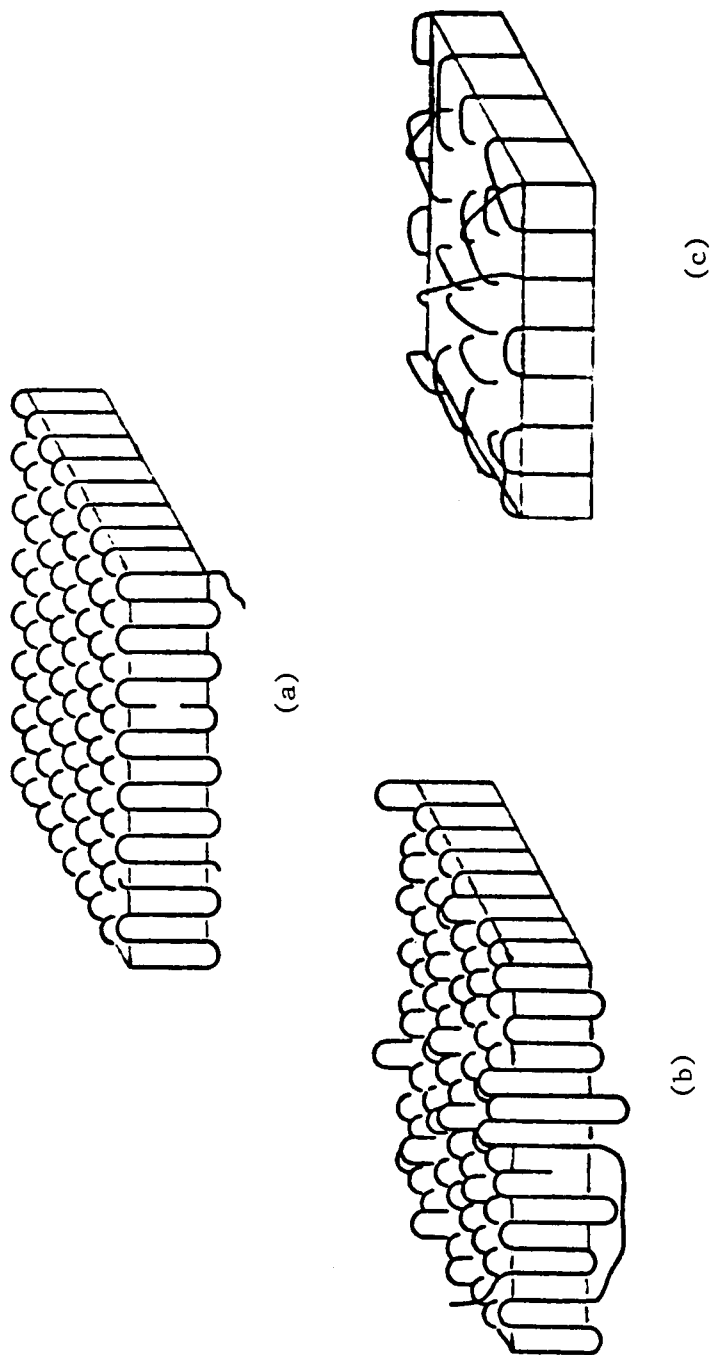


Figure 2.6. Chain Folding Models. (a) Regular, Adjacent Re-entry Model. (b) Irregular, Adjacent Re-entry Model. (c) Switchboard, or Non-adjacent Re-entry Model.

Source: Geil, P. H., "Polymer Single Crystals," Interscience (1963).

explain dynamic loss phenomena and other mechanical properties. It is important in this work and will be referred to later on.

The switchboard model was proposed by Flory (1962). This model leads to more disorder in the intercrystalline regions and resembles the fringed micelle model.

Recent studies on chain folding in polyethylene have been carried out using techniques such as small angle neutron scattering (SANS) by Sadler and Keller (1978), Schelten et al., (1974), Spelles et al., (1984) and Yoon and Flory (1977, 1979), Fourier-transformed infrared spectroscopy (FTIR) by Spelles et al., (1980, 1984b), and by ^{13}C nuclear magnetic resonance (NMR) by Ando et al., (1984, 1985).

2.5.4 Spherulites

Whether crystallization is from the melt or solution, a common feature is that the solid polymer is semi-crystalline and it contains both amorphous and crystalline phases. The spherulite was first recognized by Bunn (1945). When observed under cross-polarized light spherulites show a characteristic Maltese cross pattern. As the name itself suggests, the object is spherical in shape and the growth stops when growing spherulites impinge. The analogy can be made that grains in a metal are similar to spherulites. However, grains in metals are single crystals whereas spherulites in polymers consist of several crystals radiating from a central nucleus. Spherulites consist of chain-folded lamellae. In

other words, the lamellae are approximately parallel to the radius of the sphere and the polymer chains are normal to the radius. Lamellae in polyethylene twist about their growth axis giving rise to concentric bands of birefringence. In polyethylene, the b crystal axis is radial and as expected the c axis is perpendicular to the radius.

2.5.5 Solid-State Deformation of Polyethylene

A variety of techniques can be used to orient polyethylene, such as drawing, rolling, solid-state extrusion and melt spinning. By solid-state deformation, the original chain folded lamellar structure of polyethylene is broken by an externally applied stress, and the polymer chains are oriented in the direction of applied stress. This deformation results in the well known microfibrillar structure (Peterlin, 1983) as shown in Figure 2.7. In this microfibrillar structure, chain folded crystals are held together by tie molecules, and an increased number of taut tie molecules are responsible for the higher modulus of the deformed material (Peterlin, 1971).

A major part of solid-state deformation is plastic deformation of the crystalline phase. There are four principal mechanisms involved in plastic deformation, which are crystallographic plane slipping, twinning, martensitic transformation and melting. Slipping in the polymer crystal is limited to the slip planes and it must not result in breakage of the covalent bonds of the polymer molecules. Hence slipping occurs between chain-folded planes.

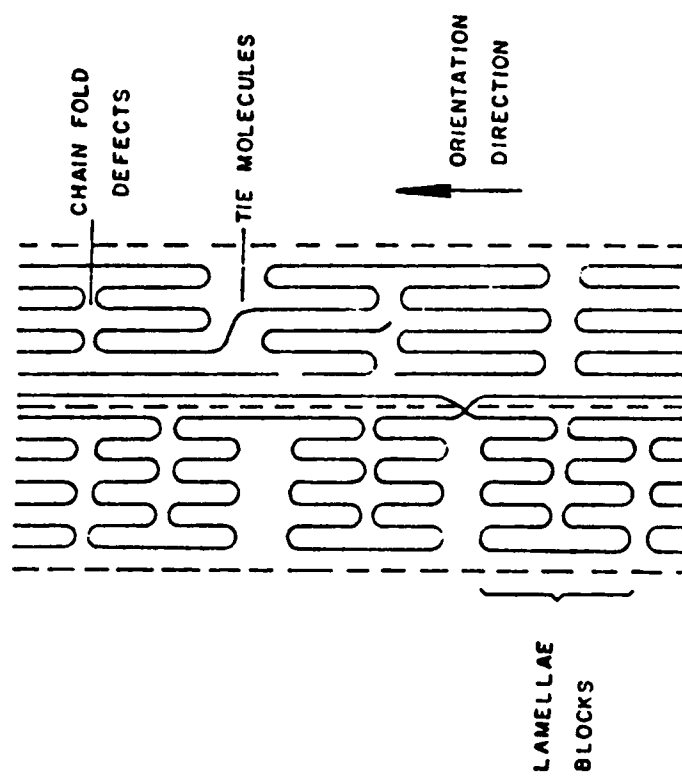


Figure 2.7. Schematic Structure of Drawn Crystalline Polymer.

Source: Peterlin, A., "The Strength and Stiffness of Polymers," Marcel Dekker Inc., New York (1983).

Twinning modes involved in the plastic deformation of polyethylene crystals are (310) and (110), as shown in Figure 2.8. Martensitic transformation, which is also known as shear transformation, results in a new crystal structure of polyethylene. It has a monoclinic unit cell with dimensions: $a = 8.09 \text{ \AA}$, $b = 2.53 \text{ \AA}$, $c = 4.79 \text{ \AA}$ and $\beta = 107.9^\circ$ as reported by Tanaka et al., (1962) and Bevis and Crellin (1971) but is not stable. In work carried out by Hay and Keller (1966) the angular relationship between the unit cell and the lamella was kept constant during rotation of the unit cell by annealing, showing that the lamella rotated as a whole with unaltered structure. This result suggested that the lamellar structure of the crystal is important in the solid-state deformation mechanism. The deformation mechanisms can be classified as lamellar separation, interlamellar slip, and intralamellar slip for LDPE according to Keller (1967). For HDPE the principal deformation mechanisms are fibrillar slip, lamellar slip and chain slip according to Young et al., (1973, 1974). They found that the angle between the chain direction and the lamellar normal was altered irreversibly by a compressional stress, which could only be explained by a (100) [001] chain slip mechanism.

The morphological changes involved in the deformation process can be observed at the level of the individual lamella, groups of lamellae or spherulites. Direct observations can be made using optical and electron microscopy and indirect observations of the process can be made using WAXS, SAXS, birefringence and light

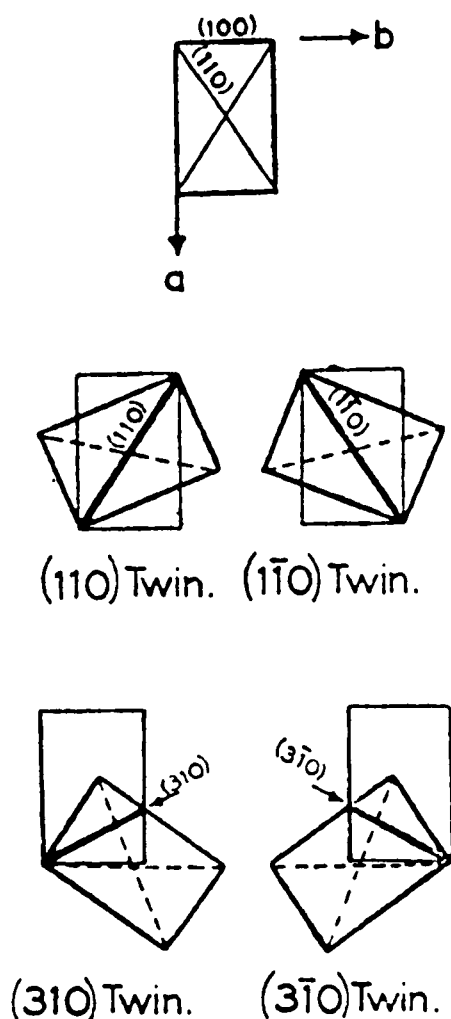


Figure 2.8. The Effect of Twinning on the Orientation of the Unit Cell When Viewed in the c-Projection.

Source: Young, R. J., Bowden, P. B., Ritchie, J. M. and Rider, J. G., J. Materials Sci., 8, 23 (1973).

Young, R. J. and Bowden, P. B., Phil. Mag., Ser. 8, 29 (2), 1061 (1974).

scattering. Stages in the deformation of a semi-crystalline polymer are illustrated in Figure 2.9 (a) to (e), (Schultz, 1974). Two adjacent chain folded lamellae and the interlamellar amorphous material are shown in (a). In the first stage of deformation lamellar ribbons slip rigidly past each other and at this stage the strain is accommodated almost entirely by the interlamellar amorphous layer as shown in (b). Figure (c) shows that the tie chains are highly extended and tilting of lamellar chain folds occurs. In the next stage (d) the crystalline blocks are pulled out and separated but still attached to each other by tie chains. In the final stage (f) the blocks become aligned along the tensile axis, i.e., block segments and tie chains are almost aligned with the tensile axis.

2.5.6 Solid-State Deformation of LLDPE

A type of low-density polyethylene which has been prepared recently is called linear low density polyethylene (LLDPE). LLDPE is a copolymer of ethylene with olefins having four to eight carbons. They are copolymerized under low pressure with Ziegler-Natta type catalysts, and, therefore, their molecular structure is linear. LLDPE has several advantages to its mechanical properties over conventional LDPE and has been discussed in a review paper by Kwack and Han (1983).

One of the earlier studies on LLDPE was carried out by Peterlin et al., (1983). They studied the drawability of LLDPE and the maximum draw ratio achieved with LLDPE at drawing temperature 60°C

LANCASTER BOND
100% COTTON FIBRE

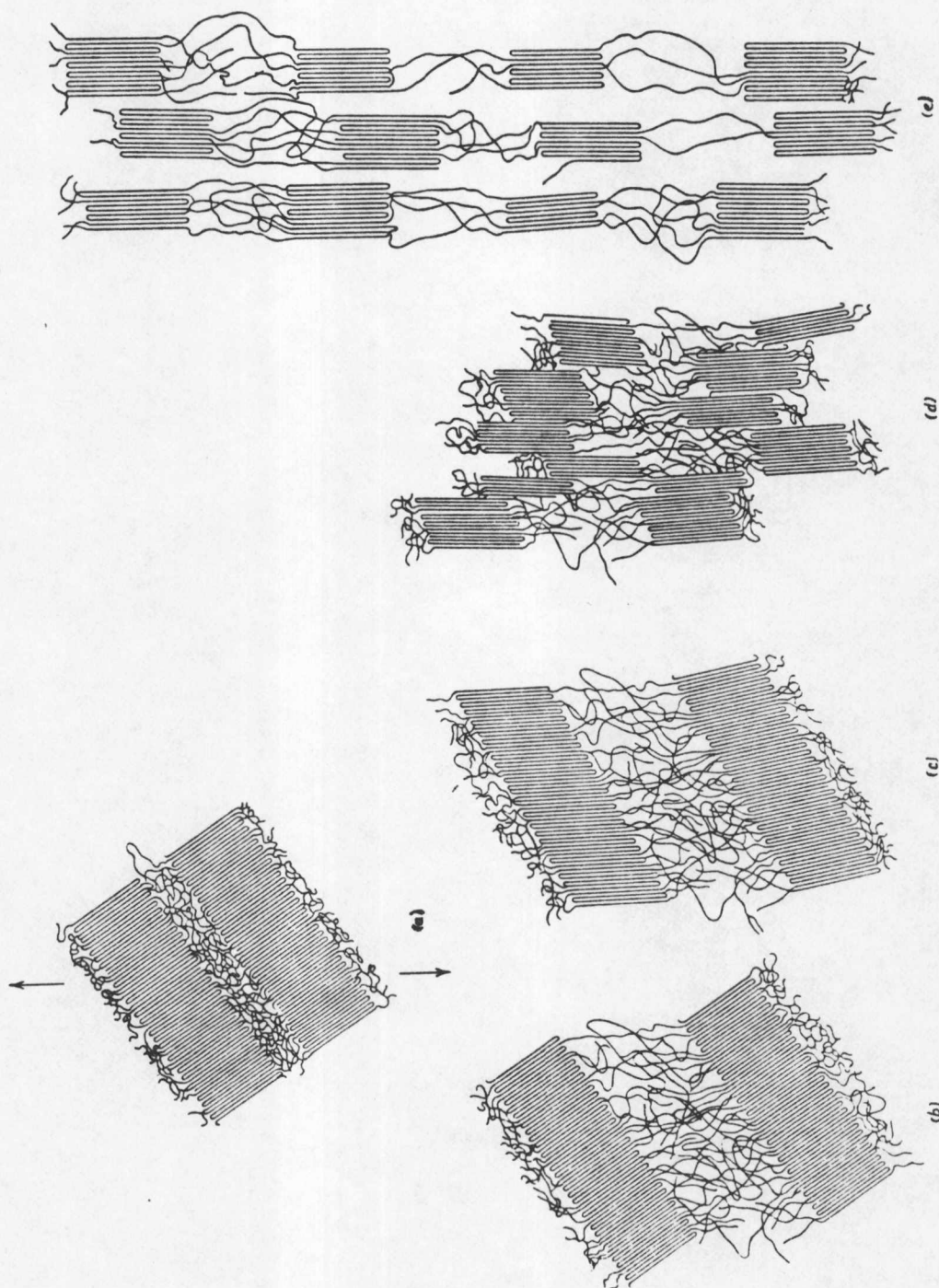


Figure 2.9. Stages of Solid-State Deformation of a Crystalline Polymer.

Source: Schultz, J., "Polymer Materials Science," Prentice-Hall, Inc., (1974).

was 8 being a little higher than that of LDPE (which was 6). The slightly better drawability of LLDPE compared to LDPE was interpreted in terms of the short branches of LLDPE.

Capaccio and Ward (1984) in their study of the drawing behavior of a variety of linear ethylene copolymers found that even a very low concentration of side chains increased strain hardening and decreased the maximum draw ratio that could be achieved. When the side chain length was increased these above-mentioned effects were noticed. This means that even a small amount of side chain reduces the molecular flexibility during plastic deformation.

2.5.7 Possible Locations for Solute Organic Molecules with Respect to Polyethylene Morphology

The incoming solute aromatic molecules can have many possible locations. In the undeformed unoriented state the crystals of a polymer are arranged in spherulites as shown in Figure 2.10. There can be four possible sites for location of organic solutes in un-oriented polyethylene (Jang and Phillips, 1982). These sites are labeled as A, the amorphous phase; B, the interior of a crystal; C, adsorption sites on the lateral surfaces of the crystal; and D, adsorption sites on the folded surfaces of the crystals. Site D is likely to be a remote possibility because of the uneven folded surface. Similarly the location of the solute molecules in the interior of crystals, i.e., site B, is not a likely site and will be discussed later.

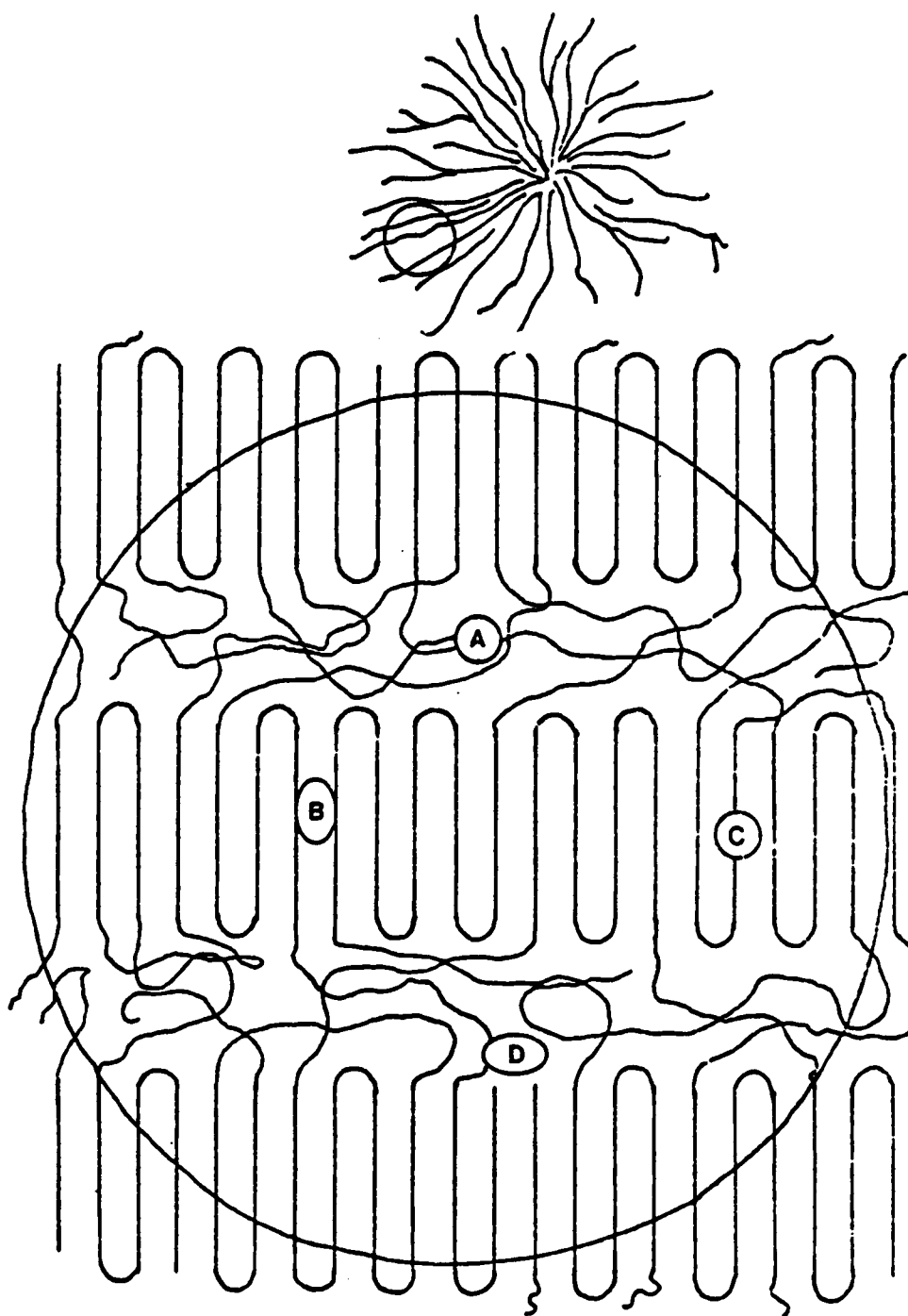


Figure 2.10. Schematic Representation of the Spherulitic Structure of an Oriented Crystalline Polymer Together with Potential Adsorption Sites.

Source: Jang, Y. T., Phillips, P. J. and Thulstrup, E. W., Chem. Phys. Lett., 93, 66 (1982).

The general model for the morphology of yielded polyethylene is represented schematically in Figure 2.11. During the yielding process the spherulites are destroyed and microfibrils are formed. The chain molecules which participate in two or more subcrystals tend to become oriented along with these subcrystals. These may crystallize on the lateral surfaces of the existing crystals or may remain in the amorphous phase. Thus it creates a new additional potential site for the aromatic molecules, namely the interfibrillar amorphous phase, which is oriented to some extent. This location is indicated as site E in Figure 2.11. Thus there are five sites for location of organic solutes in oriented polyethylene. Of these five, only three sites are capable of producing orientation of the aromatic solutes. They are B, the interior of the polymer crystals; C, the lateral surface of the crystal; and E, the interfibrillar amorphous phase. The unoriented solute aromatic molecules must be in the amorphous regions, however, the location of the oriented molecules is a matter of controversy.

2.6 Dielectric Relaxation

2.6.1 Theory of Dielectric Relaxation

The concepts and equations involved in dielectric relaxation applicable to this work will be reviewed briefly. A more detailed analysis of dielectric relaxation can be found in the books by McCrum, Read and Williams (1967) and Smyth (1955). Relaxation studies of polymers can be carried out using mechanical and

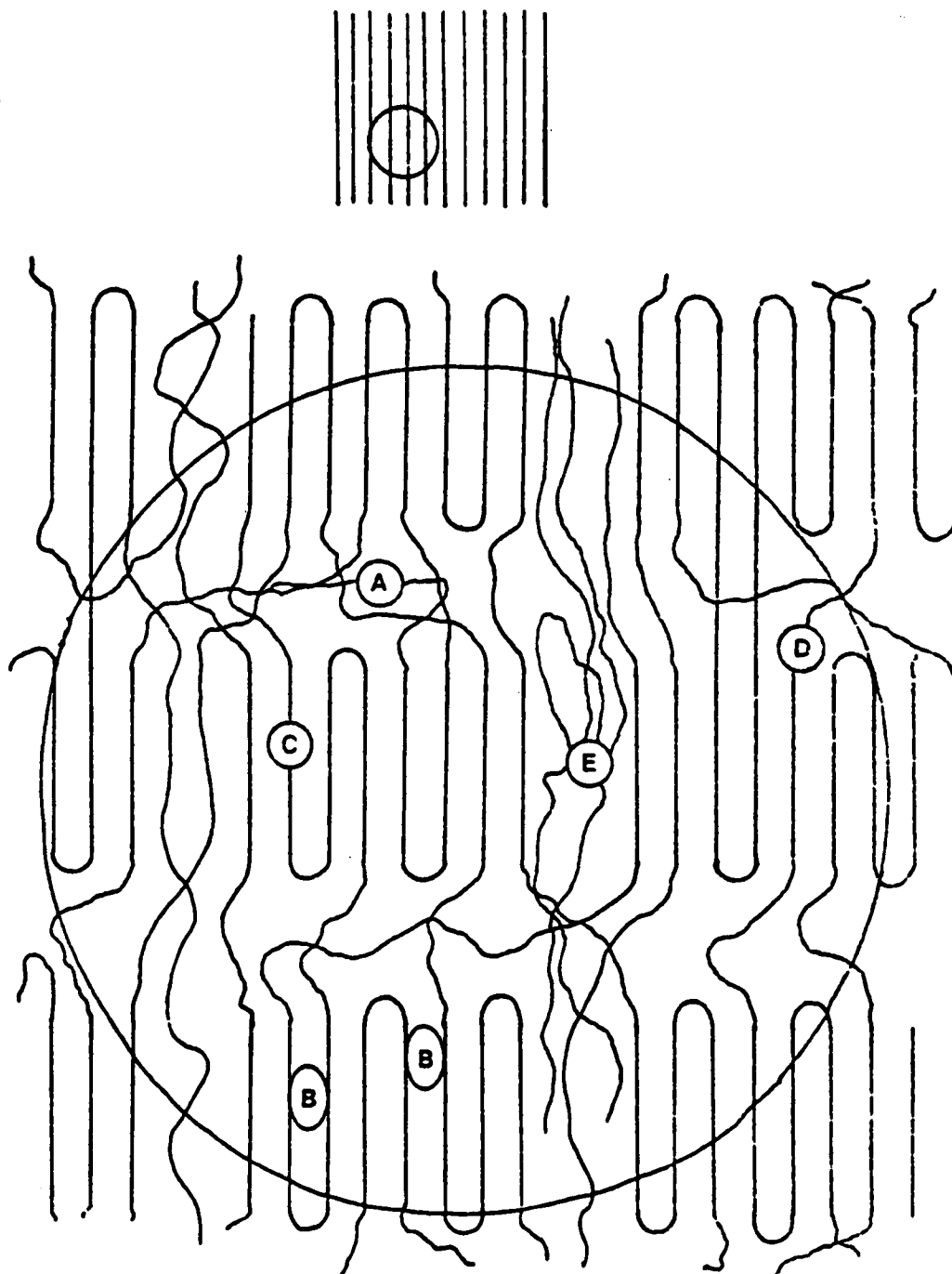


Figure 2.11. Schematic Representation of the Fibrillar Structure of an Oriented Polymer Together with Potential Adsorption Sites.

Source: Jang, Y. T., Phillips, P. J. and Thulstrup, E. W., Chem. Phys. Lett., 93, 66 (1982).

dielectric techniques among others. Dielectric relaxation is preferable for this work since the measurements can be carried out over a wide range of frequencies. Also quantitative arguments can be made linking loss peak intensities (relaxation strengths) to the number of molecular dipoles participating in the loss process.

Dielectric relaxation is an important technique for probing polymer structure. An external electrical field is applied, which induces polarization by the reorientation of permanent dipoles. There are four different types of polarization (Phillips, 1977). They are atomic, electronic, orientational and interfacial polarization. Generally polarization is time dependent. In the presence of an alternating field, the internal motion of the polymer chains controls the rate of dipolar orientation.

Let us consider a perfect loss-free parallel plate capacitor with a cross-sectional area, A , the separation of the plates is d , and a potential V_0 is applied across the plates. The equal and opposite charges Q_0 formed on each plate are given by

$$Q_0 = V_0 C_0 \quad (2.4)$$

where C_0 is defined as the capacitance of the condensor in a vacuum and is given by

$$C_0 = \epsilon_0 \frac{A}{d} \quad (2.5)$$

where ϵ_0 is the permittivity of free space.

If we introduce a specimen between the parallel plates and the same voltage is applied, then the material will become polarized due to the relative displacement of positive and negative electric charges within itself. Thus, there will be an increase in surface charge of the capacitor to Q_{total} , where,

$$Q_{\text{total}} = Q_o + Q = CV_o \quad (2.6)$$

This Q_{total} is the sum of the free charge, Q_o , and the charges formed by the dipoles in materials, Q , the bound charges.

The dielectric constant ϵ' of the material can be defined as the ratio of the capacitance C with the material placed in between the plates to the capacitance with air.

$$\epsilon' = \frac{C}{C_o} = \frac{Q_{\text{total}}}{Q_o} \quad (2.7)$$

The dielectric constant is a characteristic of the material.

The measurement of capacitance, particularly when of high accuracy, is made by a null method which uses some form of the basic ratio arm bridge shown in Figure 2.12. The capacitance of the unknown, C_x , is balanced by a calibrated variable standard capacitor, C_N , or by a fixed standard capacitor and variable ratio arms such as R_A or R_B . Such bridges with resistive ratio arms and with calibrated variable capacitors or resistors can be used over a wide range of capacitance and frequency. The system used in this

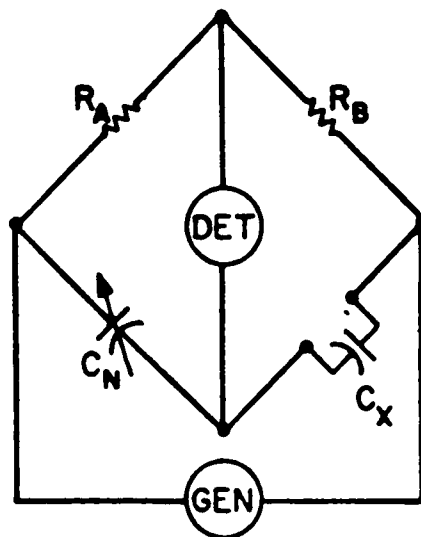


Figure 2.12. Basic Ratio Arm Bridge.

study has transformer ratio arms giving accuracy within a few parts per million.

In general, for any dielectric relaxation study measurements of the capacitance, C , and conductance, G , of the polymeric materials as a function of frequency and temperature are made.

The dielectric loss ϵ'' can be obtained as

$$\epsilon'' = \frac{G}{2\pi\nu C_0} \quad (2.8)$$

where ν is the frequency of the applied field. The angular frequency of the applied field is

$$\omega = 2\pi\nu \quad (2.9)$$

Actually, the complex dielectric constant ϵ^* is given by

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (2.10)$$

The changes in ϵ' and ϵ'' as a function of angular frequency and temperature are shown schematically in Figure 2.13.

At any particular temperature and at low frequencies, the dipoles on the polymer chains orient in phase in the direction of the applied field, hence the dielectric constant ϵ' is called the relaxed dielectric constant, ϵ_R . At the same temperature, but at high frequencies, the dipoles are not able to follow immediately the rapidly alternating field. The dielectric constant ϵ' acquires a lower value and is called the unrelaxed dielectric constant, ϵ_U .

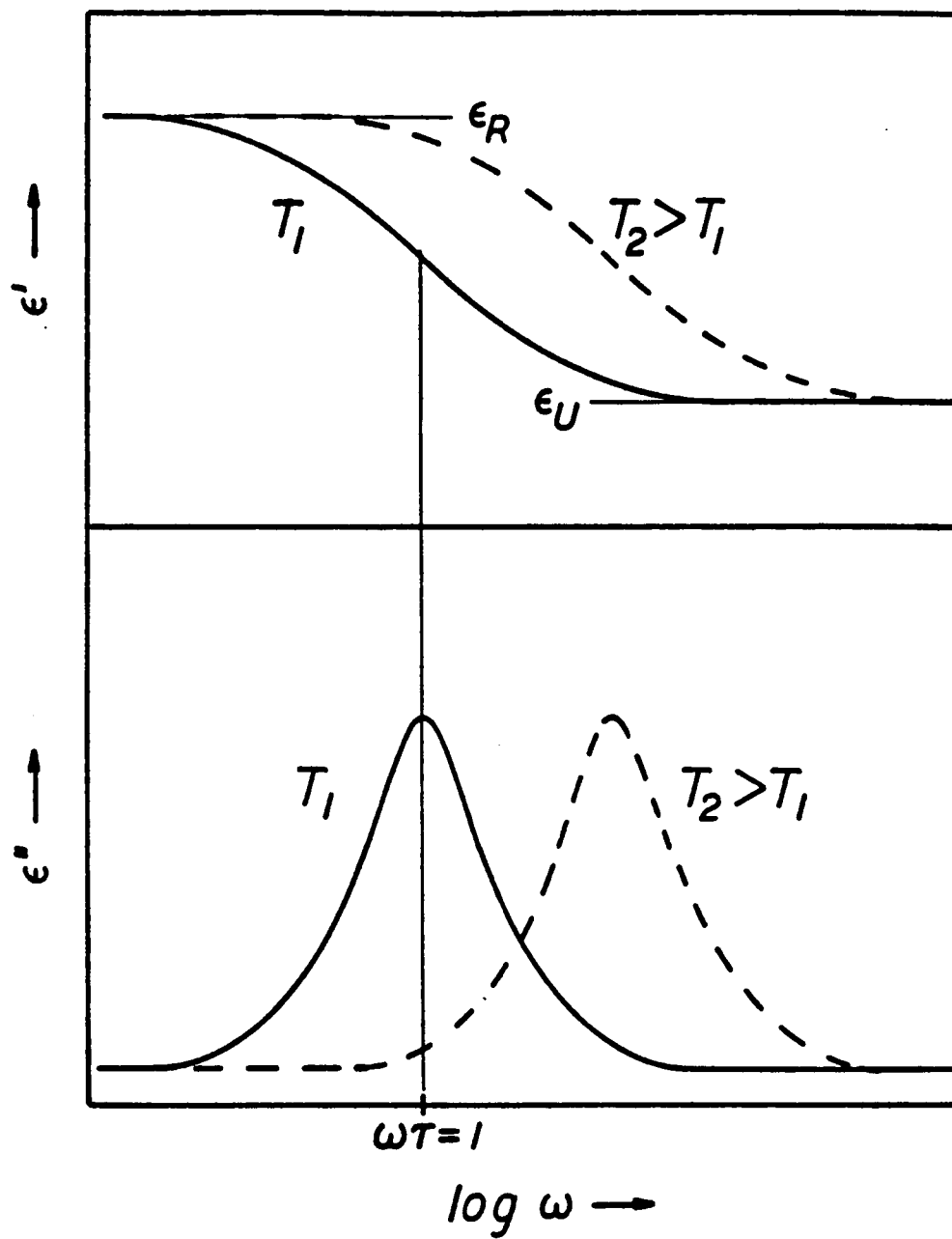


Figure 2.13. Plot of ϵ' and ϵ'' vs. $\log \omega$.

At both ϵ_R and ϵ_U the dielectric loss, ϵ'' , is negligible. The difference between ϵ_R and ϵ_U is called the relaxation strength.

Keeping in mind that the orientation of permanent dipoles in an electric field is time dependent, the simplest model we could have is one where all the dipoles orient in the same manner with the same time dependence. This is called the single relaxation time model. It is given by

$$\psi = 1 - e^{-t/\tau} \quad (2.11)$$

where ψ is the decay function, t is the time and τ is the time constant.

2.6.1.1 Empirical distributions. To check how close the relaxation of a polymer is to the single relaxation model it is usual to plot dielectric loss ϵ'' vs. dielectric constant ϵ' .

Without going into a detailed analysis, the following relationship can be obtained (Cole and Cole, 1941).

$$\left\{ \epsilon' - \frac{\epsilon_R + \epsilon_U}{2} \right\}^2 + (\epsilon'')^2 = \left(\frac{\epsilon_R - \epsilon_U}{2} \right)^2 \quad (2.12)$$

which is of the form

$$(x-a)^2 + y^2 = R^2 \quad (2.13)$$

Hence a plot of ϵ'' vs. ϵ' will give a semicircle with its center lying on the abscissa, $(\epsilon_R - \epsilon_U)/2$ away from the origin and

of a radius equal to $(\epsilon_R - \epsilon_U)/2$. This type of plot is referred to as a Cole-Cole plot (Cole and Cole, 1941). The single relaxation time (SRT) model represents dipolar relaxation in many simple liquids fairly well, but polymers usually have much broader relaxations. This model produces the following simple relation between the complex dielectric constant and the frequency of the applied field:

$$\epsilon^* = \epsilon_U + (\epsilon_R - \epsilon_U)/[1 + i\omega\tau] \quad (2.14)$$

Hence, the distributions of relaxation times present in the dielectric data of polymer must be taken into account. This is usually done by the Cole-Cole function having the parameter $\bar{\beta}$ (known as the Cole-Cole parameter) which takes values from 0 to 1. The Cole-Cole function (Cole and Cole, 1941) modified equation 2.14 by the introduction of the parameter $\bar{\beta}$.

$$\epsilon^* = \epsilon_U + (\epsilon_R - \epsilon_U)/[1 + (i\omega\tau)^{\bar{\beta}}] \quad (2.15)$$

Figure 2.14 shows a Cole-Cole diagram for various values of $\bar{\beta}$.

2.6.1.2 Temperature dependence of relaxation. Each dipole possesses at least two equilibrium positions, which are separated by an energy barrier ΔE . The dipoles oscillate with a given frequency ν about their equilibrium positions and often acquire enough energy to jump over the energy barrier from one equilibrium position to the other.

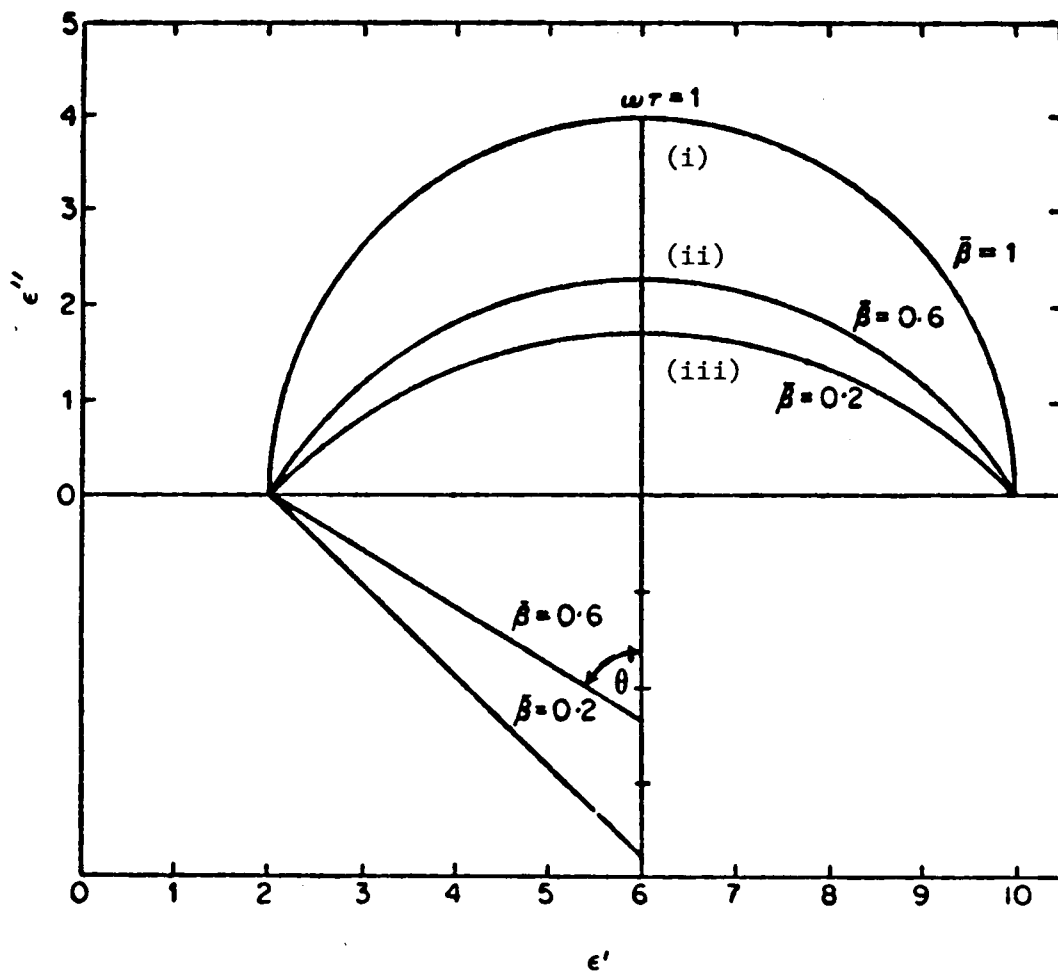


Figure 2.14. Cole-Cole Plot for Models with $\epsilon_R/\epsilon_U = 5$; (i) $\bar{\beta} = 1$ (Single Relaxation Time); (ii) $\bar{\beta} = 0.6$; (iii) $\bar{\beta} = 0.2$.

Source: McCrum, N. G., Read, B. E. and Williams G., "Anelastic and Dielectric Effects in Polymeric Solids," John Wiley & Sons, New York (1967).

The energy barrier between the equilibrium positions of the dipoles can be obtained from the temperature dependence of the frequency of maximum loss using the following equation (McCrum et al., 1967).

$$f_{\max} = Ae^{-(\Delta E/RT)} \quad (2.16)$$

Hence a plot of $\log_e f_{\max}$ vs. $1/T$ would give a straight line with a slope of $\Delta E/R$ and, if the activation energy of the process is a constant, it can be determined.

2.6.2 Dielectric Relaxation of Polyethylene

The dielectric loss data of polyethylene show three well defined loss regions as a function of temperature. A schematic diagram of the three relaxation regions of LLDPE in dielectric experiments is shown in Figure 2.15, the loss regions being labeled as α , β and γ in order of decreasing temperature. The α -loss region, located around 60°C, is due to translational motions of Mansfield-Boyd defects which have both rotational and translation motions in the crystalline phase (Mansfield and Boyd, 1978; Mikhailov et al., 1957; Sinnott, 1966). The β -loss region situated around -20°C, is believed to be associated with the amorphous regions (Flocke, 1962; Stachurski and Ward, 1968, 1969) and is related to the long range motions activated at the glass transition. The γ -loss region situated around -120°C was believed to be made up of local motions occurring in the crystalline

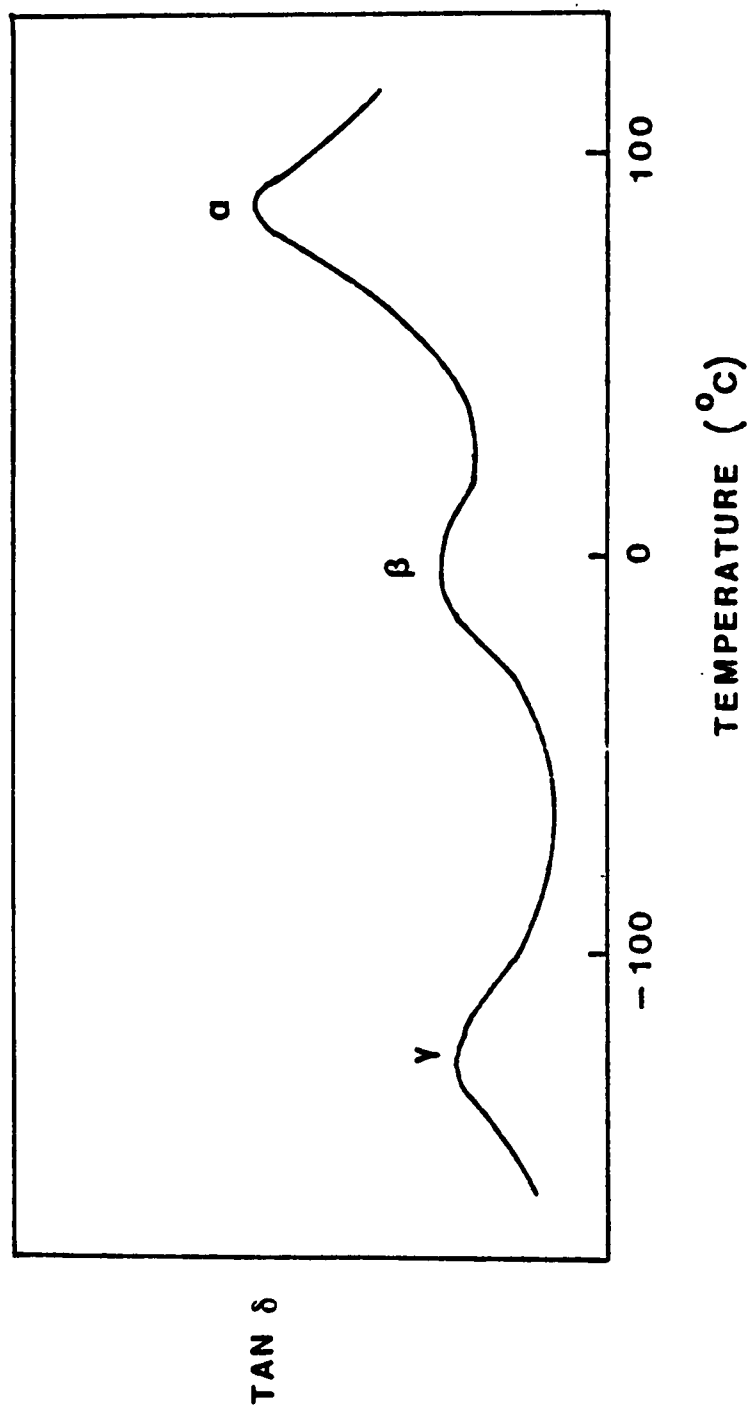


Figure 2.15. Schematic Diagram of the Three Relaxation Regions of Polyethylene in Dielectric Relaxation Studies.

as well as the amorphous phase but recently the study of Ashcraft and Boyd (1976) demonstrated that the γ -process occurs only in the amorphous phase.

2.6.3 Dielectric Relaxation of PE Containing Solute Molecules

The presence of polar aromatic molecules in polyethylene, which is practically a non-polar material itself, affects the location and intensity of peaks. Yogev and co-workers (1969, 1970, 1971a, 1971b, 1973, 1975) suggested that aromatic molecules are present inside the polyethylene crystal since the orientation functions of the solute organic molecules and polyethylene crystals are similar. Work carried out by Jang and Phillips (1982) demonstrated with the help of dielectric relaxation studies of 1-bromonaphthalene in polyethylene that the aromatic molecules are absent from the interior of the polyethylene crystals.

The dielectric loss curves for unstretched LLDPE specimens containing 0.44%, 0.89% and 1.32% by weight of 1-bromonaphthalene are shown in Figure 2.16. They observed that the β and γ loss processes are increased in magnitude whereas the α -process is decreased slightly in magnitude as the concentration of 1-bromonaphthalene was increased. If the organic molecules were located inside the PE crystals, they should intensify the α -loss process but that was not the case. This study provided strong evidence that the oriented aromatic molecules are not located inside the crystals as proposed by Yogev and his co-workers. If the molecules were present in the amorphous phase and functioning as a

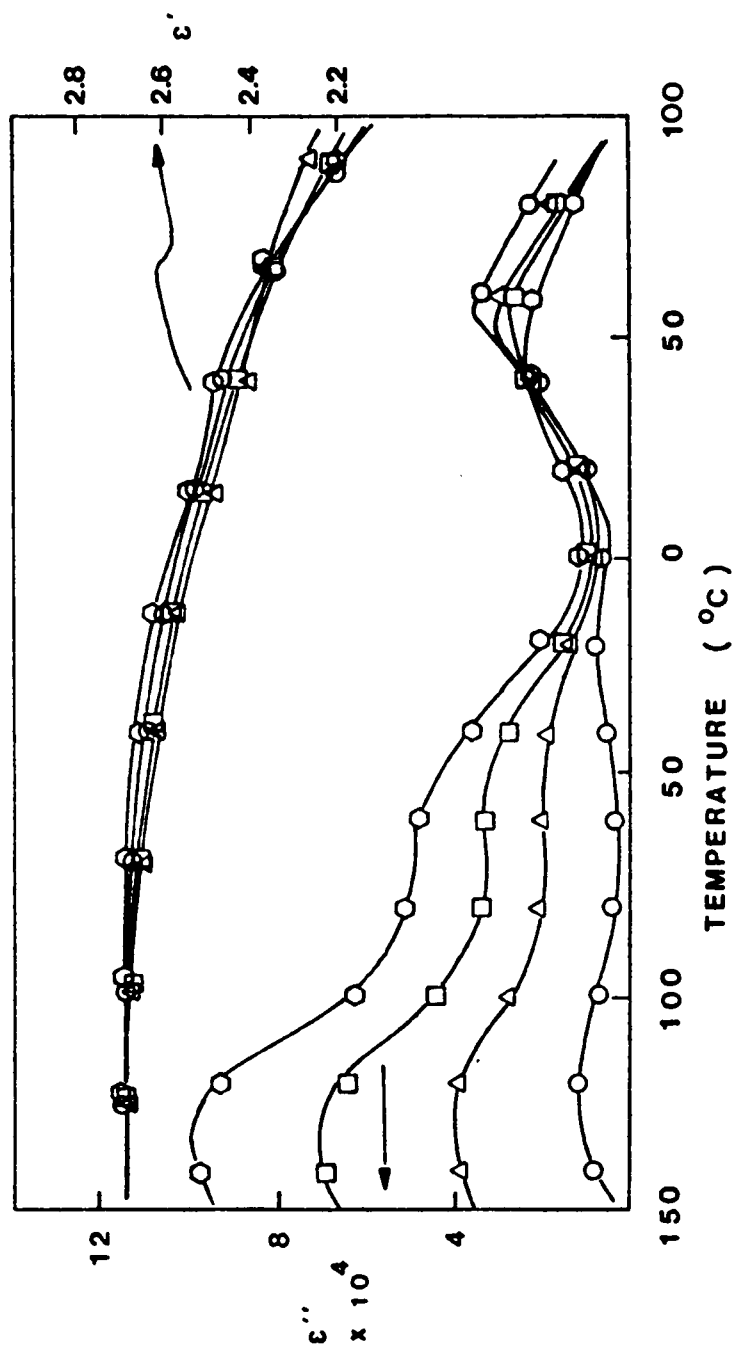


Figure 2.16. Dielectric Constant and Loss of LLDPE at 10 Hz Containing 1-bromonaphthlene. Keys: (○) 0%; (△) 0.44 wt%; (□) 0.89 wt%; (◐) 1.32 wt%.

Source: Jang, Y. T., Phillips, P. J. and Thulstrup, E. W., Chem. Phys. Lett., 93, 66 (1982).

plasticizer then they should intensify the β and γ loss processes and possibly would shift the peak locations to lower temperatures. Hence the possibility of plasticization was ruled out. Figure 2.17 shows their data for 450% stretched LLDPE containing 0.89% by weight of 1-bromonaphthalene at 10 Hz. They observed that the β and γ loss processes were reduced relative to the unstretched polymer containing the same amount of 1-bromonaphthalene, whereas the α -peak was not affected. Also adding the solute before or after stretching did not produce any change in the α -loss process leading them to the conclusion that for the oriented polymer the crystalline relaxation is unaffected by the presence of organic molecules. Data of Figure 2.17 show that the magnitudes of the β and γ loss processes are affected but not the temperature locations and no new loss processes are observed leading to the conclusion that the sites of relaxing organic molecules are not affected by stretching but that their orientation is influenced significantly. They proposed that the most likely location of oriented aromatic molecules is adsorption on the lateral (i.e., unfolded) surfaces of the polyethylene crystals.

One of the most important observations of their work which forms the basis of this work is that the γ -loss process does occur in oriented films but of a much reduced magnitude. Calculation carried out using Equation 4.6, (page 147) showed that only 40% of the molecules participating in the γ -relaxation process were detected (Jang, 1984). In other words, a large fraction of organic

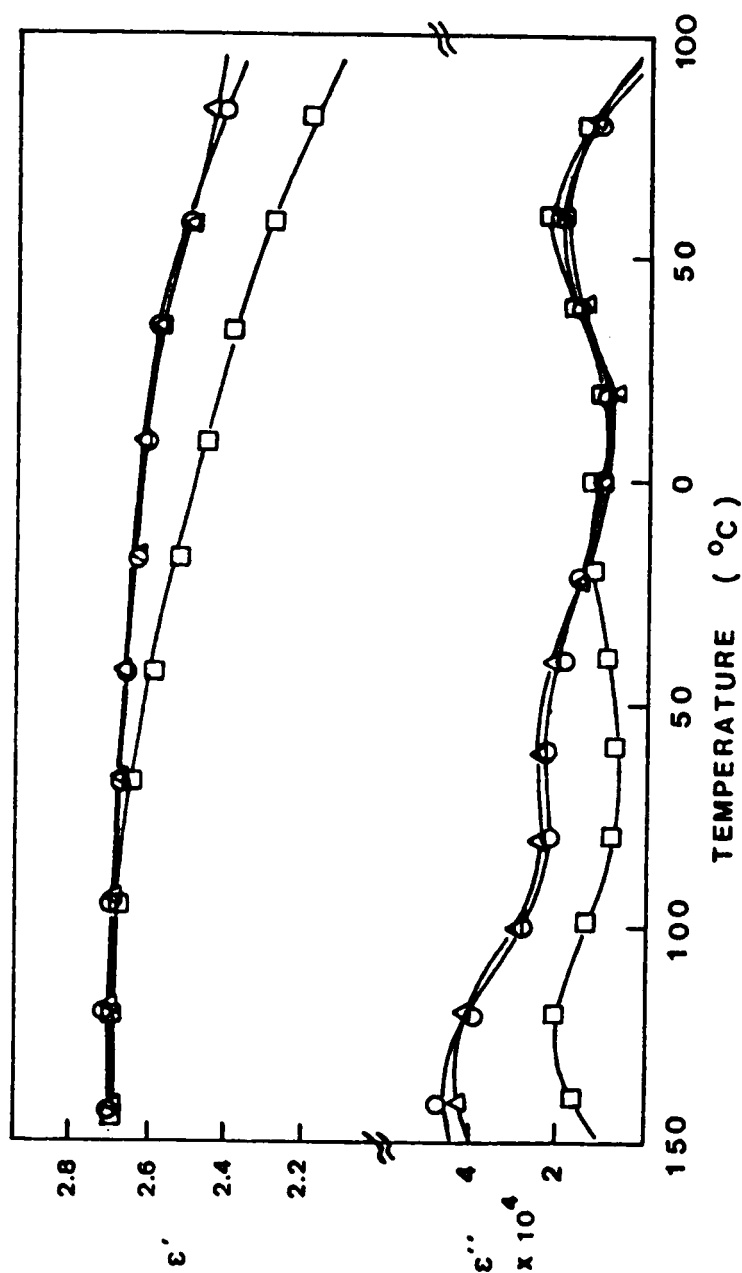


Figure 2.17. Dielectric Constant and Loss of Linear LDPE at 10 Hz.
 Keys: (□) Stretched at 450%; (Δ) Stretched to 450%, Followed by
 Adsorption of 0.89 wt% 1-bromonaphthalene; (O) Adsorption of
 0.85% by wt of 1-bromonaphthalene, Followed by Stretching to 450%.

Source: Jang, Y. T., Phillips, P. J. and Thulstrup, E. W., Chem. Phys. 93,
 66 (1982).

molecules was not able to reorient and was immobilized by the orientation process. Further investigations of this aspect are reported in this dissertation.

2.7 Epitaxial Crystallization

In work carried out by Lotz and Wittmann (1981) on the nucleating ability of organic crystals in polyethylene, it was found that polyethylene crystallizes epitaxially onto crystals of homologous series of (i) condensed aromatic hydrocarbons and (ii) linear polyphenyls.

The term 'epitaxy,' meaning 'on arrangement,' was used by Royer (1928) who developed an early theory of epitaxial growth based on structural matching. Epitaxial crystallization can be defined as the oriented overgrowth of a crystalline phase on the surface of a substrate which is also crystalline. It can also be defined as the oriented nucleation and growth of a crystalline substance on an ordered substrate. The specific adsorption and orientation of biological molecules at the surface of dust particles leads to the pathological cell metabolism which is the mechanism of the onset of the disease Silicosis. This is one of the many examples of epitaxy occurring in nature with organic molecules. The epitaxial crystallization of polymers on various substrates has been reported in the literature and discussed in detail by Williams (1967), Binsbergen (1970, 1977) and Mauritz et al., (1978) in their review articles. One of the most important aspects of epitaxial

crystallization is lattice matching. Structural similarities between organic compounds and polymers are of importance in lattice matching.

Recent investigations by Lotz and Wittmann (1981) have shown that the epitaxial crystallization of polymers onto crystallizable organic compounds can be explained using two-dimensional lattice matching of polymer and substrate organic crystal planes in contact. They also suggested that nucleating ability may result from epitaxy of the polymer onto the apolar part of the substrate. This interaction is highly specific and can affect both the structure and the morphology of the crystallizing polymer. In most cases, the action of the substrate is to enhance the nucleation of a second crystalline phase by lowering the free energy of the activation by means of the force field near the structure, according to Mauritz and Baer (1978). Mauritz et al., (1973) carried out a series of energy calculations in order to describe the epitaxial crystallization of PE from solutions in terms of molecular interactions. The total energy was computed as the sum of electrostatic, dispersion and repulsion contributions. They calculated the potential energy associated with a section of planar zig-zag polyethylene chain. Epitaxial crystallization has been observed to occur from the vapor phase, the melt and solution. It may be possible to grow organic molecules epitaxially on the external surfaces of the polymer crystals.

There are several parameters affecting the possibility of epitaxial growth, according to Mauritz and Baer (1978), being

1. molecular weight and its distribution, chemical nature, conformation and possible crystalline structure of the polymer;
2. concentration of polymer in a given solvent;
3. the chemical constitution, structural symmetry, dimensions of the substrate lattice and comparison of surface periodicities with those of the deposited phase;
4. the chemical nature of the solvent and resulting polymer-substrate interaction, and
5. temperature.

The morphology of possible epitaxial deposits, the growth kinetics, and molecular structure are a function of these parameters.

Crystals of anthracene were grown as flat platelets with top and bottom (001) faces, the lateral growth faces being (110). After melting and recrystallization of polyethylene on these crystals it was found that molecules are oriented parallel to the [110] and $[1\bar{1}0]$ directions of anthracene (Lotz and Wittmann, 1981). They also showed that polyethylene lamellae are perpendicular to the {110} growth faces of the substrate crystal and found that the periodicity along the $\langle 110 \rangle$ directions of anthracene is $5.24 \text{ \AA}$, being twice the polyethylene chain axis repeat distance of $2.54 \text{ \AA}$.

In order to understand the mechanism of orientation of aromatic molecules, epitaxial crystallization is thought to be of considerable importance, but so far there is no direct evidence of epitaxial crystallization as the mechanism of orientation of organic solutes in oriented polyethylene. Since epitaxy has been observed of polyethylene on condensed aromatic hydrocarbons, the reverse epitaxy on polyethylene may occur. One aim of this work is to investigate that possibility.

2.8 Binary Phase Diagrams and Oriented Overgrowth

Studies of polymer-organic mixtures in which both components have comparable melting points have shown eutectics. Also polymer can crystallize epitaxially onto the freshly formed organic crystals, as reported by Wittmann et al., (1977, 1978) and Rickert et al., (1978). Thus epitaxial crystallization is closely related to the formation of binary eutectic systems.

The preparation and properties of binary eutectic systems in which at least one of the components is a polymer have recently received some attention. The in-situ solid-state polymerization of organic molecules on the surface of polymer fibrils offer a possible means to create a novel type of polymer composite (Kiss et al., 1981). Interest arose in the system of polyethylene and low molecular weight organic molecules because of the fact that such a system can display both eutectic solidification and oriented growth of polymer crystals (Hodge et al., 1982).

In earlier studies by Smith and Pennings (1974) it was shown that mixtures of polyethylene and 1,2,4,5 tetrachlorobenzene form a pseudo-eutectic solid with a melting point depressed by about 15°C compared to that of the pure polymer. In another study by Wittmann and Manley (1977), the poly (ϵ -caprolactone) - trioxane system, it was observed that in hypoeutectic mixtures (organic compound rich composition), the poly (ϵ -caprolactone) crystals deposited epitaxially on the freshly grown trioxane substrate crystals providing one of the earliest examples of polymer epitaxy on freshly grown in-situ organic substrates.

In the binary system of polyethylene - 1,3,5 tribromobenzene (Hodge et al., 1982) the polyethylene component of the eutectic assumes a habit in which lamellae are highly oriented, with the chains in the (110) contact plane being parallel to the tribromobenzene needle axis. Thus well defined orientation is most likely based on an epitaxial relationship between polymer and substrate crystals. Since epitaxial growth is closely related to binary eutectic solidification it is worth exploring the phase diagram of the binary system. It may provide ideas on the possible operating mechanisms over the entire range of polyethylene and organic compound composition. Such a binary phase diagram study can provide an example of polymer/low molecular weight crystallizable solvent mixtures in which a combination of eutectic solidification and oriented overgrowth of polyethylene on freshly formed solvent crystals may result in highly anisotropic films.

CHAPTER 3

EXPERIMENTATION

3.1 Polymeric Materials

Materials used in this research are linear low density polyethylene (LLDPE, Dow Chemical 530) which has a weight-average molecular weight $\bar{M}_w = 73,342$ and $\bar{M}_w/\bar{M}_n = 9.48$ and linear polyethylene (HDPE, DuPont Sclair #2907) which has a weight-average molecular weight $\bar{M}_w = 61,000$ and a polydispersity of $\bar{M}_w/\bar{M}_n = 3.5$.

3.2 Aromatic Solutes

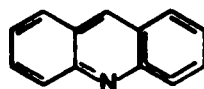
Most of the selected aromatic molecules for this work are symmetrical and have high aspect ratios, i.e., length > diameter. The aromatic molecules having a rod-like structure are known for their ability to be oriented by polyethylene into its stretch direction. For the purposes of dielectric studies, the molecules chosen contained dipolar groups in order to provide dipole moments. Table 3.1 lists their chemical and physical characteristics. Figure 3.1 shows their chemical structures.

Extensive work has been carried out using acridine in this study. For spectroscopic work acridine and 9-bromoanthracene have been used. Most of the aromatic molecules used were 'Gold label' (99.5 + % pure) from Aldrich Chemicals and were used without any further purification.

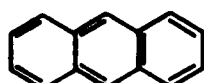
Table 3.1. Properties of Aromatic Solutes.

Solutes	M_w	M.P. (°C)	B.P. (°C)	Density (g/cm ³)	Dipole Moment (Debye)
Acridine	179.22	110	345	1.005	2.19
Anthracene	178.23	216	340	1.283	--
9-Bromoanthracene	257.14	98	--	0.998	1.61
Naphthalene	128.19	80.5	218	0.963	--
Phenanthrene	178.24	101	340	0.98	--
Phenazine	180.21	177	sub. 360	--	--
Pyrene	202.26	150	393	1.271	--
p-terphenyl	230.31	212	sub. 250	--	--

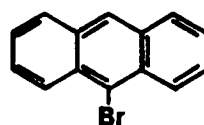
ACRIDINE



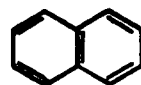
ANTHRACENE



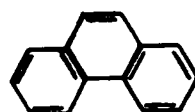
9-BROMOANTHRACENE



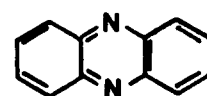
NAPHTHALENE



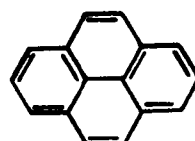
PHENANTHRENE



PHENAZINE



PYRENE



p-TERPHENYL

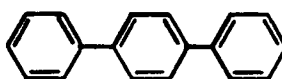


Figure 3.1. Chemical Structure of Aromatic Compounds.

3.3 Sample Preparation

3.3.1 Unoriented Films

Films of linear low density polyethylene were compression molded using a hot press at 150°C. About 30 - 35 grams of the LLDPE pellets were placed between two flat, one-foot square stainless steel plates. The plates with pellets were kept between preheated hot plates for an initial time of 4 minutes to allow complete melting to occur. Gradually a pressure of approximately 100 psi was applied for 4 minutes to press the melt into a film. The hot press was then allowed to air cool to ambient under pressure. Spacers of thickness 0.001, 0.0015 and 0.002 inches were used to obtain sheets of uniform thickness.

3.3.2 Uniaxially Stretched Films

The films produced as described in section 3.3.1 were usually unoriented. To produce orientation, the films were cut to a gauge width of 1.75 inches and a gauge length of 1.5 inches using 2 inch shoulders. These films were uniaxially stretched from 100 to 600% in a bench model Instron machine at a constant strain rate of 0.5 inch/min. The stretched sheets produced by this method have good reproducibility and consistent orientation. Reproducibility and consistent orientation effects were also obtained by Michl and co-workers (1983). After stretching, the films were retained in the Instron jaws for 30 minutes before removing them.

3.3.3 Extruded Rods

Solid-state extruded rods were produced using a modified version of the method developed by Sayre and Boyd (1978). Orientation of the polymer can be achieved by means of cold work, such as drawing, stretching, rolling, and solid-state extrusion. A stretched film could be measured dielectrically only in the perpendicular direction, whereas extruded rod can be measured dielectrically both parallel and perpendicular to the orientation direction. In solid-state extrusion the polyethylene is extruded through a tapered die at a temperature approximately 40°C below its melting point. The extrusion ratio is defined as the ratio of the cross-sectional area before extrusion to that after extrusion.

3.3.3.1 Compression molding of rods. The polyethylene to be extruded was molded into solid rods free of voids. A compression molding cell was constructed of 4140 steel hardened to 55 Rockwell C and had an inner diameter of 1 inch and an outer diameter of 3 inches. The molding cell is shown in Figure 3.2 (a). The cylinder, piston and plugs are made of 4140 steel hardened to 55 Rockwell C. Steel plugs (4140 steel hardened to 55 Rockwell C) and teflon delta rings were used as a high pressure seal in the cell. As shown in Figure 3.2 (b) the steel plug has a 45° angle while the teflon ring has a 48° angle allowing good sealing when the pressure is applied.

In order to mold the polyethylene rod, the cell was filled with LLDPE pellets and assembled as shown in Figure 3.2 (a). The cell was heated to 150°C at a heating rate of 2°C/min. The heat was

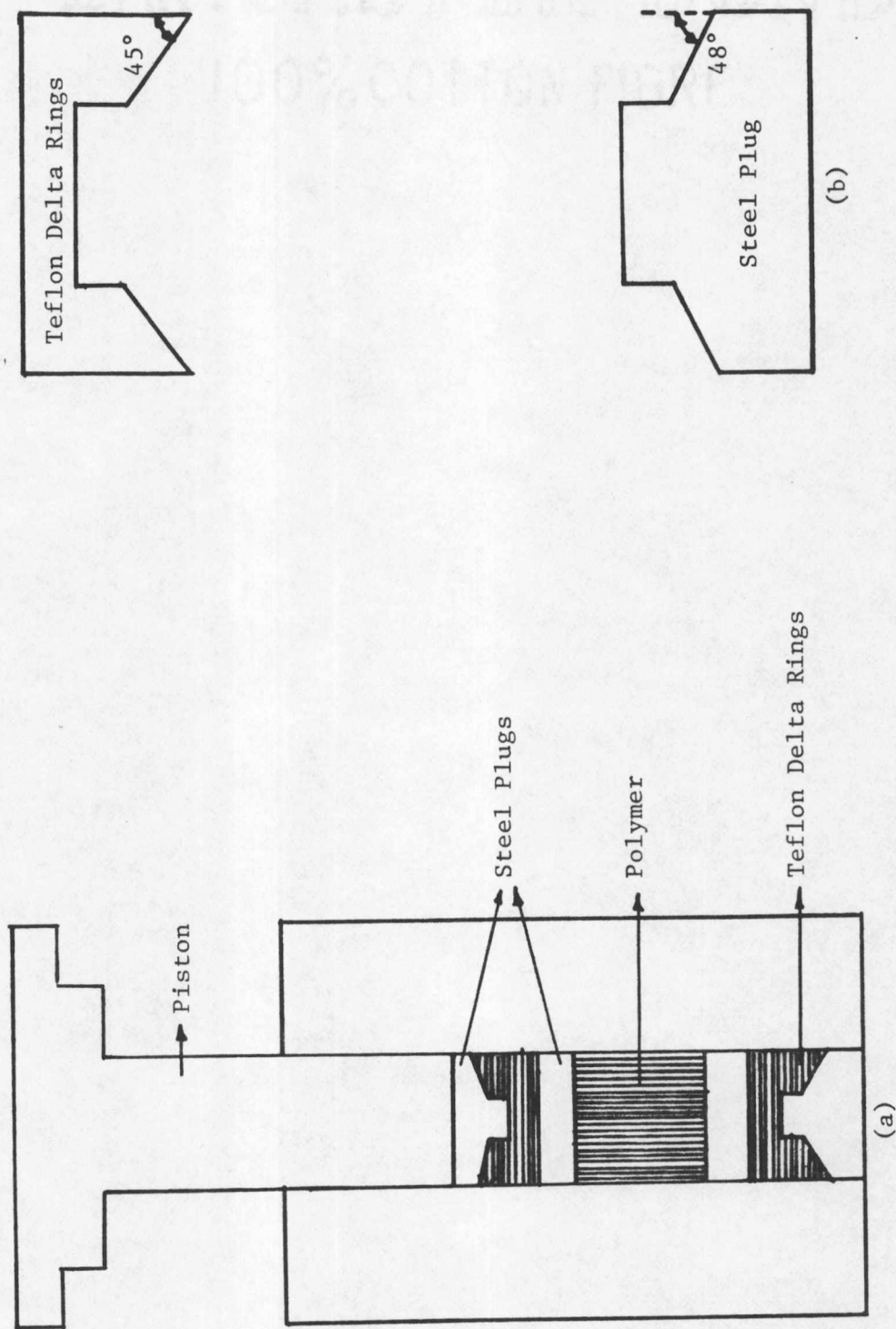


Figure 3.2. Compression Molding Cell. (a) Assembly, (b) High Pressure Seals.

provided by a heavy duty heating tape which was wrapped around the cylinder. The temperature was monitored using thermocouples. After reaching 150°C a pressure of about 10,000 psi was applied and kept at that level while the cylinder was air cooled to room temperature. This compression was carried out on a Tinius Olsen tensile testing machine.

3.3.3.2 Solid-state extrusion. The extruder used in this work was again originally designed by Sayre and Boyd (1978) and was modified as shown in Figure 3.3. The extruder has the die built into the piston, thus reducing the required extrusion pressure and avoiding slippage of the polyethylene between the piston and the barrel. The die entrance was very smoothly machined and was of a concave shape upward toward the barrel base which provided a large surface of die as well as a slow and smooth extrusion process. The die half angle was 56 degrees.

The extruder had a half diameter reduction (the die inside diameter was one-half the barrel diameter of 1 inch). The die was made of Graph-air steel hardened to 62 Rockwell C. A high extrusion ratio can be achieved by consecutive extrusions through two or three extruders which have half diameter reductions.

The extrusion temperature was measured using a thermocouple and a digital thermometer. The heating tape wrapped around the barrel was used to raise the temperature up to the extrusion temperature (70°C), the heating rate being controlled by a potentiometer. Extrusion was started when the temperature reached 70°C, an

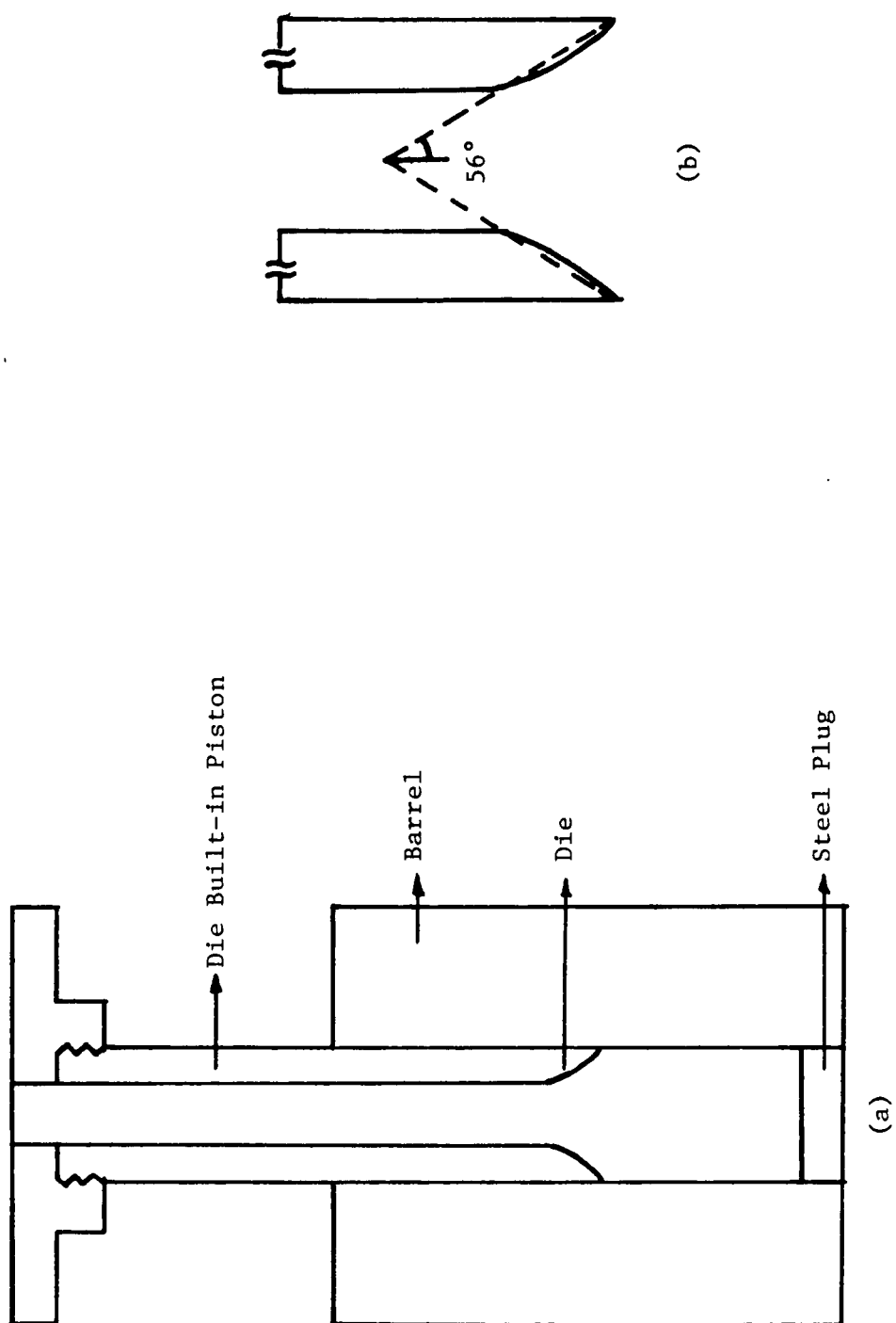


Figure 3.3. Schematic Representation of (a) Solid-State Extruder Assembly,
(b) Die Entrance.

extrusion rate of 0.05 inch/min being used. The piston was pushed into the barrel, hence forcing the polymer through the die.

3.3.4 Polyethylene Powder

Polyethylene powder was made by dissolving 5 grams of polyethylene pellets in 100 ml of p-xylene at about 130°C with magnetic stirring. When the dissolution of polyethylene was complete, the solution was added dropwise into 400 ml of methanol (which was kept cool with dry ice) and vigorously stirred. After half an hour, the polyethylene had precipitated completely in the flask. The polyethylene was recovered by filtration under vacuum and the wet powder was added to methanol with stirring for 15 minutes, again recovered by filtration and then washed with methanol twice to remove p-xylene. Complete removal was carried out in a vacuum oven at 50°C and 30 mm pressure for 48 hours. A liquid nitrogen trap was used to condense the solvent.

3.3.5 Absorption of Aromatic Compounds

3.3.5.1 Gas phase absorption. Aromatic chemicals in the solid form were placed in a small beaker, polyethylene samples being placed on a support across the edges of the beaker. This set-up was then placed in a vacuum desiccator attached to a vacuum pump. The samples were kept under vacuum for a selected period of time depending on the desired concentration of aromatic compounds in polyethylene film. The sample surfaces were then washed with spectral-grade methanol to remove all surface deposits of aromatic

materials. The amount of chemical absorbed was determined by weighing the samples before and after the above procedure using a high precision electronic balance capable of measuring up to 10^{-6} grams accuracy.

3.3.5.2 Soaking in chloroform solution. Most of the aromatic compounds used in this work can be dissolved in spectral-grade chloroform very easily at room temperature. A concentrated chloroform solution of any selected aromatic compound was made and polyethylene samples were soaked in the solution for a selected period of time. The surfaces of the samples were washed with spectral-grade methanol to remove aromatic compounds from the surfaces. The samples were then kept in a vacuum oven for an hour. Samples prepared by this method were tested by infrared spectroscopy to ensure an absence of chloroform. The amounts of aromatic compounds absorbed were determined by weight difference.

3.3.6 Mixing of PE Powder and Aromatic Compounds for Binary Phase Diagrams

The phase diagrams of polyethylene and aromatic compounds were determined using differential scanning calorimetry (DSC) and X-ray diffractometry. The polyethylene, whether HDPE or LLDPE, was used in powder form for blending. The powder was prepared as described in section 3.3.4. The polyethylene (HDPE or LLDPE) for a particular binary phase diagram was selected in such a way that the melting point difference between the polyethylene and aromatic compound was

minimized. The aluminum sample pans used for DSC study were volatile sample pans which can withstand internal pressures up to 3 atmospheres. Approximately 2 to 3 milligrams of samples of a weighed mixture having a given composition were sealed in the sample pan. The sample pans were weighed before and after each run, to check for loss of aromatic compounds.

The thermal treatments for the samples of various compositions were initial melting to at least approximately 10°C above the melting point of the higher melting component for 15 minutes (to homogenize the mixtures) followed by cooling to ambient at a rate from $2.5^{\circ}\text{C}/\text{min}$ to $80^{\circ}\text{C}/\text{min}$. Melting endotherms of above treated mixtures were recorded at a heating rate of $10^{\circ}\text{C}/\text{min}$.

Films were prepared as follows. Approximately 2 to 3 milligrams of a weighed mixture having a selected composition was placed in between two coverslips. These samples were melted to at least 10°C above the melting point of the higher melting component for 10 minutes followed by cooling to ambient at a rate of $10^{\circ}\text{C}/\text{min}$. They were weighed before and after heat treatment, to check for loss of aromatic compounds. All the heat treatments were carried out on the hot stage of an optical microscope for precise temperature control. The films prepared by the above procedure were studied using X-ray diffractometry.

3.3.7 Sample Preparation for Epitaxial Crystallization

Single crystals of acridine and anthracene were grown in the laboratory for the study of epitaxial crystallization. Acridine

crystals were dissolved in dilute methanol and the solution was kept in an ice bath to produce single crystals of acridine. Polyethylene film was obtained on a glass slide by drying a 0.5% dilute solution in p-xylene. This solvent cast film was treated at 80°C for 24 hours to eliminate p-xylene. This very thin solvent cast film was placed on the single crystal of acridine following a thermal treatment under vacuum to eliminate p-xylene. This preparation was subject to melting of the polyethylene film but not of the substrate single crystal. Afterwards the polyethylene was recrystallized during slow cooling to room temperature. All the heat treatments were carried out on the hot stage of an optical microscope for precise temperature control. Samples prepared by the above procedure were studied using X-ray diffractometry.

3.3.8 Ethylene-Propylene Rubber Films

Ethylene-propylene rubber (EPR), available in the block form (VISTALON 404, Exxon Chemicals), was dissolved in p-xylene at 130°C. After complete dissolution of the EPR, the solution was added dropwise into methanol (which was kept cool with dry ice) and vigorously stirred. After 15 minutes, the EPR had precipitated completely in the flask. The EPR was recovered by filtration under vacuum and the wet EPR was added to methanol with stirring for 15 minutes, again recovered by filtration and then washed with methanol three times to remove p-xylene. Dicumyl peroxide (DCP) was crystallized from aqueous methanol. The EPR powder was then mechanically mixed with dicumyl peroxide as follows. Typically,

10 grams of EPR and 50 ml of methanol were placed in a beaker, and DCP in methanol was added to give the desired concentration. This assembly was stirred with a magnetic stirrer until the slurry dried.

The powder samples were mixed with a spatula and compression molded into a sheet of 0.01" thickness. This was carried out on a hot press using a mold made of stainless steel plates with a steel separator template having a hole of area 10 cm^2 . The mold had been preheated to 170°C for 2 minutes. The polymer-peroxide reaction was carried out for 5 minutes at 210°C . Decomposition of DCP was expected to be at least 99.9% based on the known reaction kinetics. Upon curing at the above conditions, the crosslinked polymer was allowed to cool in air before removal from the mold. Sol fractions were extracted by boiling in p-xylene at 140°C for 72 hours.

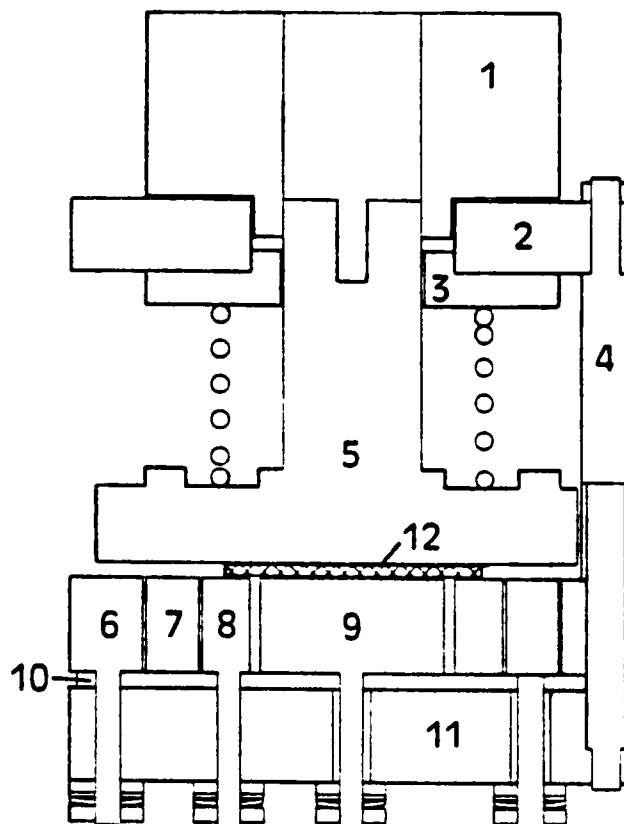
3.4 Dielectric Relaxation Studies

3.4.1 Equipment

Dielectric measurements were made using a system consisting of an oscillator, a detector, a capacitance bridge and a dielectric cell. Capacitance and conductance measurements were carried out on a General Radio 1621 capacitance measurement assembly which consists of a 1616 capacitance bridge with 1316 audio oscillator, 1238 tuned amplifier and null detector. The 1616 bridge is a transformer ratio arm bridge with a capacitance range of 10^{-19} F to 10^{-7} F , having $\pm 0.01\% + 0.00003 \text{ pF}$ accuracy at 1 KHz and a

conductance range of $10^{-12} \Omega$ to $10^{-4} \Omega$ having accuracy equal to $\pm 1\%$ measured value. The 1616 Capacitance Bridge can be used in a three terminal mode in which the lead capacitance is grounded out. The 1316 oscillator is a high performance audio oscillator with an output of 10 to 10^5 Hz having $\pm 1\%$ accuracy at an output voltage of 125 v. It is specifically designed for use with the 1238 detector and 1616 capacitance bridge. The 1238 detector is a sensitive, low-noise instrument particularly suited for null detection in a high precision bridge system like this one. This detector can be tuned to the oscillator over its entire range of frequency.

The dielectric cell used in this study was originally designed by Coburn (1984) as a three terminal parallel plate capacitor to measure sample capacitance and conductance (see Figure 3.4). The parallel plate capacitor consisted of a central brass disc surrounded by three concentric brass rings. The central disc served as a low lead electrode and the middle concentric ring as the air capacitor electrode. The inner and outer concentric rings served as the guard lead electrodes which are used to eliminate fringe fields and surface conduction across the edge of the sample. The air gap between the central disc and the three concentric rings electrically isolated the sample low electrode from the inner guard electrode and the air capacitor the low electrode from the outer guard electrode. The top surfaces of the central disc and the three concentric rings were polished to obtain coplanar surfaces. To measure accurately the temperature of the sample a Cu-Constantan thermocouple was



1	Top Brass Screw	7	Air Capacitor Low Electrode
2	Top Disc	8	Inner Guard Ring
3	Phenolic Insulating Collar	9	Low Electrode
4	Brass Column	10	Pyrex Sheet
5	High Electrode	11	Base Brass Plate
6	Outer Guard Ring	12	Sample

Figure 3.4. Dielectric Cell.

Source: John Coburn (1984) Ph.D. Dissertation, Univ. of Utah.

placed in the inner concentric ring through a hole in the bottom disc. The top brass disc was aligned parallel to the coplanar surface of the central disc and three concentric rings with the help of three brass columns. This top brass electrode served as a high lead electrode for both the sample and air capacitors. Whenever necessary, pyrex sheets were used to electrically insulate the electrode since they have excellent thermal stability over the entire range of experimentation.

3.4.2 Experimental Procedure

3.4.2.1 Unoriented films. A flat sample of uniform thickness (usually in the range 0.0015 to 0.002 inches) approximately 0.6 inch in diameter was cut from the compression molded specimen. This sample was placed in between the two electrodes and the spring loaded high electrode was lowered slowly until it fully rested on the sample ensuring firm contact of the sample with both electrodes. The required connections for the high and low lead electrodes were made and a thermocouple was placed at the bottom of the dielectric cell. This assembly was placed in a brass container and nitrogen purged through the gas inlet. The heating tape was mounted on the outer surface of the brass container which was placed in a Dewar flask. Thermal insulation was provided by fiberglass. Liquid nitrogen was poured slowly to cool the assembly to liquid nitrogen temperature (-196°C). The heating tape was connected to a transformer which was used to raise the temperature at a heating

rate of approximately 20°C/hr . The capacitance and conductance of the sample were measured at intervals of 2°C from -190°C to 100°C at frequencies of 10, 20, 50, 100, 1000 and 5000 Hz.

3.4.2.2 Stretched films. The uniaxially stretched film was cut into a circular disc of diameter ca. 0.6 inch and thickness of 0.001 to 0.0015 inches. Exactly the same procedure was followed as described in section 3.4.2.1 for capacitance and conductance measurements.

3.4.2.3 Extruded rods. The extruded rods permit the acquisition of capacitance and conductance data in the directions parallel and perpendicular to the extrusion direction. A stretched film can be measured dielectrically only perpendicular to orientation. A diamond rotary blade was used to cut the extruded rods. Since the diamond wafering blade itself has a thickness of 0.006 inches it was difficult to obtain a uniform sample thickness below 0.0015 inches. A special mount was designed to hold the extruded rod for cutting, water being used as a cooling agent. Again the sample procedure was followed as described in section 3.4.2.1 for acquisition of capacitance and conductance data.

3.5 Dynamic Mechanical Studies

3.5.1 Equipment

Dynamic mechanical experiments were carried out using a TMI Rheovibron DDV-II, which is a direct reading dynamic viscoelastomer.

With the help of this equipment the temperature dependence of the complex modulus of polymer at a definite frequency can be measured. This instrument deforms the sample with a small sinusoidal pulse of a set frequency. Measurement is made of the phase angle and the difference in magnitude between the applied wave and the transmitted wave. From these measurements the storage and loss moduli can be calculated. For the DDV-II model, the $\tan \delta$ value is read off directly on the meter. Four frequencies are provided: 3.5, 11, 35 and 110 Hz, however the 35 Hz cannot be used since it corresponds to a machine resonance. The complex modulus E^* is given by the equation: $E^* = E' + iE''$.

A schematic representation of the arrangement of the DDV-II Rheovibron is shown in Figure 3.5. Cooling was provided by liquid nitrogen and heating by use of heating elements controlled by a transformer. A Cu-Constantan thermocouple was used to detect the temperature using a digital thermometer.

3.5.2 Experimental Procedure

Dynamic mechanical relaxation spectra were obtained only for the extrusion direction for specimens of length of 2.5 cm, width 0.5 cm and thickness of approximately 0.0015 inches being normally used. The spectra in the direction perpendicular to the extrusion direction could not be obtained because of the small specimen size. The sample was clamped between the strain gauges and a dry nitrogen flush was maintained throughout each experiment to prevent water condensation. The whole assembly was cooled to liquid nitrogen

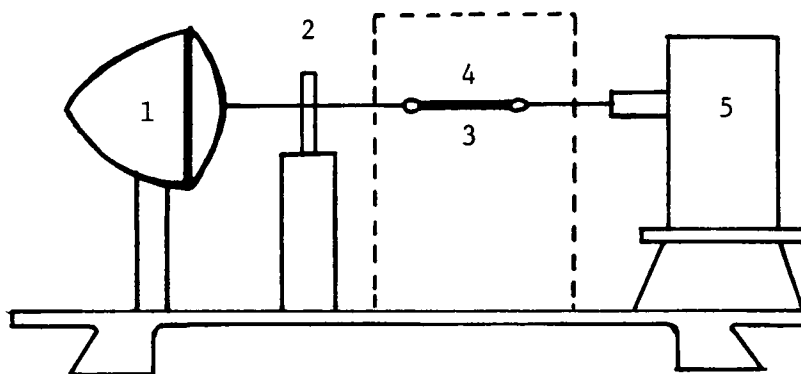


Figure 3.5. Schematic Representation of the Arrangement of the Rheovibron. (1) Driver, (2) Strain Gauge, (3) Sample Furnace, (4) Sample, (5) Stress Gauge.

temperature by pouring liquid nitrogen into the sample furnace. $\tan \delta$ values were measured at every 2°C interval from -160°C to 100°C at a heating rate of 30 to 35°C/hr . When the temperature was raised, it produced a lowering of Young's modulus. For this reason, the amplitude of the applied wave was adjusted at each temperature.

3.6 Infrared Spectroscopy

3.6.1 Equipment

All the infrared spectra were recorded on a Nicolet 7000 Fourier-Transform Spectrometer (4000 – 200 cm^{-1}) with a resolution of 1 cm^{-1} , using aluminum grid polarizers (Cambridge Physical Sciences, Ltd.) and a HARRICK quadruple diamond polarizer. The polarizer was mounted in the path of the light beam prior to its passing through the sample. Infrared spectroscopy, in conjunction with infrared dichroism techniques, have been used to study the orientation of aromatic molecules using a quantitative analysis of infrared absorption bands. The orientation of the aromatic compounds was measured as a function of dichroic ratio.

The phenomenon of infrared dichroism occurs in polymer samples which have chemical bonds preferentially oriented in a particular direction. Infrared radiation plane polarized in a direction parallel to the transition moment of the oriented bonds will have a greater absorption than light polarized in any other direction. In general, infrared absorption spectra are measured with plane polarized light in two mutually perpendicular directions. The ratio

of the parallel to perpendicular polarized absorption intensities is known as the dichroic ratio.

Fourier Transform Infrared Spectroscopy (FTIR) uses a Michelson interferometer which preserves both frequency and intensity information, collimated radiation from the source being partially transmitted by a beam splitter. The transmitted beam is reflected from a moving mirror and the reflected beam is reflected from a fixed mirror. These two beams are recombined at the beam splitter, where one goes back to the source and the other goes to the detector through the sample. Constructive interference is obtained if the traveling distance of these two beams is equal.

3.6.2 Experimental Procedure

The unoriented sample with or without aromatic molecules in it was mounted on an aluminum holder over a circular hole for beam passage. Absorbance spectra were obtained for the stretched sample (with or without aromatic molecules in it) with light polarized parallel and perpendicular to the direction of stretch. Before performing any experiment using FTIR, the spectra were checked for the presence of water and carbon dioxide. Dichroic ratios were determined from the intensity of parallel polarized light and the corresponding intensity of perpendicularly polarized light for any absorption band.

3.7 Ultra-violet Spectroscopy

3.7.1 Experimental Procedure

All the ultraviolet absorption spectra were measured on a Cary 17 spectrophotometer. The absorption spectra were recorded for two mutually perpendicular positions of a Glan-Thompson polarizer located at 45° from the vertical, one having the electric vector of the light parallel and the other perpendicular to the stretching direction of the film. A second polarizer was placed in the reference compartment. The sample size was 1.5 square centimeters. Each sample was scanned over the 250 - 450 nm range.

3.8 Differential Scanning Calorimetry

3.8.1 Equipment

All experiments were carried out using Perkin-Elmer Differential Scanning Calorimeters model 2 and model 7. The instruments were calibrated using the melting transitions of pure indium (156.6°C) and tin (231.9°C). The DSC has two platinum sample holders, one for an empty aluminum pan used as a reference, the other for an aluminum pan containing a sample. When the DSC is programmed to heat or cool at a constant rate, both sample holders maintain the same temperature. The amount of energy which has to be supplied or withdrawn from the sample to maintain a zero temperature differential between the sample and the reference is the ordinate of the DSC plot. The temperatures of both the microfurnaces are compared, and the electrical power supplied to

each microfurnace (heater) is adjusted so that the temperature of both pans remains equal to the specified temperature. The power used to balance the pans is plotted as the abscissa. DSC can be used to measure heats of transition, temperatures of transitions, specific heats, crystallinity, glass transition temperatures, purity, crystallization kinetics, thermal and oxidative degradation, and characterization. The DSC-7 is one component of the Perkin-Elmer 7 series thermal analysis system which includes PE 7500 Professional Computer, TAC 7 (Thermal Analysis Instrument Controller) and Graphics Plotter 2. The DSC-7 can be operated from -170°C to 725°C with heating and cooling rates from $0.1^{\circ}\text{C}/\text{min}$ to $500^{\circ}\text{C}/\text{min}$ with the temperature accuracy of $\pm 0.1^{\circ}\text{C}/\text{min}$.

3.8.2 Experimental Procedure

All samples have been made either as film or powder of weight in the range 2 to 4 milligrams. In the case of volatile materials the volatile aluminum sample pans were used to prevent the loss of the materials. These pans can withstand internal pressures of up to 3 atmospheres. The samples sealed in aluminum pans were weighed before and after the DSC runs. All experiments were conducted with the sample enclosed in a sealed aluminum pan under flowing dry nitrogen gas at ambient pressure. In most of the experiments the temperature programmed heating rate of $10^{\circ}\text{C}/\text{min}$ was used to measure the melting temperature.

3.9 Wide Angle X-ray Diffraction

3.9.1 Equipment

Two types of X-ray diffractometer have been used during the course of this work. They are a Philips X-ray unit and a Rigaku X-ray diffractometer system. Monochromatic Radiation Cu K α ($\lambda = 1.5418^{\circ}\text{A}$) was generated at 35 KV and 20 mA and a nickel filter was used.

3.9.2 Flat Film Patterns

For the flat film diffraction patterns a sample was placed between the X-ray source and the camera with a sample to camera distance of 3 centimeters. A very useful device designed by Professor E. S. Clark was used for mounting the samples. This device was used during the study of the diffraction patterns for single crystals and epitaxially crystallized samples. Kodak BB-5 (Blue Brand) films were used to record the diffraction pattern. Oriented films (stretched films and extruded rods) exhibit X-ray patterns consisting of arcs. A quantitative analysis of the orientation requires angular intensity scanning of the arcs. The intensity of the diffraction pattern was measured using a microdensitometer. The azimuthal intensity distributions of the (hk0) reflection of PE were determined over one quadrant of the pattern. The intensity measurements were obtained using a Joyce-Lobel automatic recording microdensitometer model MKIII C.S., radial scans

being carried out and the maximum intensity being taken at each azimuthal angle.

3.9.3 Diffractometry

The X-ray diffractometer system used is mainly composed of an X-ray generator, a goniometer, an electronic circuit panel and control/data processor. A schematic diagram of the X-ray diffractometer system is shown in Figure 3.6. The X-ray generator produces a high voltage to be applied to the X-ray tube and controls the voltage and current applied to the X-ray tube. The X-ray generator employs a solid-state negative feed back control constant potential system by which the variation of the current and voltage applied to the X-ray tube is directly detected and the input power supply is controlled accordingly. The data processor controls the goniometer and the electronic circuit panel. The electronic circuit panel accepts pulses from the counter and records X-ray intensities.

The goniometer used is a horizontal type that allows installation of various diffractometer attachments. The goniometer performs remote-controlled automatic scanning over a preset angular range. Whenever necessary 'Duco Cement' was used to attach sample to the sample holder.

3.9.4 High Temperature X-ray Diffraction

X-ray diffraction experiments at higher temperatures were carried out on thermally treated samples of various compositions of the acridine-LLDPE system prepared as described in section 3.3.6.

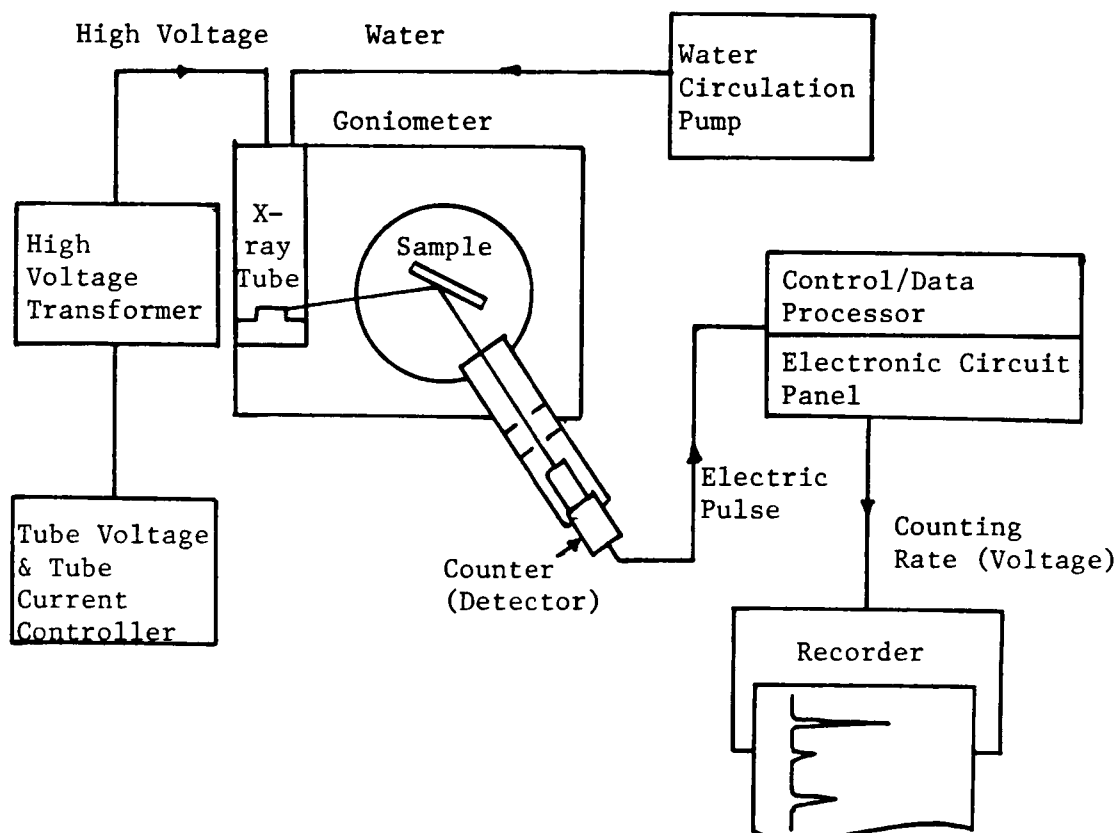
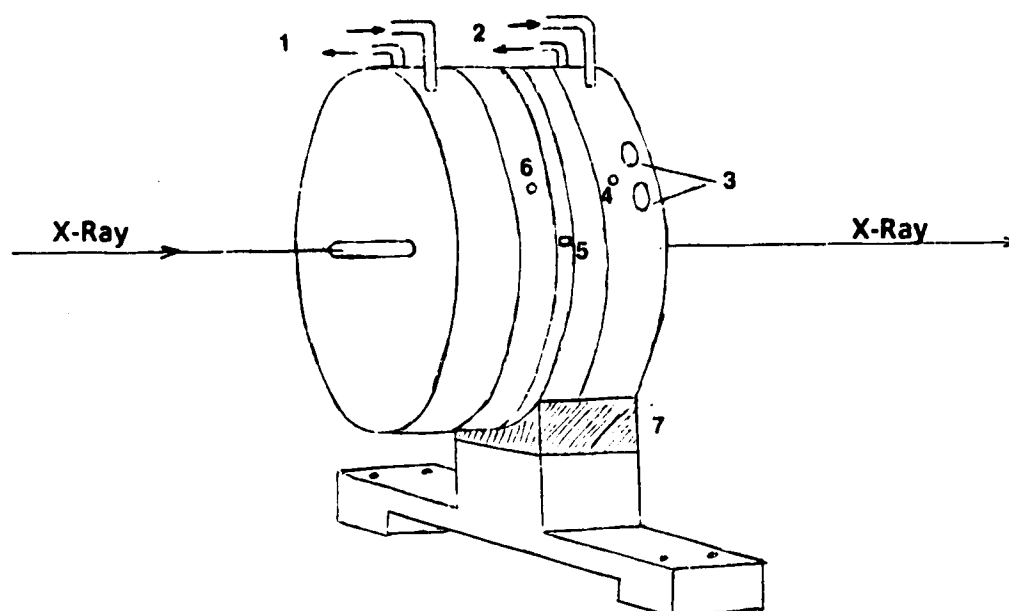


Figure 3.6. Schematic Diagram of X-ray Diffractometer System.

All the X-ray diffraction patterns at high temperatures were obtained in the transmission mode. The high temperature cell was mounted in a Rigaku X-ray diffraction system. The sample was placed in a high temperature cell and gradually heated and controlled with the help of a circulating oil bath. X-ray diffraction patterns were obtained at intervals of 15°C from ambient to approximately 106.5°C .

The high temperature cell (see Figure 3.7) used in this study is made up of aluminum. It has inbuilt heat exchangers. Hot silicone oil circulates through the grooves of a heat exchanger and circulator bath. The Cu-constantan thermocouple was placed very close to the sample to monitor the exact temperature of the sample. The high temperature cell was mounted on a fiberglass insulation base which was mounted on the goniometer. The assembly was covered with insulation material to prevent heat losses at high temperature.



- 1, 2 CIRCULATOR CONNECTIONS
- 3 CARTRIDGE HEATERS
- 4, 5, 6 THERMOCOUPLE INLETS
- 7 FIBERGLASS INSULATION

Figure 3.7. High Temperature Cell for X-ray Diffraction Studies.

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Polyethylene4.1.1 Unoriented Films

4.1.1.1 Characterization of LLDPE films. The films prepared as described in section 3.3.1 were characterized using standard techniques such as differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS). The DSC curve shows that LLDPE melts over the range 55° to 115°C at a heating rate of 10°C/min with the peak position located at 110.2°C (see Figure 4.1). The heat of fusion (ΔH) for LLDPE determined from the DSC melting curve is 21.5 cal/gm. Percent crystallinity can be determined from heat of fusion using the following equation

$$\% \text{ crystallinity} = \frac{\text{heat of fusion of specimen}}{\text{latent heat of fusion}} \quad (4.1)$$

To determine the latent heat of fusion of LLDPE WAXS was used. Figure 4.2, obtained using a flat plate camera, shows a series of concentric circles representing diffraction of crystallographic planes. The innermost ring with the highest intensity corresponds to the (110) plane, the next ring corresponds to the (200) plane. Inside the (110) ring, a hazy area represents the presence of the amorphous phase in LLDPE. This figure shows the absence of

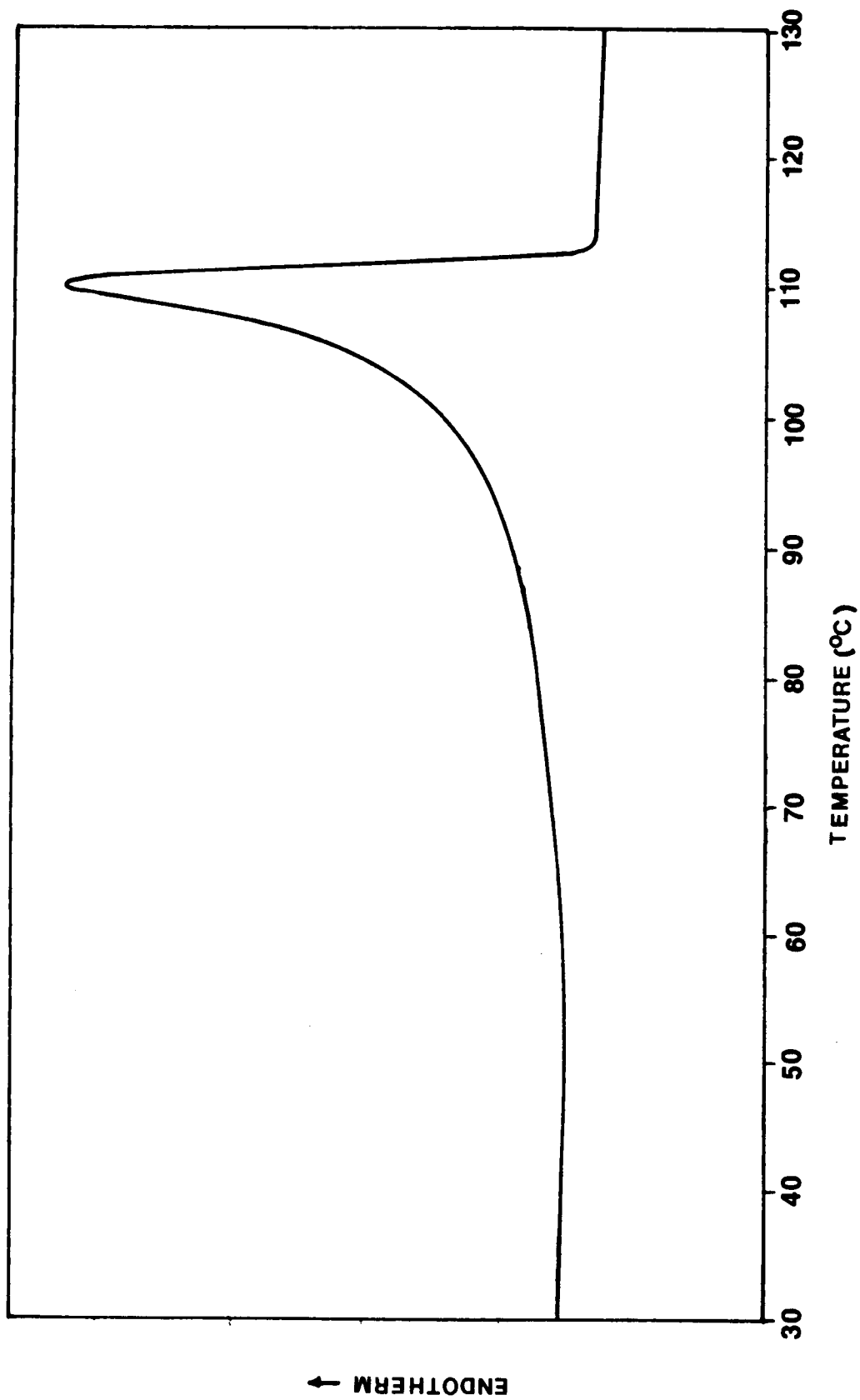


Figure 4.1. Melting Curve of LLDPE.

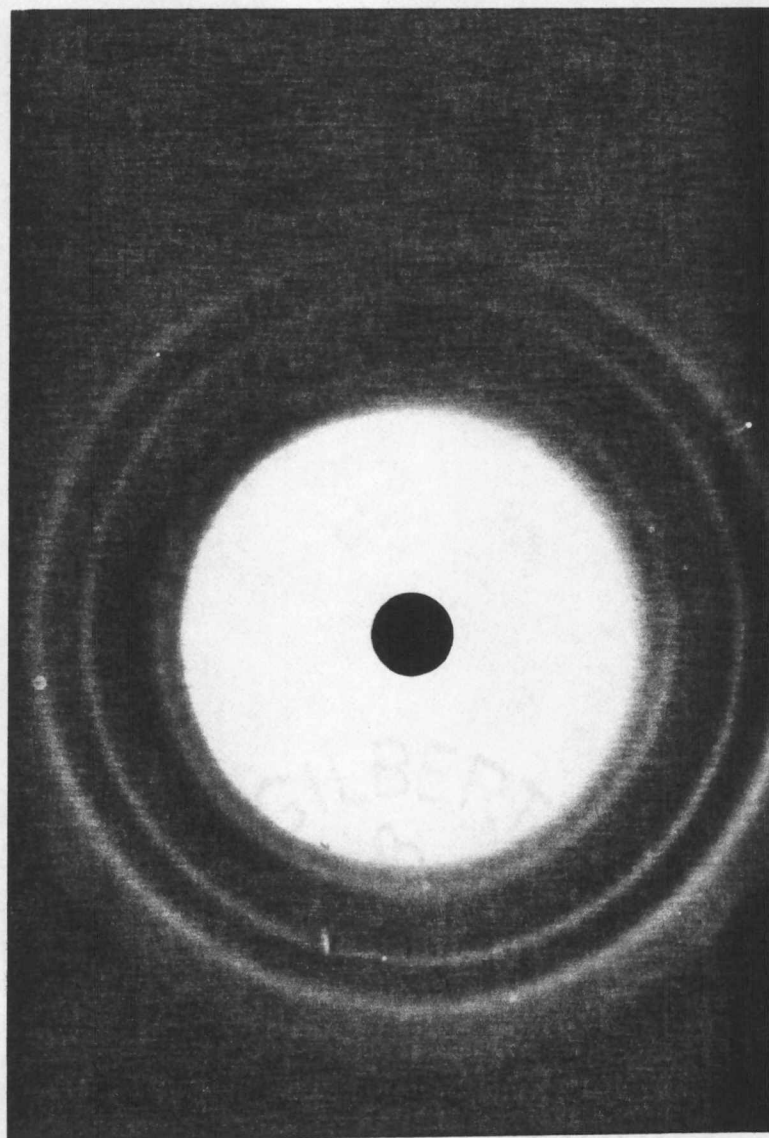


Figure 4.2. Wide Angle X-ray Diffraction Pattern of LLDPE Obtained Using a Flat Plate Camera.

orientation as there is no intensity change as a function of the azimuthal angle. Figure 4.3 shows a result of a wide angle X-ray diffractometer study on unoriented LLDPE, being a plot of intensity vs. 2θ angle. The 2θ scan range was chosen from 10° to 40° . The amorphous peak overlaps the diffracted peaks from the (110) and (200) planes. The peak positions of the (110) and (200) planes are at $2\theta = 21.62^\circ$ and $2\theta = 23.82^\circ$, respectively. Using Bragg's law, $2d\sin\theta = \lambda$, d_{110} and d_{200} were determined. The values for d_{110} and d_{200} are $4.11 \text{ \AA}$ and $3.705 \text{ \AA}$, respectively. Assuming that the diffraction peaks of both (110) and (200) planes have Gaussian shapes, they can be resolved symmetrically. By measuring the relative amounts of energy diffracted by crystalline and amorphous regions of polymer, the percent crystallinity can be determined. The areas of these three peaks are measured and corrected for atomic scattering factor, absorption and temperature. The combined correction factors calculated for amorphous, (110) and (200) peaks are 0.69, 1.00 and 1.43, respectively (Nichols, 1954). The percent crystallinity of polyethylene can be expressed by the following equation

$$\% \text{ crystallinity} = \frac{I_{110} + I_{200}}{I_A + I_{110} + I_{200}} \quad (4.2)$$

where I_A , I_{110} and I_{200} are relative intensities after correction. By using equation 4.2, a percent crystallinity of 61% was obtained. The heat of fusion of 100% crystalline LLDPE was calculated to be 35.3 cal/gm using WAXS.

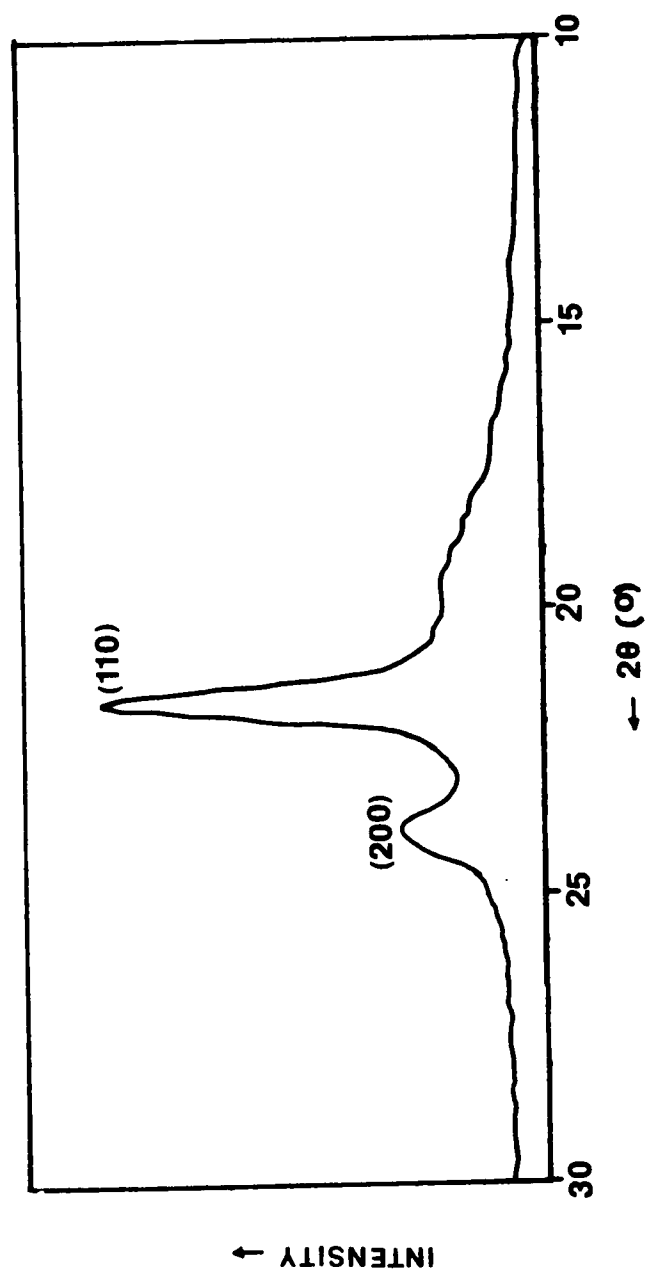


Figure 4.3. Wide Angle X-ray Diffraction Pattern of LLDPE Obtained using a Diffractometer.

4.1.1.2 Characterization of HDPE films. HDPE films were prepared as described in section 3.3.1. These films were characterized with WAXS and DSC. Figure 4.4 is a DSC melting curve of HDPE with the peak position location at 131.5°C. Figure 4.5 shows a result of a wide angle X-ray diffractometer scan on unoriented HDPE film. Percent crystallinity determined by using equation 4.2 is 70%. By using equation 4.1, a percent crystallinity of 69% was obtained using the known value of the latent heat of fusion of 69 cal/gm (Brandrup and Immergut, 1975). The lower intensity of the amorphous peak of HDPE (see Figure 4.5) gives a higher crystallinity for HDPE compared to LLDPE.

4.1.1.3 Characterization of cross-linked EPR. Extraction of crosslinked (2% dicumyl peroxide) ethylene-propylene rubber (EPR) using boiling xylene over a period of three days removed 18.7% of the material. All the dried samples had been investigated by infrared spectroscopy to verify the solvent removal. Crosslinked EPR was tested for the appearance of permanent set on elongation. The measured values of permanent set increase linearly from 100 to 600% elongation, producing a maximum permanent set of 8% after 600% elongation.

4.1.2 Oriented Polyethylene

4.1.2.1 Uniaxially stretched LLDPE films. Figure 4.6 shows the result of a DSC experiment on the uniaxially stretched LLDPE film. The melting temperature is very close to that of the

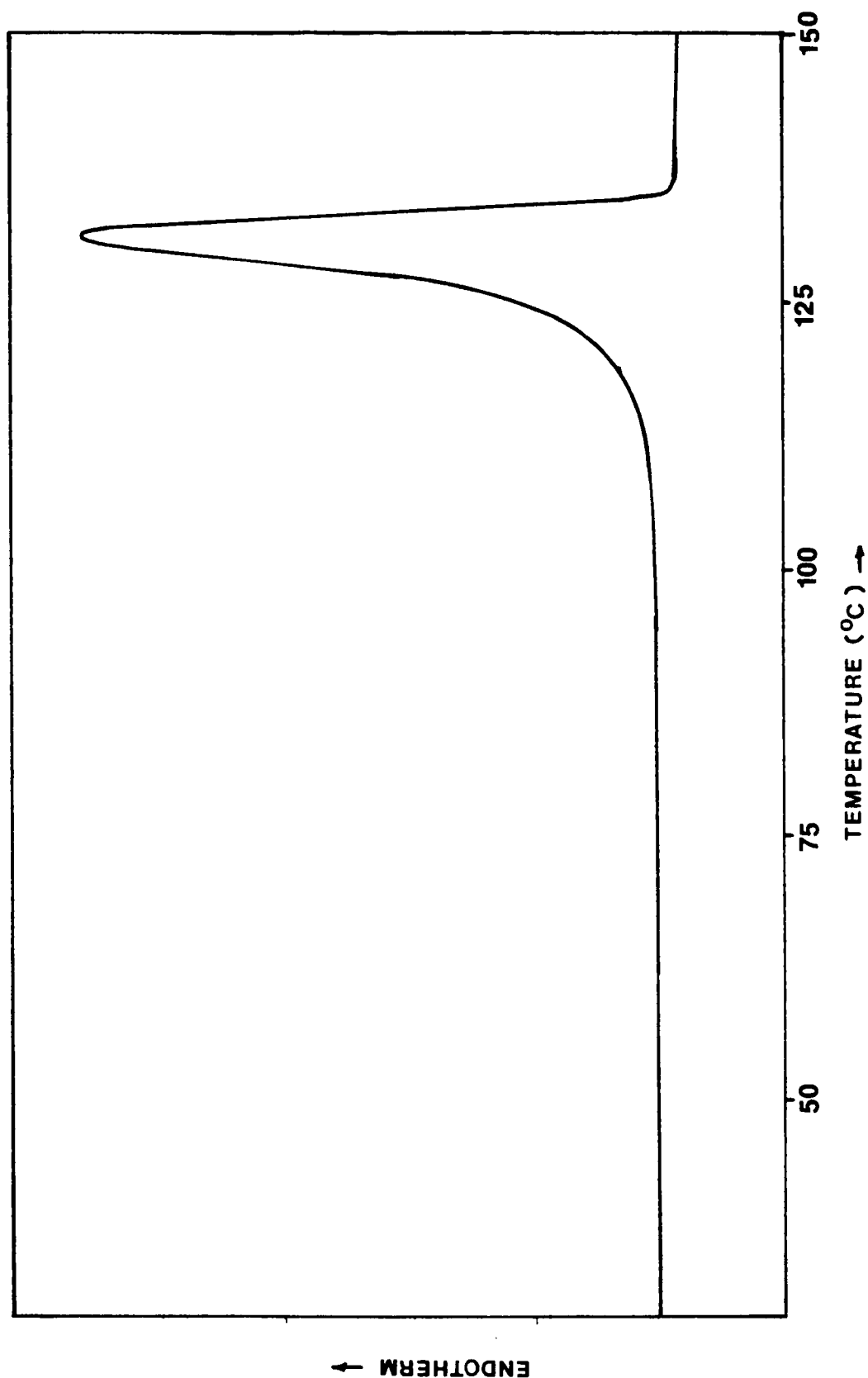


Figure 4.4. Melting Curve of HDPE.

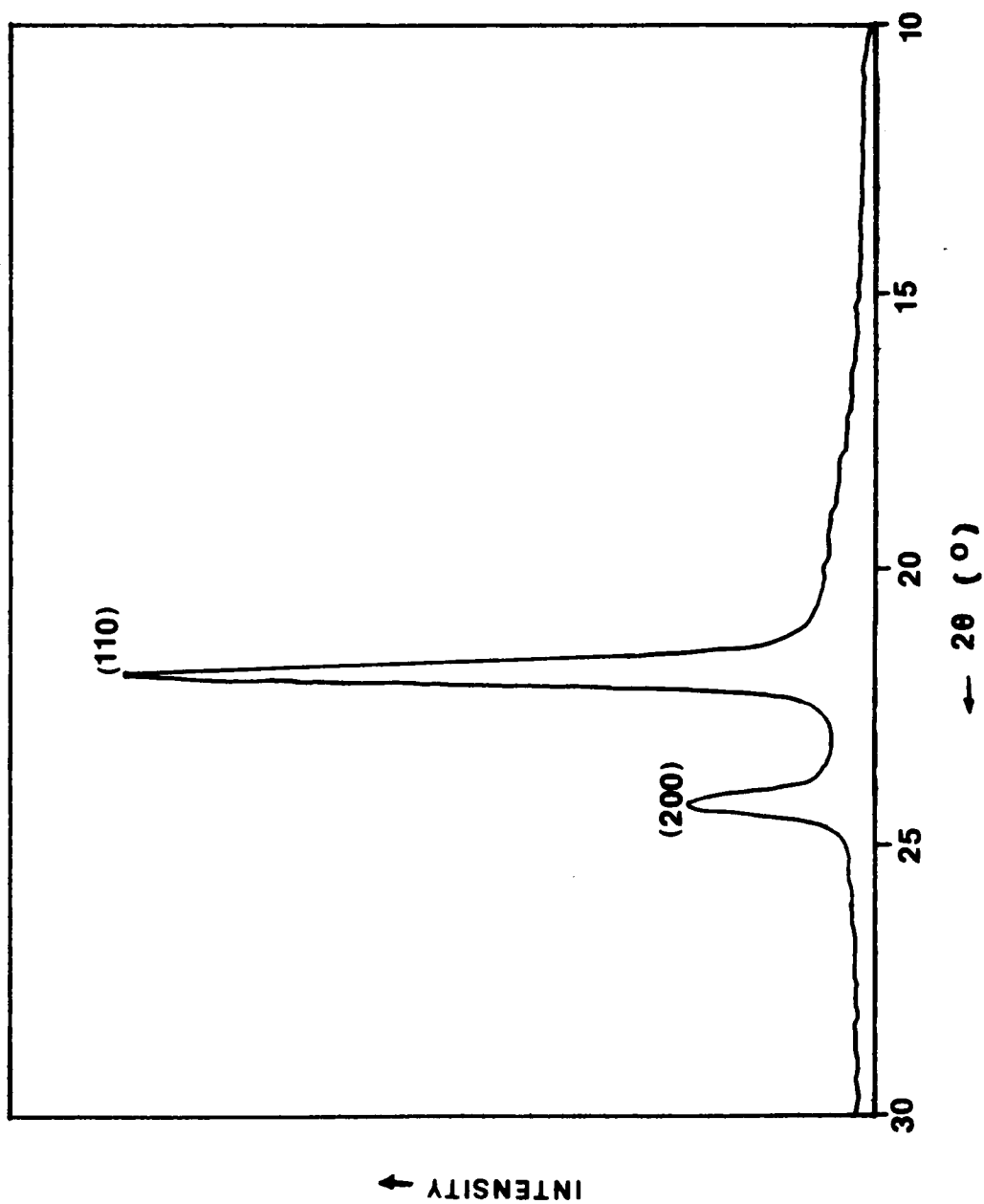


Figure 4.5. Wide Angle X-ray Diffraction Pattern of HDPE Obtained using a Diffractometer.

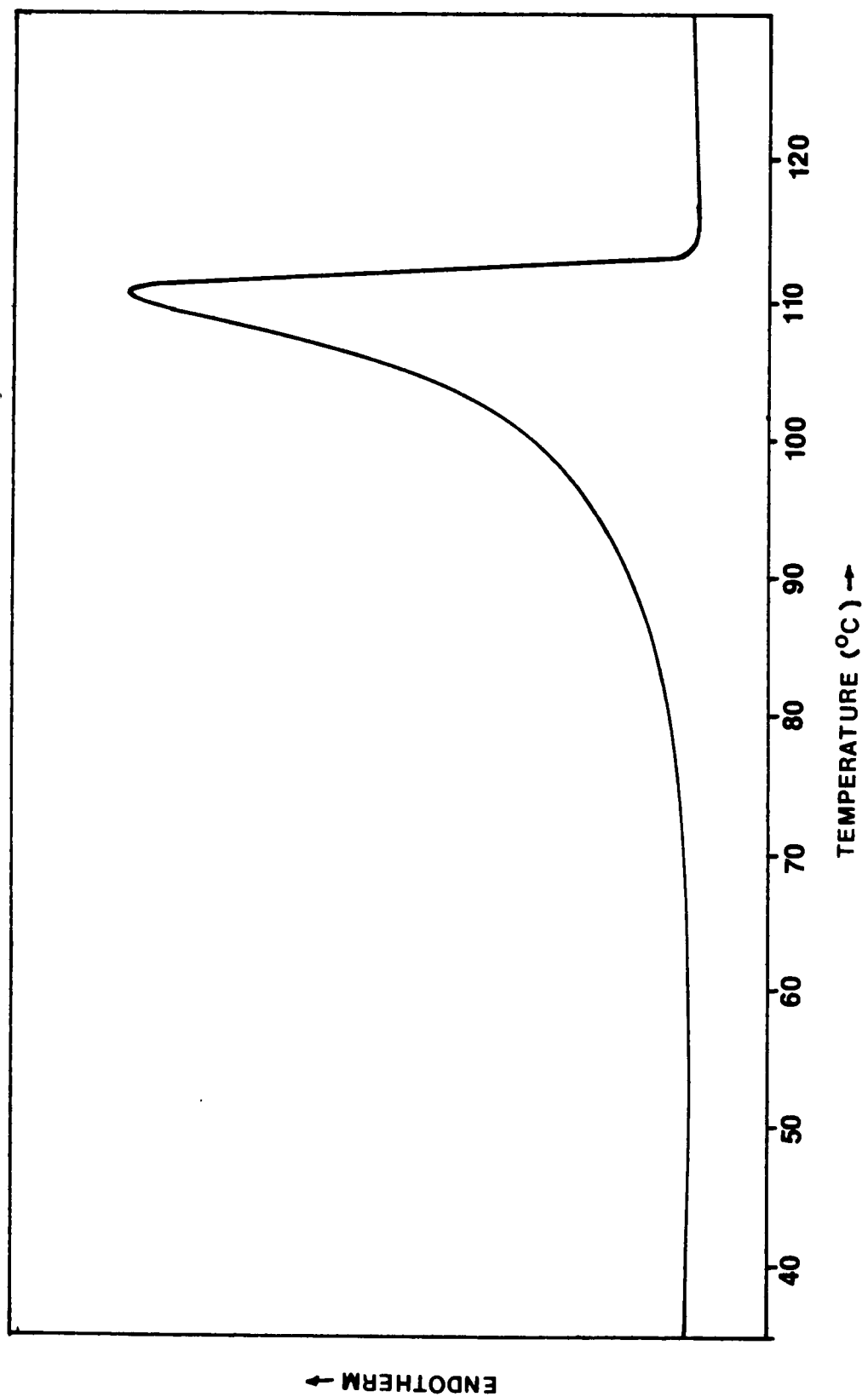


Figure 4.6. Melting Curve of Uniaxially Stretched LLDPE Film.

unoriented sample, but the heat of fusion has increased, and hence the crystallinity is 67%.

Figure 4.7 is a wide angle X-ray diffraction pattern of a uniaxially stretched LLDPE film obtained using a flat plate camera. This diffraction pattern of the stretched film is different from that of the unoriented film (see Figure 4.2) in that the concentric rings of the unoriented film are now short arcs. The lengths of the arcs are dependent on the degree of orientation, the more a film is stretched the shorter the arcs. Specification of orientation is based on the concepts of Hermans et al. (1946). The orientation in the crystalline region is commonly expressed using the Herman's orientation function (Equation 4.3). The general form of the orientation function for the uniaxial (cylindrically averaged) case is:

$$f_{c,z} = \frac{1}{2} [3\langle \cos^2 \phi \rangle_{c,z} - 1] \quad (4.3)$$

where ϕ is the angle between the c-axis of the PE unit cell (chain axis) and the stretching direction (commonly denoted by z). The degree of orientation of the c-axis, f_c , varies from -0.5 to 1. In the case of random orientation value of $\langle \cos^2 \phi \rangle_{c,z}$ is equal to 1/3 and $f_{c,z}$ is equal to zero whereas in the perfectly oriented sample $\langle \cos^2 \phi \rangle_{c,z}$ has a value equal to one and $f_{c,z}$ is equal to 1.

In an orthogonal system,

$$f_{a,z} + f_{b,z} + f_{c,z} = 0 \quad (4.4)$$

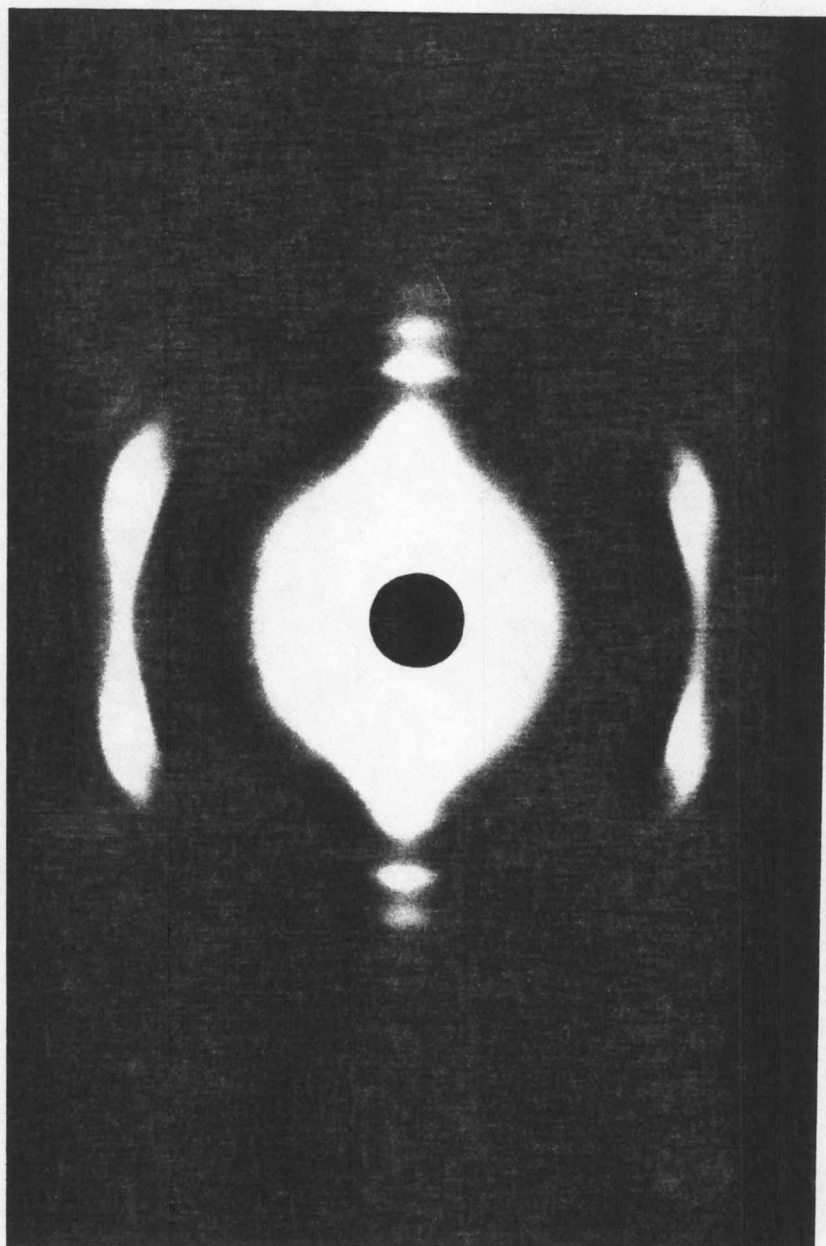


Figure 4.7. Wide Angle X-ray Diffraction Pattern of Uniaxially Stretched Film Obtained using a Flat Plate Camera.

Values of the mean square cosine in Equation 4.3 are calculated from the intensity distribution of reflection planes obtained using a flat plate camera. The method used to estimate the mean square cosine is to measure the intensity distribution as a function of the azimuthal angle of the diffraction arc over a quadrant of pattern using a microdensitometer. $\langle \cos^2 \phi \rangle_{hkl,z}$ can be calculated using the following equation:

$$\langle \cos^2 \phi \rangle_{hkl,z} = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi \, d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi \, d\phi} \quad (4.5)$$

The orientation functions calculated from Figure 4.7 are $f_c(110) = 0.989$ and $f_c(200) = 0.981$.

4.1.2.2 Characterization of extruded rods. Solid-state extruded rods prepared as described in section 3.3.3 were characterized with FTIR, DSC and WAXS. The extruded rods were characterized in directions parallel and perpendicular to the extrusion direction. Since extrusion was carried out at a higher temperature (70°C), it was necessary to check the presence of carbonyl groups due to oxidation. For the same reason, a Fourier transform infrared spectrum was obtained for the extruded rod. Figure 4.8 shows the FTIR result for extruded rod which did not detect any carbonyl groups through the absorption at a wavenumber equal to 1720 cm⁻¹. The DSC result (see Figure 4.9) shows that the extruded rod of LLDPE melts at 110.5°C. The heat of fusion of the extruded rod of LLDPE determined from the DSC melting curve is 24.3

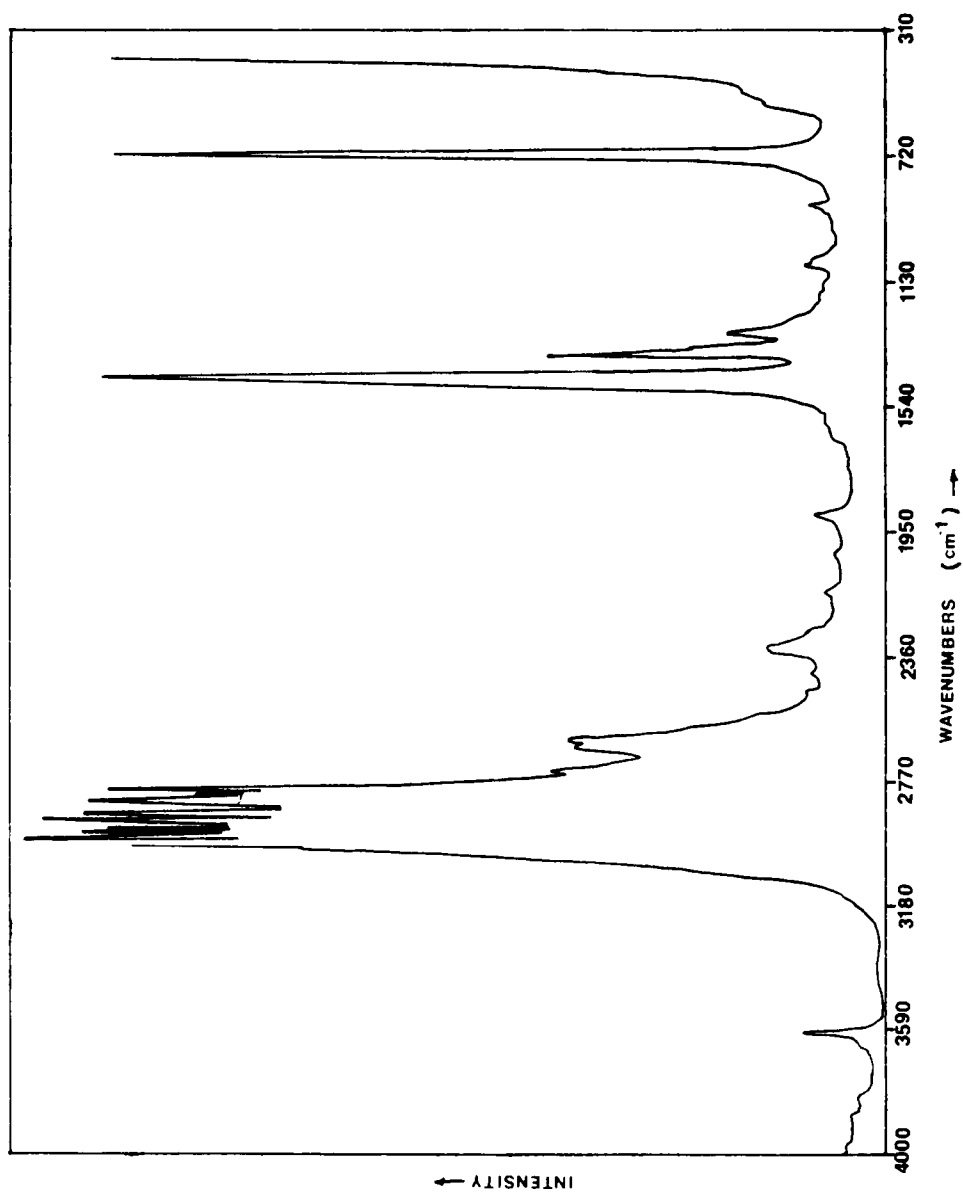


Figure 4.8. FTIR Spectra of Extruded Rod of LLDPE.

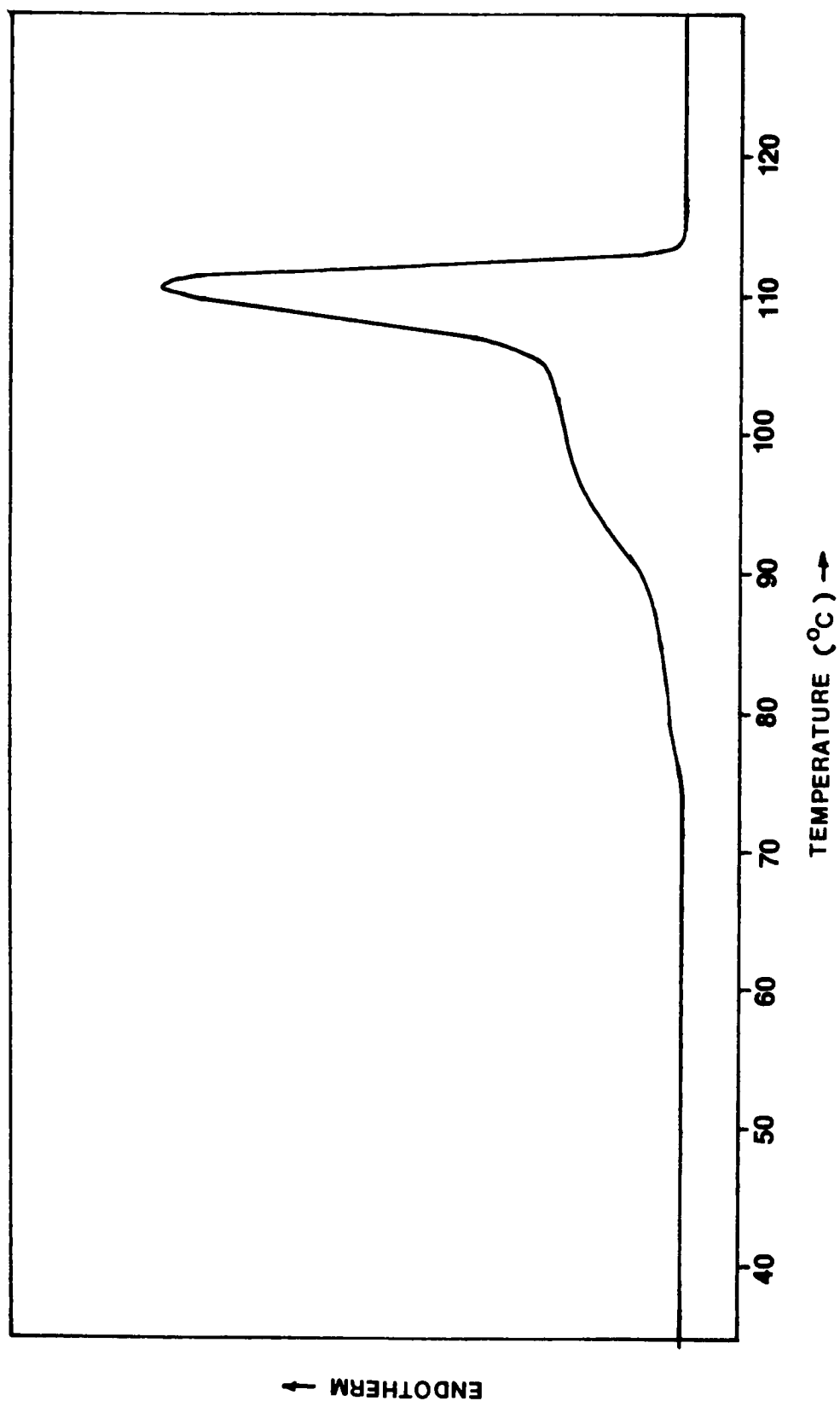


Figure 4.9. Melting Curve of Extruded Rod of LLDPE.

cal/gm. Percent crystallinity determined by using equation 4.1 is 69%. Figures 4.10 and 4.11 were obtained using a flat plate camera for sections cut parallel and perpendicular to the extrusion direction. Figure 4.10 shows orientation whereas Figure 4.11 does not show orientation. In other words, there is no preferred orientation in the direction perpendicular to the extrusion direction. The orientation functions calculated, from Figure 4.10, are $f_c(110) = 0.991$ and $f_c(200) = 0.984$.

4.2 Dielectric Data

4.2.1 Dielectric Constant and Loss

Dielectric data obtained directly from the bridge consisted of capacitance (C) and conductance (G) values at different frequencies (ν) and temperatures (T). These data were converted to dielectric constant (ϵ') and dielectric loss (ϵ'') values using equations 2.7 and 2.8 (pages 41 and 43, respectively).

4.2.1.1 Residual d.c. conductivity. D.C. conductivity becomes significant at lower frequencies and higher temperatures. The following method was used to correct for it. Low-frequency conductance data at each temperature were extrapolated to zero frequency and the zero-frequency conductance was obtained. At low temperature the value of d.c. conductivity was very small and at the higher temperature d.c. conductivity was significant. At any given temperature, the value of d.c. conductivity calculated was

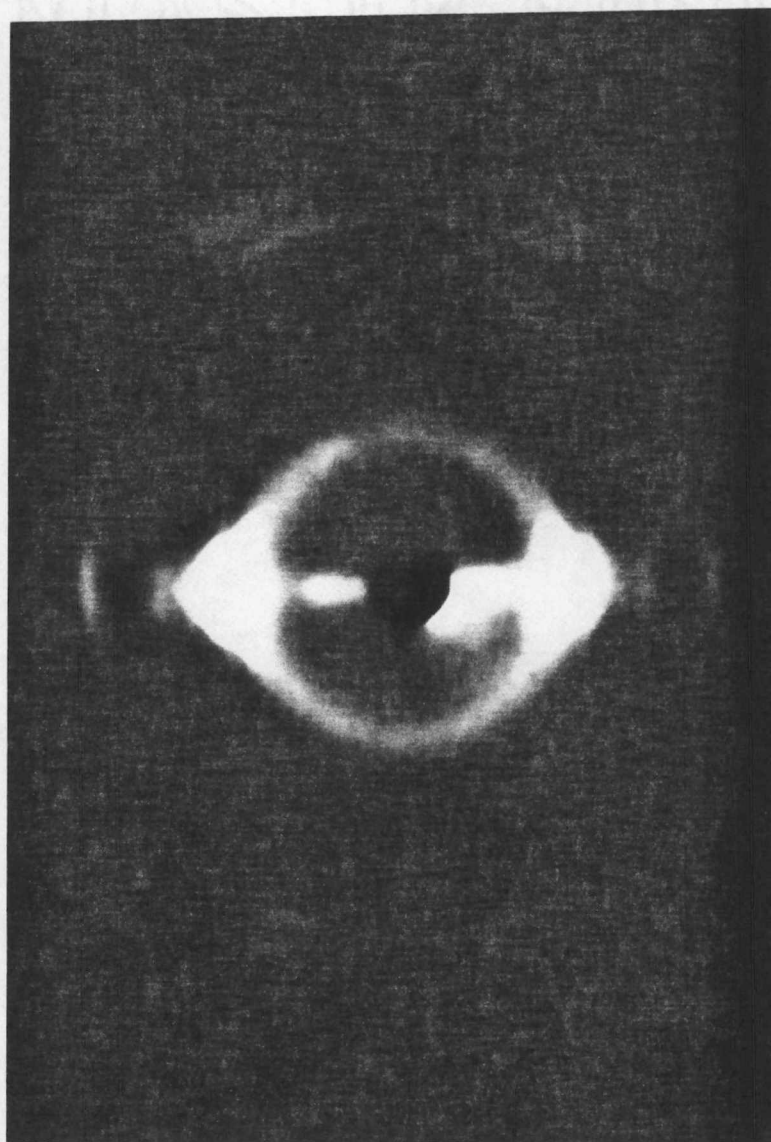


Figure 4.10. Wide Angle X-ray Diffraction Pattern of Extruded Rod of LLDPE Cut Along the Extrusion Direction Obtained using a Flat Plate Camera.

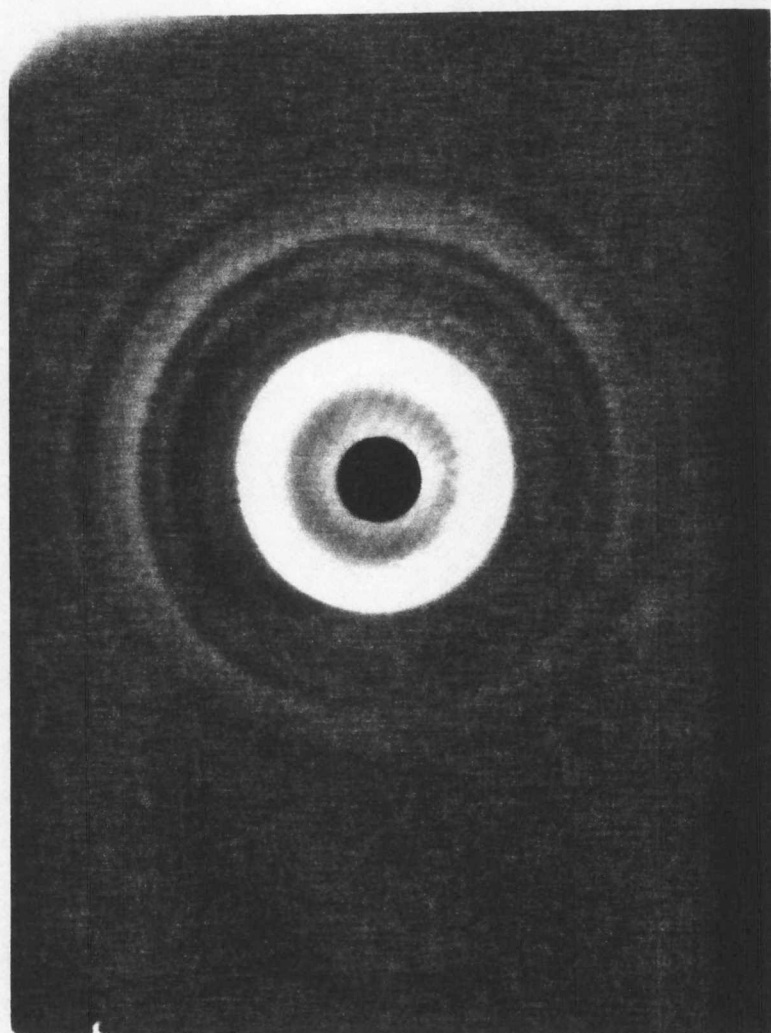


Figure 4.11. Wide Angle X-ray Diffraction Pattern of Extruded Rod of LLDPE Cut Perpendicular to the Extrusion Direction Obtained using a Flat Plate Camera.

subtracted from the bridge conductance data. This procedure helped to minimize errors due to d.c. conductivity.

4.2.2 Cole-Cole Parameters

The single relaxation time (SRT) model represents an ideal system where all the relaxation processes have the same relaxation time τ .

The SRT model represents dipolar relaxation in many simple liquids fairly well, but polymers usually have much broader relaxations. Hence, the equation has to be modified to take into account the distribution of relaxation times present in the dielectric data of a polymer. This is usually carried out by empirical functions of the type described by equation 2.15 (page 46).

The Cole-Cole parameter $\bar{\beta}$ takes values $0 < \bar{\beta} < 1$. $\bar{\beta}$ is the measure of the width of a symmetric distribution. Cole-Cole plots are generated for an isothermal condition. Frequencies increase from right to left in these plots. The Cole-Cole parameters were determined geometrically from these plots. Over the temperature range chosen, an uncertainty in the value of the Cole-Cole parameter $\bar{\beta}$ of about $\pm 1\%$ was caused by the scatter in the data points.

4.2.3 Dielectric Relaxation Studies of Polyethylene

4.2.3.1 Unoriented LLDPE films. Figure 4.12 shows the dielectric constant and loss of LLDPE as a function of temperature at several frequencies. There are three loss peaks at about 60°C ,

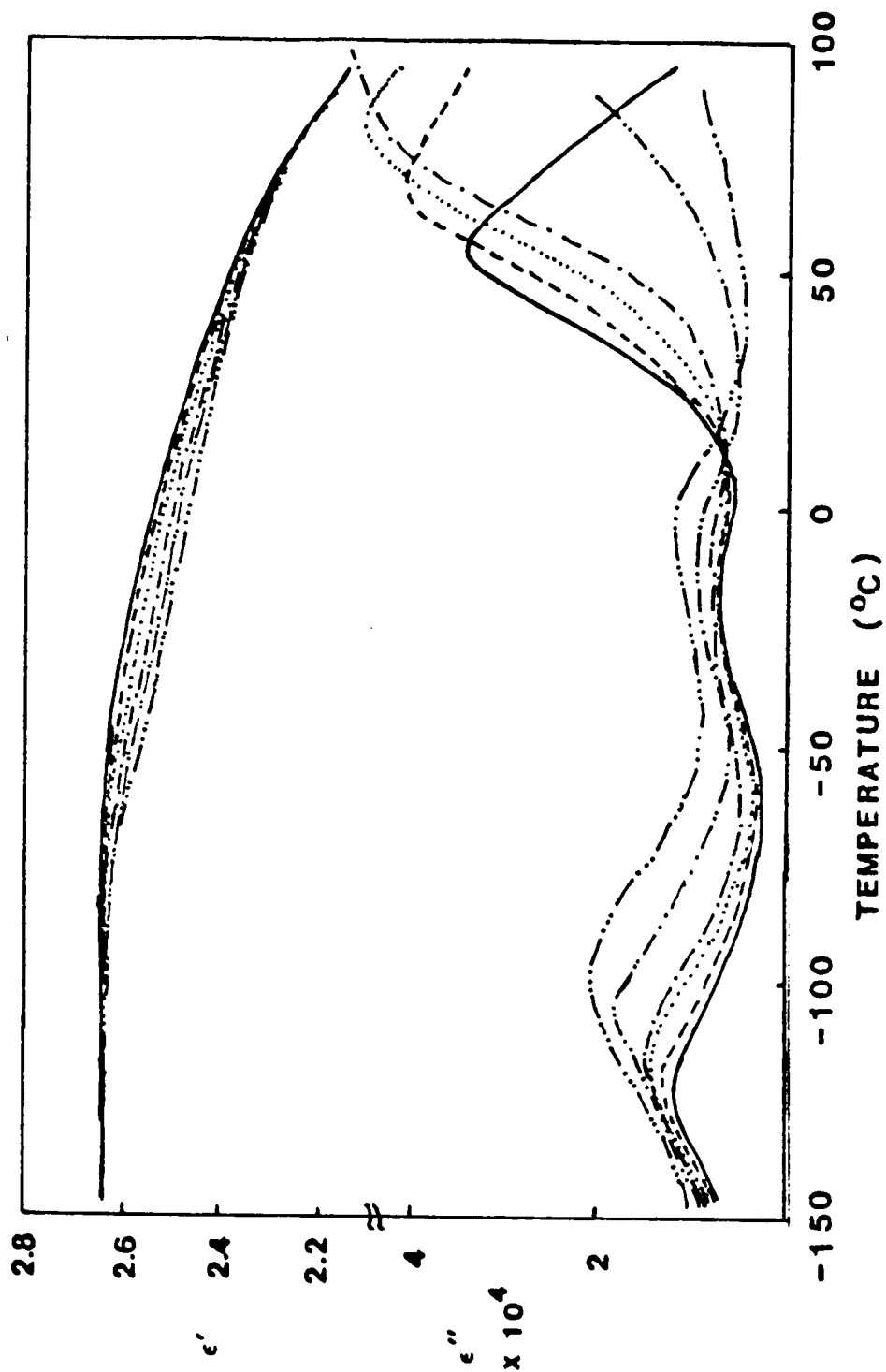


Figure 4.12. Dielectric Constant and Loss of Unstretched LLDPE as a Function of Temperature. (—) 10 Hz, (---) 20 Hz, (.....) 50 Hz, (-.-.-) 100 Hz, (-.-.-) 1 kHz, (-.-.-) 5 kHz.

-20°C and -120°C and are labeled α , β and γ , respectively, in order of decreasing temperature. The γ loss peaks at frequencies higher than 100 Hz are located at temperatures higher than 100°C which is very close to the melting temperature of LLDPE. At higher frequencies, it was difficult to obtain the α loss peak temperatures experimentally. The value of dielectric loss is about a decade lower than those of chlorinated or oxidized polyethylenes (Ashcraft and Boyd, 1976; Yemni and Boyd, 1979). The activation energies of loss processes can be estimated from Arrhenius plots of the logarithm of applied frequency vs. the reciprocal of the absolute temperature of maximum loss. Figure 4.13 is the Arrhenius plot of LLDPE, obtained from the dielectric loss data of Figure 4.12. The α relaxation has an activation energy of 14.8 kcal/mole, which is lower than those reported earlier (20 to 26 kcal/mole by Tuijnman (1963), 21 to 22 kcal/mole by Phillips et al., (1971), 24 to 30 kcal/mole by Ashcraft and Boyd (1976) and 26 kcal/mole by Boyd and Yemni (1979)). The β relaxation has an activation energy of 76.3 kcal/mole which is similar to 76 kcal/mole reported by Boyd and Yemni (1979) and higher than 50 kcal/mole reported by Ashcraft and Boyd (1976). The γ relaxation has an activation energy of 9.5 kcal/mole which is similar to those reported in the literature by Tuijnman (1963) and Lowell et al. (1971). Activation energies for the α , β and γ relaxation processes are tabulated in Table 4.1. Cole-Cole plots generated at 60°C , -20°C and -120°C for the α , β and γ relaxation respectively. Cole-Cole plots were obtained by

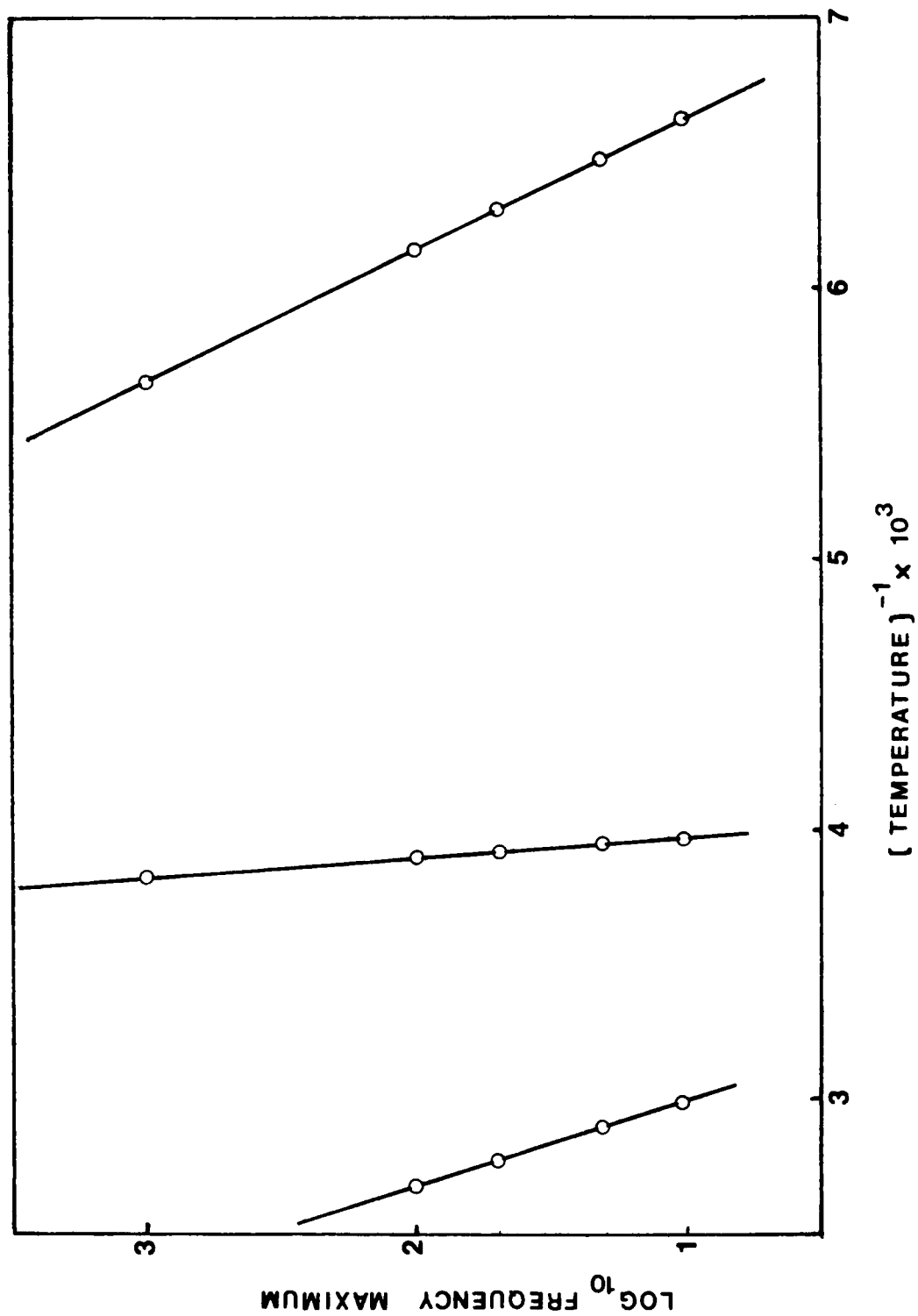


Figure 4.13. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.12.

Table 4.1. Activation Energies of LLDPE (kcal/mole).

	Unoriented	Stretched Sheet	Extruded Rod	
			to Extrusion Direction	⊥ to Extrusion Direction
α	14.8	17.0	17.5	19.6
β	76.3	57.2	60.2	67.1
γ	9.5	15.0	12.1	14.1

interpolating the data in Figure 4.12 and are shown in Figure 4.14. The relaxation magnitudes ($\Delta\epsilon'$) and Cole-Cole parameters obtained from the Cole-Cole plots for the α , β and γ relaxation processes are listed in Table 4.2.

4.2.3.2 Uniaxially stretched films. Dielectric constant and loss of an LLDPE film stretched to 500% are shown in Figure 4.15. The α loss peak is decreased in magnitude relative to the unoriented LLDPE films whereas the β and γ loss processes have increased somewhat. Most noticeable is the decrease in the magnitude of the peak. This behavior is quite the opposite of that of low-density polyethylene in that orientation of a polymer in which the active groups are carbonyls (Phillips et al., 1971) produces an increase in the magnitude of the α loss process. The positions of the loss peaks are essentially unchanged from those of the unoriented material. Arrhenius plots of the logarithm of applied frequency vs. the reciprocal of the temperature of maximum loss of Figure 4.15 are constructed to obtain the activation energies (see Figure 4.16). The activation energies of the α and γ relaxation processes have increased in magnitude by 15% and 37%, respectively. The activation energy of the β process has been reduced by 25%. The Cole-Cole plots generated at 60°C, -20°C, and -120°C for the α , β and γ relaxation processes, respectively, are shown in Figure 4.17. Values of relaxation magnitudes and Cole-Cole parameters are tabulated in Table 4.2.

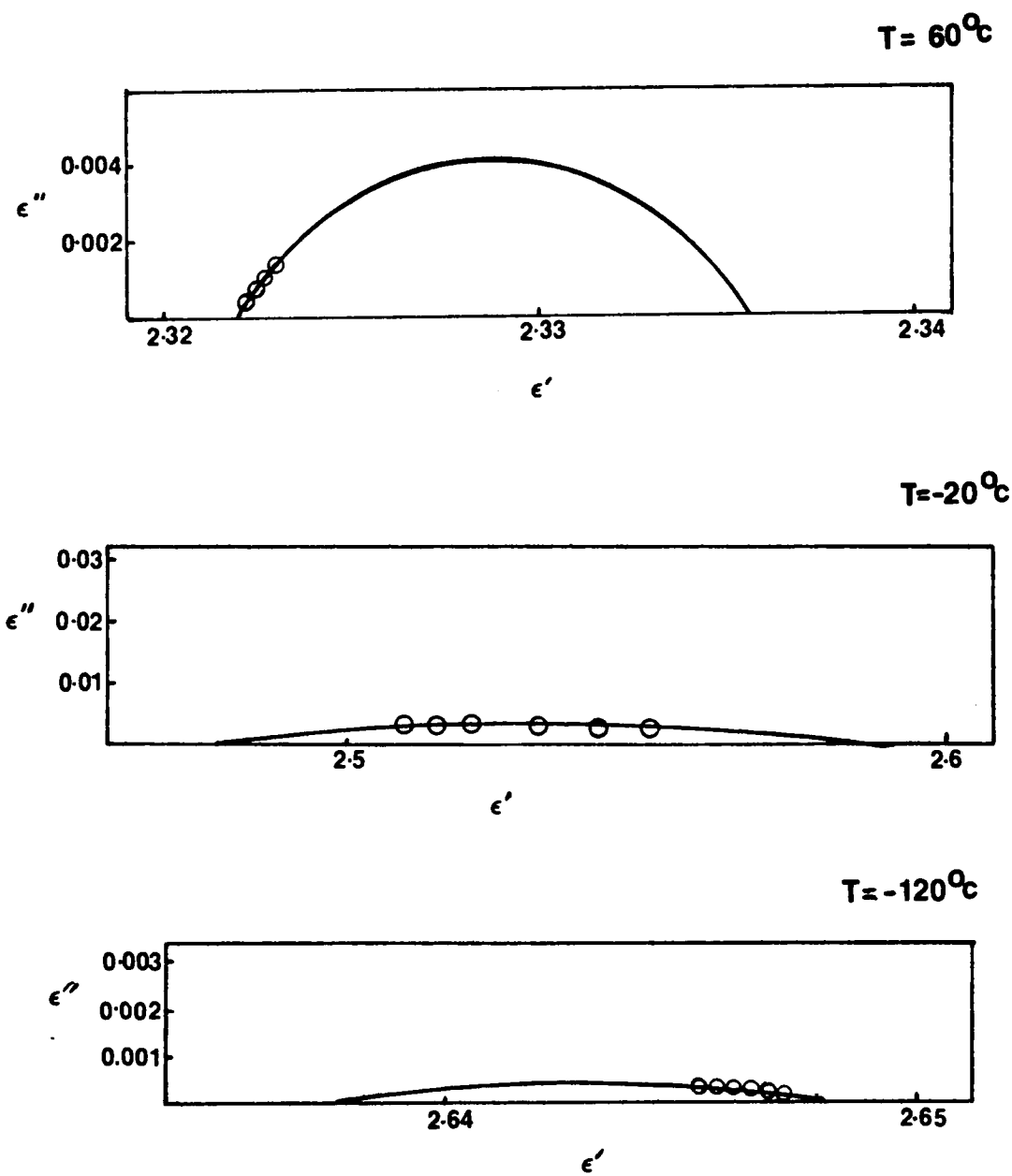


Figure 4.14. Cole-Cole Plots of Unoriented LLDPE.

Table 4.2. Relaxation Magnitudes ($\Delta\epsilon'$) from Cole-Cole Plots and Williams' Plots and Cole-Cole Parameters (β) for LLDPE.

		Extruded Rod		
	Unoriented	Stretched Sheet	Parallel to Extrusion Direction	Perpendicular to Extrusion Direction
Relaxation Magnitudes ($\Delta\epsilon'$) from Cole-Cole Plots				
$\alpha(60^{\circ}\text{C})$	0.014	0.0086	0.0235	0.0059
$\beta(-20^{\circ}\text{C})$	0.104	0.0093	0.0096	0.078
$\gamma(-120^{\circ}\text{C})$	0.0096	0.0047	0.008	0.011
Relaxation Magnitudes ($\Delta\epsilon'$) from Williams' Plots				
$\alpha(60^{\circ}\text{C})$	0.0147	0.0079	0.0223	0.0064
$\beta(-20^{\circ}\text{C})$	0.098	0.0091	0.0098	0.081
$\gamma(-120^{\circ}\text{C})$	0.0087	0.0055	0.0075	0.0124
Cole-Cole Parameters (β)				
$\alpha(60^{\circ}\text{C})$	0.678	0.056	0.510	0.122
$\beta(-20^{\circ}\text{C})$	0.072	0.067	0.078	0.050
$\gamma(-120^{\circ}\text{C})$	0.089	0.133	0.078	0.083

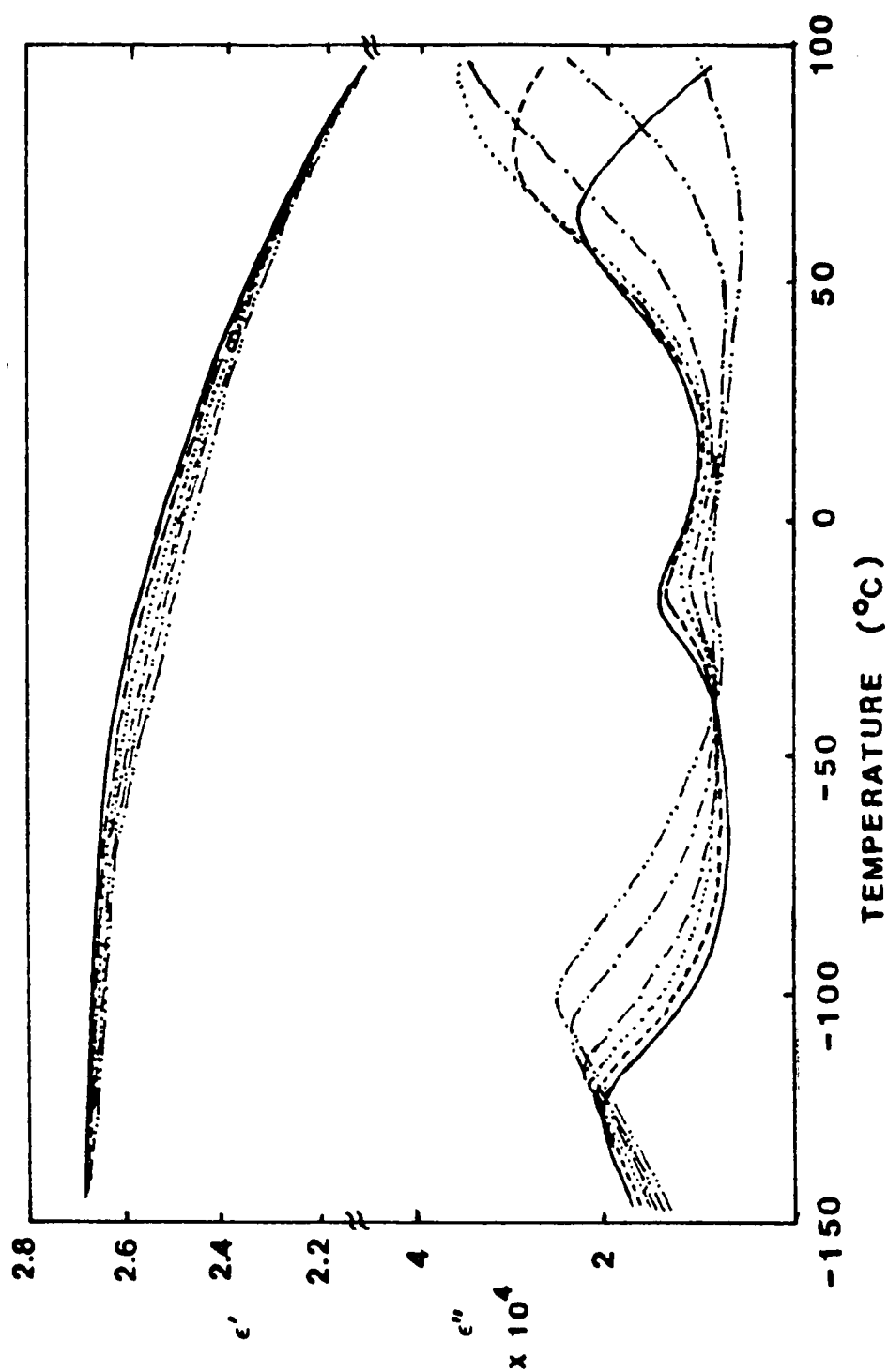


Figure 4.15. Dielectric Constant and Loss of 500% Stretched LLDPE as a Function of Temperature. (—) 10 Hz, (---) 20 Hz, (.....) 50 Hz, (— · —) 100 Hz, (— · — · —) 1 kHz, (— · — · — · —) 5 kHz.

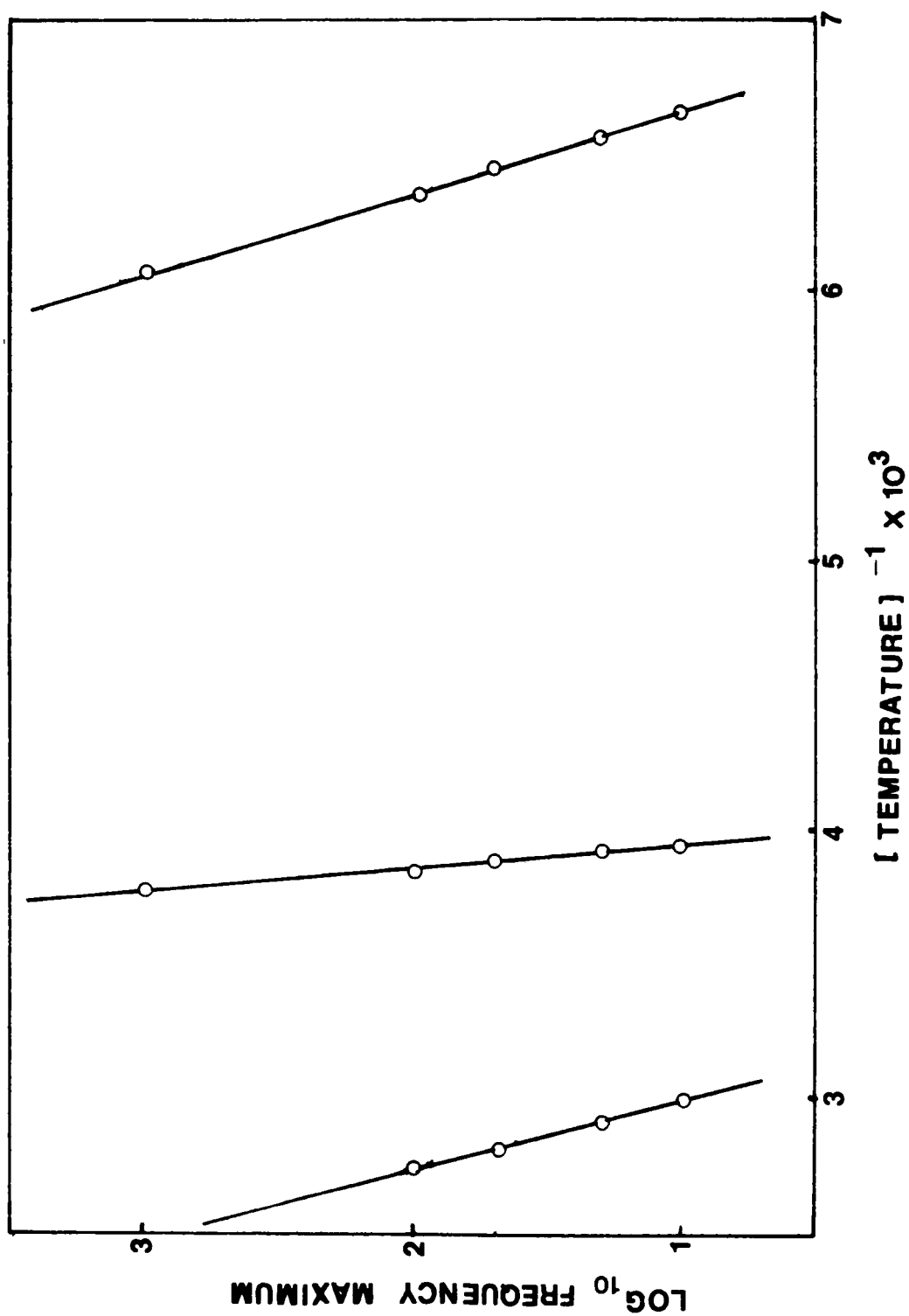


Figure 4.16. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.15.

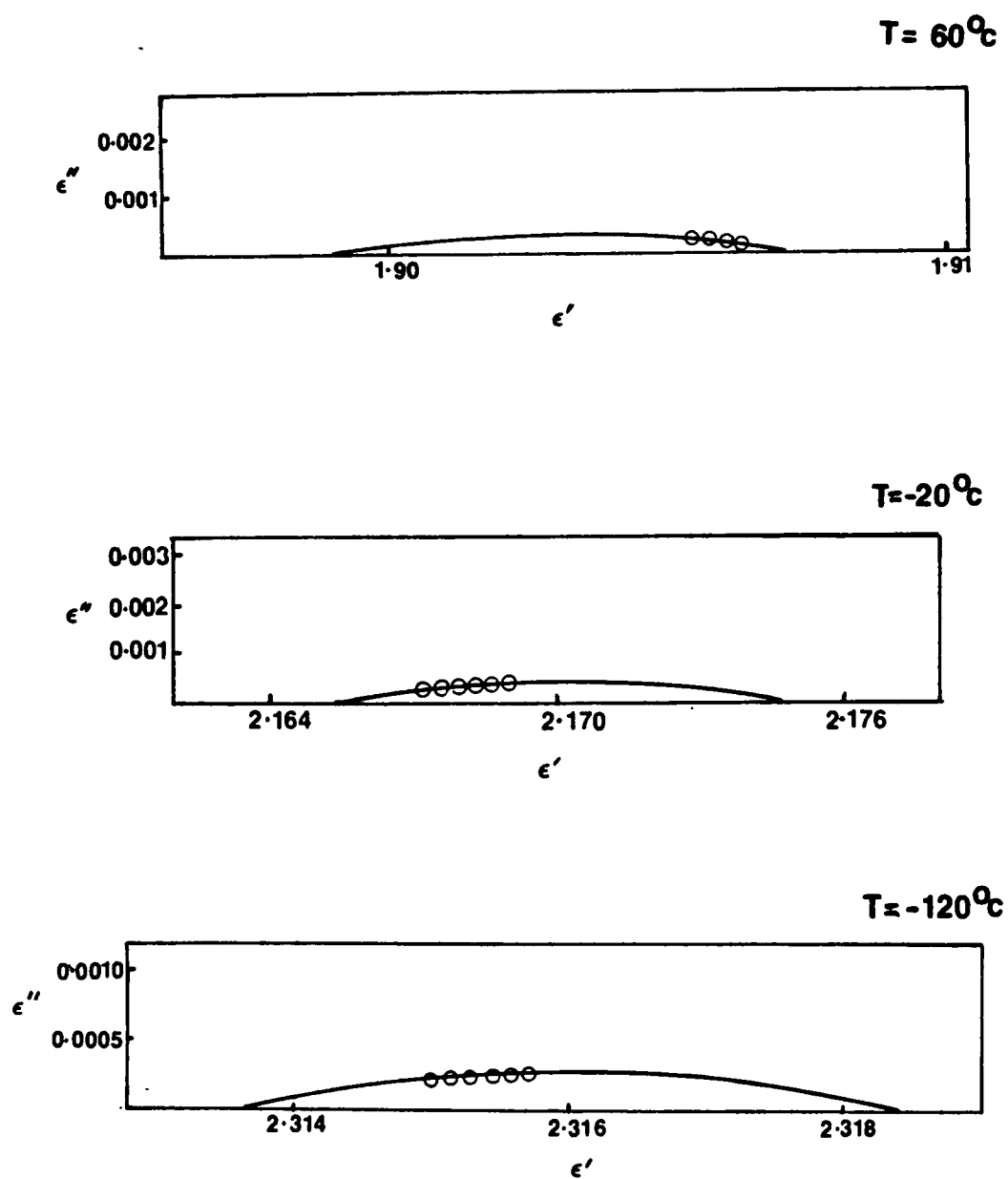


Figure 4.17. Cole-Cole Plots of 500% Stretched LLDPE.

4.2.3.3 Solid-state extruded materials. The use of solid-state extruded material permits the acquisition of dielectric data parallel and perpendicular to the orientation direction. Dielectric constant and loss of extruded rod LLDPE measured with the field along the extrusion direction and the field perpendicular to the extrusion direction are presented in Figures 4.18 and 4.19 respectively. It is apparent that the magnitudes of the β and γ peaks are larger in the direction perpendicular to the extrusion direction. The α peak shows the opposite effect, the magnitude in the extrusion direction being almost double that normal to the extrusion direction. The enhancement of the α peak in the orientation direction was large for the extruded rod, however, the magnitude normal to the extrusion direction was the same as for the stretched sheet. An important effect lies in the positions of the loss maxima. For the α process, at 10 Hz the loss maxima are located at 51 and 59°C for the perpendicular and parallel-to-orientation directions, respectively. Although enhancement of the β and γ peaks in the normal-to-stretch direction of the stretched sheets occurred, the magnitude of the effect was not as large as observed here. Figures 4.20 and 4.21 are the Arrhenius plots of the logarithm of applied frequency vs. the reciprocal of the absolute temperature of maximum loss of Figures 4.18 and 4.19, respectively. Activation energies for the α , β and γ processes for extruded rods are tabulated in Table 4.1 (page 108). Cole-Cole parameters and relaxation magnitudes for the α , β and γ relaxation processes are

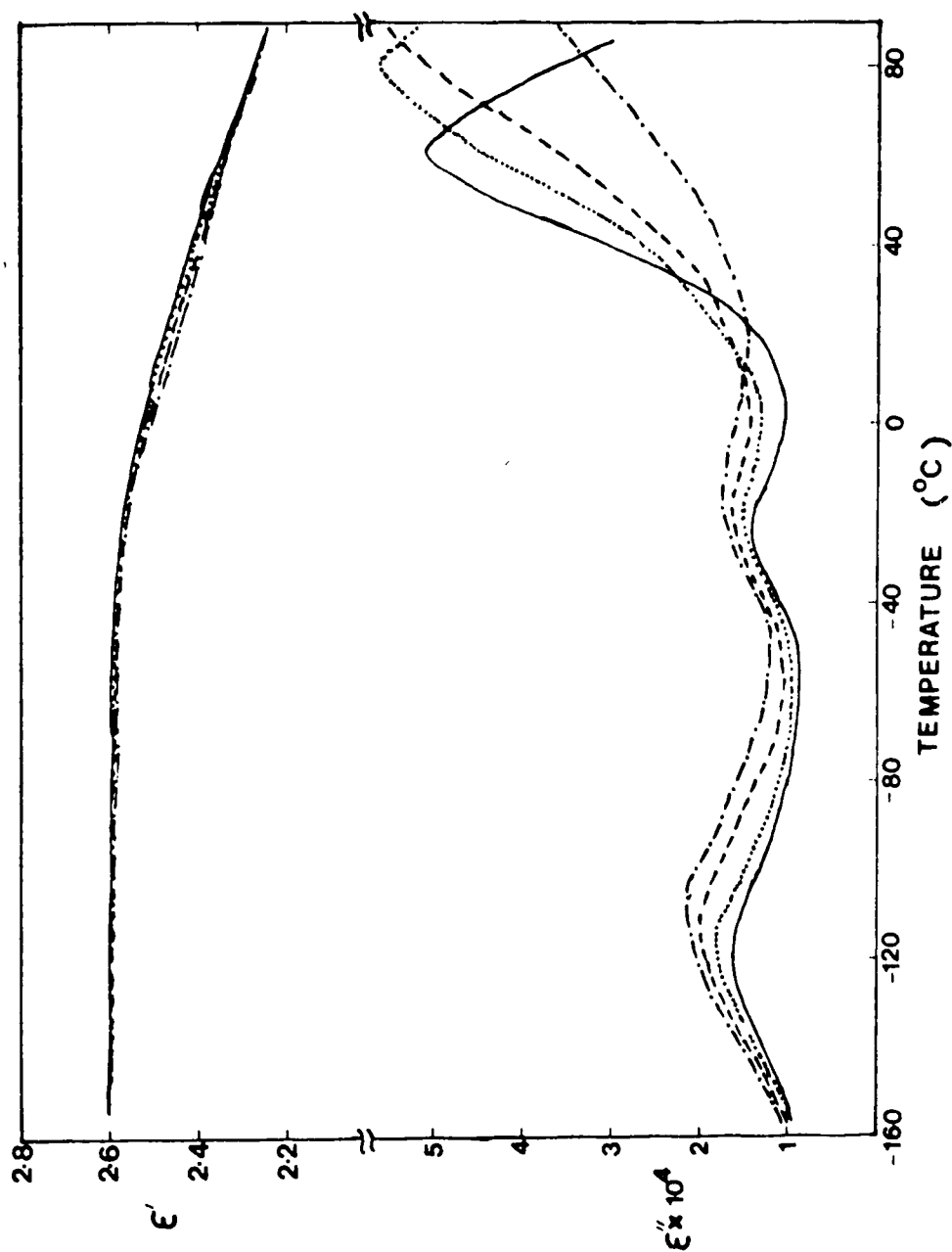


Figure 4.18. Dielectric Spectra of Extruded Rod LLDPE Measured with the Field Along the Extrusion Direction. (—) 10 Hz, (.....) 20 Hz, (---) 50 Hz, (-.-.-) 100 Hz.

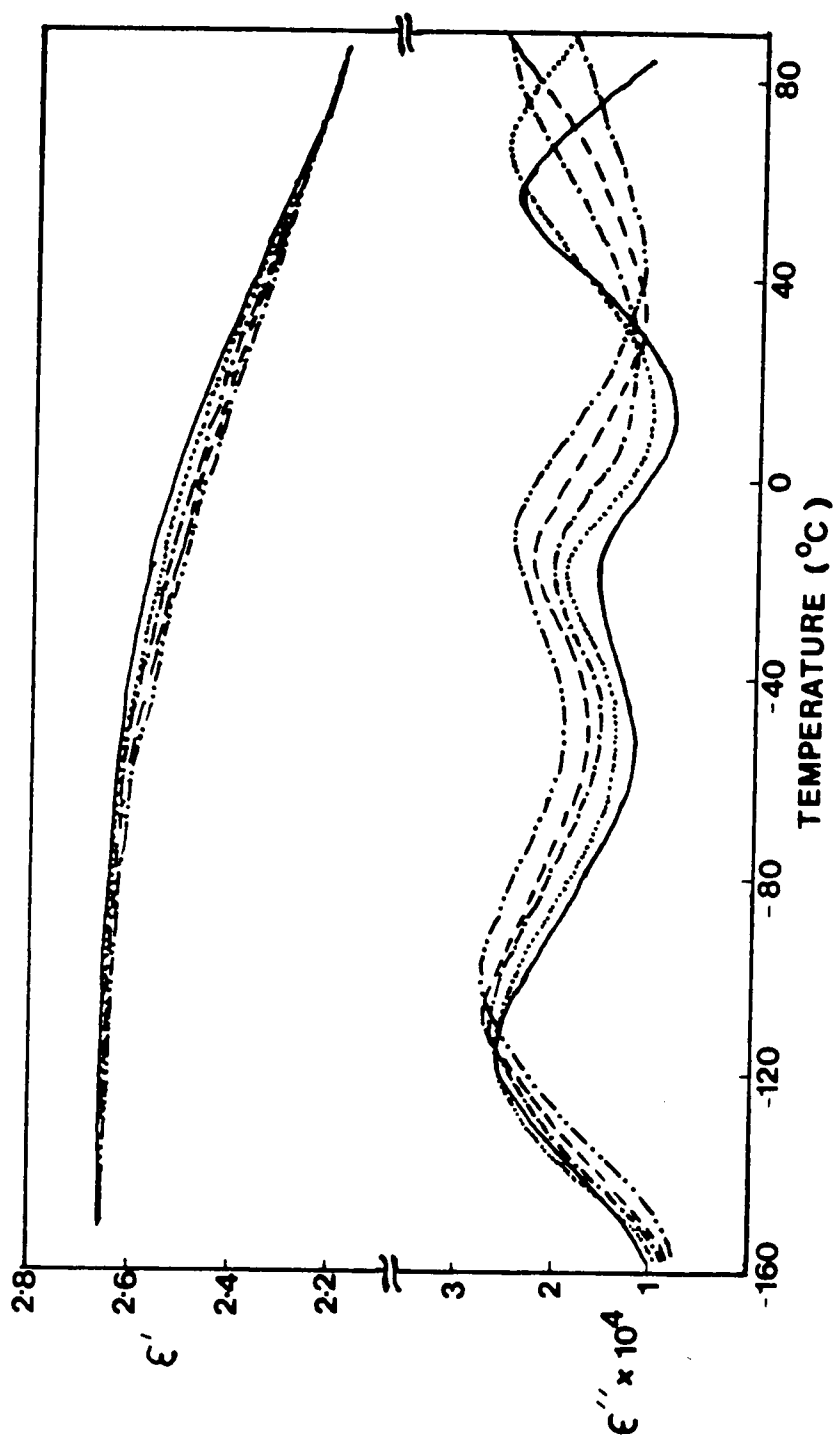


Figure 4.19. Dielectric Spectra of Extruded Rod LLDPE Measured with the Field Perpendicular to the Extrusion Direction.
 (—) 10 Hz, (.....) 20 Hz, (---) 50 Hz, (----) 100 Hz,
 (---) 1 kHz.

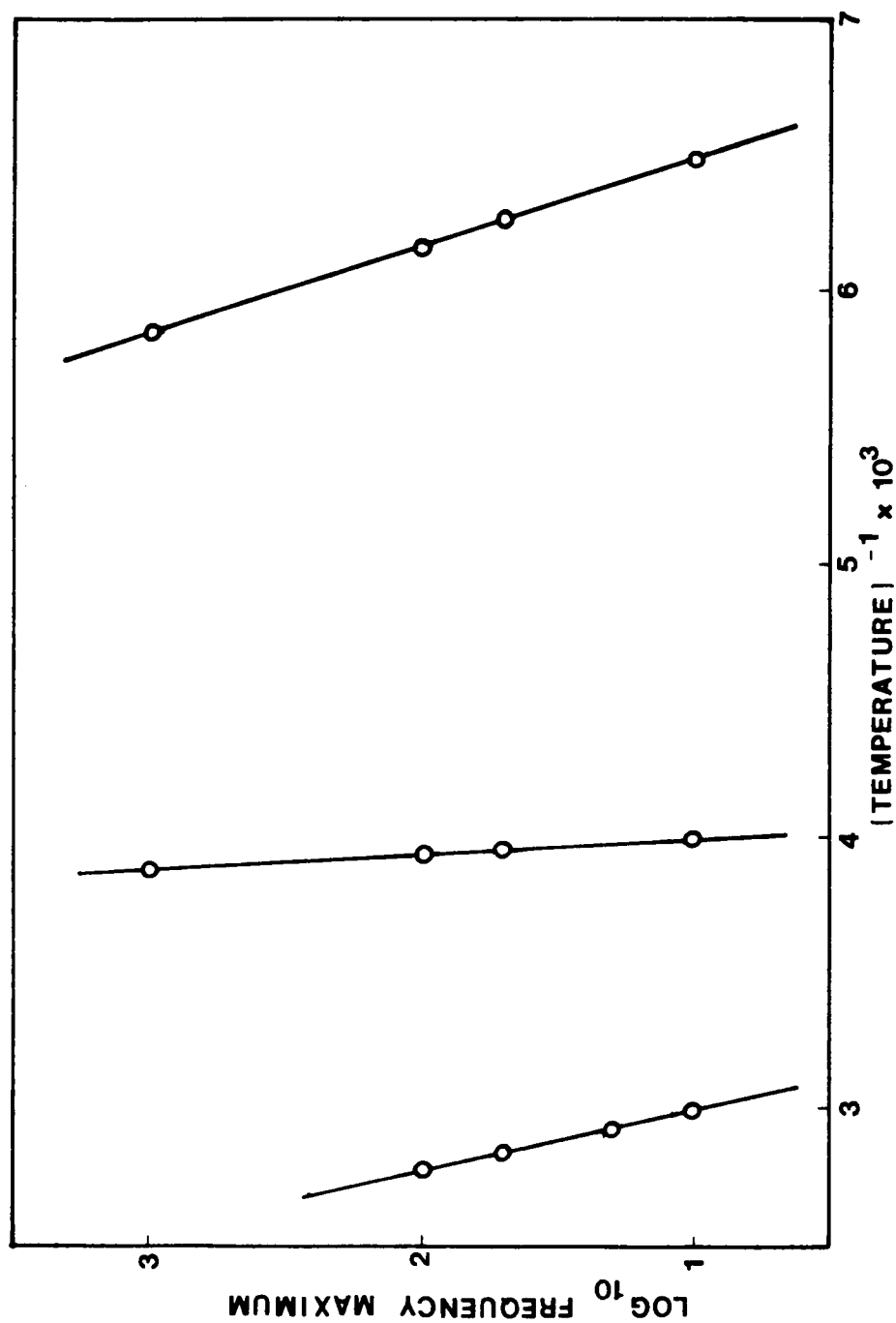


Figure 4.20. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.18.

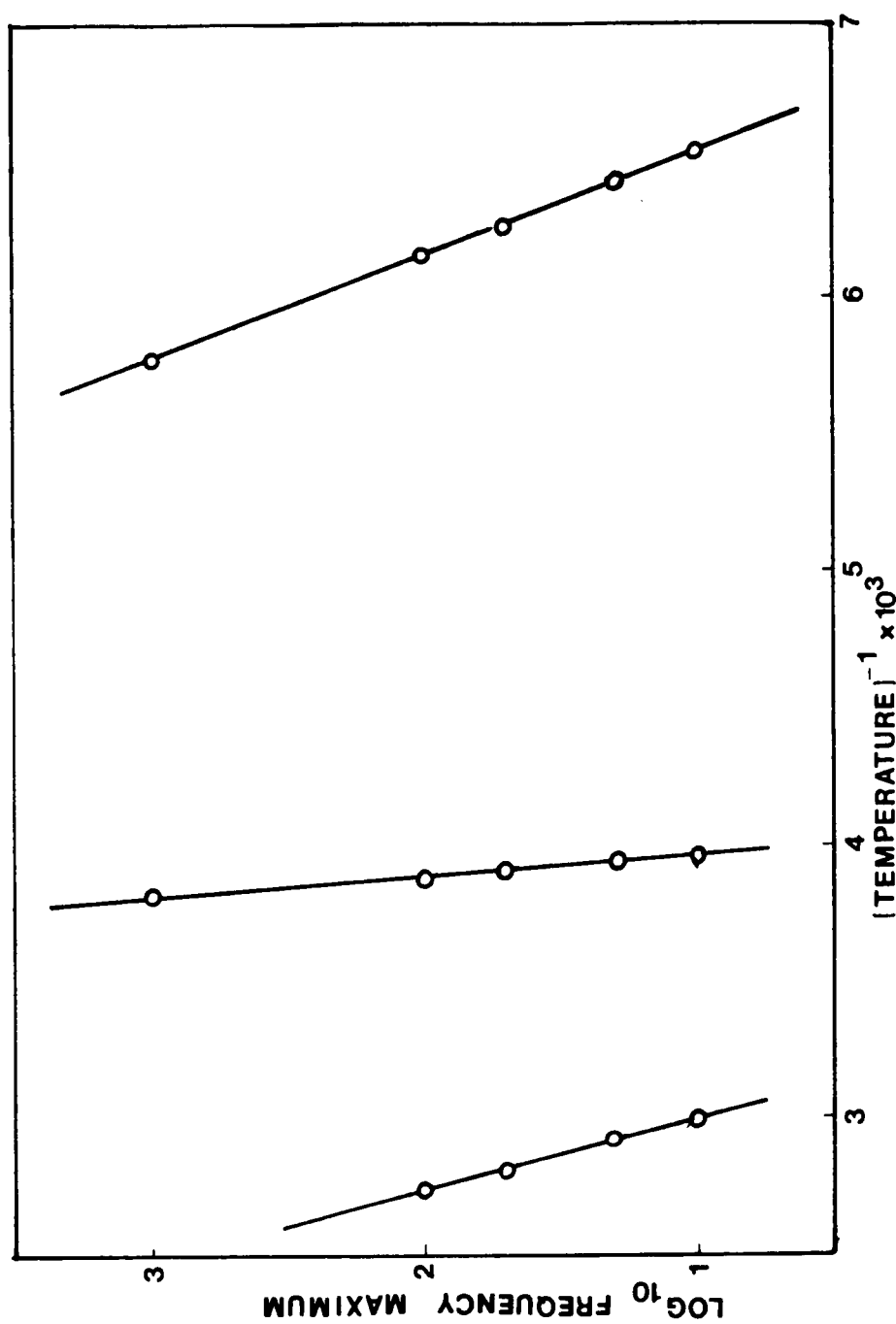


Figure 4.21. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.19.

tabulated in Table 4.2 (page 111). The Cole-Cole plots of extruded rods generated at 60°C, -20°C and -120°C for the α , β and γ relaxation processes, respectively, are shown in Figures 4.22 and 4.23.

4.3 Dynamic Mechanical Relaxation of Extruded Rods

Dynamic mechanical studies of polyethylene were first reported by Schmieder and Wolf (1953) followed by Flocke (1962). For low density polyethylene three loss peaks were reported. Schneider and Wolf (1953) found that the magnitude and the position of the α peak were dependent on percent crystallinity. Samples with higher crystallinity tend to have the α peak of higher magnitude and higher peak position.

Dynamic mechanical spectra could be obtained only for the extrusion direction because of the specimen size. Dynamic modulus and loss modulus as a function of temperature at 110 Hz are shown in Figure 4.24. Three major relaxation regions are present and are labeled similarly to those of the dielectric loss curve. As can be seen from Figure 4.24, the peaks overlap continuously, hence the shift of any peak becomes difficult to quantify. This result is compared with unoriented LLDPE films and stretched sheets (Jang et al., 1985). The major differences between the specimen of extruded rod and the stretched sheet lie in the slightly higher modulus and the large high-temperature extension of the α loss peak.

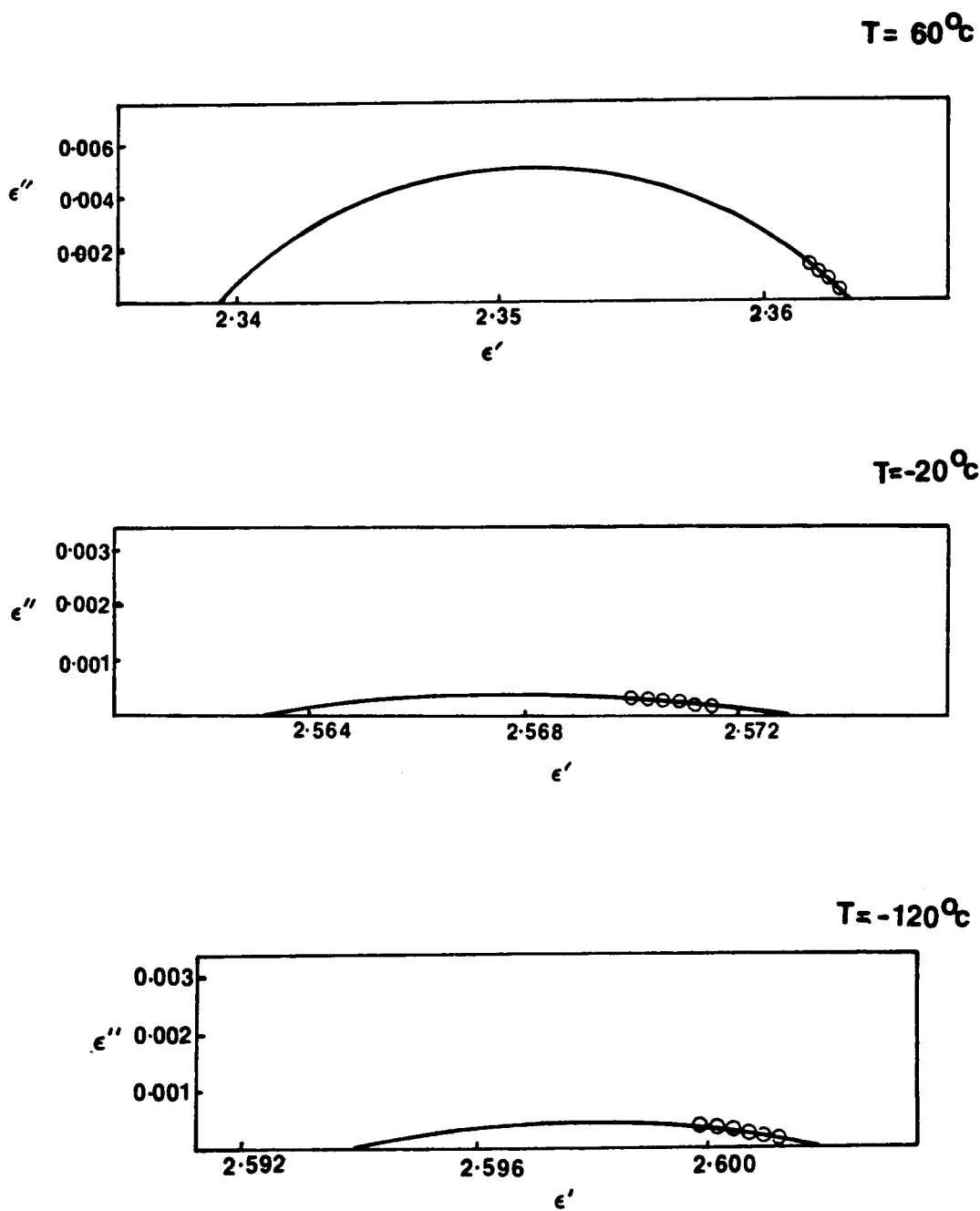


Figure 4.22. Cole-Cole Plots of Extruded Rod from the Data in Figure 4.18.

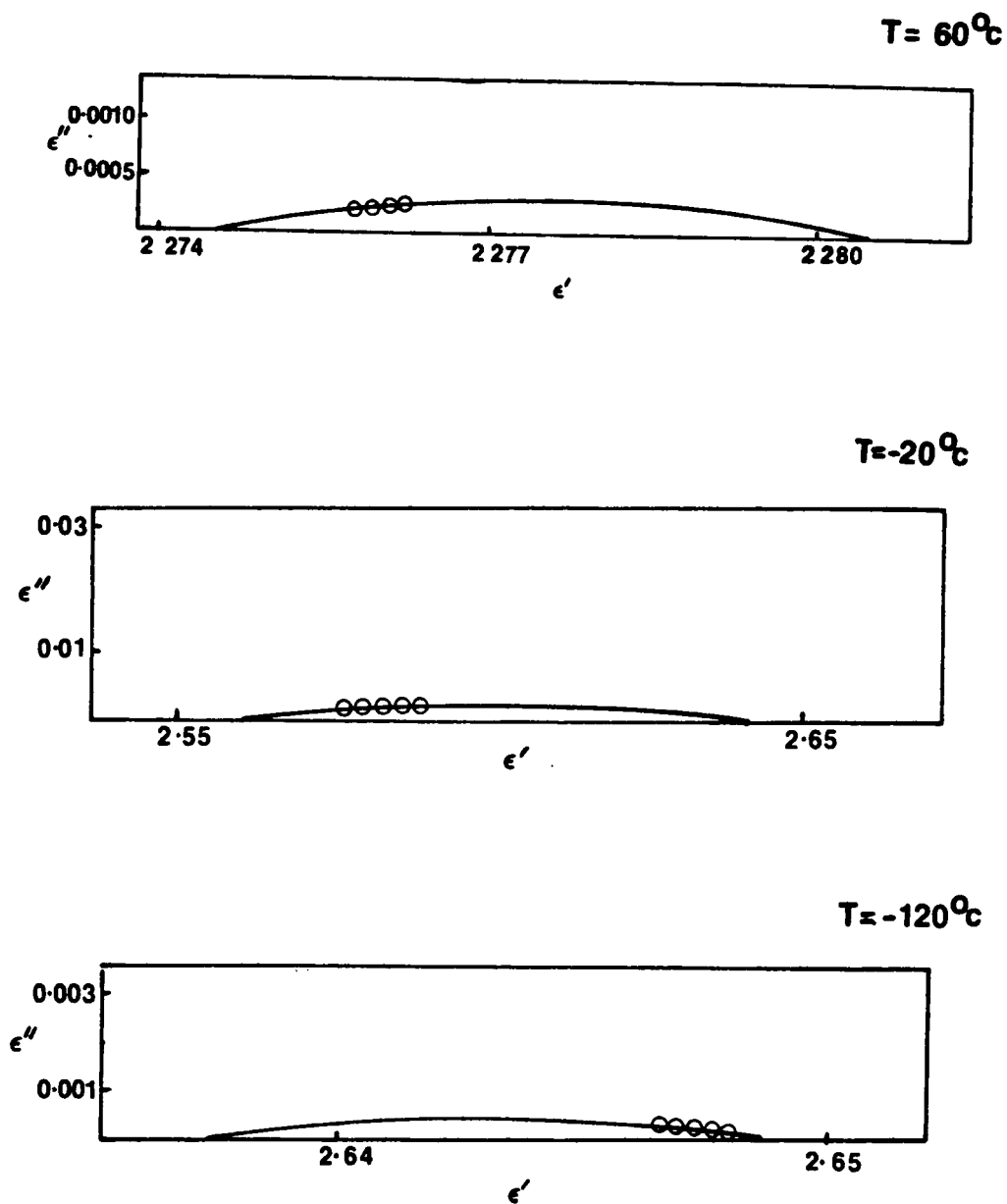


Figure 4.23. Cole-Cole Plots of Extruded Rod from the Data in Figure 4.19.

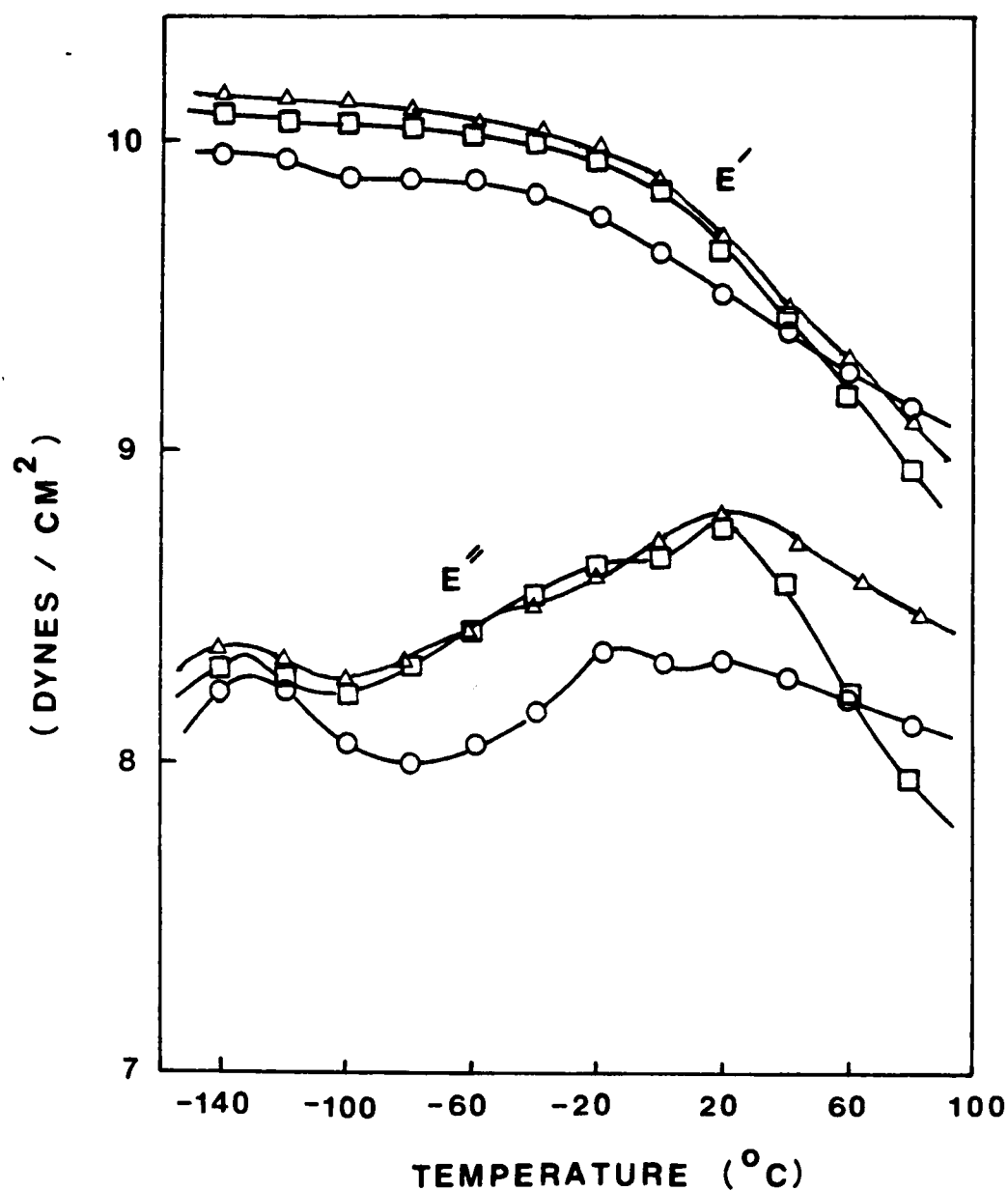


Figure 4.24. Storage and Loss Moduli at 110 Hz as a Function of Temperature for Unoriented (O), Oriented by Stretching (□) and Extruded Rod (Δ) of LLDPE in Extrusion Direction.

Source: (O) and (□) Jang, Y. T., Ph.D. Dissertation, Univ. of Utah, 1984.

4.4 PE Containing Solute Molecules

4.4.1 Unoriented Films

4.4.1.1 Characterization. The wide-angle X-ray diffraction pattern of an unoriented LLDPE film containing 1.5% acridine taken using a diffractometer is shown in Figure 4.25. There was no change in peak positions when compared to the LLDPE film without acridine molecules (see Figure 4.3, page 91). Arrows in Figure 4.25 indicate the possible acridine diffraction 2θ values. Since the X-ray diffraction pattern is unchanged even after dissolving solute molecules, it is an indication that solute molecules are excluded from the crystalline region.

Figure 4.26 shows DSC studies of unoriented LLDPE films containing 0.6%, 1.1% and 1.8% of acridine. The melting temperatures are 110.12, 110.03 and 110.05°C and the heats of fusion are 21.47, 21.53 and 21.38 cal/gm for samples containing 0.6%, 1.1% and 1.8% of acridine, respectively. The melting curves are very similar regardless of the concentration of the solute molecules. There are no major changes in the melting point and the heat of fusion with acridine molecules in the sample compared to the unoriented LLDPE film (see Figure 4.1, page 88).

4.4.1.2 Spectroscopic analysis. Figure 4.27 shows the ultraviolet spectra of unoriented polyethylene containing 0.15%, 0.21% and 0.68% of acridine. For unoriented LLDPE containing up to a few percent acridine, the spectra are sharp and well resolved.

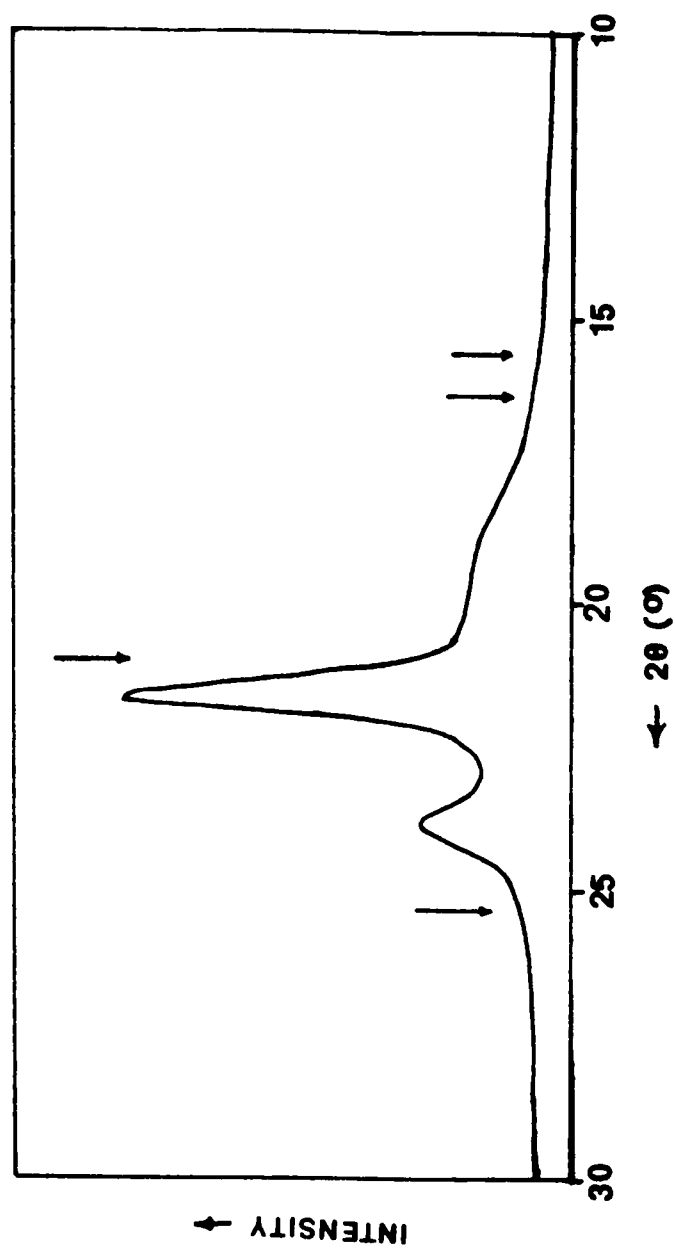


Figure 4.25. Wide Angle X-ray Diffraction Pattern of Unoriented LLDPE Containing 1.5% Acridine.

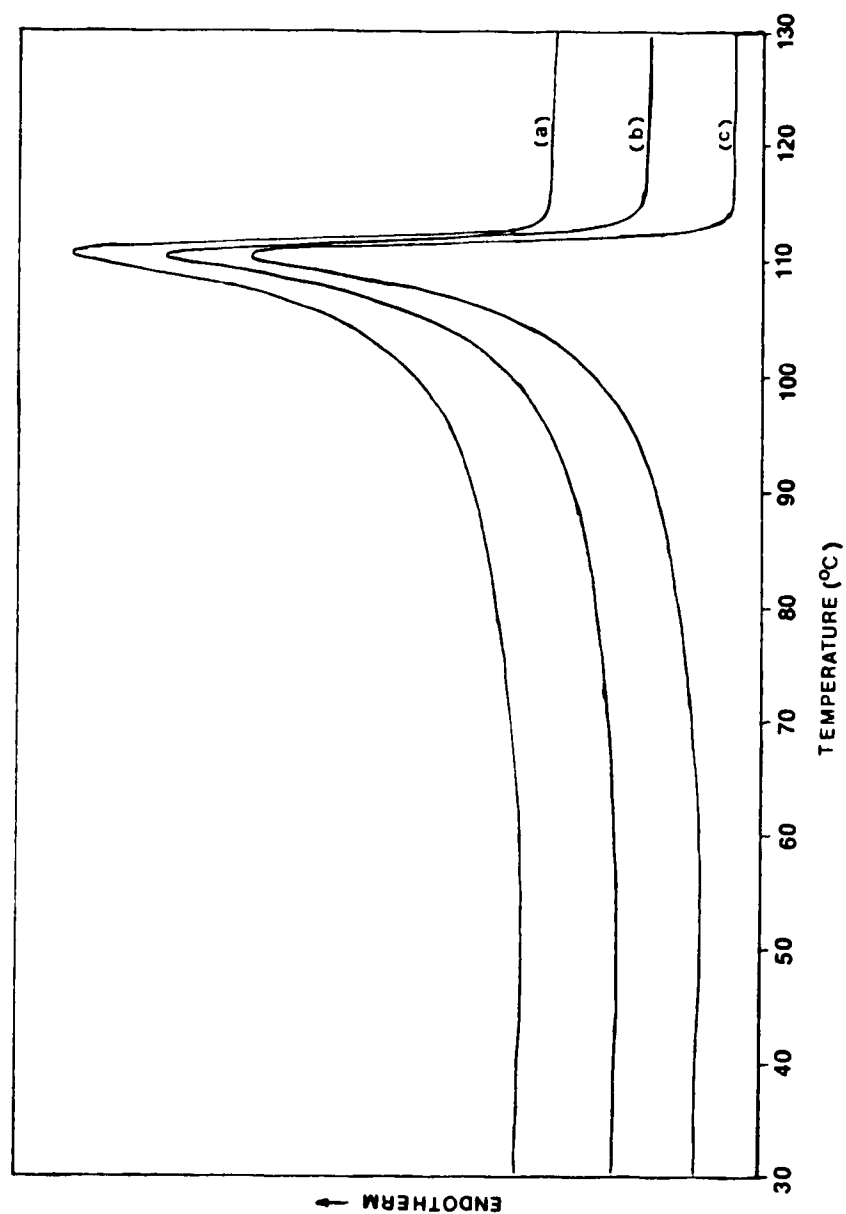


Figure 4.26. Melting Curves of LLDPE Containing Acridine. (a) 0.6%, (b) 1.1%, (c) 1.8%.

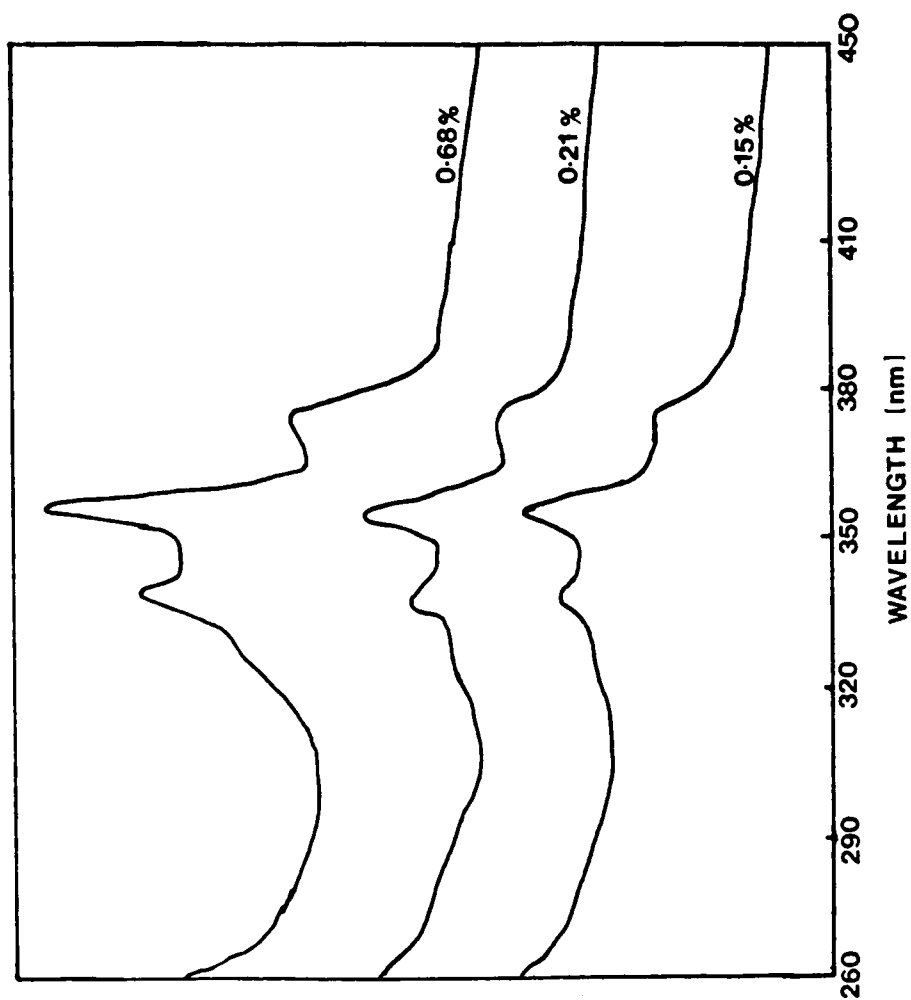


Figure 4.27. Ultraviolet Spectra of Unoriented LLDPE as a Function of Acridine Concentration.

The ultraviolet spectra are sensitive to association of aromatic molecules, becoming smeared if microcrystals are formed. Lack of smearing of ultraviolet spectra indicates that aromatic molecules are not able to associate in unoriented LLDPE.

4.4.2 Uniaxially Stretched Films

4.4.2.1 Characterization. Figure 4.28 shows the DSC melting curve of acridine. Acridine shows both a melting point at 110°C and a solid-state crystal transformation at 104°C, the latter being a change from the monoclinic to the orthorhombic crystal form. A melting curve of 500% elongated LLDPE containing 0.66% acridine is shown in Figure 4.29. The melting point of acridine is very close to that of polyethylene, however, the crystal transformation has a much larger latent heat. Oriented LLDPE containing 0.66% acridine shows the crystal transformation of acridine and a hint of the acridine melting point. Unoriented LLDPE containing acridine does not show evidence of the crystal transformation and melting of acridine (see Figure 4.26).

4.4.2.2 Spectroscopic analysis. Infrared study considered the 956 cm^{-1} band of acridine, typical of the long axis of the acridine molecule. Dichroic ratios were determined from the infrared spectra of stretched LLDPE containing acridine molecules up to a few percent. Both the directions parallel and perpendicular to the stretching direction were measured through the use of a polarizer. Dichroic ratios of the 956 cm^{-1} band of acridine vs. percent

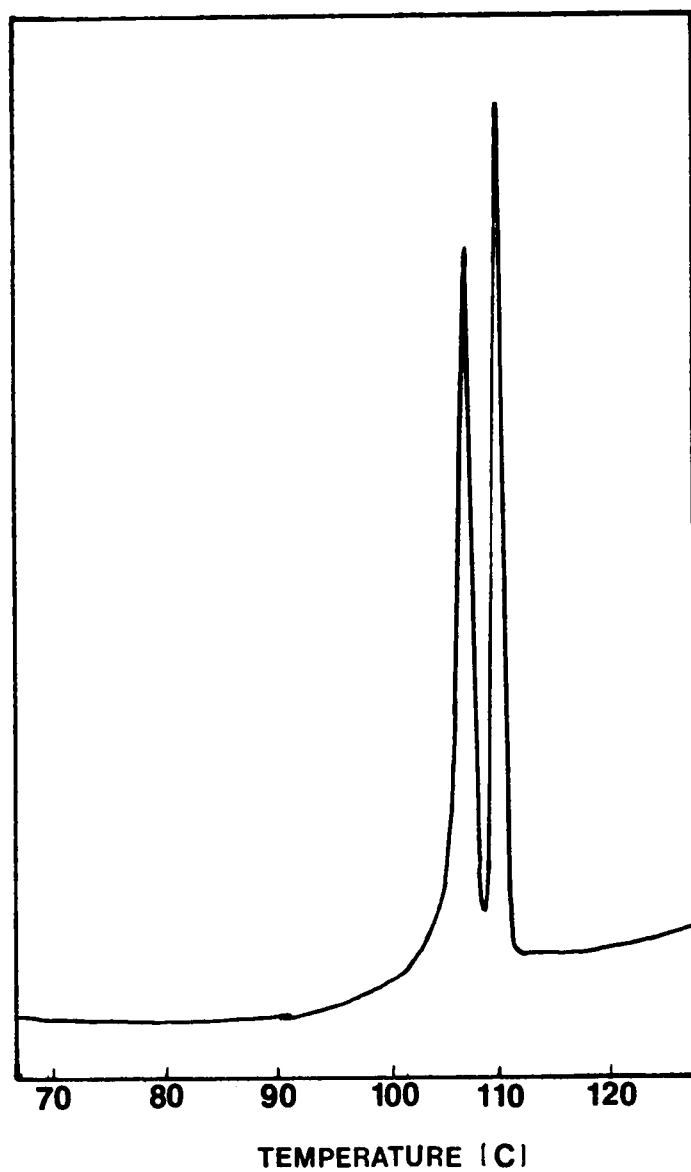


Figure 4.28. Melting Curve of Acridine.

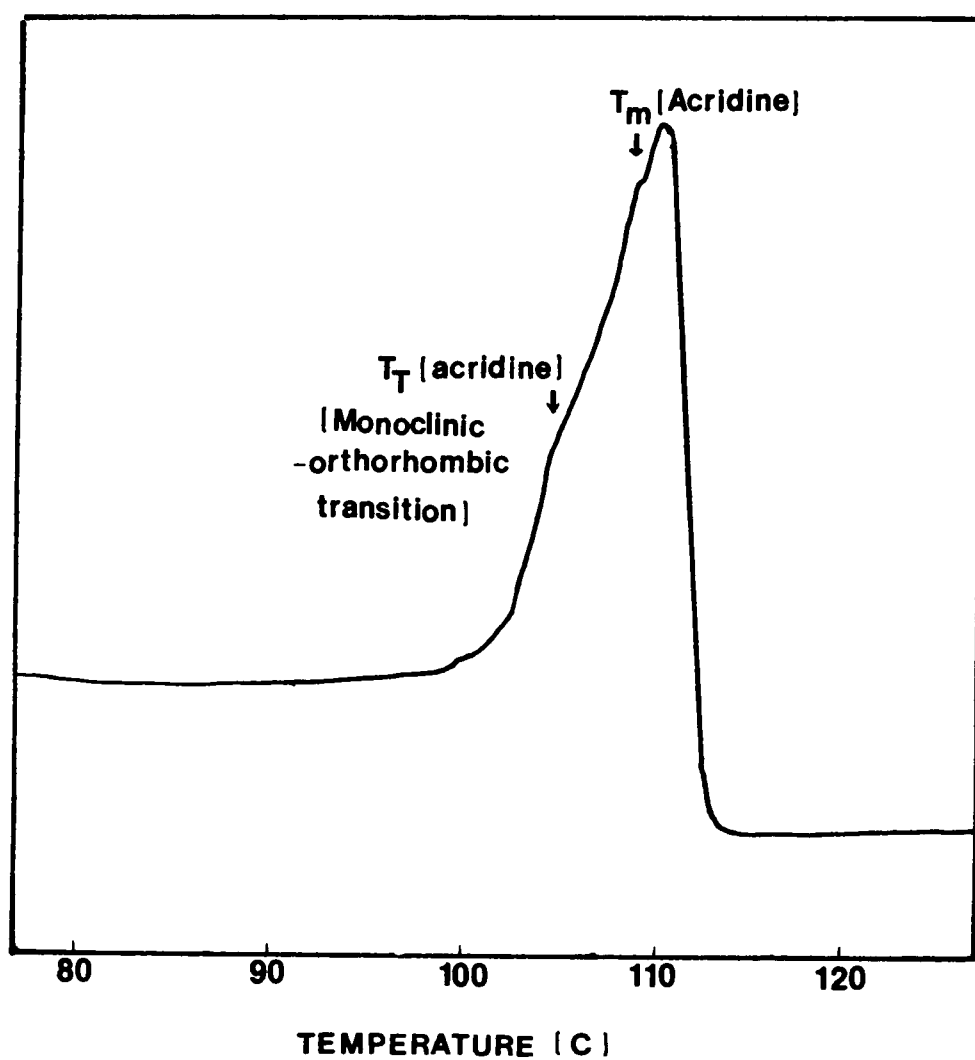


Figure 4.29. Melting Curve of 500% Elongated LLDPE Containing 0.66% Acridine.

acridine for polyethylene elongations of 275%, 450% and 600% are presented in Figure 4.30. Dichroic ratio increases both with concentration of acridine and applied elongation. This result could indicate a better orientation of individual molecules or an increasing fraction of oriented molecules.

Infrared dichroism was used by Read et al., (1968) to study orientation in the crystalline and amorphous phases of polyethylene. They found that the crystalline (1894 cm^{-1}) and amorphous (1368 cm^{-1}) regions of polyethylene gave different dichroic ratios on stretching. The dichroic ratios of the crystalline (1894 cm^{-1}) and amorphous (1368 cm^{-1}) regions of polyethylene as well as the 956 cm^{-1} band of acridine as a function of acridine concentration are shown in Figure 4.31. Dichroic ratios of CH_2 stretching in the crystalline and amorphous regions remain unchanged as a function of acridine concentration whereas the dichroic ratio of the 956 cm^{-1} band increases.

Infrared dichroism studies were also carried out on uniaxially stretched gel fractions of crosslinked ethylene-propylene rubber (EPR) having acridine concentrations up to 2%. The dichroic ratio of the 956 cm^{-1} band of acridine vs. percent acridine for an elongation of 600% is presented in Figure 4.32. Dichroic ratios of the amorphous regions (1368 cm^{-1}) of polyethylene were also obtained as a function of stretching and are presented in Figure 4.33.

Ultraviolet spectra are sensitive to the association of aromatic molecules and can easily be detected if their spectra are

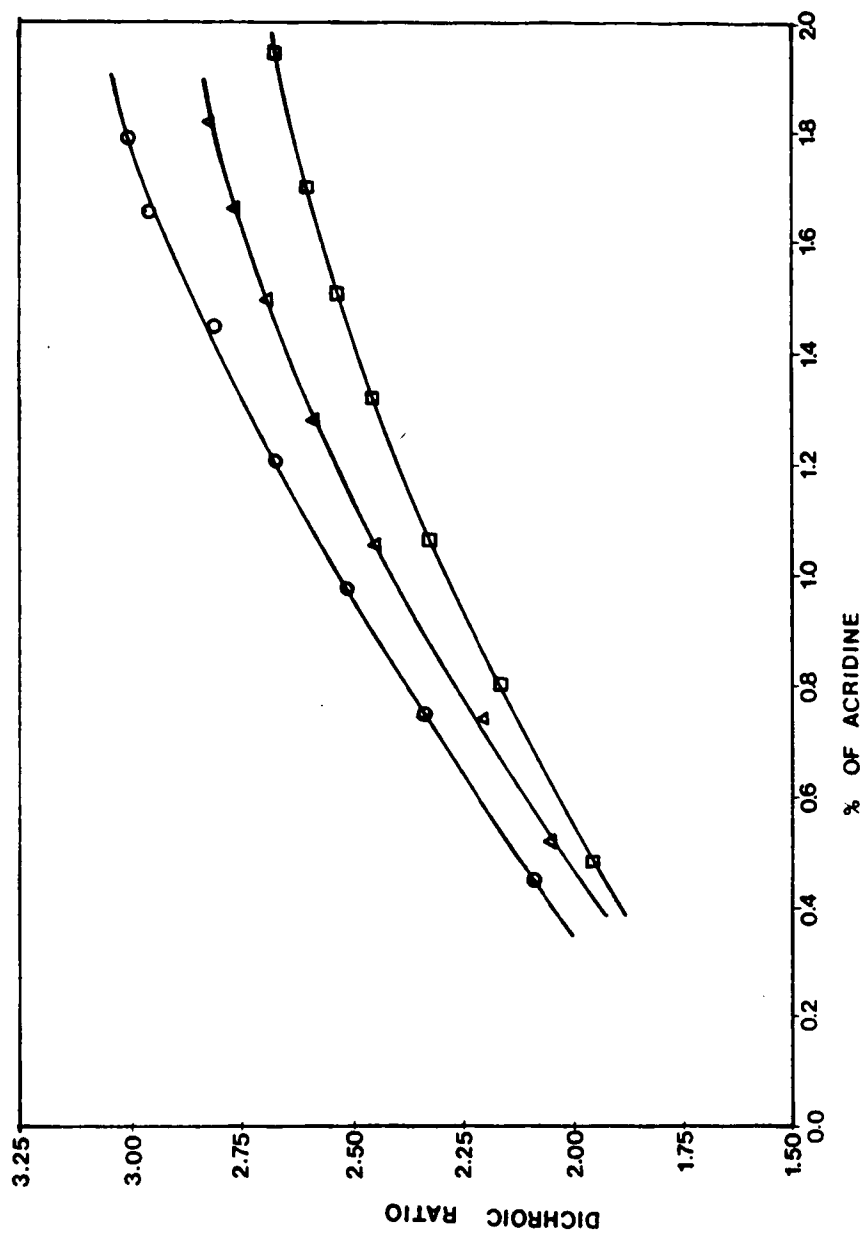


Figure 4.30. Dichroic Ratio vs. % of Acridine. (□) 275 Elongation, (Δ) 450% Elongation, (O) 600% Elongation.

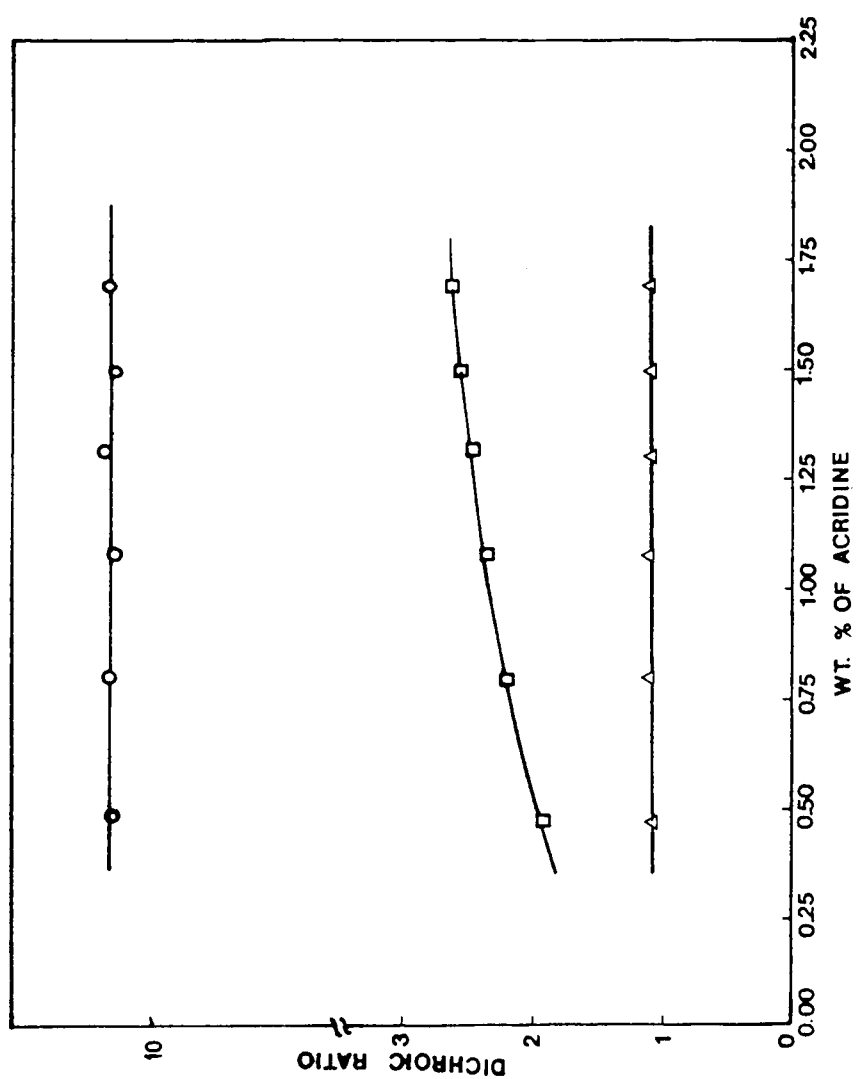


Figure 4.31. Dichroic Ratio as a Function of Acridine Concentration for 275% Elongated LLDPE. (o) Crystalline (1894 cm^{-1}) Band, (Δ) Amorphous (1368 cm^{-1}) Band, ($\square$) Acridine (956 cm^{-1}) Band.

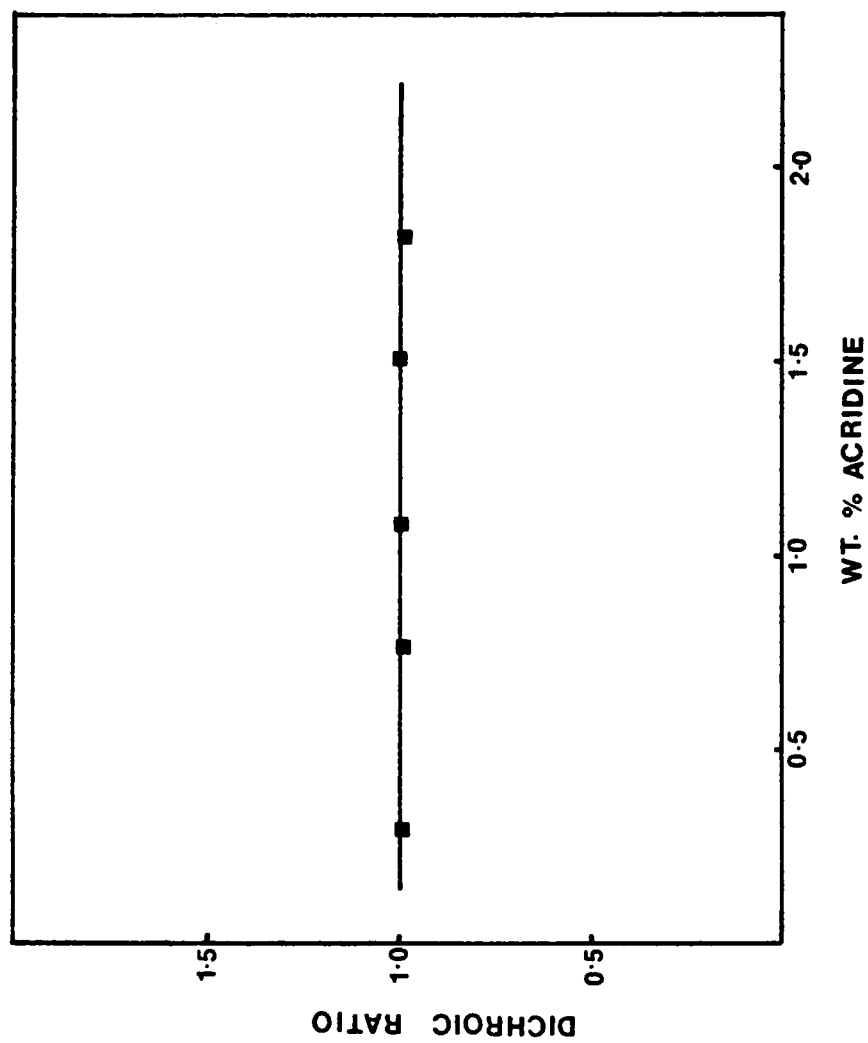


Figure 4.32. Dichroic Ratio as a Function of Acridine Concentration for 540% Elongated Cross-linked Ethylene-Propylene Rubber (EPR).

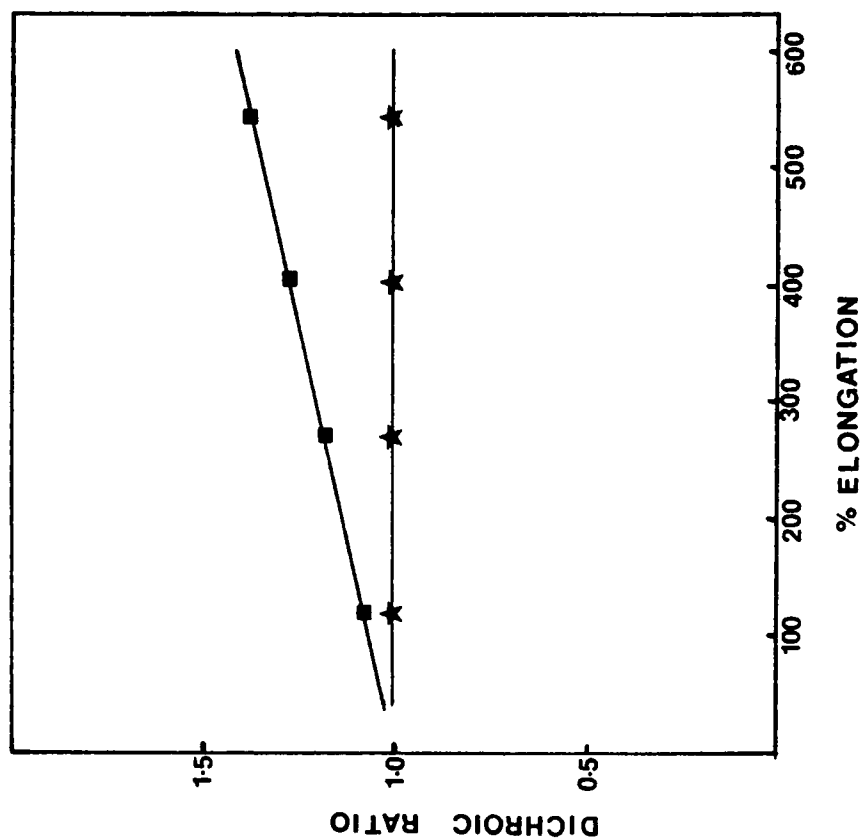


Figure 4.33. Dichroic Ratio for Cross-linked EPR (■) and acridine (★) as a Function of Draw Ratio.

smeared. Figure 4.34 shows the ultraviolet spectra of 900% elongated polyethylene containing 0.12%, 0.16% and 0.8% acridine. For unstretched LLDPE film containing acridine, the spectra are sharp and well resolved even for relatively high solute concentration whereas for stretched sheets, they become smeared for concentrations in excess of 0.15% acridine. The association of molecules is dependent on the shape of the aromatic molecule and is demonstrated with the help of 9-bromoanthracene. Figure 4.35 shows ultraviolet spectra of oriented LLDPE containing 0.56%, 1.82%, 2.57% and 3.07% of 9-bromoanthracene. The spectra are sharp and very well resolved even up to 3.00% of 9-bromoanthracene. The spectra of 9-bromoanthracene and acridine are quite different in terms of the smearing effect. Thus, different shaped aromatic molecules in oriented polyethylene behave in different ways.

4.4.3 Extruded Rods

DSC studies of extruded rod of LLDPE containing 0.0%, 1.04%, 2.75% and 3.27% of acridine are shown in Figure 4.36. It can be seen that the solid-state crystal transformation (at about 105°C) becomes quite evident with increase in acridine concentration. The use of extruded rod polyethylene, which is known to orient molecules better than the stretched film, produces very clear evidence of the crystal transformation from monoclinic to orthorhombic crystal form. Figure 4.37 shows a comparison of extruded rods of LLDPE with 4.0% acridine and without acridine. In this case, the solid-state crystal transformation is quite evident and even the melting of the

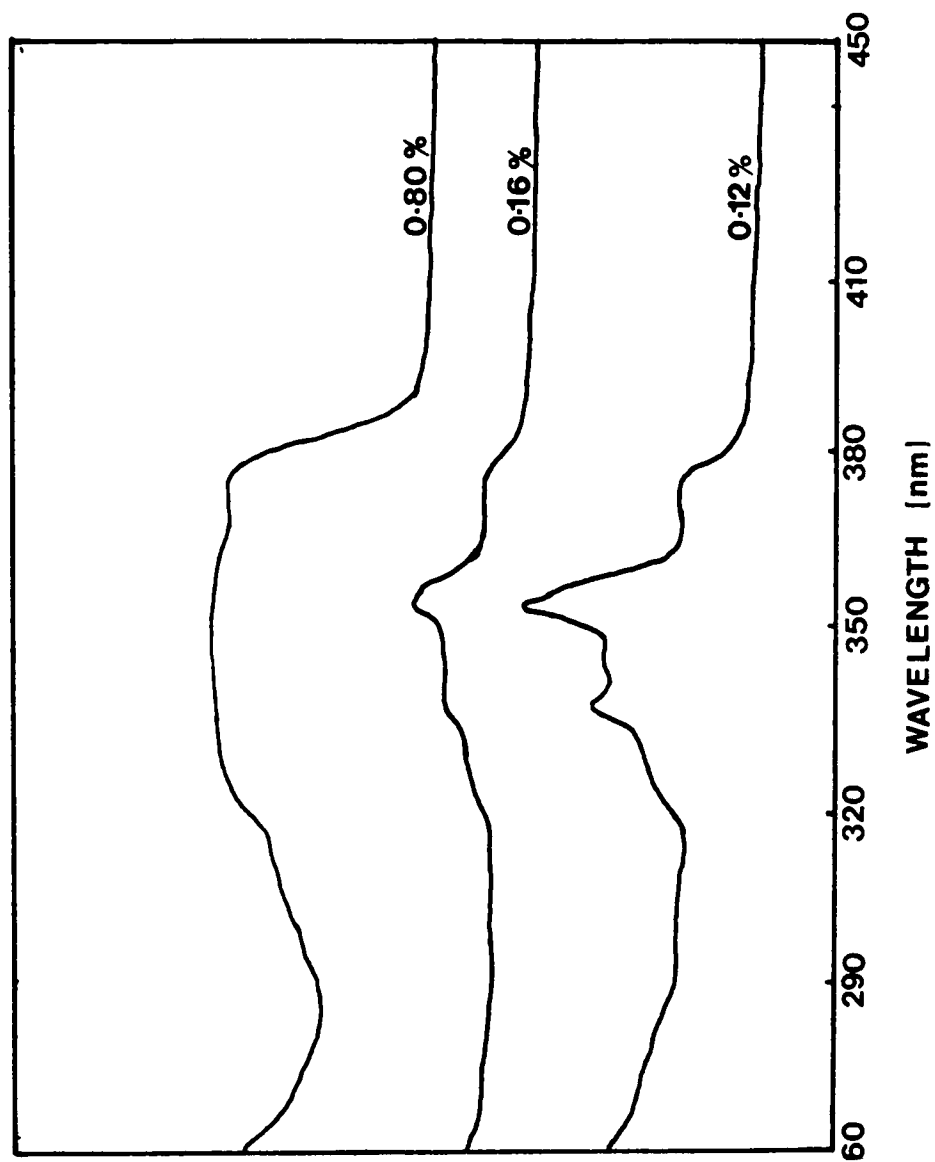


Figure 4.34. UV Spectra for 900% Elongated LLDPE as a Function of Acridine Concentration.

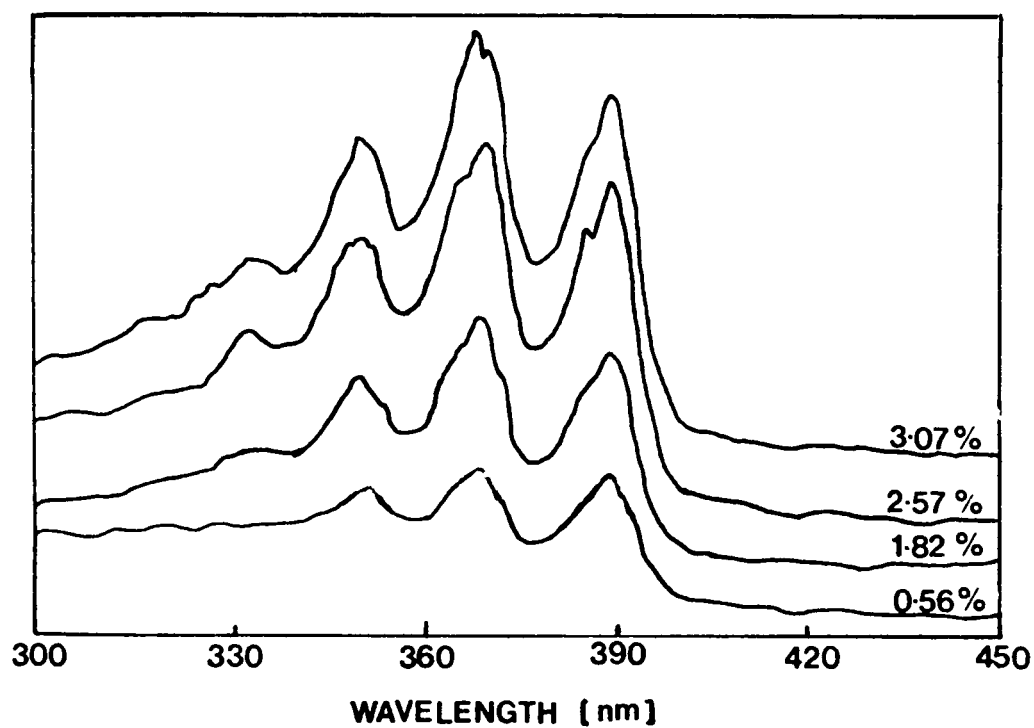


Figure 4.35. UV Spectra for 900% Elongated LLDPE as a Function of 9-Bromoanthracene Concentration.

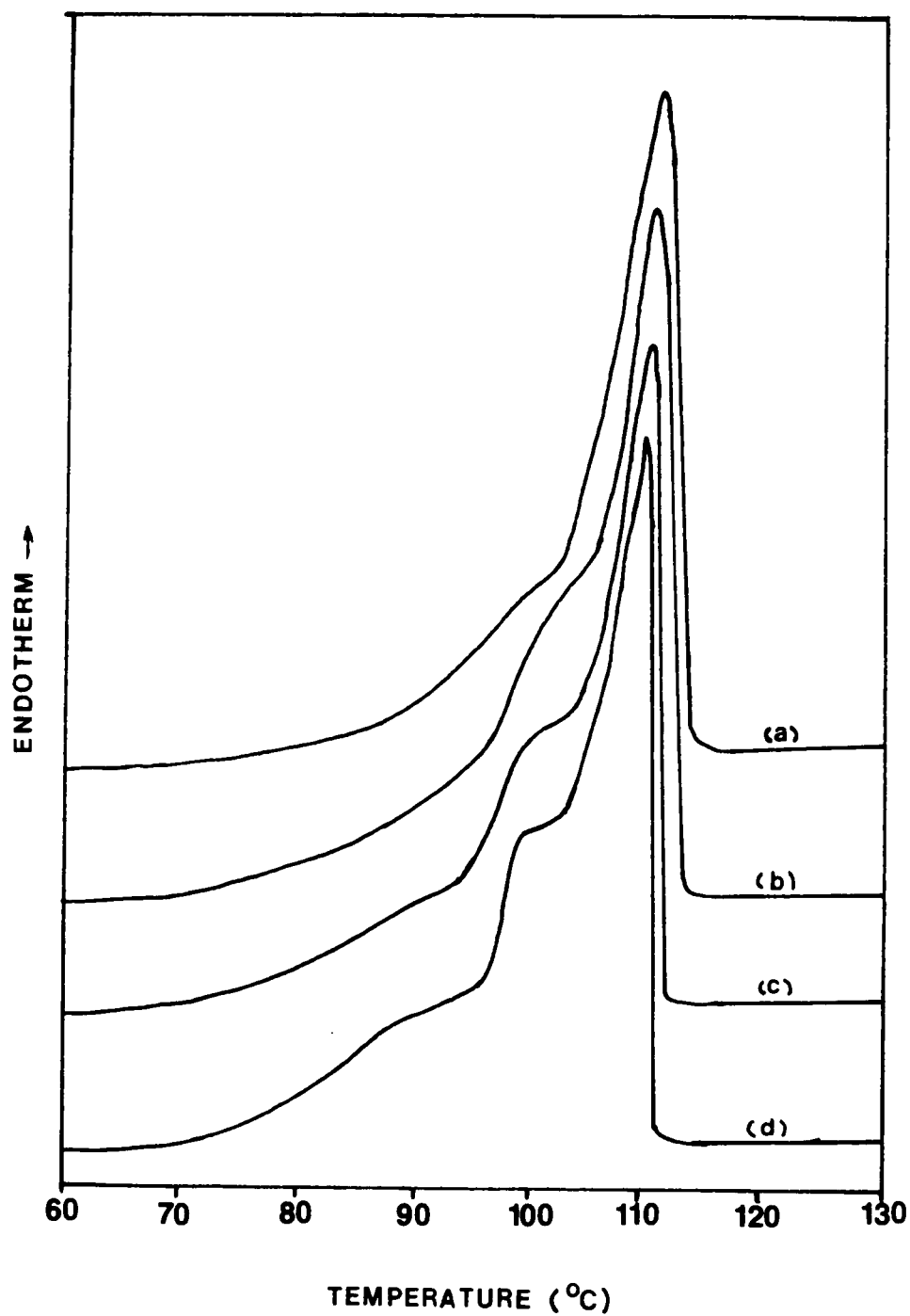


Figure 4.36. Melting Curves of Extruded Rod of LLDPE Containing Acridine. (a) 0%, (b) 1.04%, (c) 2.75%, (d) 3.27%.

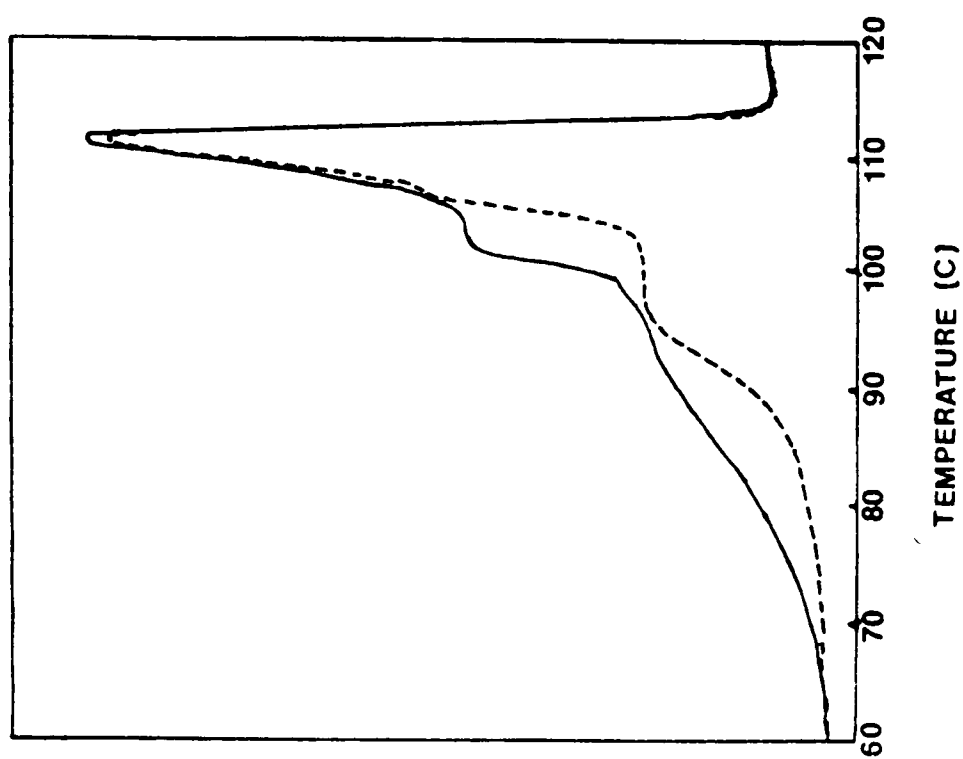


Figure 4.37. Melting Curve for Extruded Rod Polyethylene (---) and Con-taining 4.0% Acridine (—).

acridine crystals can be discerned very close to the polyethylene melting peak. Extruded rods and stretched sheets, containing acridine molecules, show both transitions (solid-state crystal transformation and melting of acridine). Thus, irrespective of the method used to induce orientation in polyethylene, similar behavior is observed.

4.5 Dielectric Data of PE Containing Solute Molecules

4.5.1 Unoriented LLDPE

Figure 4.38 shows the dielectric loss of unoriented LLDPE containing 0.17% acridine at various frequencies. In this case, the α -process remains about the same in magnitude as in unoriented LLDPE (see Figure 4.12, page 105) whereas the β and γ loss processes increase in magnitude but overlap one another. The peak positions of the α and β processes are unchanged whereas the location of the γ peak shifts to higher temperature compared to LLDPE. Figures 4.39 and 4.40 show a comparison of the unoriented LLDPE with and without acridine, at 10 Hz and 1 kHz, respectively. Both of these figures show the relaxation due to acridine, which was obtained by subtracting the dielectric loss of unoriented LLDPE from dielectric loss of LLDPE containing 0.17% acridine (at the same frequency).

An Arrhenius plot of the data in Figure 4.38 was constructed to obtain the activation energies (see Figure 4.41). Activation energies for the α , β and γ relaxation processes of LLDPE containing acridine molecules are tabulated in Table 4.3. The

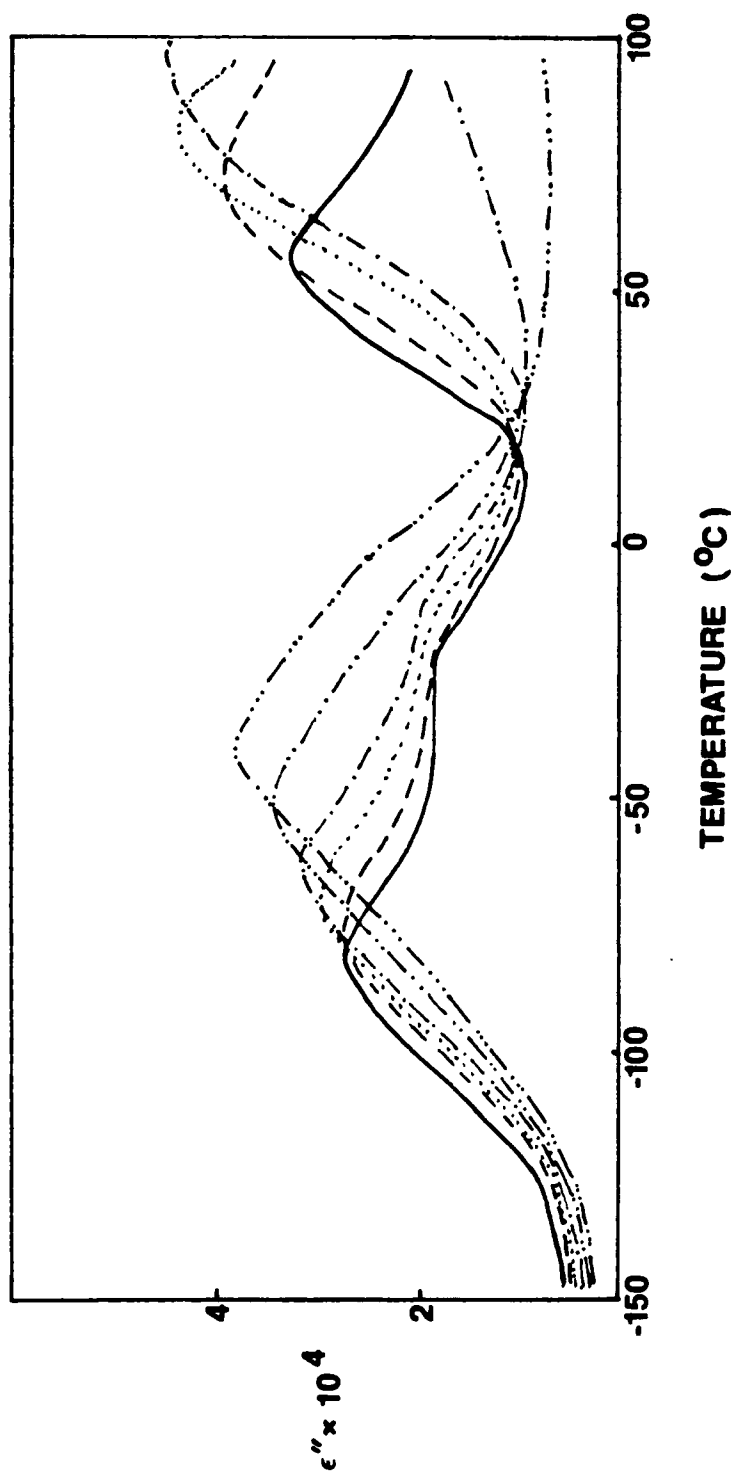


Figure 4.38. Dielectric Loss of Unoriented LLDPE Containing 0.17% Acridine. (—) 10 Hz, (---) 20 Hz, (.....) 50 Hz, (-.-.-) 100 Hz, (-.-.-) 1 kHz, (-.-.-) 5 kHz.

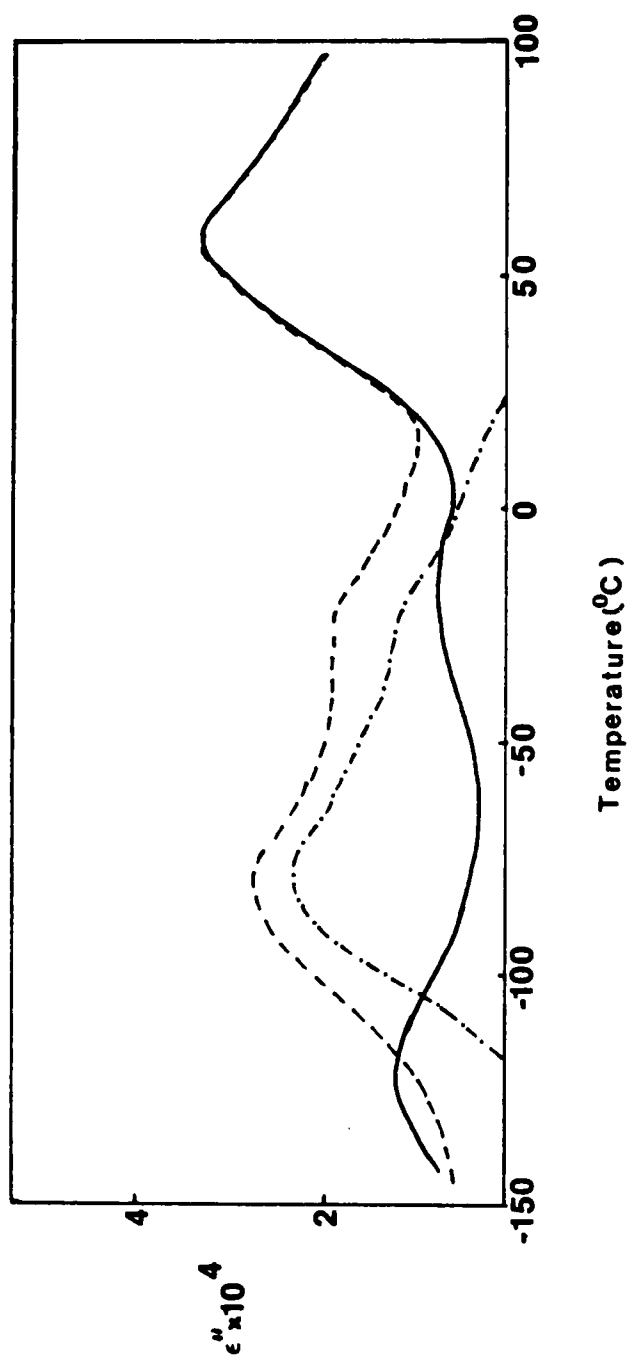


Figure 4.39. Comparison of Dielectric Loss of Unoriented LLDPE (—), with 0.17% Acridine (---) and Dielectric Loss Due to Acridine (-.-.-) at 10 Hz.

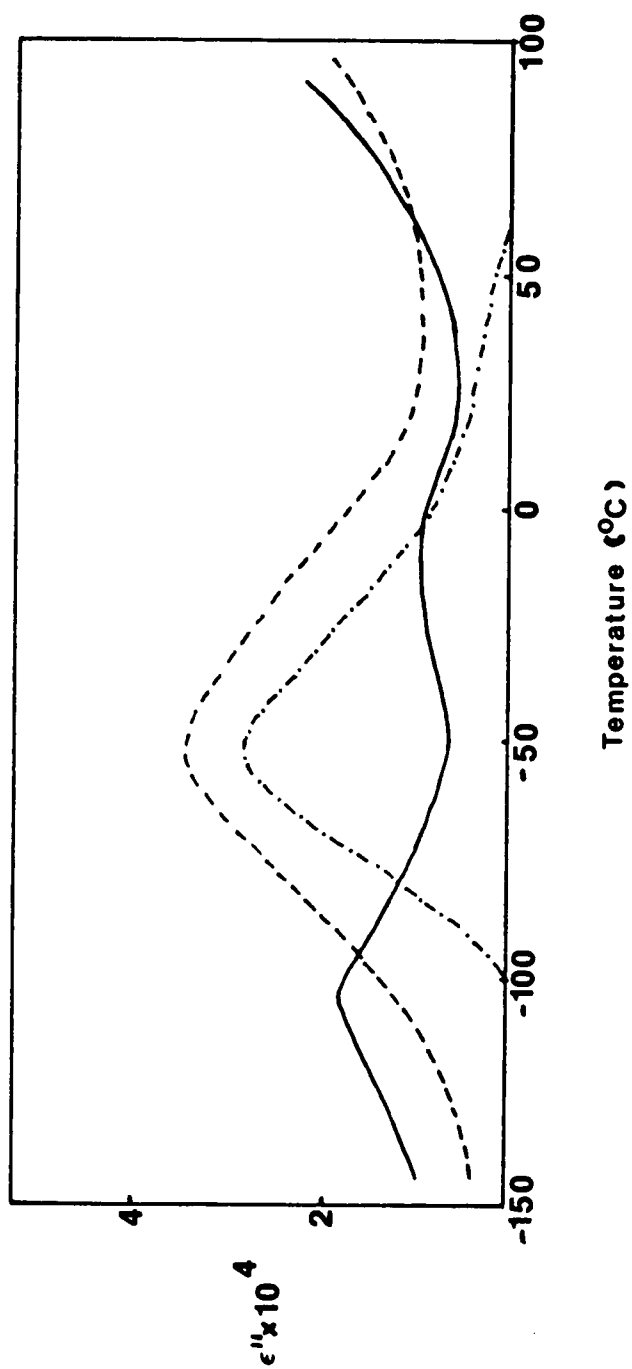


Figure 4.40. Comparison of Dielectric Loss of Unoriented LLDPE (—), with 0.17% Acridine (---) and Dielectric Loss Due to Acridine (-.-) at 1 kHz.

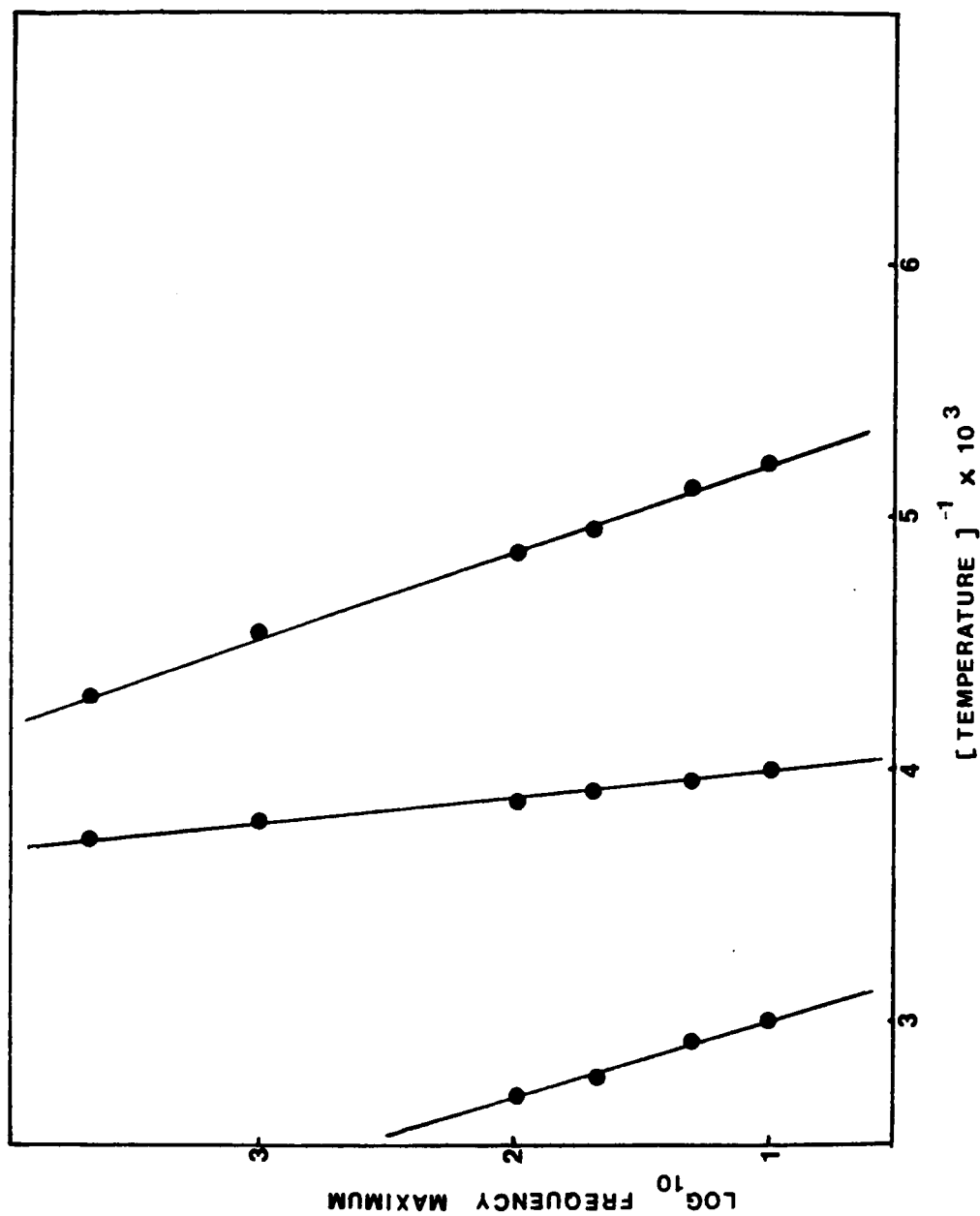


Figure 4.41. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.38.

Table 4.3. Activation Energies for LLDPE Containing Acridine (kcal/mole).

	Unoriented	Stretched Sheet	Extruded Rod	
			Parallel to Extrusion Direction	Perpendicular to Extrusion Direction
α	14.8	17.1	17.5	18.6
β	45.1	38.3	39.1	34.6
γ	13.9	15.3	16.2	14.6

activation energy of the β process with acridine molecules in LLDPE is 45.1 kcal/mole. If compared to that of the unoriented LLDPE without acridine molecules (76.3 kcal/mole), it is considerably lower. The activation energies of the γ process with and without acridine in LLDPE are 13.9 kcal/mole and 9.5 kcal/mole, respectively whereas the activation energy of the α process is unaffected in spite of acridine molecules being present. The slope and region of the Arrhenius plot for the γ process and the slope of the β process of unoriented LLDPE containing 0.17% acridine are different from those of LLDPE. The activation energies due to relaxation processes of acridine molecules dissolved in LLDPE were also obtained by constructing Arrhenius plots (see Figure 4.42) from Figures 4.39, 4.40 and similarly at other frequencies (from the dielectric loss data which correspond to acridine only). Their values are listed in Table 4.4 together with results of acridine in oriented samples for comparison.

Number of dipoles (related to number of molecules) participating in relaxation processes can be calculated from the Onsager Equation (Onsager, 1936) which is

$$N = \frac{3KT}{4\pi\mu_o^2} \left(\frac{2\epsilon_R + \epsilon_U}{3\epsilon_R} \right) \left(\frac{3}{\epsilon_U + 2} \right)^2 (\epsilon_R - \epsilon_U) \quad (4.6)$$

where N is the number of dipoles per unit volume, K is the Boltzman constant, T is the absolute temperature, μ_o is the dipole moment of the molecule. The Onsager equation was derived for dilute solutions in non-polar solvents.

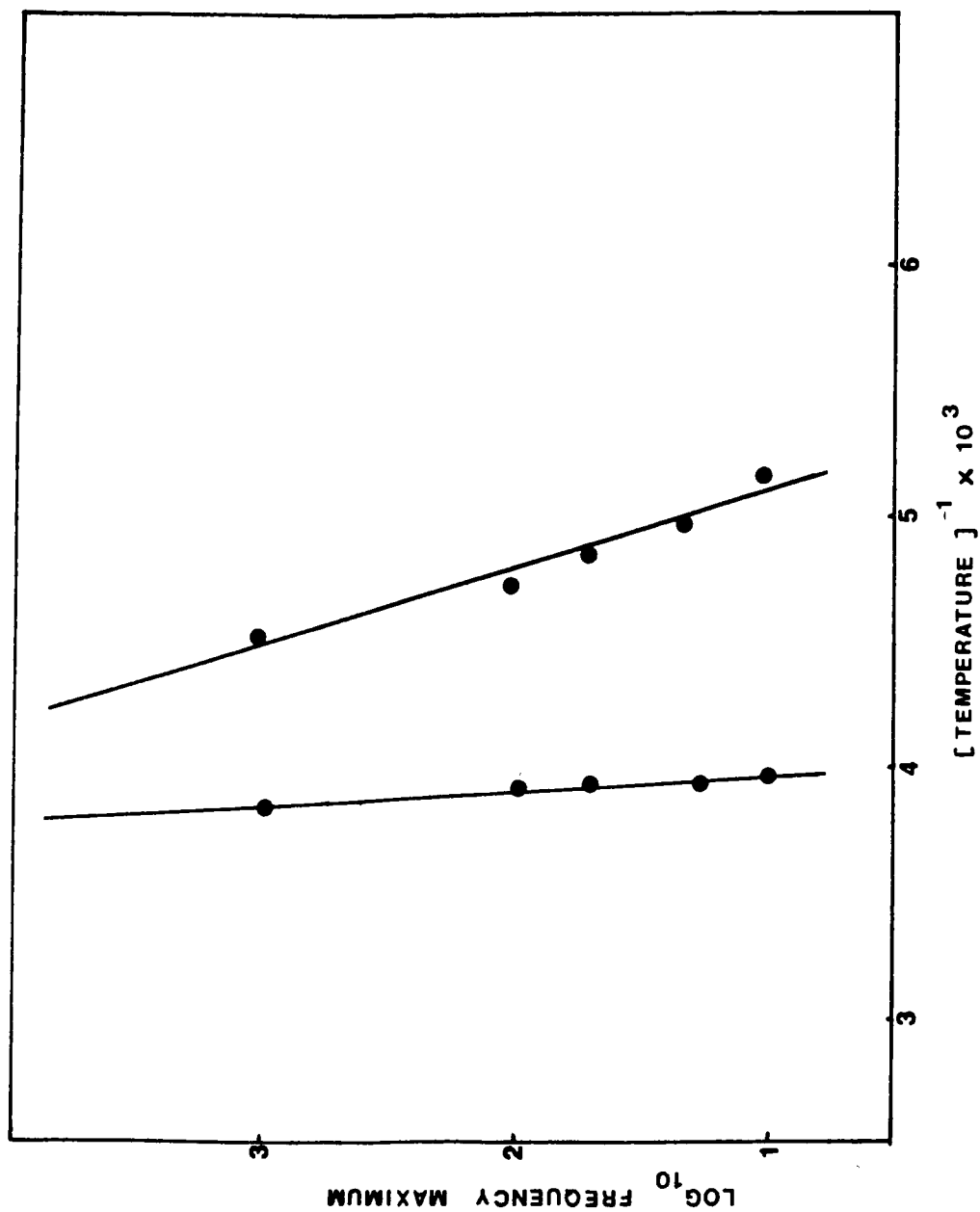


Figure 4.42. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to Acridine in Unoriented LLDPE.

Table 4.4. Activation Energies for Acridine (kcal/mole).

	Unoriented (0.17% Acridine)	Stretched Sheet (0.183% Acridine)	Extruded Rod	
			" to Extrusion Direction (0.179% Acridine)	⊥ to Extrusion Direction (0.186% Acridine)
β	85.7	81.9	92.9	46.4
γ	15.2	14.0	14.6	15.8

Equation (4.6) is a special case of the Frohlich equation (Frohlich, 1958)

$$N = \frac{3KT}{4\pi g \mu_o^2} \left(\frac{2\epsilon_R + \epsilon_U}{3\epsilon_R} \right) \left(\frac{3}{\epsilon_U + 2} \right)^2 (\epsilon_R - \epsilon_U) \quad (4.7)$$

where g is the Kirkwood dipole correlation factor and can be expressed as

$$g = 1 + Z \overline{\cos \gamma} \quad (4.8)$$

Z is the number of nearest neighbours and $\cos \gamma$ is the average of the cosine of the angle γ made between the reference molecule and nearest neighbours. In a very dilute solution, one can assume no correlation between solutes; therefore, g equals to 1. When $g = 1$, equation (4.7) reduces to the Onsager Equation (4.6). The number of molecules participating in relaxation processes are calculated using equation (4.6) and are tabulated in Table 4.5.

$(\epsilon_R - \epsilon_U)$ can be obtained by constructing Cole-Cole plots as described in section 2.6.1.1 and 4.2.2 or using the equation given by Read and Williams (1961) and Adam and Muller (1962).

$$(\epsilon_R - \epsilon_U) = \frac{2\Delta E}{\pi R} \int_0^{\infty} \epsilon'' d(1/T) \quad (4.9)$$

The area under the curve of the ϵ'' versus $1/T$ plot gives the value of the integral and using the activation energy, $(\epsilon_R - \epsilon_U)$ can be obtained.

Table 4.5. Number of Acridine Molecules Participating in Relaxation Processes.

	Unstretched	Stretched Sheet	Extruded Rod	
			" to Extrusion Direction	⊥ to Extrusion Direction
Concentration (%)	0.170	0.183	0.179	0.186
Number of molecules ($\times 10^{18}$)	5.713	6.151	6.016	6.253
Number of molecules ($\times 10^{18}$)	2.457	1.537	1.985	1.8127
% of molecules detected	43	25	33	29

Relaxation magnitudes ($\Delta\epsilon'$) obtained by constructing the Williams' plots are presented in Table 4.6.

Figure 4.43 shows the dielectric loss of unoriented LLDPE containing 0.196 % 9-bromoanthracene at various frequencies. In this case, the β and γ loss processes are increased in magnitude whereas the α loss process remains about the same in magnitude as in unoriented LLDPE. The peak position of the γ process shifts to higher temperature compared to LLDPE. Figure 4.44 shows a comparison of the unoriented LLDPE with and without 0.196 % 9-bromoanthracene at 10 Hz. This figure also shows the relaxation due to 9-bromoanthracene, which was obtained by subtracting the dielectric loss of unoriented LLDPE from the dielectric loss of LLDPE containing 0.196 % 9-bromoanthracene (at the same frequency).

Arrhenius plots of the data in Figure 4.43 were constructed to obtain the activation energies (see Figure 4.45). These activation energies are tabulated in Table 4.7. The activation energy of the γ process with 9-bromoanthracene molecules in LLDPE is 25.6 kcal/mole. If compared to that of the unoriented LLDPE without 9-bromoanthracene molecules (9.53 kcal/mole), it is considerably higher. The activation energy of the β process is reduced from 76.3 kcal/mole for unoriented LLDPE to 58.0 kcal/mole for unoriented LLDPE containing 9-bromoanthracene. The slopes and the regions of Arrhenius plots for the β and γ processes of unoriented LLDPE containing 9-bromoanthracene are different from those of LLDPE. The activation energies due to the relaxation processes of

Table 4.6. Relaxation Magnitude ($\Delta\epsilon'$) from Williams' Equation for LLDPE Containing Acridine.

	Unoriented	Stretched Sheet	Extruded Rod	
			" to Extrusion Direction	⊥ to Extrusion Direction
$\alpha(60^\circ\text{C})$	0.0135	0.0081	0.0228	0.0065
$\beta(-20^\circ\text{C})$	0.097	0.0081	0.0087	0.072
$\gamma(-90^\circ\text{C})$	0.0149	0.0092	0.0131	0.0115

$3 (\Delta\epsilon') \text{ unoriented}$			$2 (\Delta\epsilon'_I) + \Delta\epsilon'_H$
α	0.0405		0.0358
β	0.2910		0.1527
γ	0.0447		0.0361

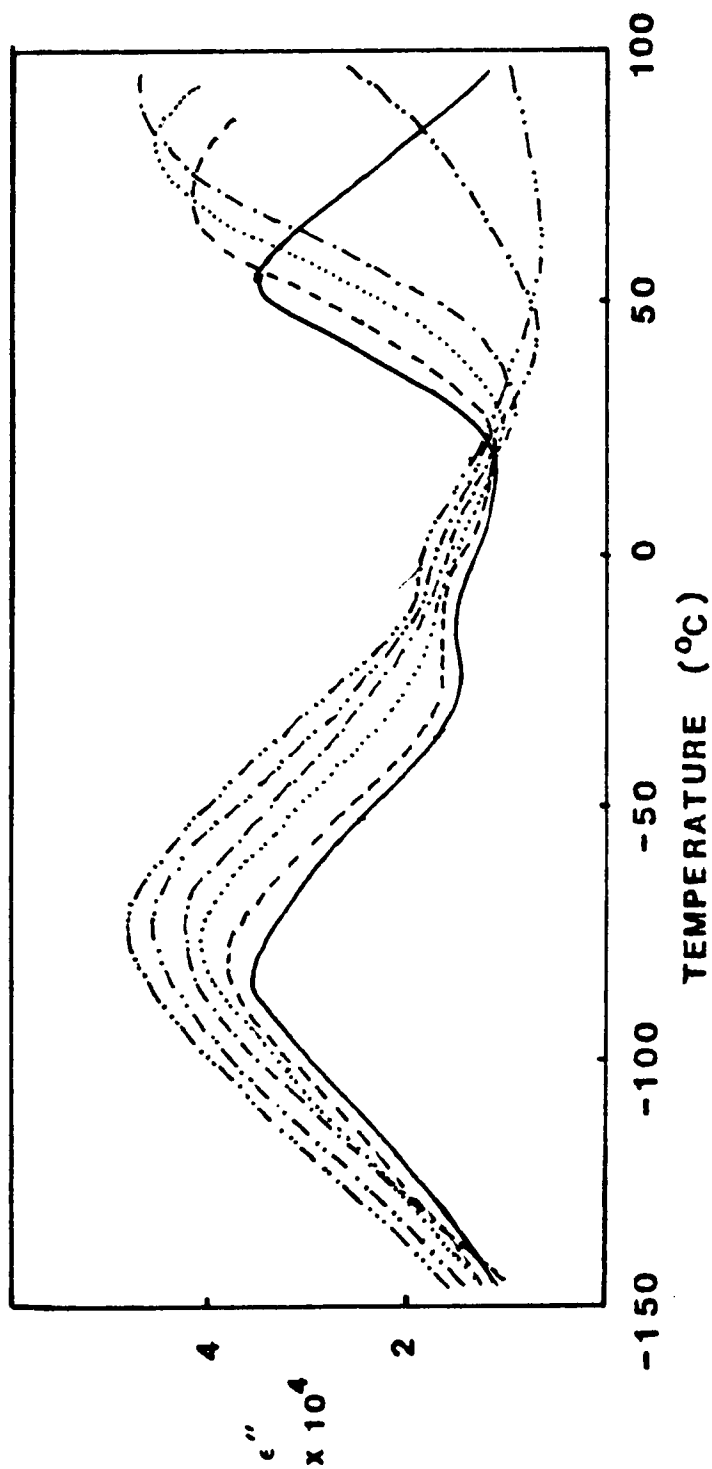


Figure 4.43. Dielectric Loss of Unoriented LLDPE Containing 0.196% 9-Bromoanthracene. (—) 10 Hz, (---) 20 Hz, (.....) 50 Hz, (-.-.-) 100 Hz, (-.-.-) 1 kHz, (-.-.-) 5 kHz.

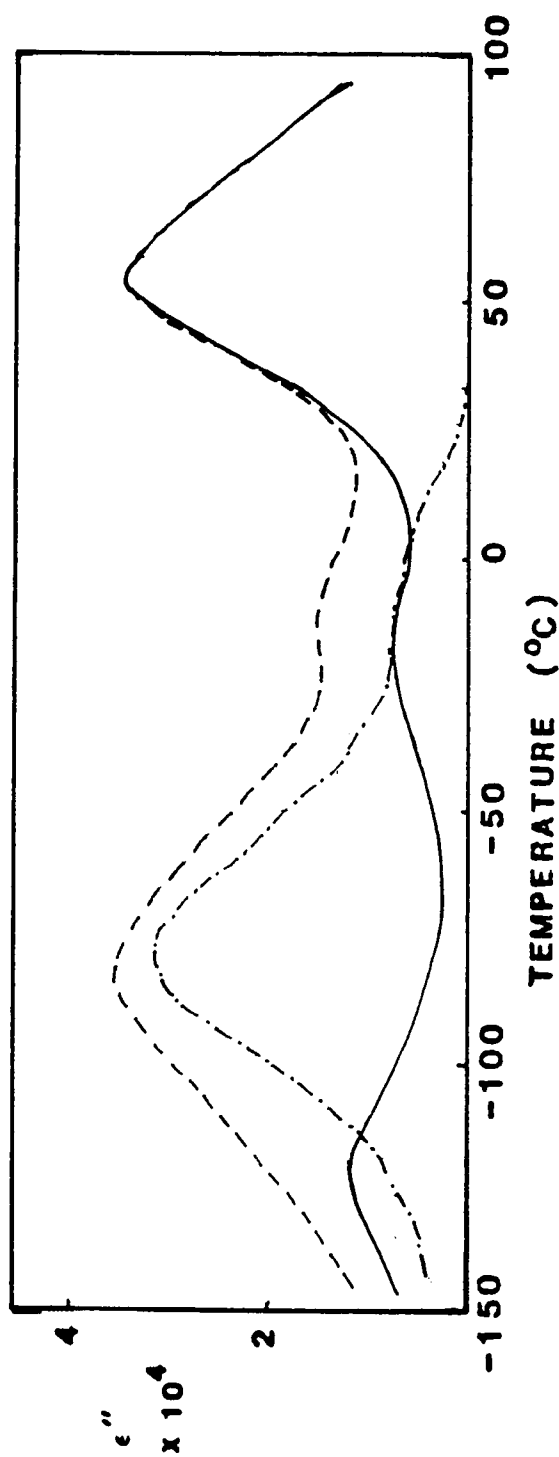


Figure 4.44. Comparison of Dielectric Loss of Unoriented LLDPE (—), with 0.196% 9-Bromoanthracene (---) and Dielectric Loss Due to 9-Bromoanthracene (-.-) at 10 Hz.

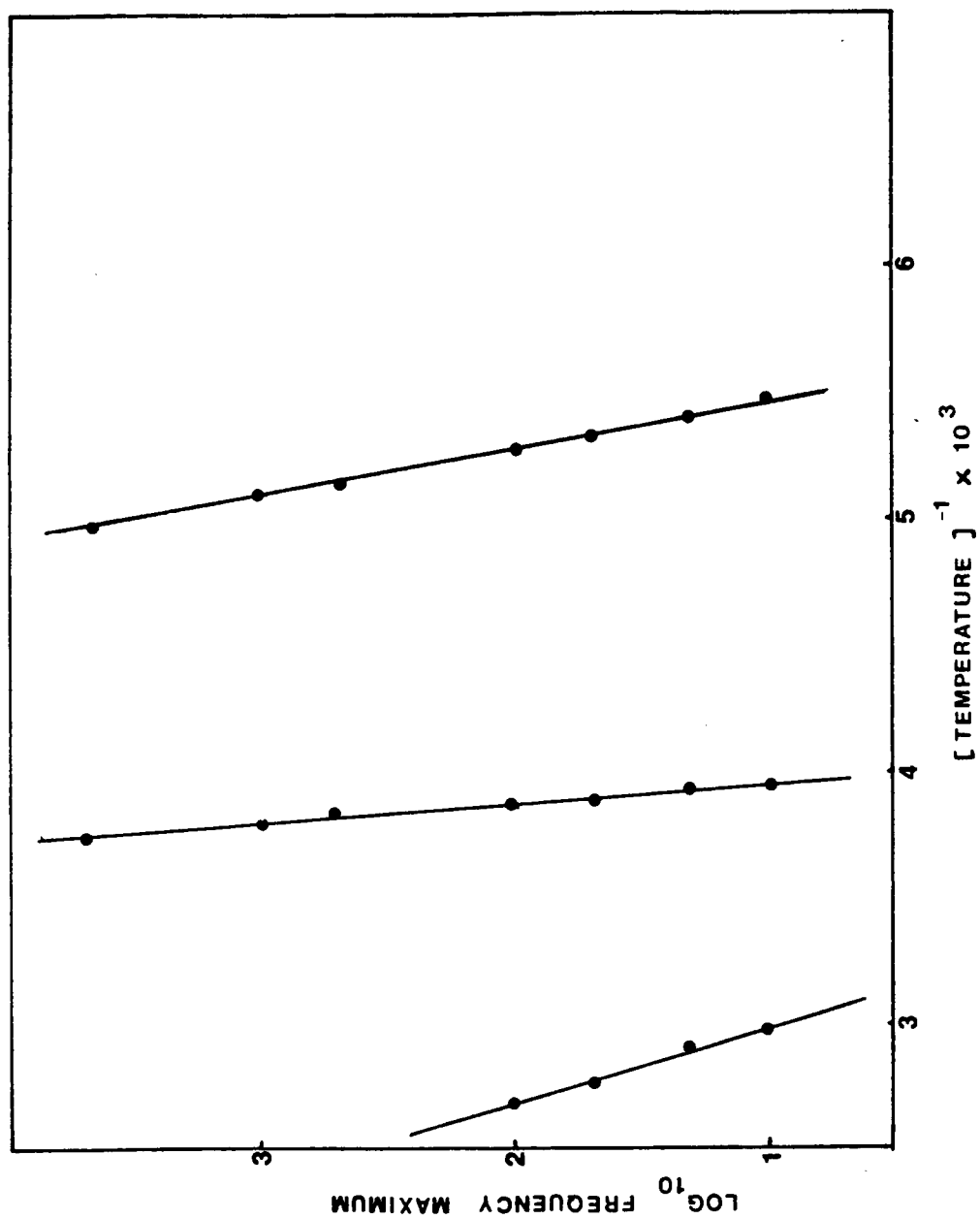


Figure 4.45. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.43.

Table 4.7. Activation Energies for LLDPE Containing 9-Bromoanthracene (kcal/mole).

	Unoriented	Extruded Rod	
		Parallel to Extrusion Direction	Perpendicular to Extrusion Direction
α	14.9	17.2	19.2
β	58.0	56.0	60.1
γ	25.6	29.2	24.8

9-bromoanthracene molecules dissolved in LLDPE were also obtained by constructing Arrhenius plots (see Figure 4.46) from Figure 4.44 and similarly at other frequencies (from the dielectric loss data which correspond to 9-bromoanthracene only). Their values are listed in Table 4.8 together with results of 9-bromoanthracene in oriented specimens for comparison. Relaxation magnitudes ($\Delta\epsilon'$) obtained by constructing the Williams' plots are presented in Table 4.9.

4.5.2 Uniaxially Stretched Films

Dielectric loss curves of LLDPE containing 0.183 wt% acridine molecules stretched to 500% elongation are shown in Figure 4.47. Clearly the α process remains almost unchanged whereas the β and γ processes are affected in magnitude and peak position compared to 500% stretched LLDPE. Locations of the peak positions of the β and γ processes are shifted by a few degrees to higher temperatures. Figures 4.48 and 4.49 (page 164) show the dielectric loss of LLDPE with and without acridine in LLDPE films elongated to 500%, at 10 Hz and 1 kHz, respectively. Both of these figures also show the relaxation due to acridine. In the case of unoriented LLDPE containing acridine, the peak position of the acridine relaxation has shifted to very high temperatures compared to the acridine relaxation in stretched films. In the case of stretched film containing acridine (see Figure 4.47), the β and γ peaks are reduced when compared to the unoriented LLDPE sample containing almost the same amount of acridine molecules (see Figure 4.38, page 142).

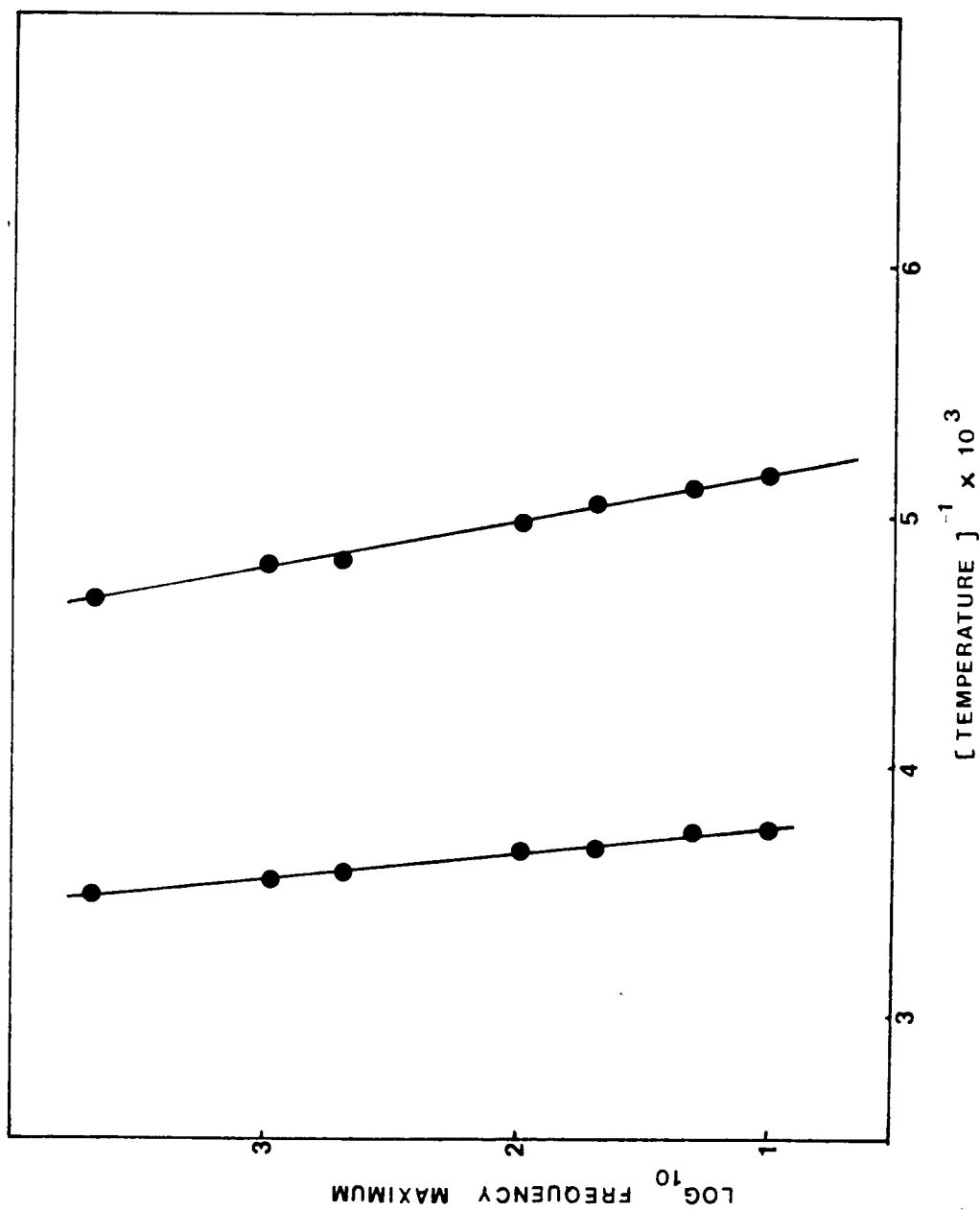


Figure 4.46. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to 9-Bromoanthracene in Unoriented LLDPE.

Table 4.8. Activation Energies for 9-Bromoanthracene (kcal/mole).

	Unoriented	Extruded Rod	
		" to Extrusion Direction	⊥ to Extrusion Direction
β	91.2	89.4	103.3
γ	25.2	25.0	28.1

Table 4.9. Relaxation Magnitudes ($\Delta\epsilon'$) from Williams' Equation for LLDPE Containing 9-Bromoanthracene.

	Extruded Rod		
	Unoriented	to Extrusion Direction	$\perp$ to Extrusion Direction
α	0.031	0.0231	0.0057
β	0.0087	0.074	0.097
γ	0.023	0.029	0.0196

$3 (\Delta\epsilon') \text{ unoriented} \quad 2 (\Delta\epsilon'_{\perp}) + \Delta\epsilon'_{\parallel}$		
α	0.0387	0.0345
β	0.324	0.268
γ	0.069	0.0682

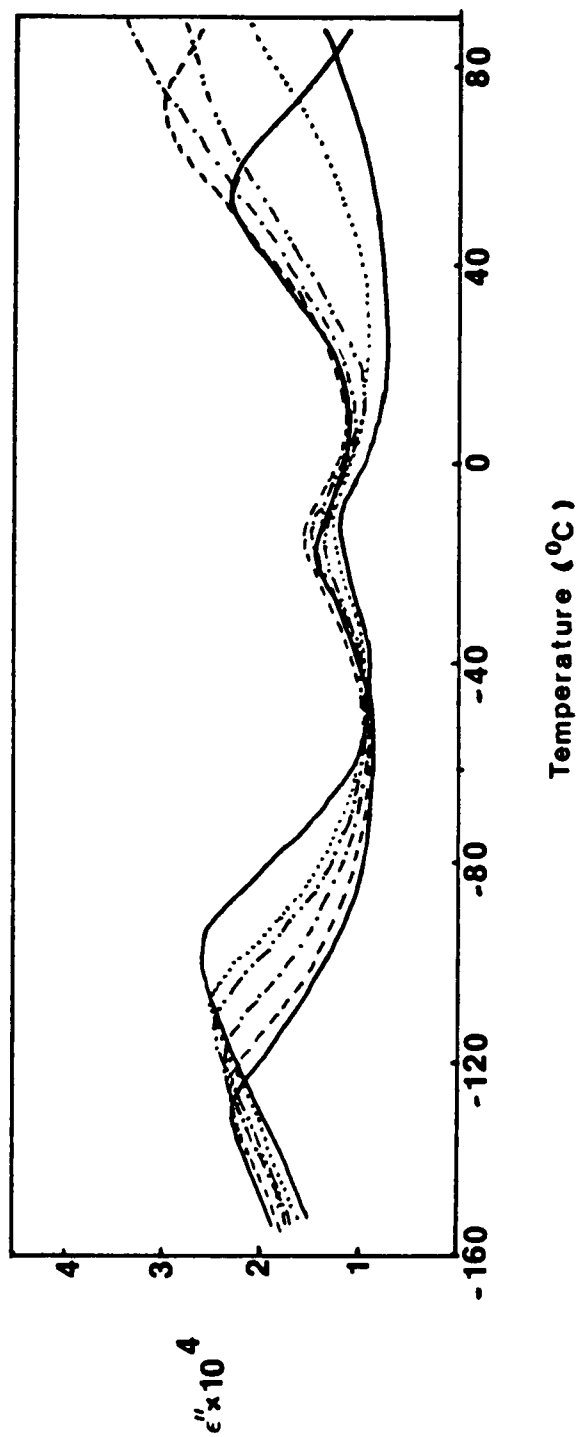


Figure 4.47. Dielectric Loss of 500% Stretched LLDPE Containing 0.183% of Acridine. (—) 10 Hz, (---) 20 Hz, (-.-.-) 50 Hz, (.....) 100 Hz, (.....) 1 kHz, (—) 5 kHz.

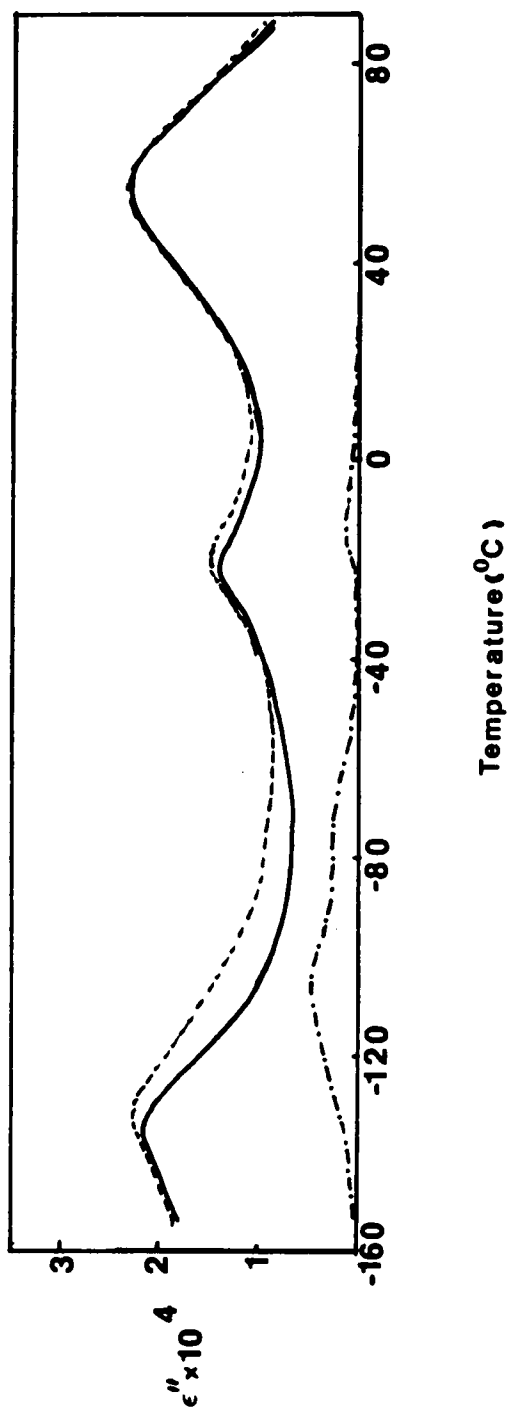


Figure 4.48. Comparison of Dielectric Loss of 500% Stretched LLDPE (—), with 0.183% Acridine (---) and Dielectric Loss Due to Acridine (-.-.-) at 10 Hz.

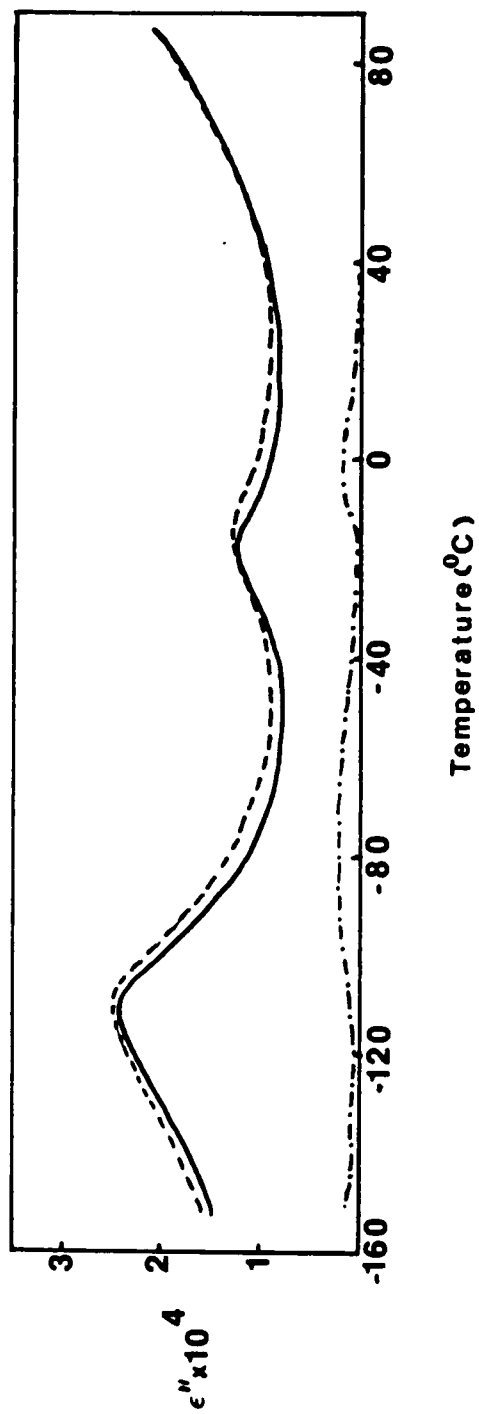


Figure 4.49. Comparison of Dielectric Loss of 500% Stretched LLDPE (—), with 0.183% Acridine (---) and Dielectric Loss Due to Acridine (-.-.) at 1 kHz.

Arrhenius plots were constructed from the data of Figure 4.47 to obtain the activation energies (see Figure 4.50). The activation energy of the β process with acridine molecules in stretched LLDPE is 38.3 kcal/mole compared to 57.2 kcal/mole of 500% elongated LLDPE whereas the activation energies of the α and γ processes are nearly the same with or without acridine molecules in stretched film. Arrhenius plots of relaxation processes of acridine in stretched LLDPE were constructed (see Figure 4.51) from Figures 4.48, 4.49 and similarly at other frequencies (from the dielectric loss due to acridine only). These activation energies are presented in Table 4.4 (page 149).

The number of dipoles participating in relaxation processes are calculated using equation (4.6) (page 147) and tabulated in Table 4.5 (page 151). Relaxation magnitudes ($\Delta\epsilon'$) for all relaxation processes were calculated by constructing Williams' plots and values are tabulated in Table 4.6 (page 153).

4.5.3 Extruded Rods of LLDPE

Figure 4.52 shows the dielectric loss of a section of extruded rod containing 0.179 wt% acridine having the electric field parallel to the extrusion direction at various frequencies. The magnitudes of the β and γ loss processes are increased compared to a section of extruded rod cut in the same direction. The peak positions of the β and γ processes are also affected in the presence of acridine molecules. The β peak shows a shift but it is much more prominent for the γ peak. The γ peak is shifted by almost 30°C compared to

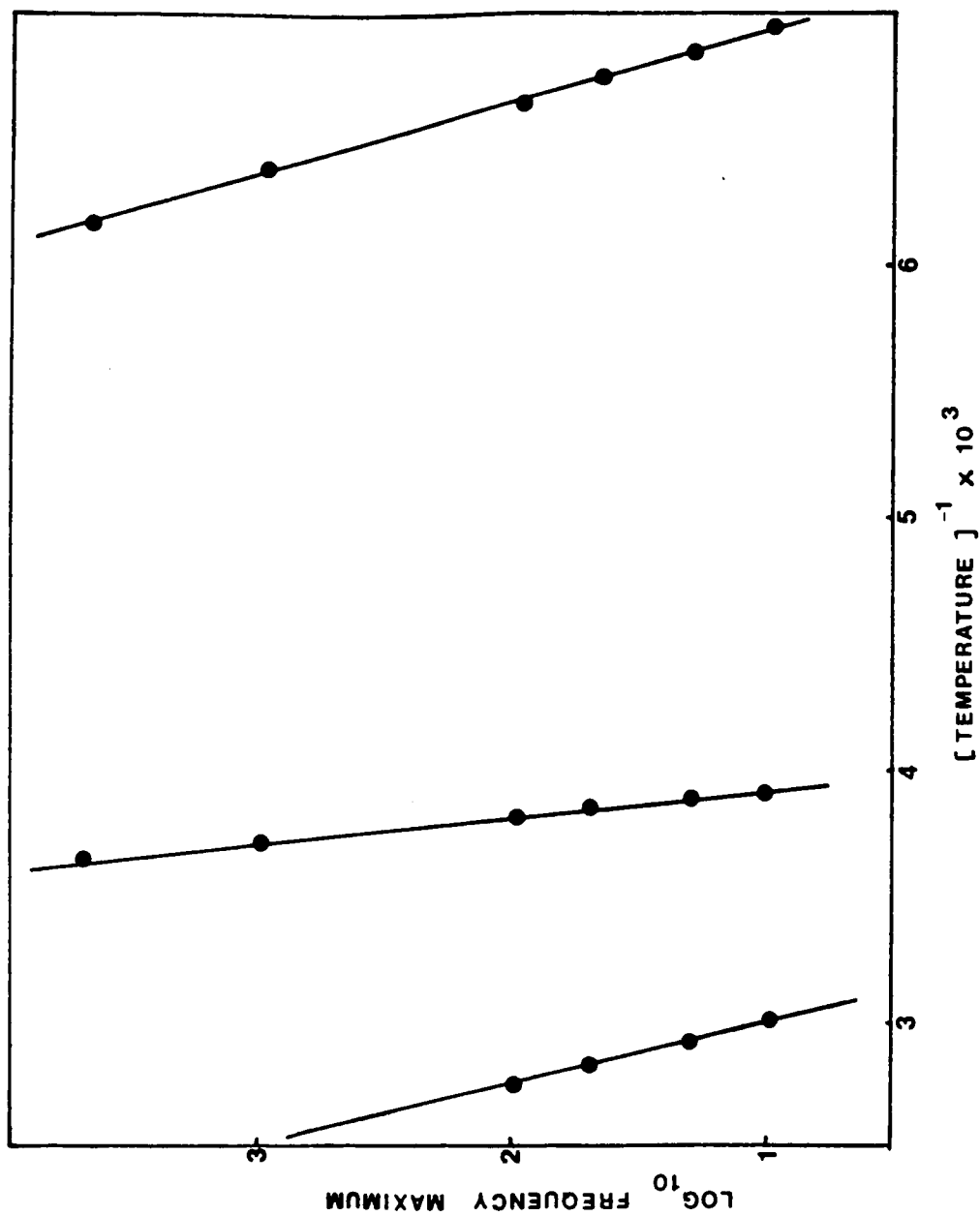


Figure 4.50. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.47.

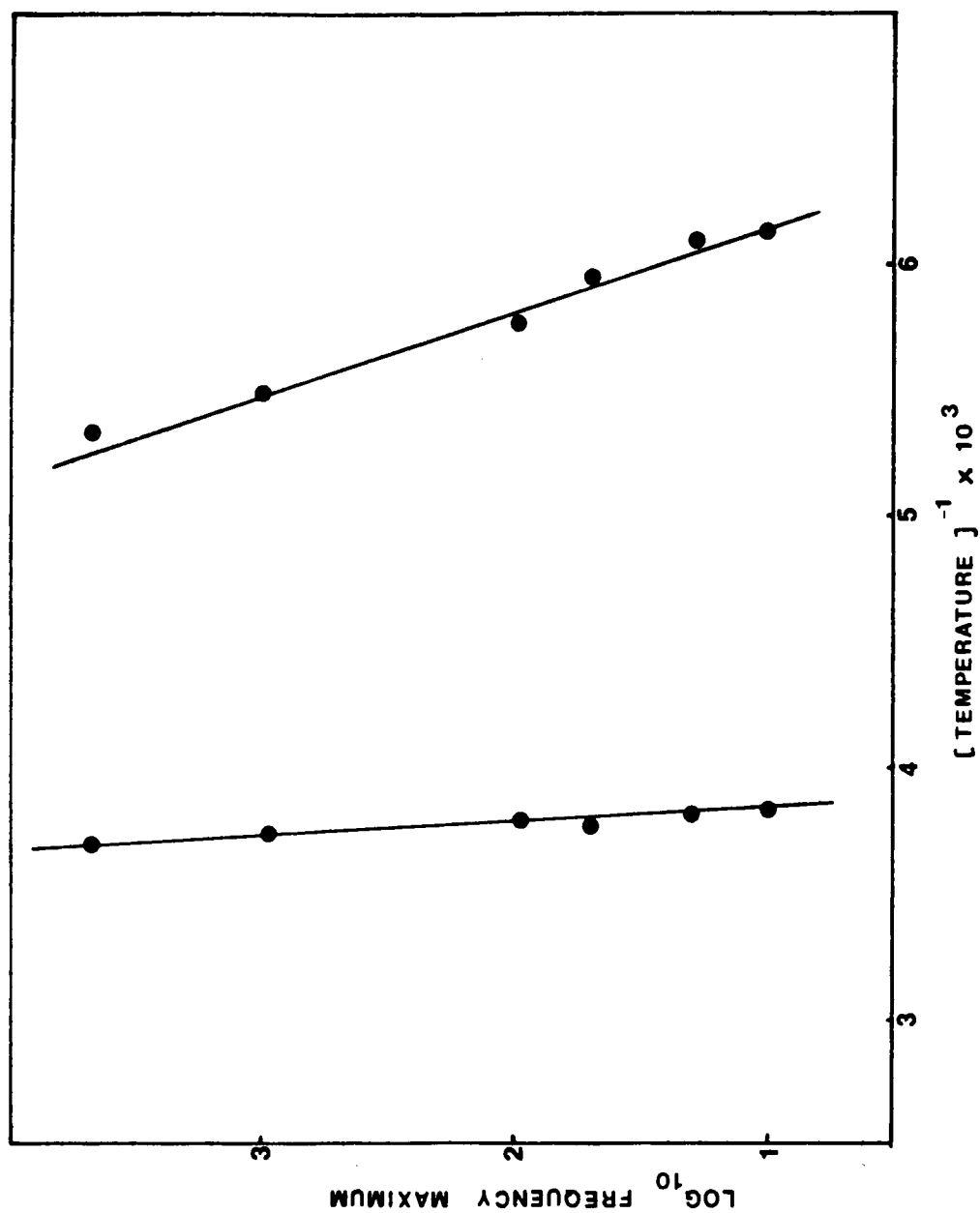


Figure 4.51. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to Acridine in 500% Stretched LLDPE.

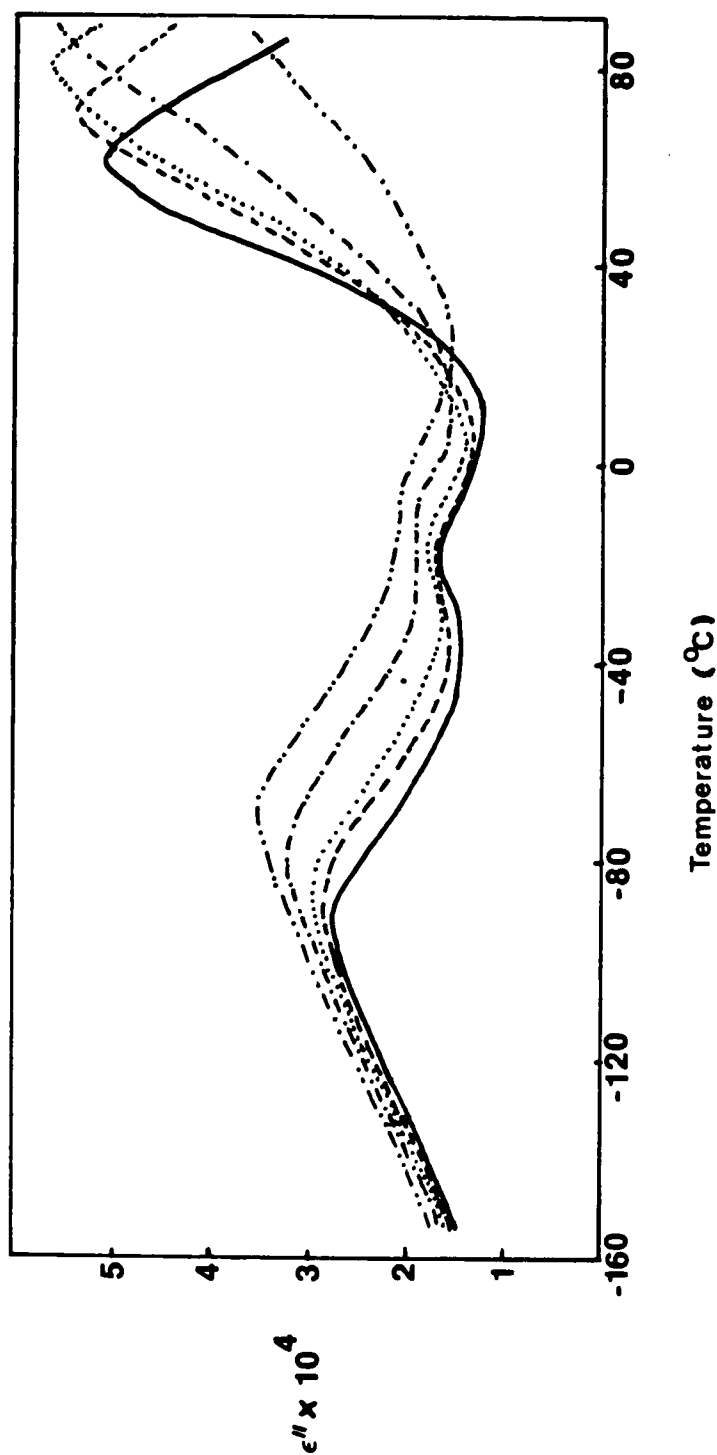


Figure 4.52. Dielectric Loss of a Section of Extruded Rod of LLDPE Having the Electric Field Parallel to the Extrusion Direction Containing 0.179% Acridine. (—) 10 Hz, (---) 20 Hz, (.....) 50 Hz, (-.-.-) 100 Hz, (-.-.-.-) 1 kHz.

extruded rod of LLDPE whereas the α peak does not show any significant change.

Figures 4.53 and 4.54 show a comparison of a section of extruded rod of LLDPE having the electric field parallel to the extrusion direction with and without 0.179% acridine, at 10 Hz and 1 kHz, respectively. The dielectric loss of extruded rod of LLDPE cut in the same direction was subtracted from the one containing acridine molecules to obtain the loss due to acridine molecules. It is also presented in Figures 4.53 and 4.54. The loss peaks of acridine are situated at -90°C (for the γ peak) and -11°C (for the β peak) at 10 Hz whereas they are located at -66°C (for the γ peak) and -5°C (for the β peak) at 1 kHz.

Arrhenius plots of the relaxation processes of the dielectric loss data of Figure 4.52 are shown in Figure 4.55. The activation energy for the β peak (39.1 kcal/mole) is affected very much when compared to a section of extruded rod of LLDPE (60.2 kcal/mole) whereas the α process does not show much change. The activation energy of the γ peak increased from 12.1 kcal/mole to 16.2 kcal/mole with the addition of 0.179% of acridine. Arrhenius plots of relaxation processes due to acridine molecules (in a section of extruded rod having electric field parallel to the extrusion direction) are shown in Figure 4.56. These activation energies are presented in Table 4.4 (page 149).

The dielectric data were also obtained of a section of extruded rod containing 0.186% acridine having the electric field

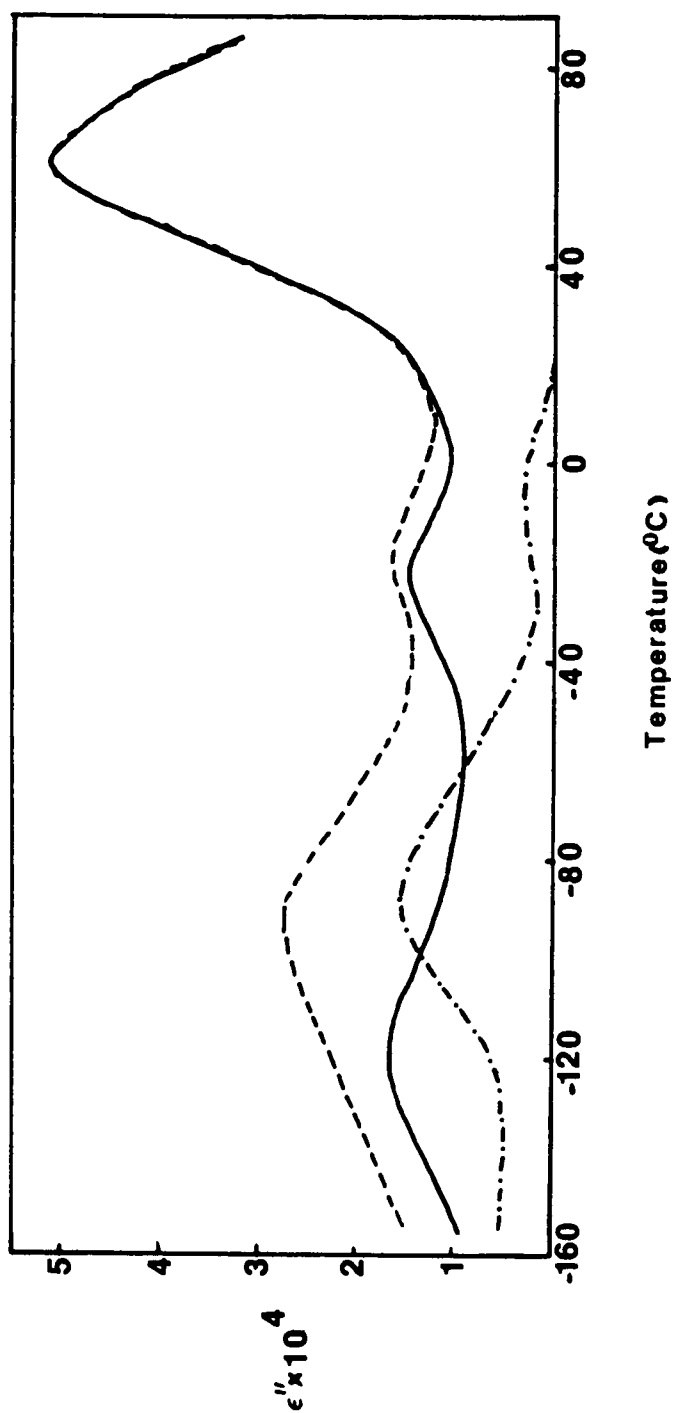


Figure 4.53. Comparison of Dielectric Loss of Extruded Rod of LLDPE Having the Electric Field Parallel to the Extrusion Direction (—), with 0.179% Acridine (---) and Dielectric Loss Due to Acridine (-.-) at 10 Hz.

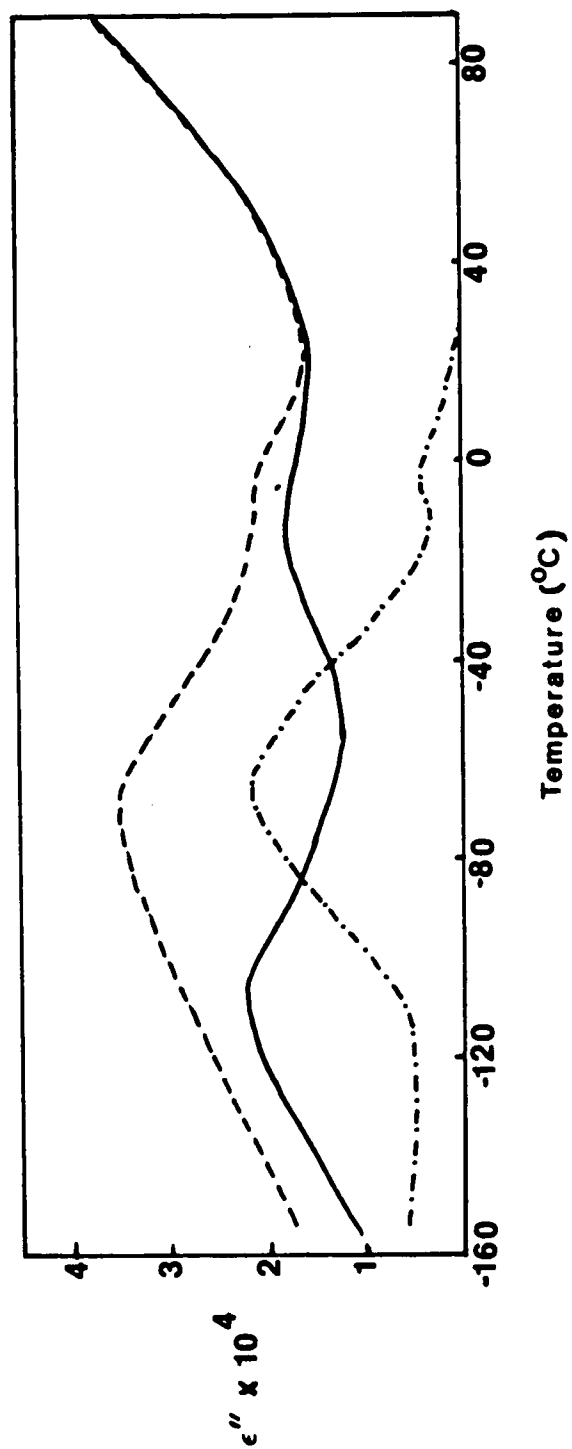


Figure 4.54. Comparison of Dielectric Loss of Extruded Rod of LLDPE Having the Electric Field Parallel to the Extrusion Direction (—), with 0.179% Acridine (---) and Dielectric Loss Due to Acridine (-.-) at 1 kHz.

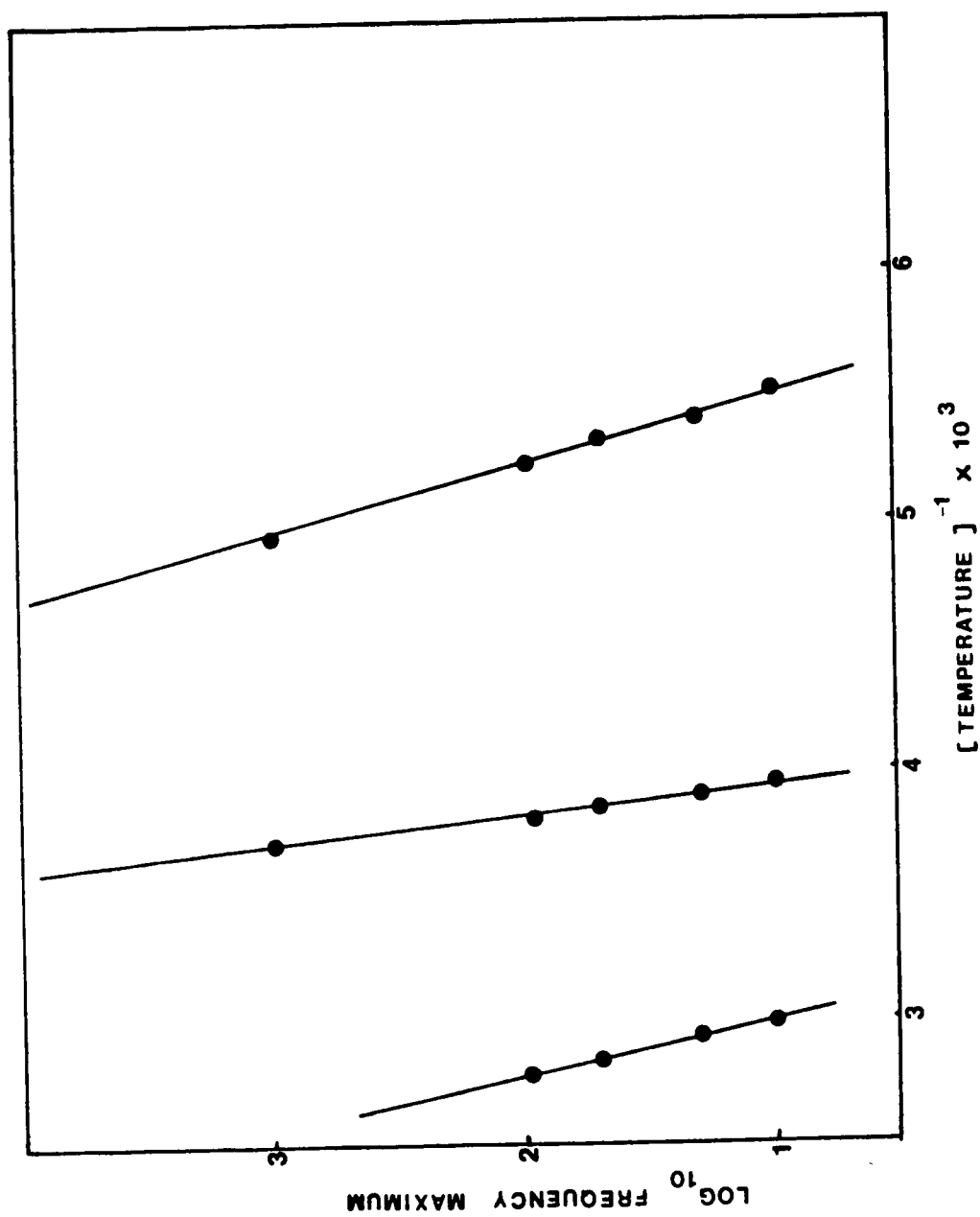


Figure 4.55. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.52.

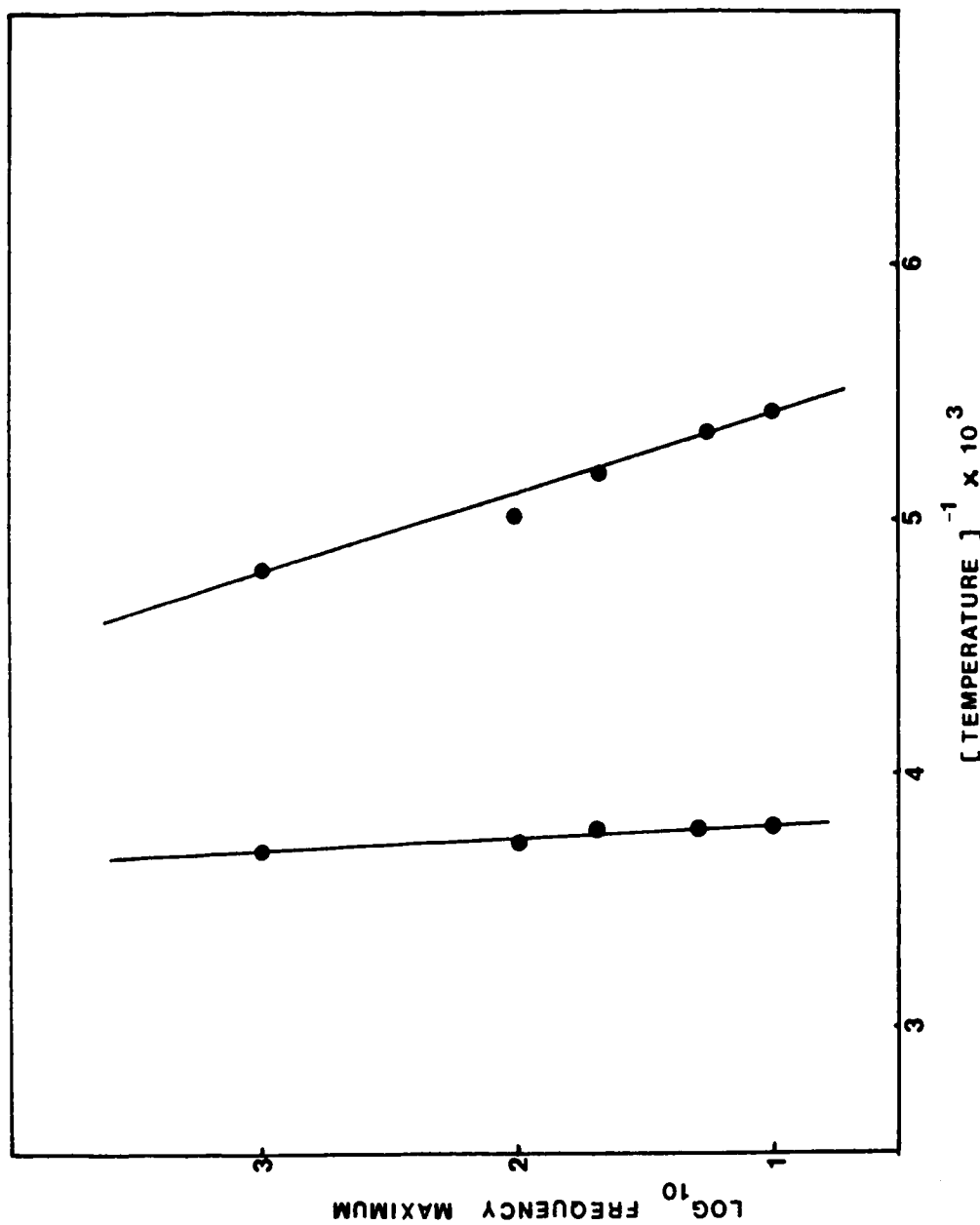


Figure 4.56. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to Acridine in a Section of Extruded Rod Having the Electric Field Parallel to the Extrusion Direction.

perpendicular to the extrusion direction (see Figure 4.57). Peak positions and the magnitudes of the β and γ peaks are affected due to the presence of acridine molecules. For the β peak, a small increase in magnitude is associated with a shift in peak position to higher temperature when compared to a section of extruded rod of LLDPE cut in the same direction. Figures 4.58 and 4.59 give a comparison of the dielectric loss data of a section of extruded rod with and without 0.186% acridine at 10 Hz and 1 kHz, respectively having the electric field perpendicular to the extrusion direction. The loss peaks of acridine are situated at -84°C (for the γ peak) at 10 Hz and at -59°C (for the γ peak) at 1 kHz. The relaxation due to acridine molecules alone (see Figures 4.58 and 4.59) shows a major loss peak.

Activation energies obtained from the Arrhenius plots (see Figure 4.60) show that the slope and the region of the β process of extruded rod (cut in the direction perpendicular to the extrusion direction) containing acridine is significantly different from that of a section of extruded rod of LLDPE. The activation energy of the β peak is reduced to almost half that of LLDPE.

Arrhenius plots were constructed to obtain activation energies of acridine molecules alone (see Figure 4.61) from the data of Figures 4.58, 4.59 and data obtained at other frequencies. Activation energies due to acridine molecules in unoriented, stretched films and extruded rods are presented in Table 4.4 (page 149). A section of extruded rod having the electric field

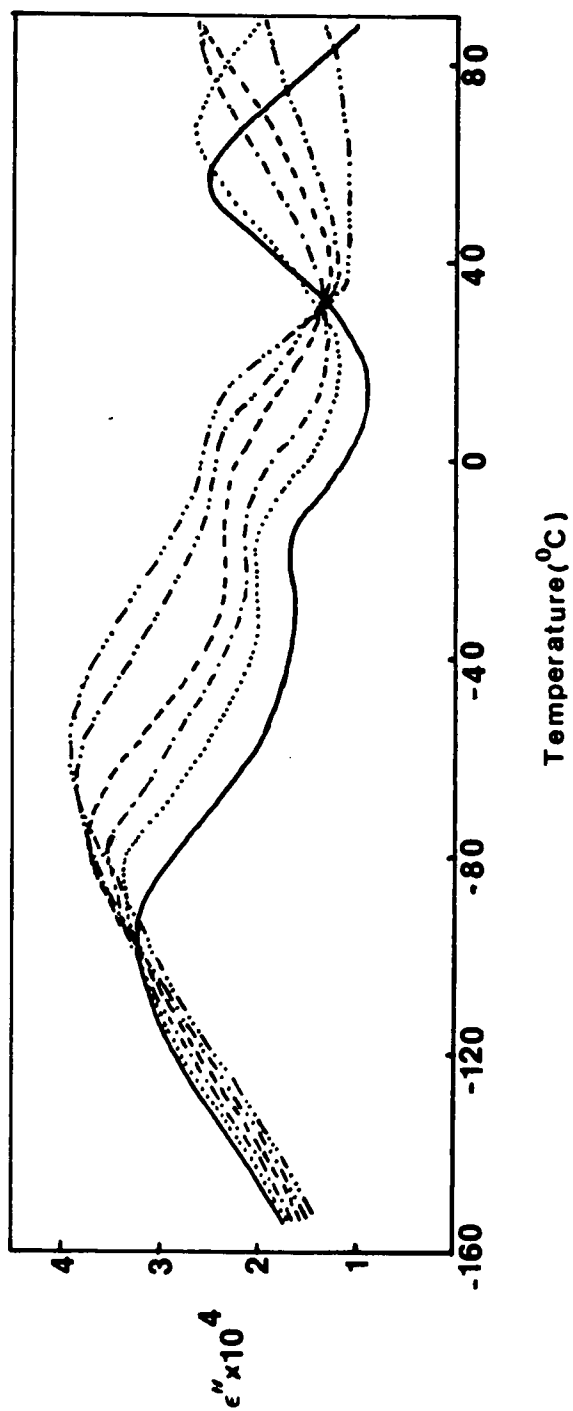


Figure 4.57. Dielectric Loss of a Section of Extruded Rod of LLDPE Having the Electric Field Perpendicular to the Extrusion Direction Containing 0.186% Acridine. (—) 10 Hz, (.....) 20 Hz, (— · —) 50 Hz, (--- · ---) 100 Hz, (---) 1 kHz, (--- · ---) 5 kHz.

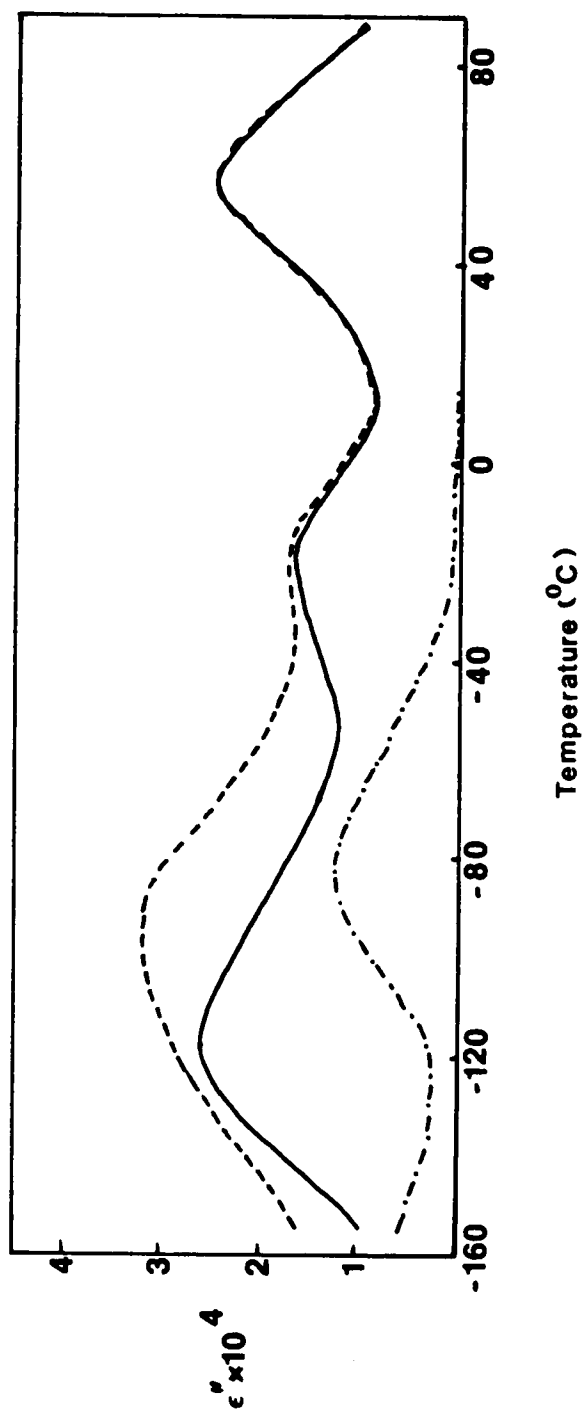


Figure 4.58. Comparison of Dielectric Loss of Extruded Rod of LLDPE Having the Electric Field Perpendicular to the Extrusion Direction (—), with 0.186% Acridine (---) and Dielectric Loss Due to Acridine (-.-) at 10 Hz.

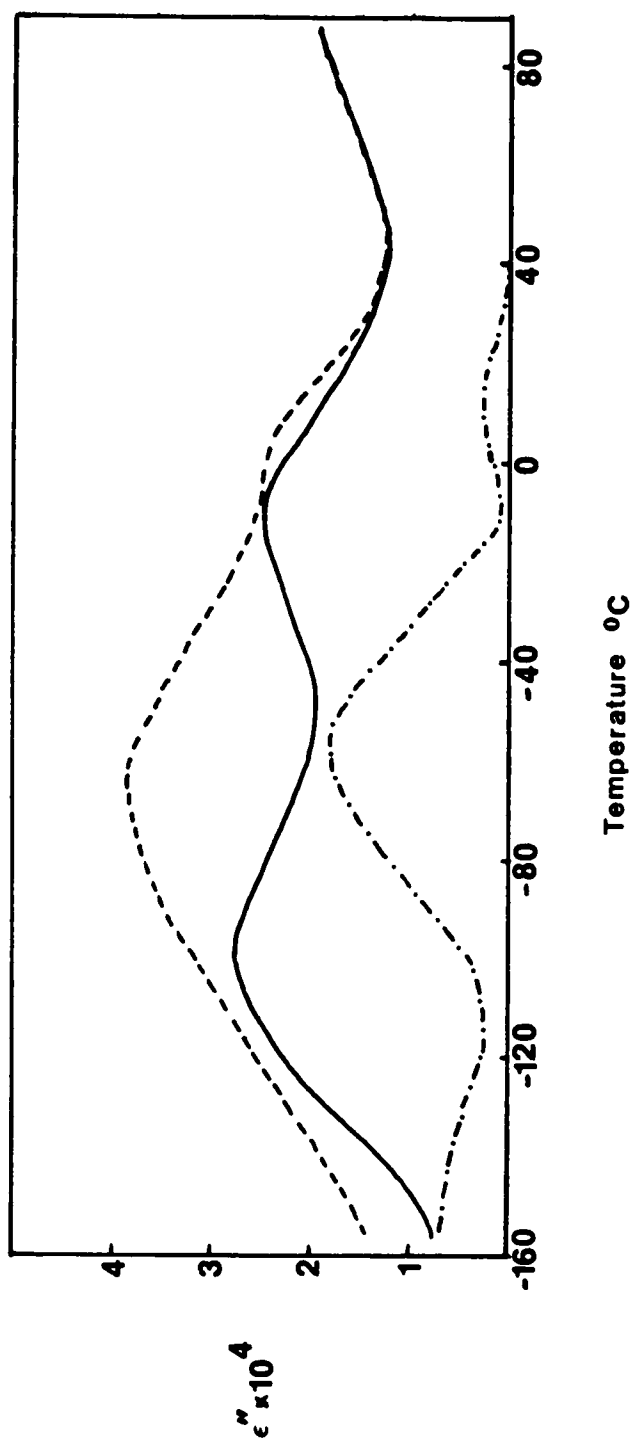


Figure 4.59. Comparison of Dielectric Loss of Extruded Rod of LLDPE Having the Electric Field Perpendicular to the Extrusion Direction (—), with 0.186% Acridine (---) and Dielectric Loss Due to Acridine (-.-.) at 1 kHz.

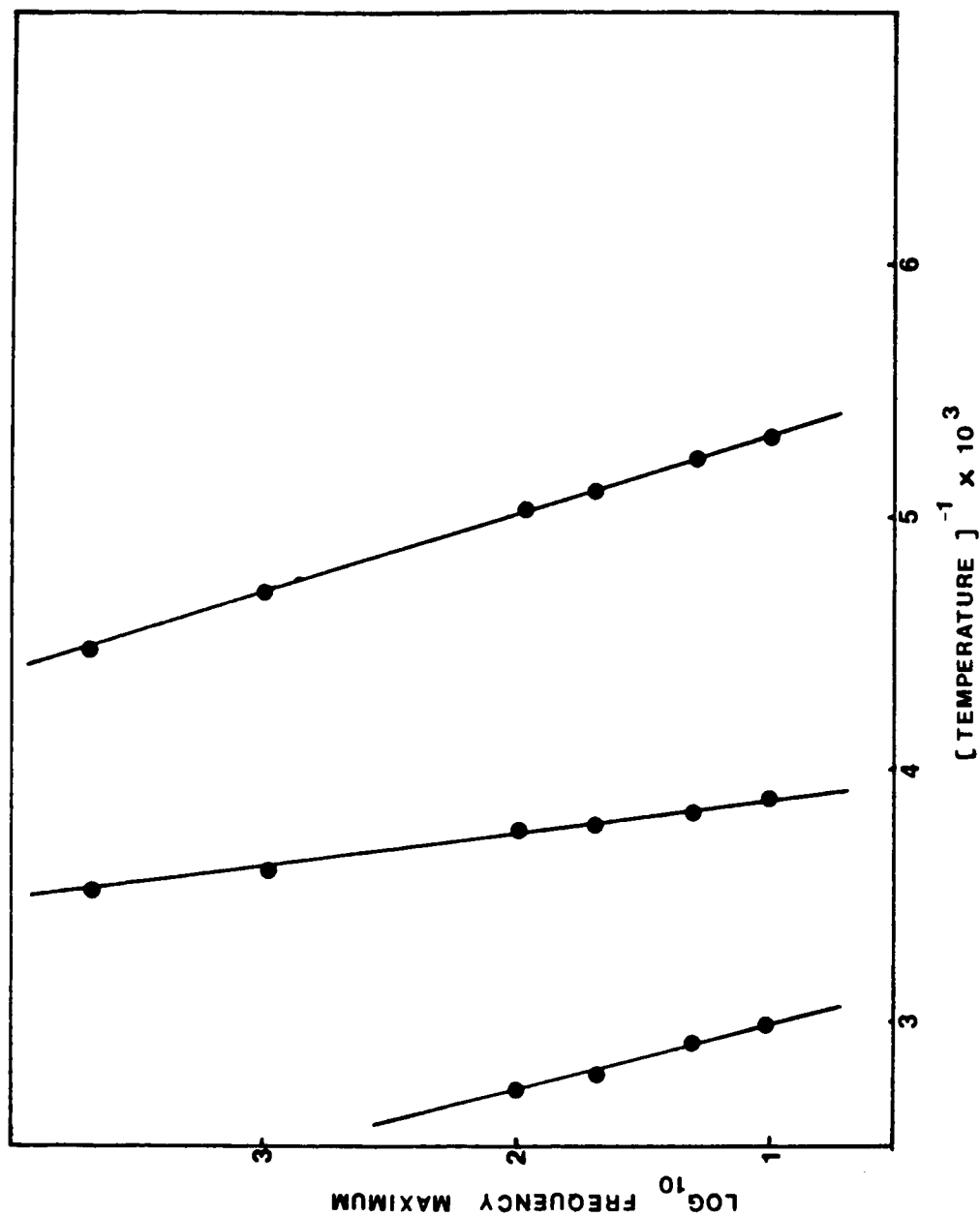


Figure 4.60. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.57.

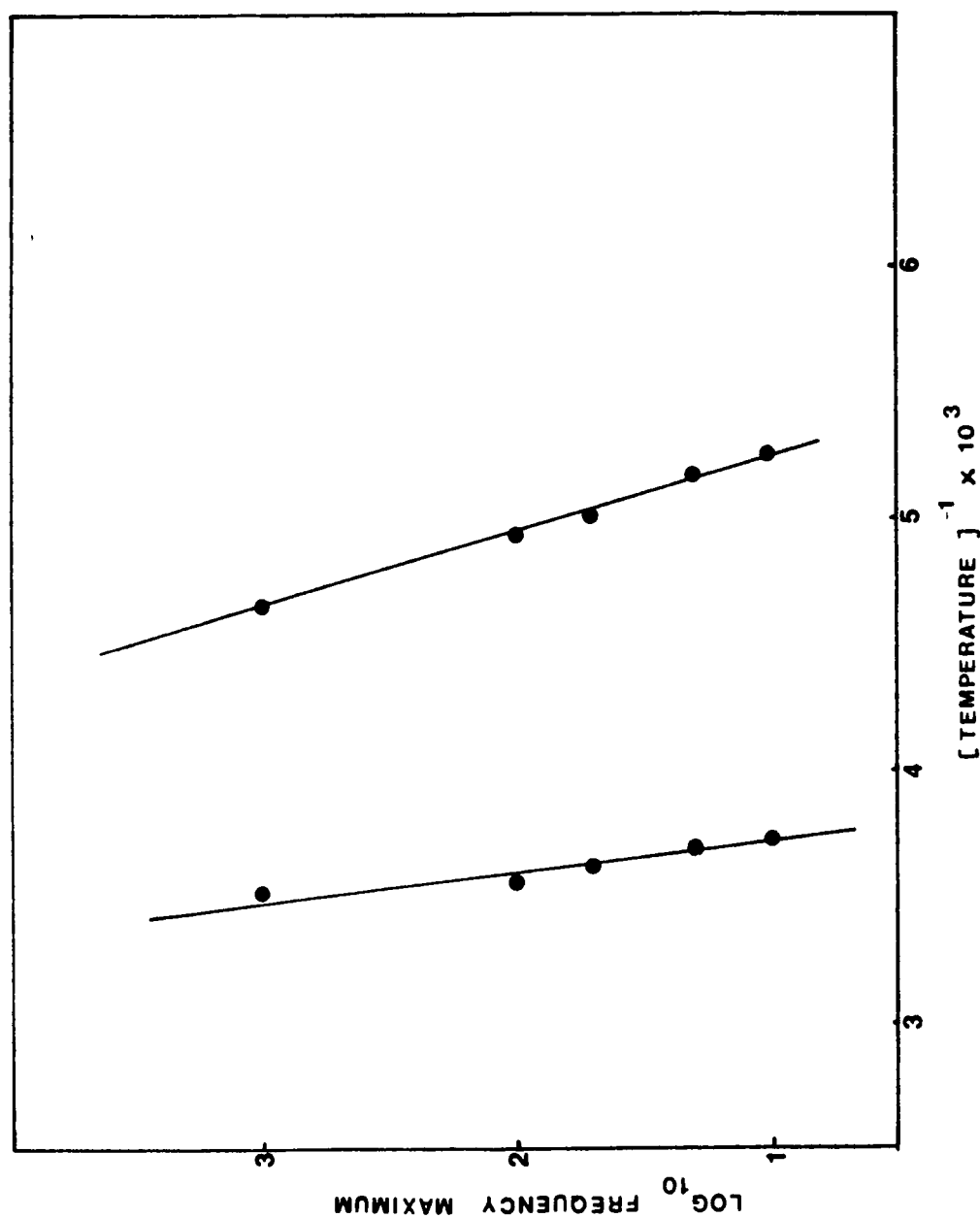


Figure 4.61. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to Acridine in a Section of Extruded Rod Having the Electric Field Perpendicular to the Extrusion Direction.

parallel to the extrusion direction shows the largest activation energy for the β process (92.9 kcal/mole) which is double that of the activation energy in the perpendicular direction.

The number of molecules participating in the relaxation processes for the specimens cut in both the directions calculated using equation (4.6) (page 147) is presented in Table 4.5, page 151. Relaxation magnitudes ($\Delta\epsilon'$) for all relaxation processes were obtained from Williams' plots and are also presented in Tables 4.6 (page 153).

Figure 4.62 shows the dielectric loss of a section of extruded rod containing 0.198 % 9-bromoanthracene having the electric field parallel to the extrusion direction at various frequencies. The magnitudes of the β and γ loss process are increased relative to a section of extruded rod cut in the same direction. The β peak shows an increase in magnitude but it is much more prominent for the γ peak. The peak position of the γ process is affected significantly in the presence of 9-bromoanthracene molecules. The γ peak is shifted by almost 35°C (at 10 Hz) compared to extruded rod of LLDPE whereas the α and β peak positions do not show any significant changes.

Figure 4.63 shows a comparison of a section of extruded rod of LLDPE having electric field parallel to the extrusion direction with and without 0.198% 9-bromoanthracene at 10 Hz. The dielectric loss of extruded rod of LLDPE cut in the same direction was subtracted from the one containing 9-bromoanthracene molecules to obtain the

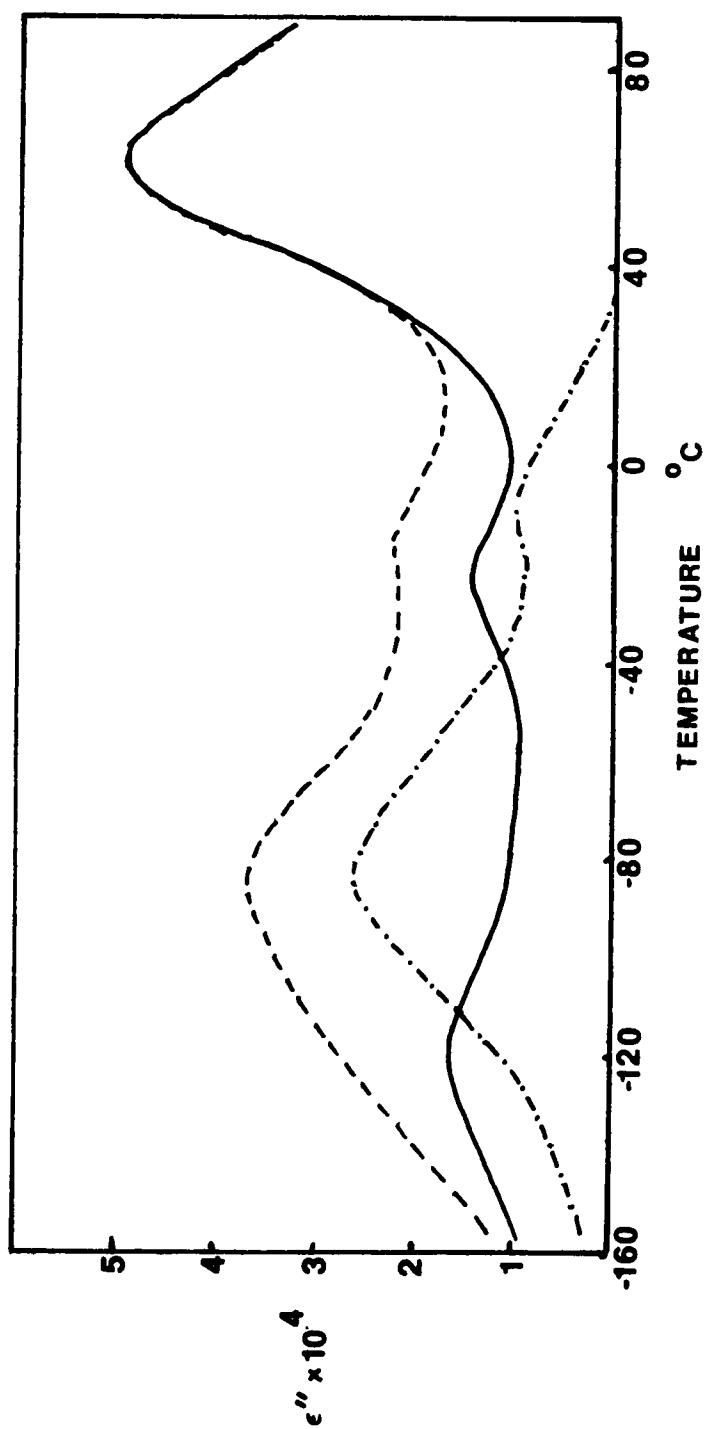


Figure 4.63. Comparison of Dielectric Loss of Extruded Rod of LLDPE Having the Electric Field Parallel to the Extrusion Direction (—), with 0.198% 9-Bromoanthracene (---) and Dielectric Loss Due to 9-Bromoanthracene (-.-) at 10 Hz.

loss due to 9-bromoanthracene and it is also presented in Figure 4.63. The loss peaks of 9-bromoanthracene are situated at -84°C (for the γ peak) and -10°C (for the β peak) at 10 Hz.

Arrhenius plots of the relaxation processes of the dielectric loss data of Figure 4.62 are shown in Figure 4.64. The activation energy of the γ loss (29.2 kcal/mole) is increased significantly when compared to that of a section of extruded rod of LLDPE (12.1 kcal/mole) whereas the β and γ loss processes do not show significant changes. Arrhenius plots of the relaxation processes due to 9-bromoanthracene molecules (in a section of extruded rod having electric field parallel to the extrusion direction) are shown in Figure 4.65. These activation energies are presented in Table 4.8, page 160. Relaxation magnitudes ($\Delta\epsilon'$) for all the relaxation processes were obtained from the Williams' plots and are also presented in Table 4.9, page 161.

The dielectric data were also obtained for a section of extruded rod containing 0.194 wt % 9-bromoanthracene having the electric field perpendicular to the extrusion direction (see Figure 4.66). Peak position of the γ peak is affected by the presence of 9-bromoanthracene molecules. The magnitudes of the γ and β peaks are increased by the presence of 9-bromoanthracene molecules. For the γ peak, an increase in magnitude is associated with a shift in the peak position to higher temperature (to -90°C) when compared to a section of extruded rod of LLDPE cut in the same direction. Figure 4.67 gives a comparison of the dielectric loss data of a

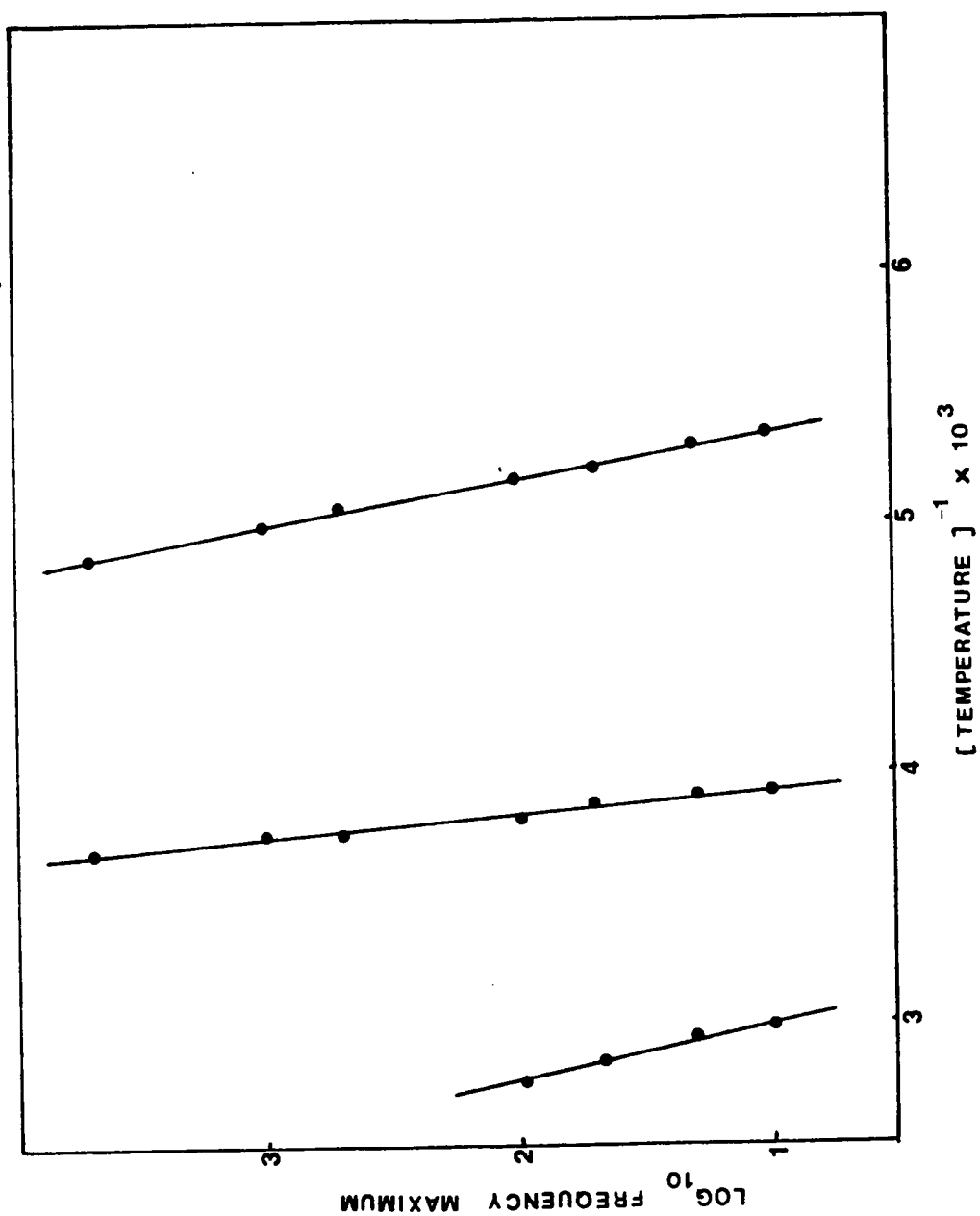


Figure 4.64. Plot of $\log f_{\text{max}}$ vs. $1/T$ using the Data in Figure 4.62.

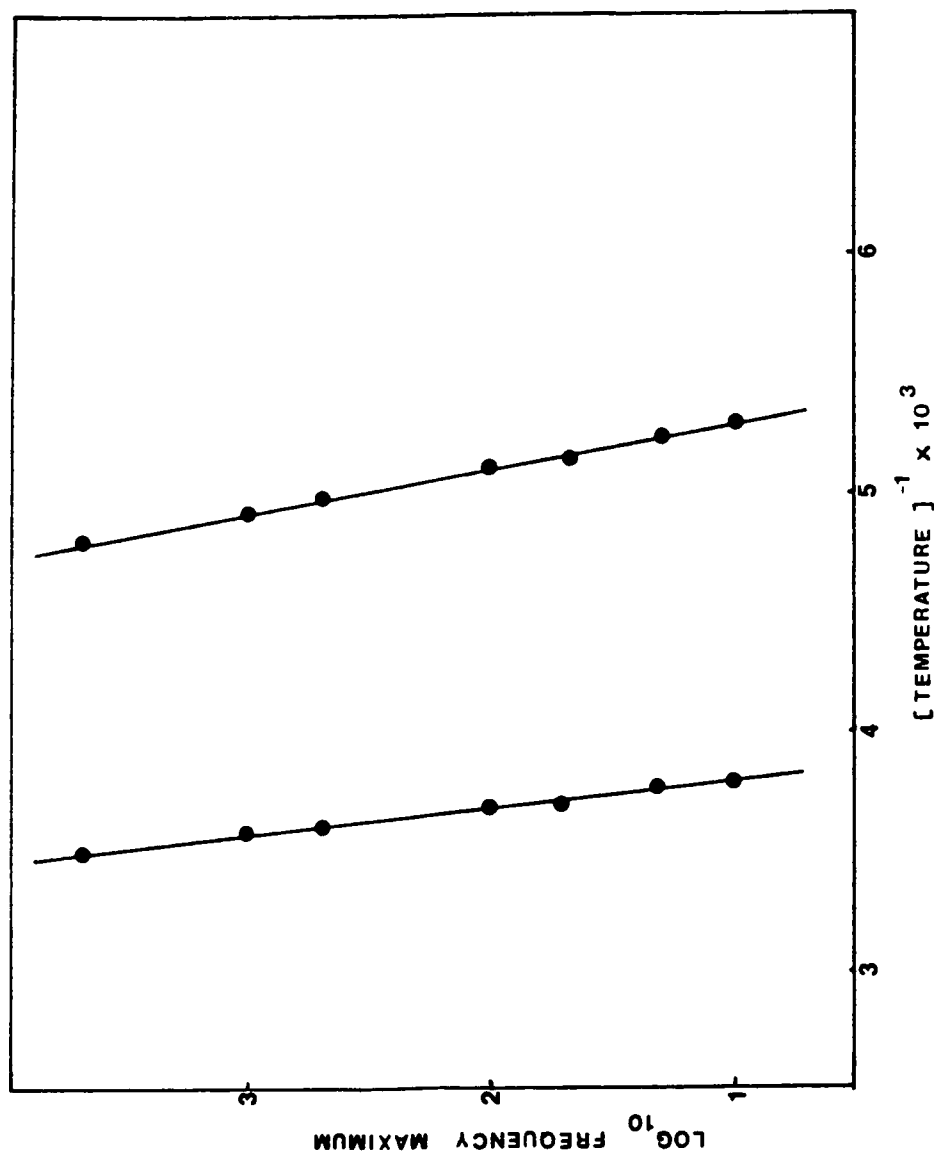


Figure 4.65. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to 9-Bromoanthracene in a Section of Extruded Rod Having the Electric Field Parallel to the Extrusion Direction.

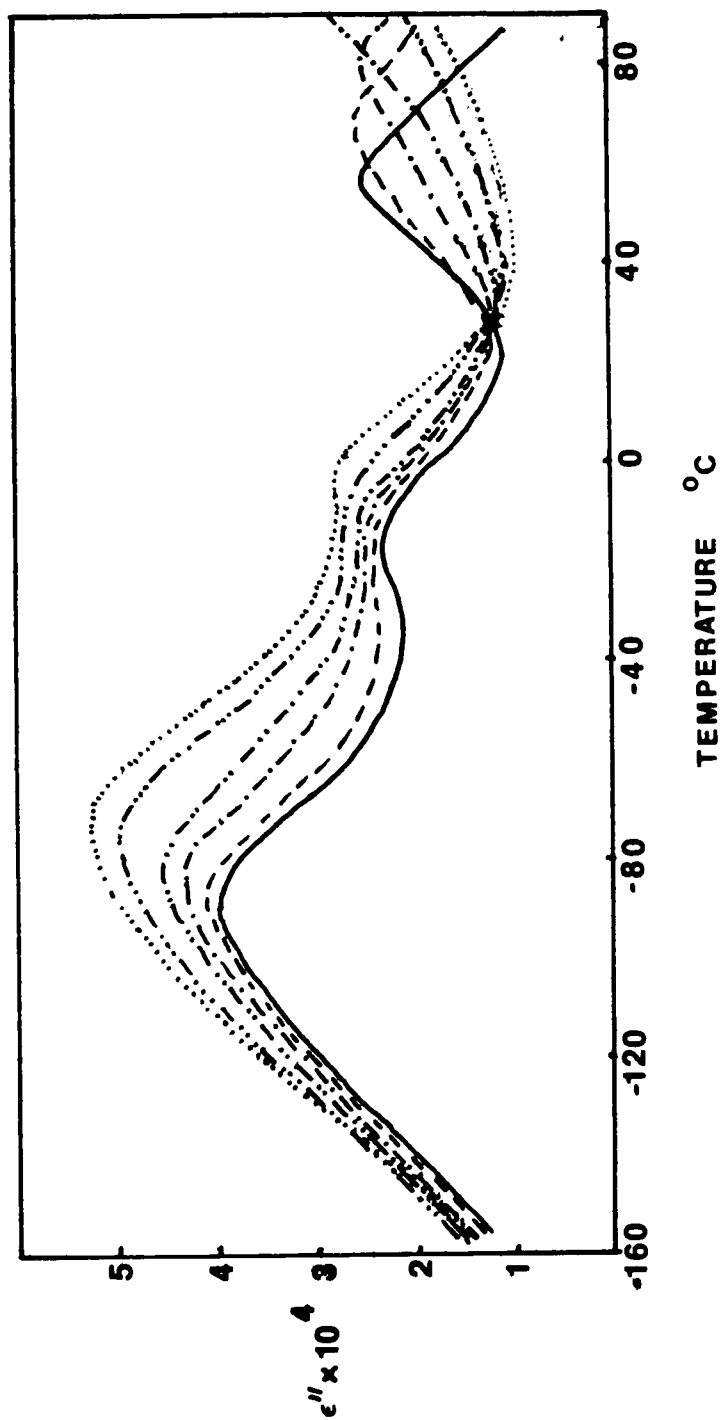


Figure 4.66. Dielectric Loss of a Section of Extruded Rod of LLDPE Having the Electric Field Perpendicular to the Extrusion Direction Containing 0.194% 9-Bromoanthracene. (—) 10 Hz, (---) 20 Hz (— · —) 50 Hz, (.....) 100 Hz, (— · — · —) 1 kHz.

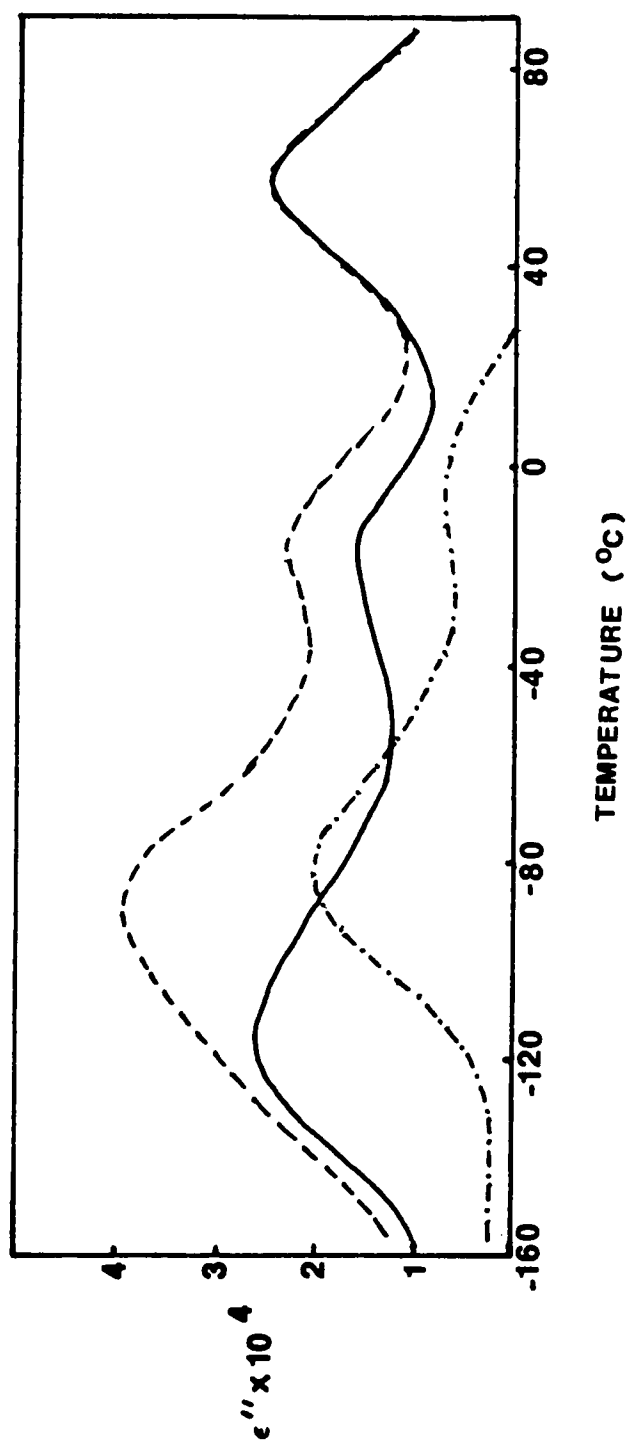


Figure 4.67. Comparison of Dielectric Loss of Extruded Rod of LLDPE Having the Electric Field Perpendicular to the Extrusion Direction (—), with 0.194% 9-Bromoanthracene (---) and Dielectric Loss Due to 9-Bromoanthracene (-.-.) at 10 Hz.

section of extruded rod with and without 0.194% 9-bromoanthracene having the electric field perpendicular to the extrusion direction. The dielectric loss of 9-bromoanthracene was also obtained by subtracting the loss due to LLDPE extruded rod from that of LLDPE extruded rod containing 9-bromoanthracene. The loss peaks of 9-bromoanthracene are situated at -80°C (for the γ peak) and -9°C (for the β peak) at 10 Hz.

Activation energies obtained from Arrhenius plots (see Figure 4.68) show the slope and the region of the γ process of extruded rod containing 9-bromoanthracene having the electric field perpendicular to the extrusion rod is significantly different from that of a section of extruded rod of LLDPE. The activation energy of the γ peak is almost doubled compared to LLDPE whereas the activation energies of the α and β processes are unaffected. Activation energies are presented in Table 4.7, page 157 and relaxation magnitudes ($\Delta\epsilon'$) obtained from Williams' plots are presented in Table 4.9, page 161.

Arrhenius plots were constructed to obtain the activation energies of 9-bromoanthracene molecules alone (see Figure 4.69) from the data of Figure 4.67 and similarly at other frequencies. Activation energies due to 9-bromoanthracene molecules in unoriented, and extruded rods are presented in Table 4.8, page 160.

The number of molecules participating in the relaxation processes for the specimens cut in both the directions calculated using equation (4.6) are presented in Table 4.10.

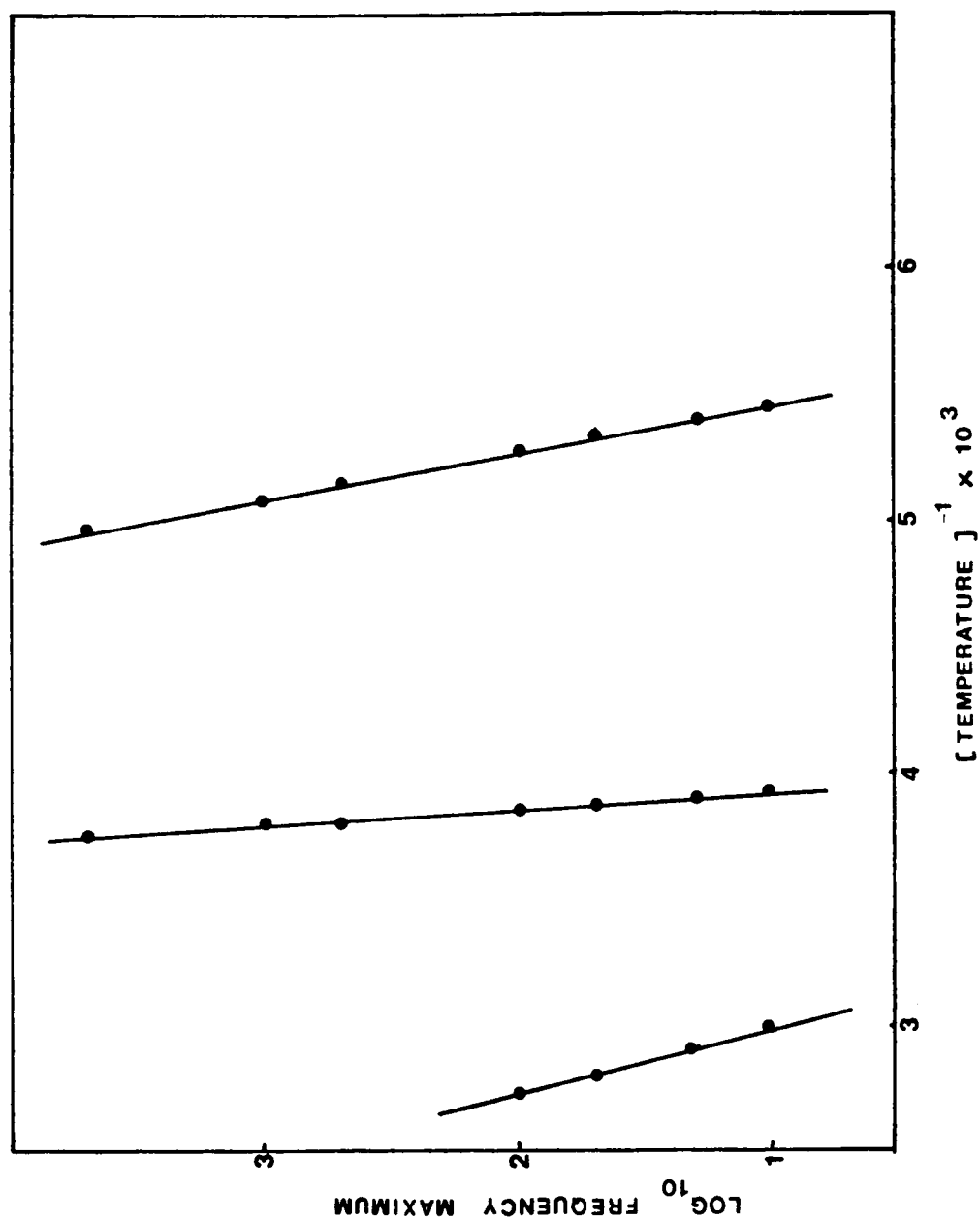


Figure 4.68. Plot of $\log f_{\max}$ vs. $1/T$ using the Data in Figure 4.66.

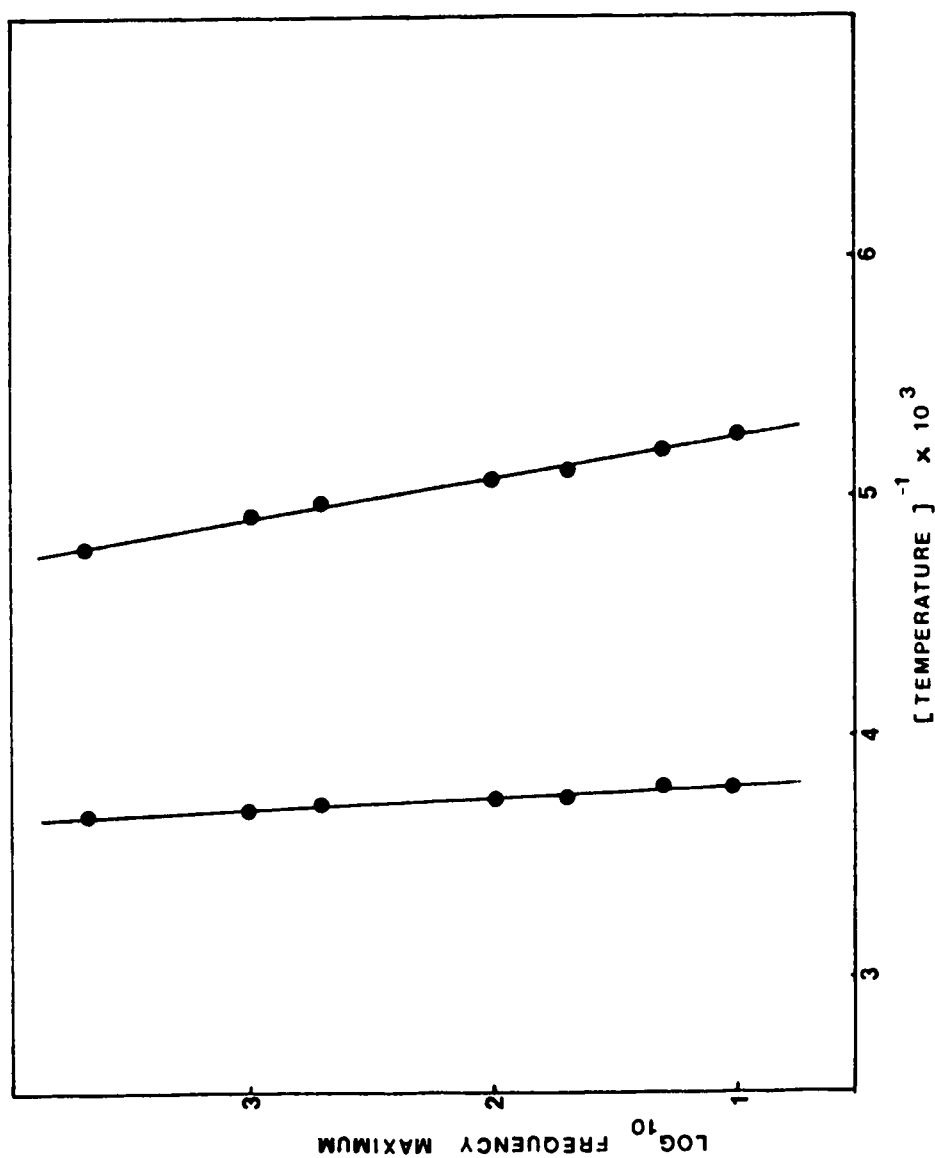


Figure 4.69. Plot of $\log f_{\max}$ vs. $1/T$ using the Dielectric Loss Due to 9-Bromoanthracene in a Section of Extruded Rod Having the Electric Field Perpendicular to the Extrusion Direction.

Table 4.10. Number of 9-Bromoanthracene Molecules Participating in Relaxation Processes.

	Unstretched	Extruded Rod	
		" to Extrusion Direction	⊥ to Extrusion Direction
Concentration (%)	0.196	0.198	0.194
Number of molecules ($\times 10^{18}$)	4.675	4.723	4.627
Number of molecules ($\times 10^{18}$)	2.244	2.031	2.082
% of molecules detected	48	43	45

4.6 Epitaxial Crystallization

4.6.1 PE Grown on a Single Crystal of Acridine

Single crystals of acridine are obtained as flat platelets with top and bottom (001) faces, the lateral growth faces being 110 planes. X-ray diffraction patterns of such single crystals are characterized by rows of sharp spots (see Figure 4.70).

After melting and recrystallization of polyethylene in contact with the (001) acridine surface, the X-ray diffraction pattern clearly shows a double orientation of polyethylene lamellae (see Figure 4.71). In the X-ray diffraction pattern (Figure 4.71) most of the slightly arced reflections due to PE overgrowth can be indexed as h00. The polyethylene reflections in Figure 4.72 correspond to a superposition of two diffraction patterns rotated by an angle of ca. 56° . This angle of 56° corresponds to the angle made by the [110] and $[\bar{1}\bar{1}0]$ directions in the ab plane of acridine, i.e., in the contact plane with PE. The PE molecules are therefore oriented parallel to the [110] and $[\bar{1}\bar{1}0]$ directions of acridine. The polyethylene chain axis lies parallel to the acridine surface and the contact plane of the polyethylene with the substrate is (100).

The epitaxial relationship between polyethylene and acridine structure can be analyzed in greater detail with the help of lattice matching. The matching is achieved between the polyethylene interchain distance (b-axis repeat distance $4.94 \text{ \AA}$) and the acridine [110] inter-row distance of $5.298 \text{ \AA}$. The matching of the two

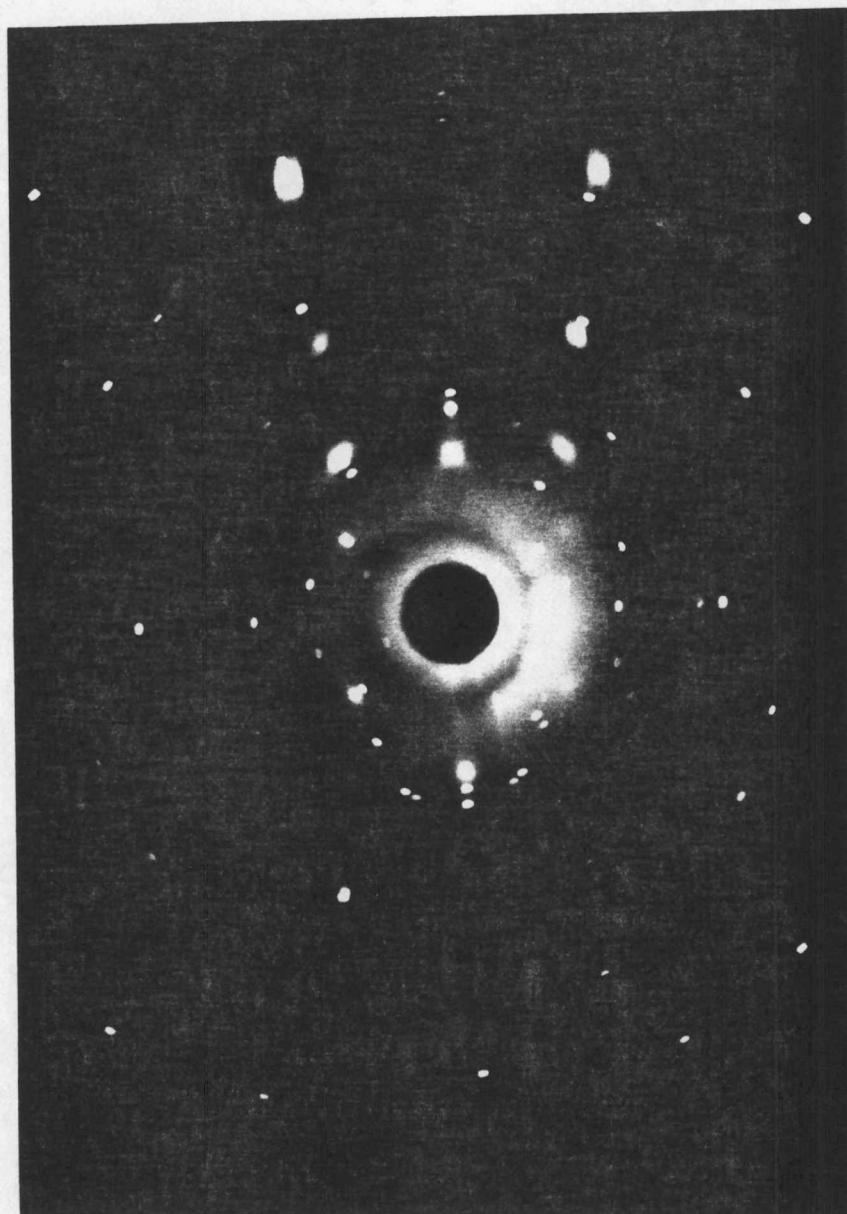


Figure 4.70. X-ray Diffraction Pattern of an Acridine Single Crystal.

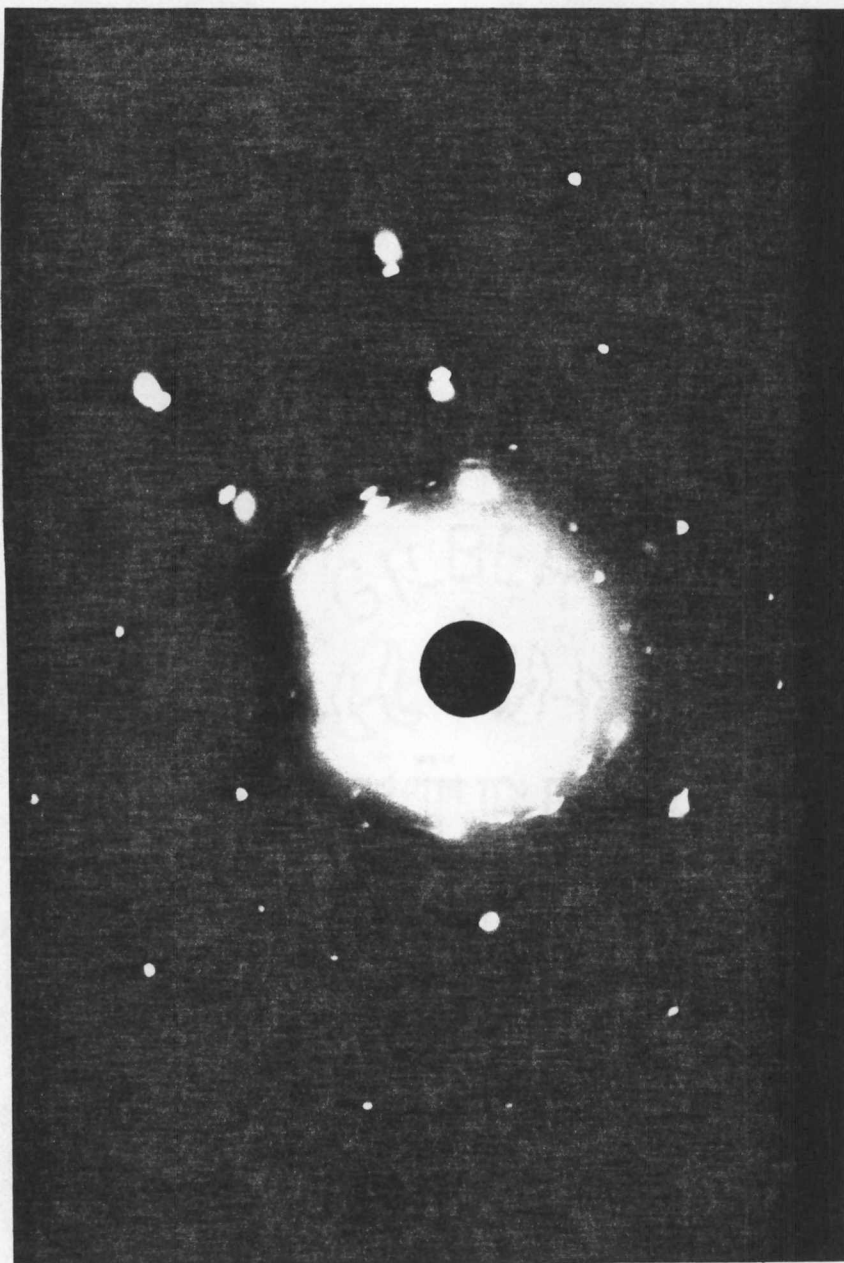


Figure 4.71. Wide-angle X-ray Pattern of Epitaxially Grown PE on the Single Crystal of Acridine.

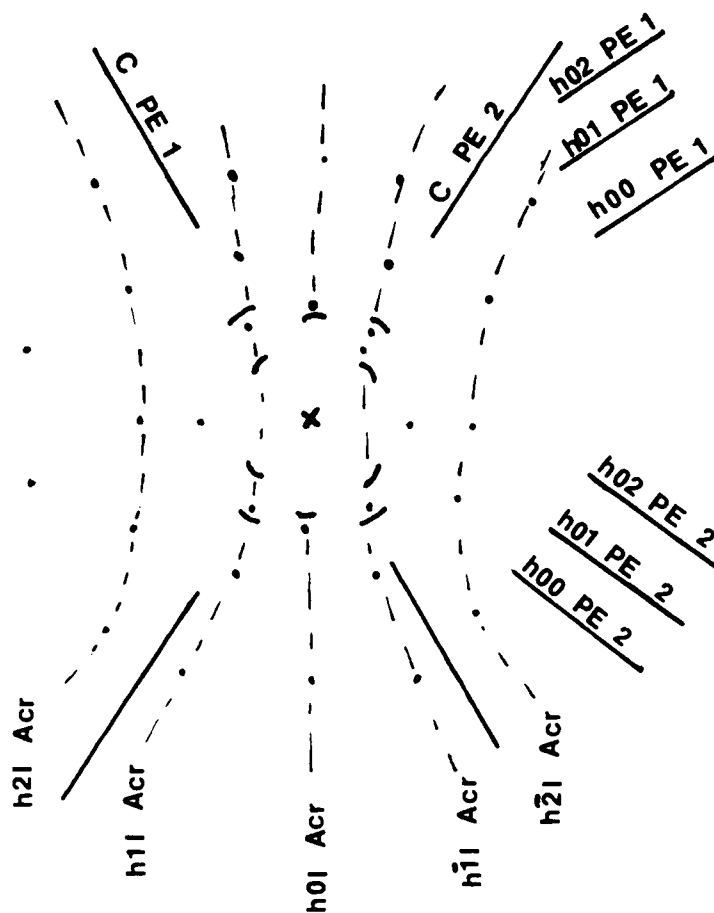


Figure 4.72. Sketch of the Pattern in Figure 4.71 with Indexing of the Reflections.

periodicities is usually measured by $\Delta = 100(d_p - d_s)/d_s$, expressed as a percentage, where d_p and d_s are the matching distances of the polymer and substrate, respectively. In the present case, the mismatch is -6.7%, i.e., well within the accepted range of lattice mismatches for epitaxy ($\Delta < \pm 15\%$).

The thin film of PE, which was melted and recrystallized on the single crystal of acridine, was recovered by detaching the film from the sides of the single crystal of acridine under vacuum. In the present case, it was possible to obtain the X-ray diffraction patterns of the recovered films from the sides and top of the single crystal. Figures 4.73 and 4.74 are the X-ray diffraction patterns of the polyethylene film recovered from the sides of the single crystal and top of the single crystal, respectively. These figures also show the indexing of the arced reflections of polyethylene.

This epitaxial relationship between acridine and substrate PE can be analyzed in detail with the help of lattice matching. The (110) plane of acridine is in contact with the (110) plane of polyethylene in such a way that the polyethylene chain axis lies parallel to the long axis of the acridine molecules. The C-axis of acridine is equal to $13.69 \text{ \AA}$ which is very nearly five times the polyethylene chain axis repeat distance of $2.54 \text{ \AA}$ provides the lattice matching required for the epitaxial crystallization. In this case, the lattice mismatch for epitaxy was found to be -7.23%.

Probably, a second quasiperfect lattice matching is achieved between the polymer interchain distance along [110] direction of $4.45 \text{ \AA}$

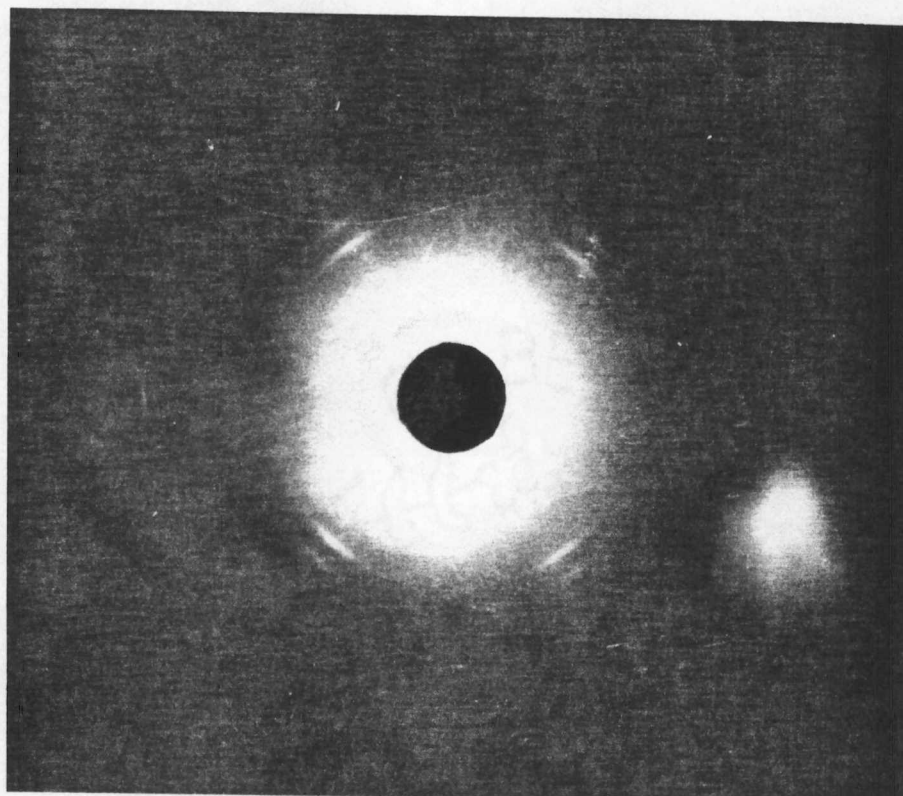


Figure 4.73. X-ray Diffraction Pattern with Indexing of Reflections of Polyethylene Film Recovered from the Sides of a Single Crystal of Acridine.

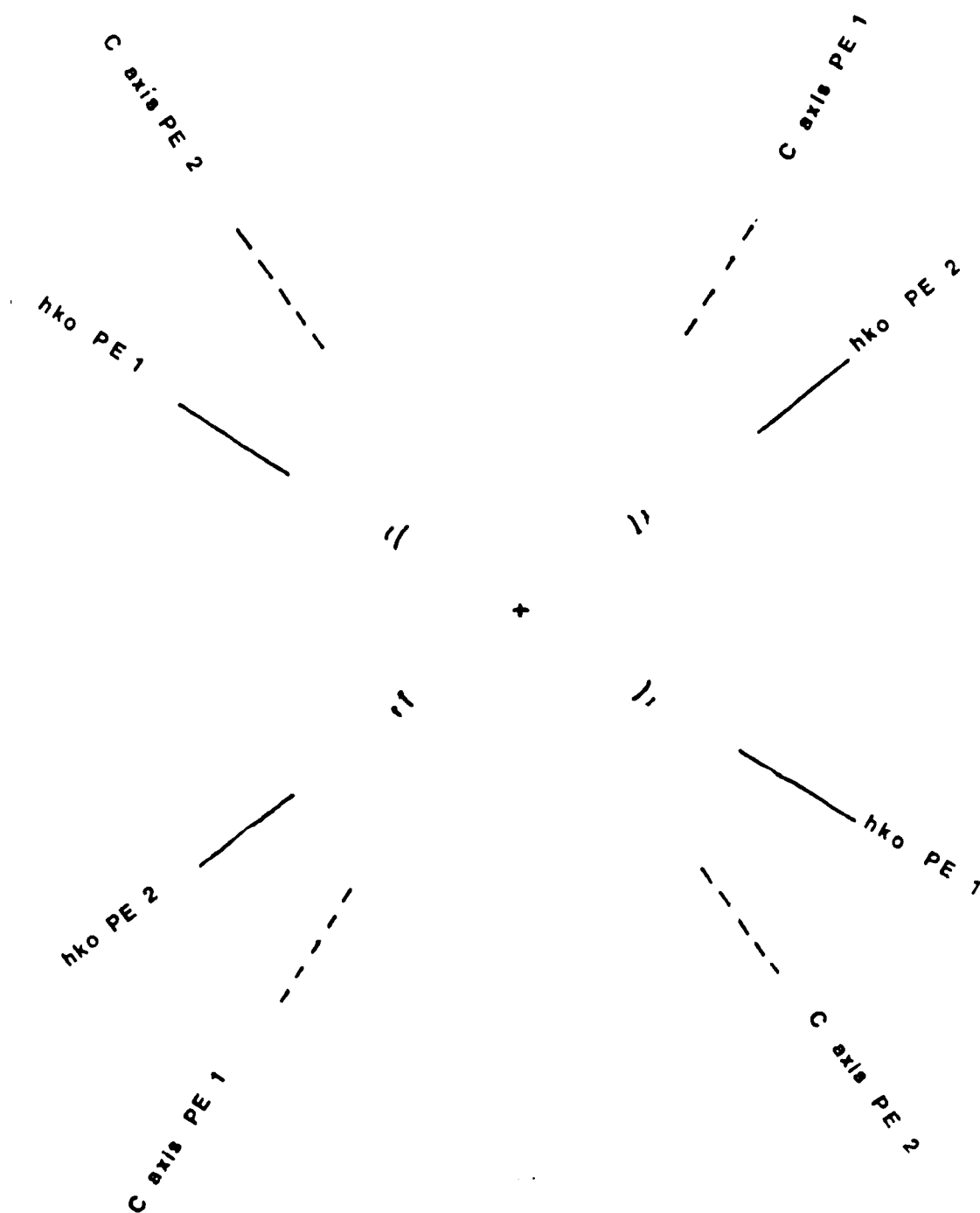


Figure 4.73. (Continued)

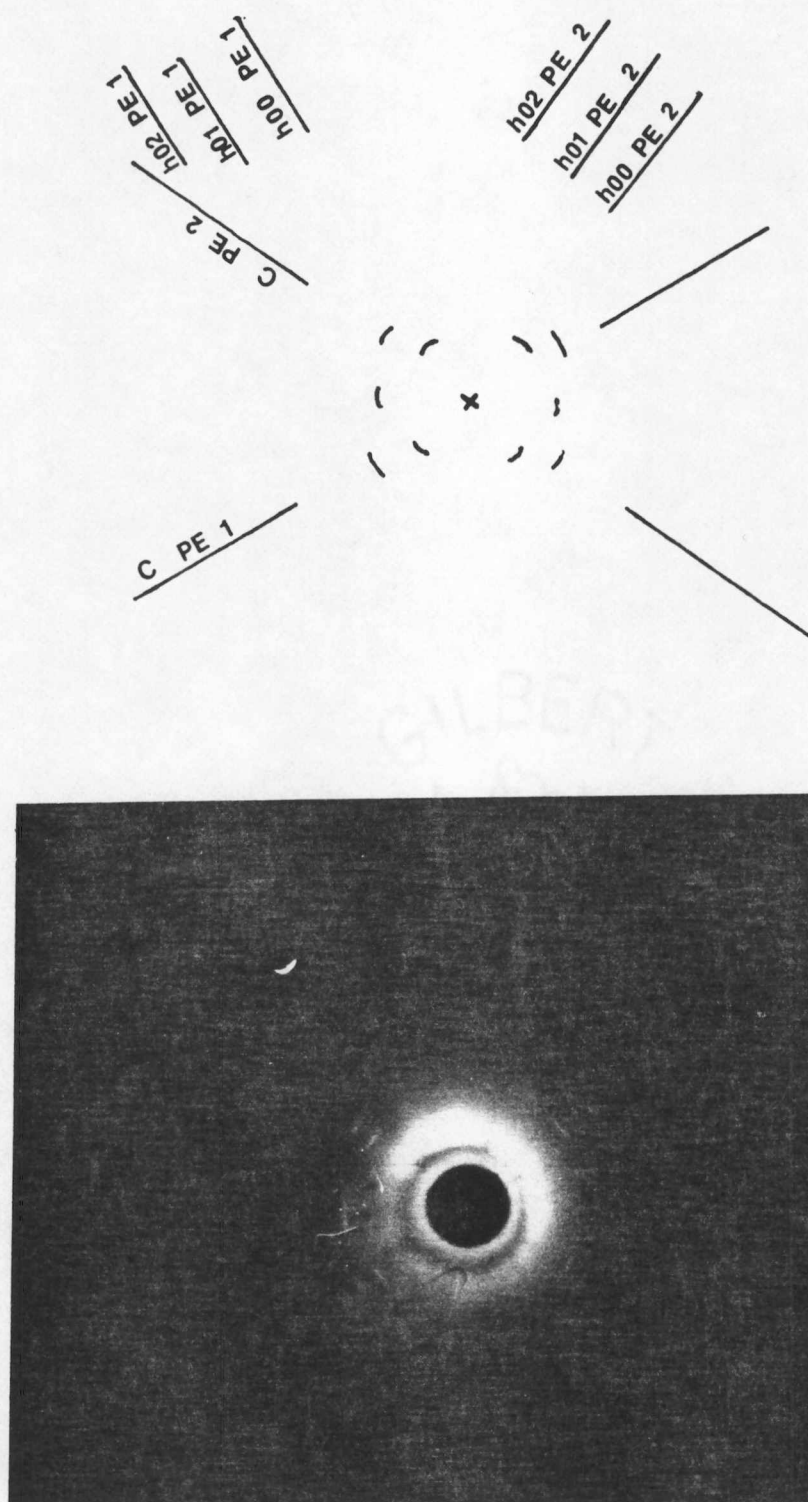


Figure 4.74. X-ray Diffraction Pattern with Indexing of Reflections of Polyethylene Film Recovered from the Top of a Single Crystal of Acridine.

and the acridine [120] inter-row distance of $4.29 \text{ \AA}$ providing lattice matching with a misfit of 3.4%.

4.6.2 Acridine Grown on PE

After ensuring that removal of the original acridine, acridine was vapor deposited on these thin films. X-ray diffraction pattern of acridine crystals grown epitaxially on the thin film of polyethylene recovered from the sides of an acridine single crystal is shown in Figures 4.75 and 4.76. In this X-ray diffraction pattern all the slightly arced reflections are due to PE and can be indexed as (hk0) reflections and the spots result from oriented overgrowth of acridine. The PE reflections in Figure 4.76 correspond to a superposition of two diffraction patterns rotated by an angle of 56° . This angle of 56° corresponds to the angle made by the (110) and ($1\bar{1}0$) planes of acridine. Thin films of PE recovered from the lateral surfaces, i.e., (110) and ($1\bar{1}0$) planes of acridine single crystal (which are along $[1\bar{1}0]$ and $[110]$ directions, respectively) makes the angle of 56° . These (110) and ($1\bar{1}0$) planes of acridine are in contact with the (110) plane of substrate PE. The substrate PE chain axis lies parallel to the long axis of acridine molecules which lies in the {110} planes of acridine. In the present case, the contact plane of the polyethylene with acridine is (110).

The X-ray diffraction pattern of acridine crystals grown epitaxially on the thin film of PE recovered from the top of an acridine single crystal is shown in Figure 4.77.

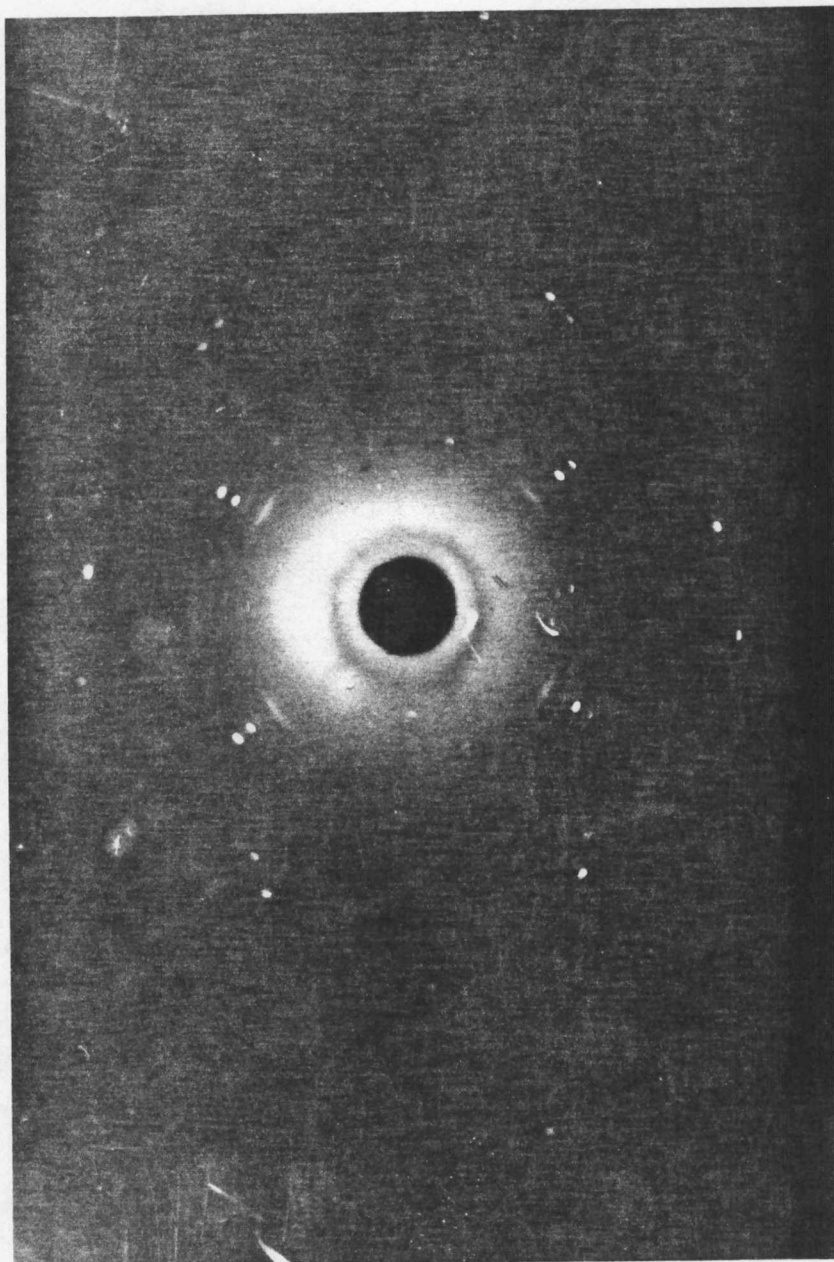


Figure 4.75. X-ray Diffraction Pattern of Acridine Crystals Grown Epitaxially on the Thin Film of PE Recovered from the Sides of an Acridine Single Crystal.

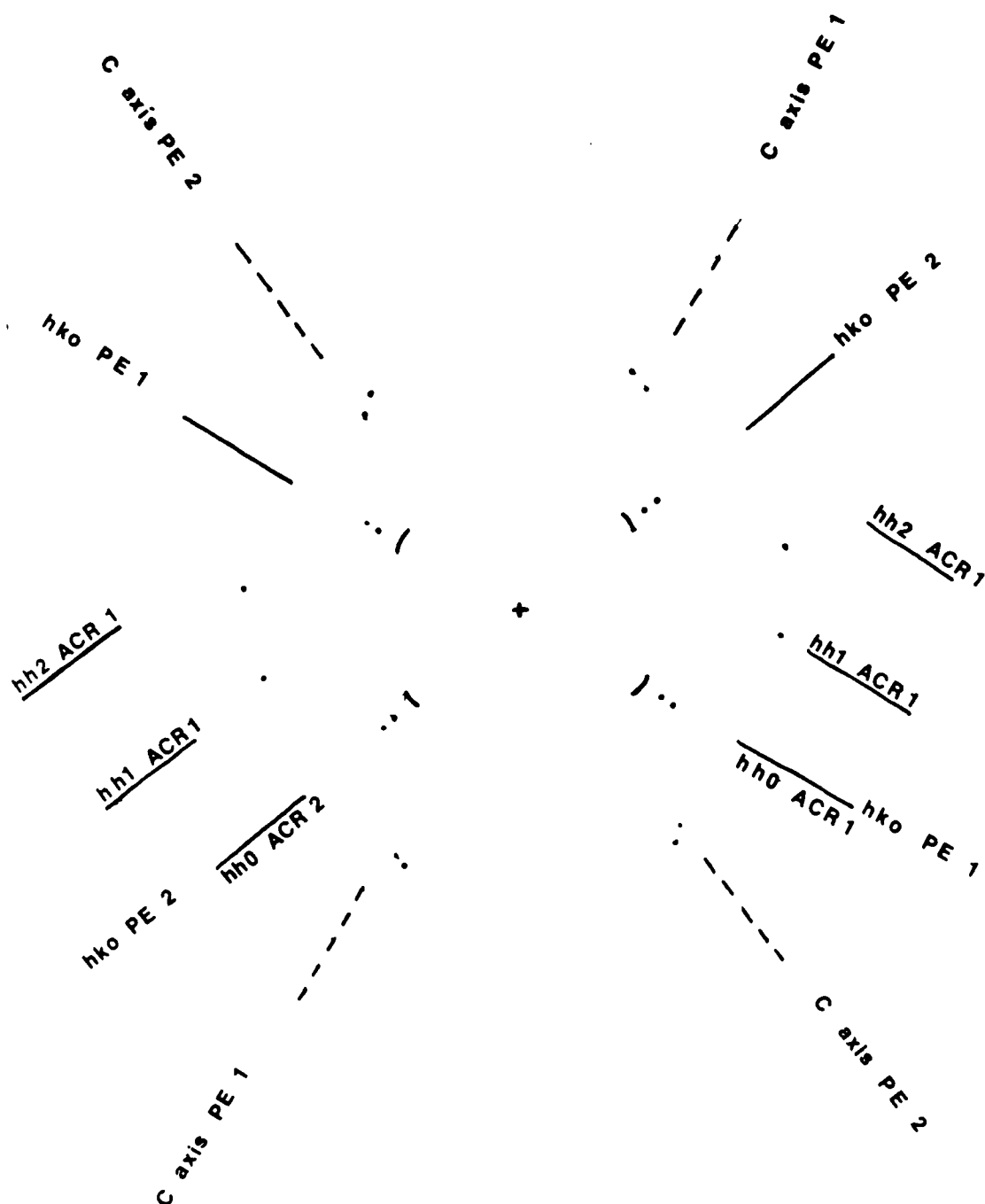


Figure 4.76. Indexing of the Reflection of Figure 4.75.

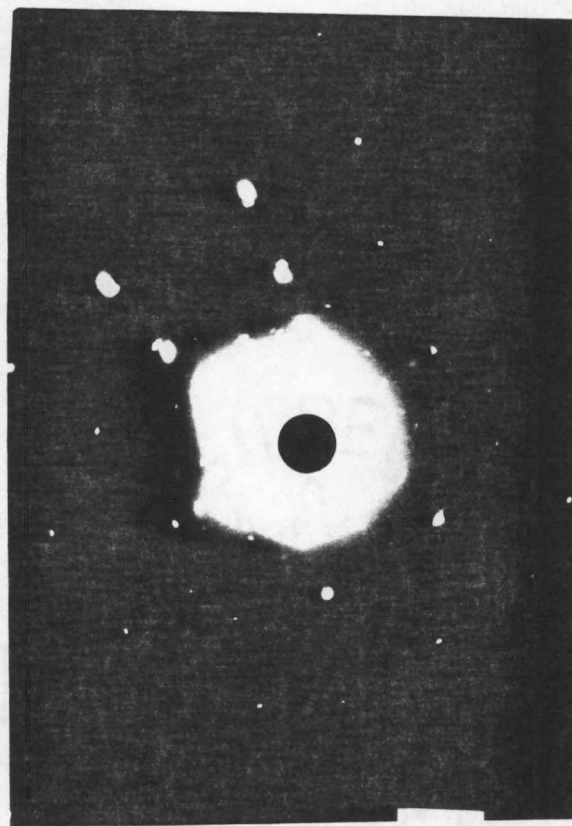


Figure 4.77. X-ray Diffraction Pattern of Acridine Crystals Grown Epitaxially on the Thin Film of PE Recovered from the top of an Acridine Single Crystal.

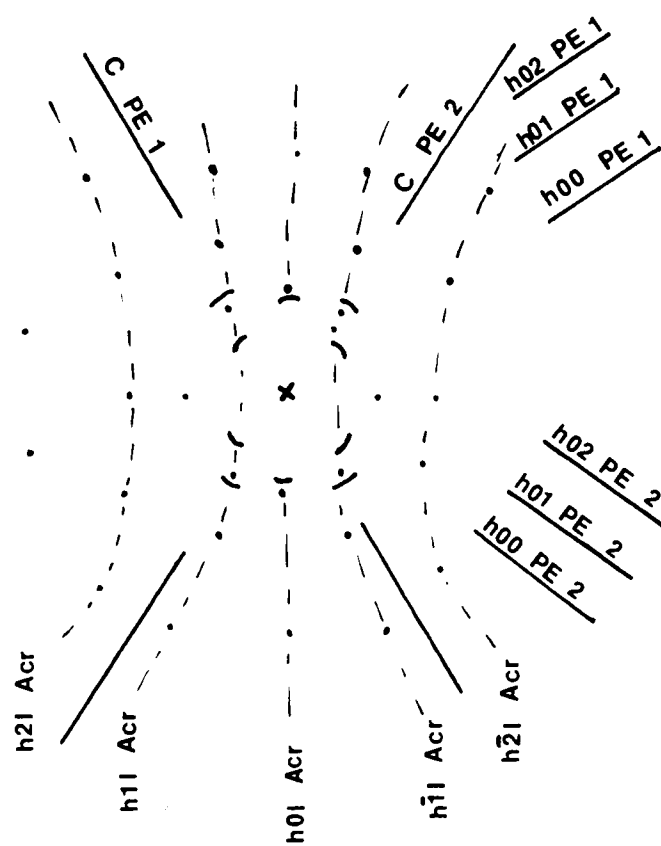


Figure 4.77. (Continued)

4.7 Binary Phase Diagrams

In order to obtain a better understanding of the fundamental interactions occurring in the binary systems, phase diagrams have been constructed using differential scanning calorimetry and X-ray diffractometry. Binary phase diagrams have been constructed over the entire range of the composition of polyethylene and aromatic compound. In this section three systems are considered. They are (i) linear low density polyethylene/acridine, (ii) high density polyethylene/phenazine and (iii) high density polyethylene/p-terphenyl.

4.7.1 Polyethylene/Acridine System

4.7.1.1 Thermal analysis. Powder of linear low density polyethylene prepared as described in section 3.3.4 had a melting point of 109.0°C . As shown in Figure 4.28, (page 129) acridine has a melting point at 110°C and a crystal transformation at 104°C . The thermal treatments for the samples of various compositions were initial melting of polyethylene and acridine at 120°C (above the melting points of both the components) for 15 minutes (to homogenize the mixtures) followed by cooling to ambient at a rate of $80^{\circ}\text{C}/\text{min}$. Melting endotherms of the above treated mixtures were recorded at a heating rate of $10^{\circ}\text{C}/\text{min}$. A typical melting curve of the composition 54.82% acridine and 45.18% linear low density polyethylene is shown in Figure 4.78. This particular plot shows two peaks at 104.85 and 108.85°C . These peak temperatures are

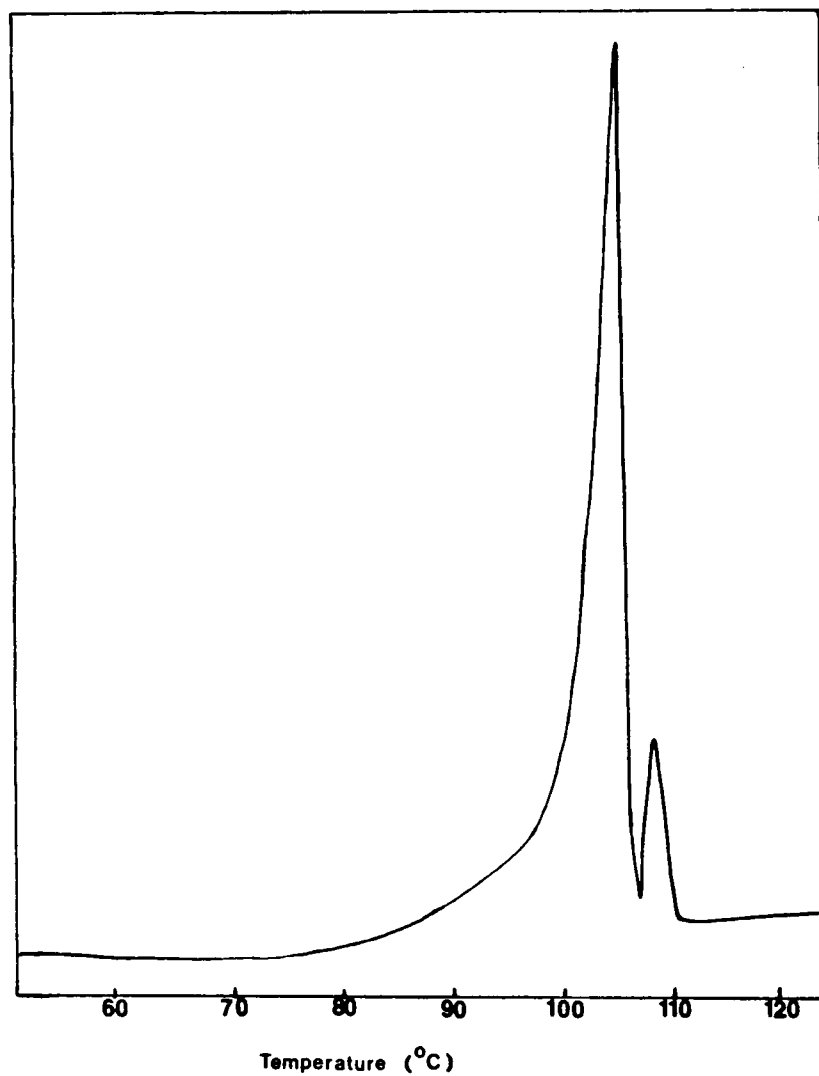


Figure 4.78. A Typical Melting Curve of the Composition 54.82% Acridine-45.18% LLDPE.

represented as the points in the phase diagram at 54.82% acridine. Similarly melting curves were obtained for other compositions. From these data of peak temperatures for all compositions the phase diagram was constructed as shown in Figure 4.79. This non-equilibrium binary phase diagram is plotted for weight percentage of acridine. Figure 4.79 shows two eutectic points at 28.5% and 78% acridine being located at 104°C and 104.9°C, respectively. This system shows two eutectics and a compound crystal containing approximately equal proportions of two constituents.

The melting curves of various compositions (which are cooled at 10°C/min from the melt instead of quenching) produce the equilibrium phase diagram (see Figure 4.80 which is different from the phase diagram produced by quenching). Figure 4.80 shows three eutectic points at 28.5%, 78% and 96% acridine being located at 104°C, 104.9°C and 108.85°C, respectively. In this case, there is a possibility of having two compound crystals of different crystal structures. This phase diagram can be divided into three different sections: 0 to 50% acridine, 50 to 84% acridine and 84 to 100% acridine. For the composition of acridine from 0 to 28%, above 104°C the liquidus line separates the melt and the mixture of polymer crystals and liquid melt. Below 104°C polymer crystals are present with the eutectic phase. For the composition from 28 to 50% acridine, above 104°C compound I is present by itself which is defined by another liquidus line, below 104°C compound I exists with the eutectic. For the composition from 50 to 84% acridine, above

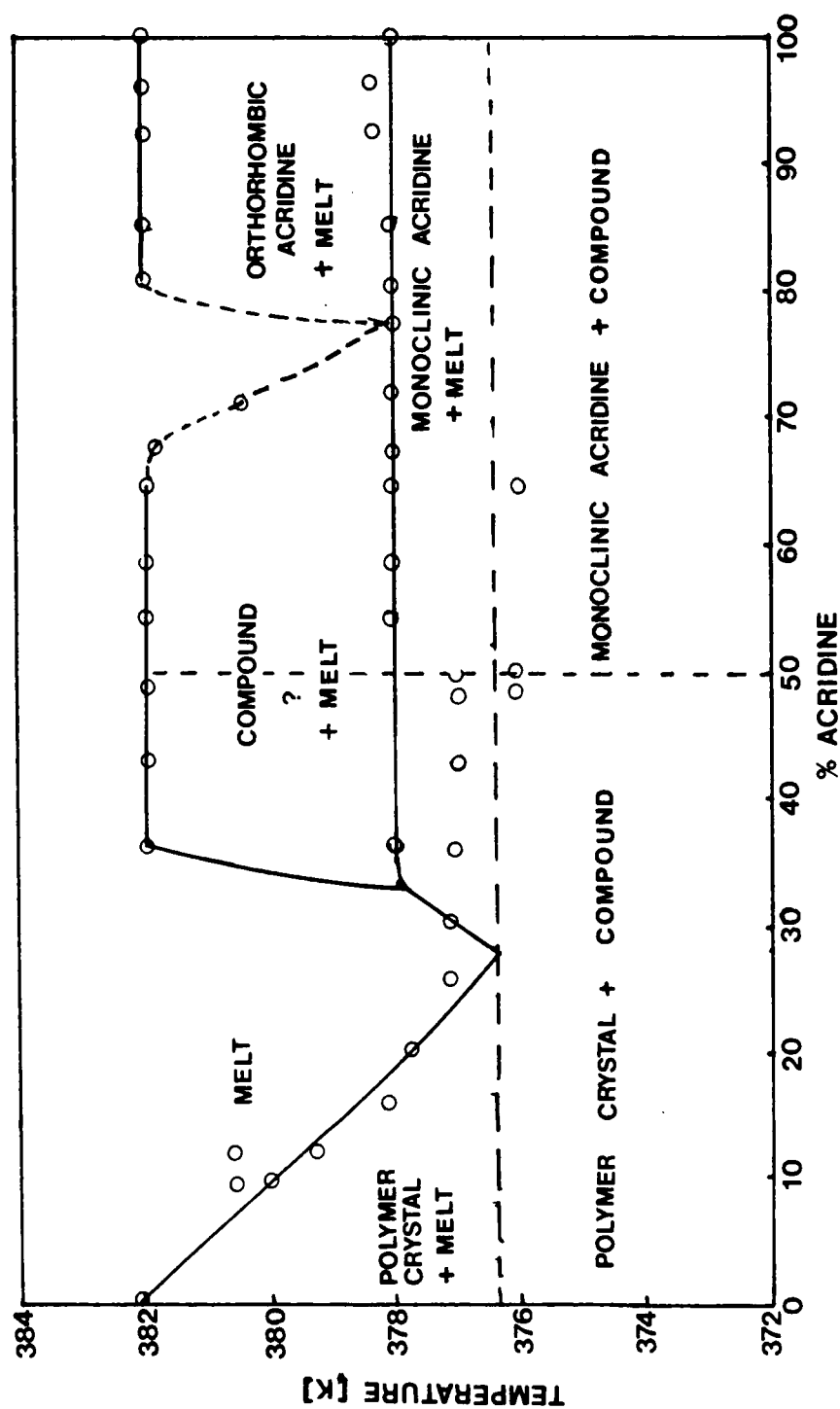


Figure 4.79. Non-equilibrium Phase Diagram of Acridine and LLDPE (from Quenched Melt).

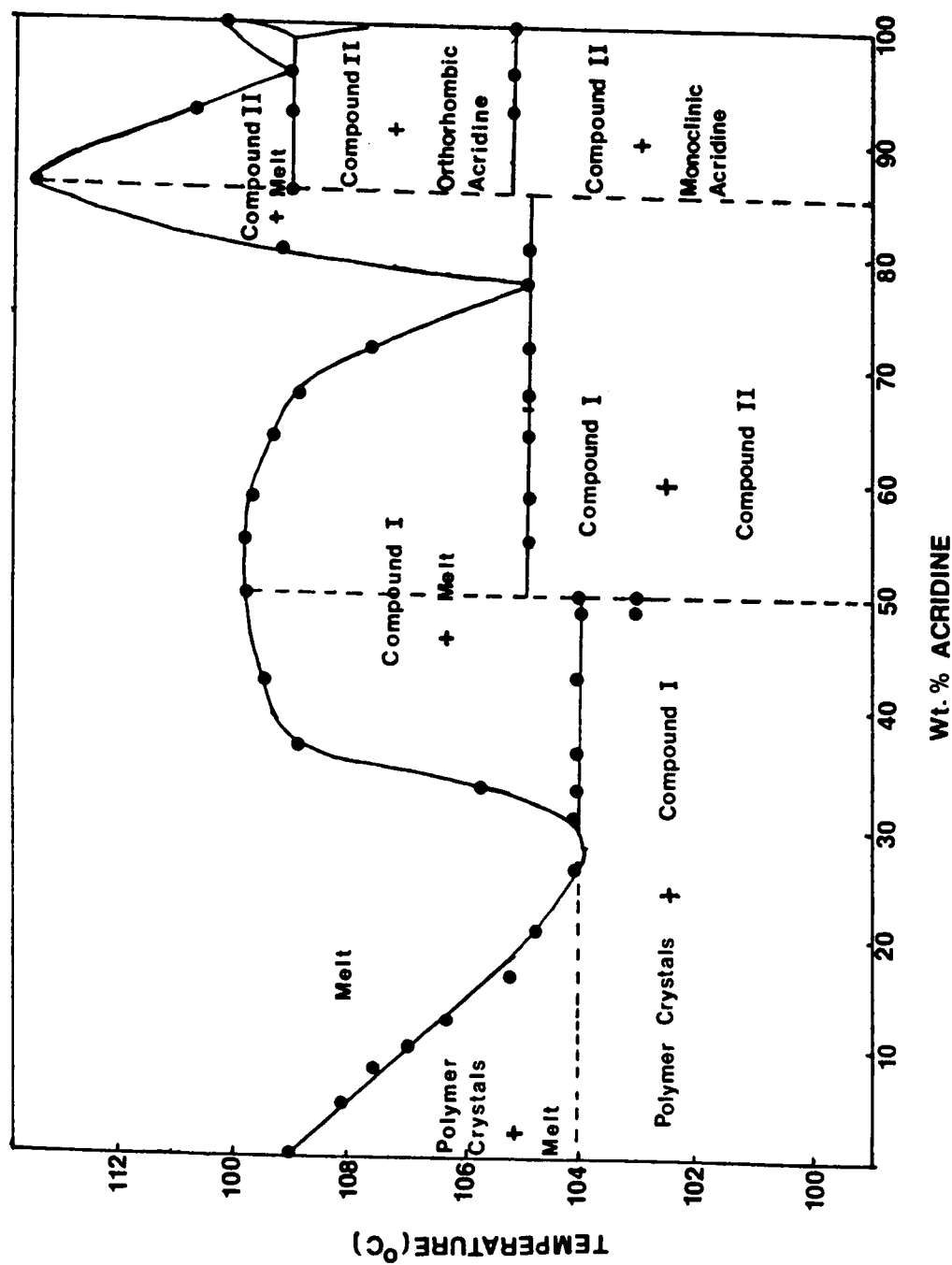


Figure 4.80. Phase Diagram of Acridine and LLDPE (from Slow Cooled Melt).

104.9°C compound I exists below 78% acridine composition which is separated by a liquidus line from the melt. Compound II exists above 78% acridine which is separated by a liquidus line. For the same range of composition, below 104.9°C compound I exists together with compound II. For the composition range from 84 to 100% acridine, compound II exists above 109°C, compound II exists with the orthorhombic acridine crystals from 105 to 109°C and below 105°C monoclinic acridine crystals are present with the compound II.

4.7.1.2 X-ray diffraction study at ambient temperature.

Acridine has a monoclinic crystal structure at room temperature with the unit cell parameters as follows: $a = 11.375 \text{ \AA}$, $b = 5.988 \text{ \AA}$, $c = 13.647 \text{ \AA}$ and $\beta = 98^\circ 58'$ (Lowde et al., 1953; Phillips et al., 1960; Phillips, 1956). All diffraction angles and corresponding d-spacings are presented in Table 4.11. Polyethylene shows two diffraction peaks at $2\theta = 21.6^\circ$ and 23.8° and corresponding d-spacings are $4.11 \text{ \AA}$ and $3.705 \text{ \AA}$, respectively. Various compositions of LLDPE and acridine were studied using X-ray diffraction. Some of these results are presented here. Figure 4.81 is a comparison of X-ray diffraction curves of pure LLDPE, pure acridine and a composition of 34% acridine and 66% LLDPE. There are three diffraction peaks for the composition of 34% acridine and 66% LLDPE located at 2θ values equal to 19° , 22.3° and 23.6° which do not correspond to LLDPE or acridine. These diffraction peaks are shown with arrows in Figure 4.81. A similar study was carried out for the composition 47% acridine, 53% LLDPE (see Figure 4.82). There are

Table 4.11. Crystal Structure of Acridine.

Acridine:

Crystal Structure: Monoclinic

$$a = 11.375 \text{ \AA}$$

$$b = 5.988 \text{ \AA}$$

$$c = 13.647 \text{ \AA}$$

$$\beta = 98^\circ 58'$$

2θ values	$d \text{ \AA}$
10.1	8.75
10.45	8.46
15.6	5.68
16.4	5.40
21.0	4.23
22.0	4.04
23.4	3.80
25.6	3.48
30.1	2.97
30.9	2.89

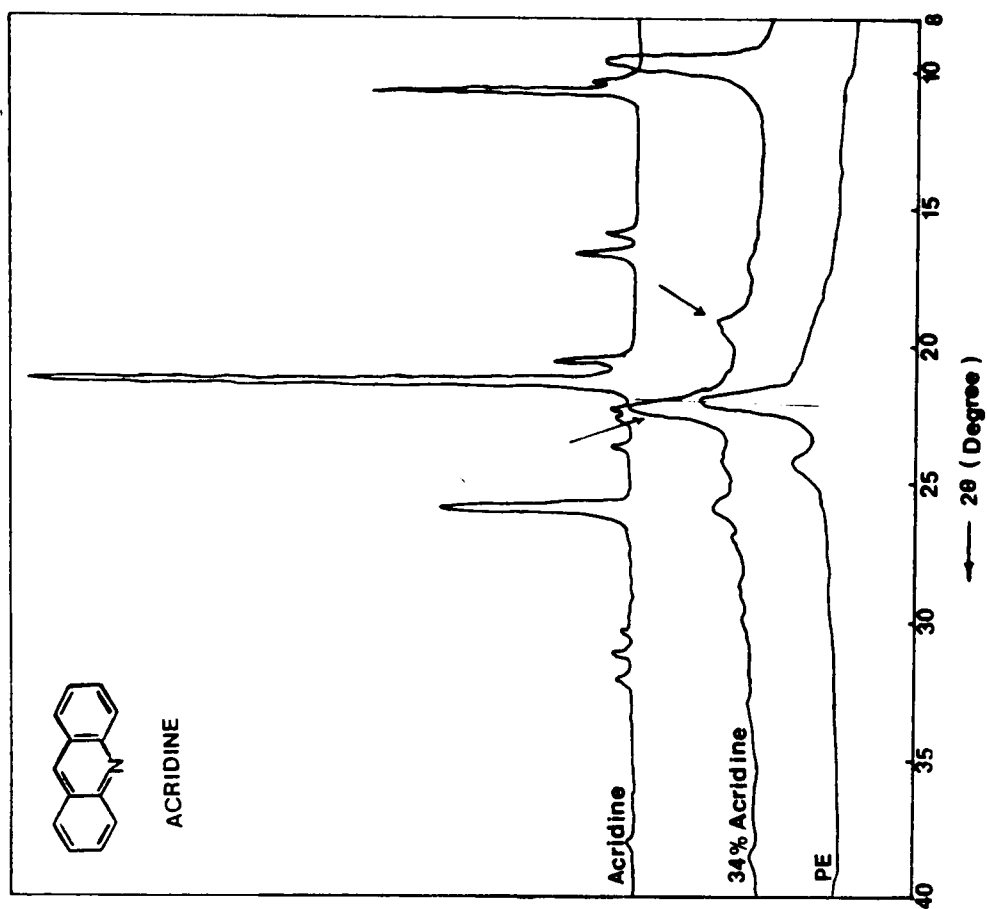


Figure 4.81. X-ray Diffraction Patterns of the LLDPE/Acridine System---
(a) Pure Acridine, (b) 34% Acridine, (c) Pure LLDPE.

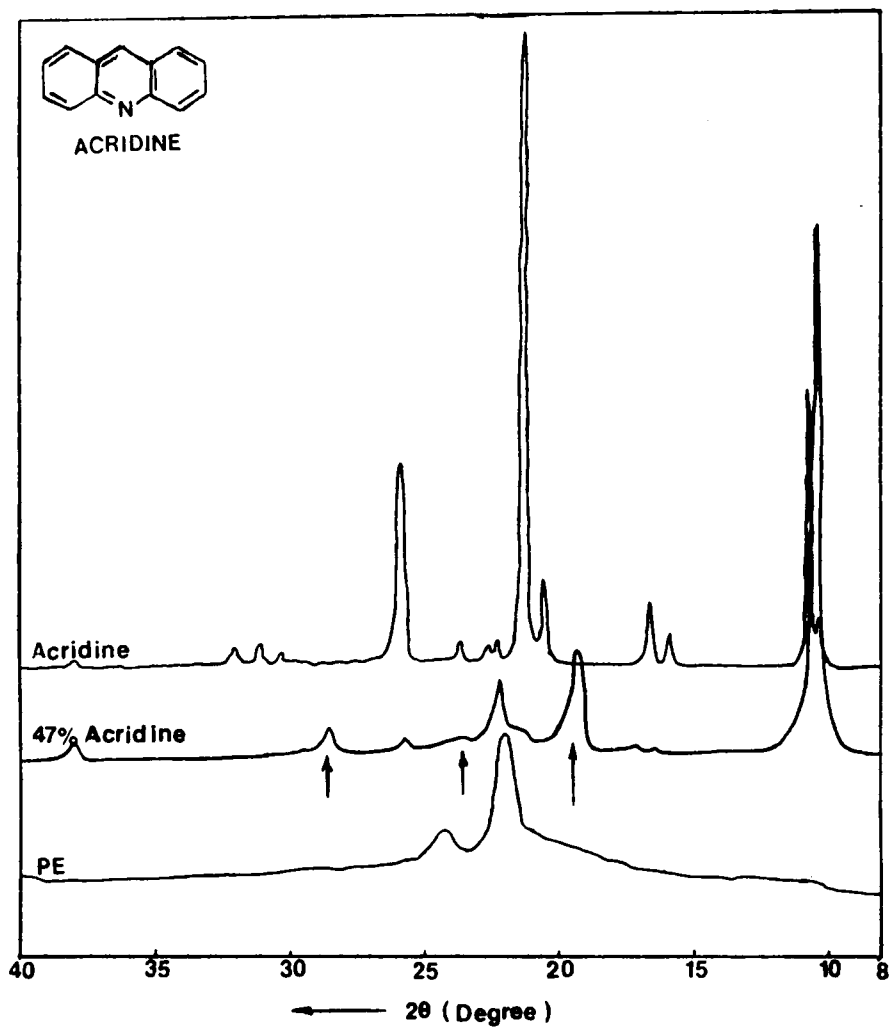


Figure 4.82. X-ray Diffraction Patterns of the LLDPE/Acridine System—(a) Pure Acridine, (b) 47% Acridine, (c) Pure LLDPE.

four diffraction peaks located at 2θ values of 19.1° , 22.4° , 23.6° and 29° which cannot be assigned to acridine or LLDPE. These two results at the compositions of 34% and 47% acridine might be reflecting the presence of compound I in the range of 28 to 50% acridine as shown in Figure 4.80.

4.7.1.3 X-ray diffraction study at higher temperatures. High temperature X-ray work was carried out in a high temperature cell which was mounted on the goniometer of a diffractometer as described in section 3.9.4. High temperature X-ray studies were carried out for two compositions of 62.8% acridine-37.2% LLDPE and 82.1% acridine-19.9% LLDPE. According to the phase diagram (see Figure 4.80) compound I and compound II exist above 104.9°C at 62.8% acridine-37.2% LLDPE and 82.1% acridine-19.9% LLDPE, respectively. The principal reason in selecting these compositions was to obtain the possible diffraction angles arising solely due to compound I and compound II. Another reason was to study the changes which might be occurring at higher temperatures. Figure 4.83 shows the X-ray diffraction patterns of the composition 62.8% acridine-37.2% LLDPE as a function of temperature. The X-ray diffraction pattern at 106°C in Figure 4.83 can be assigned to compound I. Figure 4.84 shows the X-ray diffraction patterns of the composition 82.1% acridine-19.9% LLDPE as a function of temperature. The X-ray diffraction pattern at 106.4°C in Figure 4.84 can be assigned to compound II. Thus it is possible to confirm the existence of a different structure with the high temperature X-ray results.

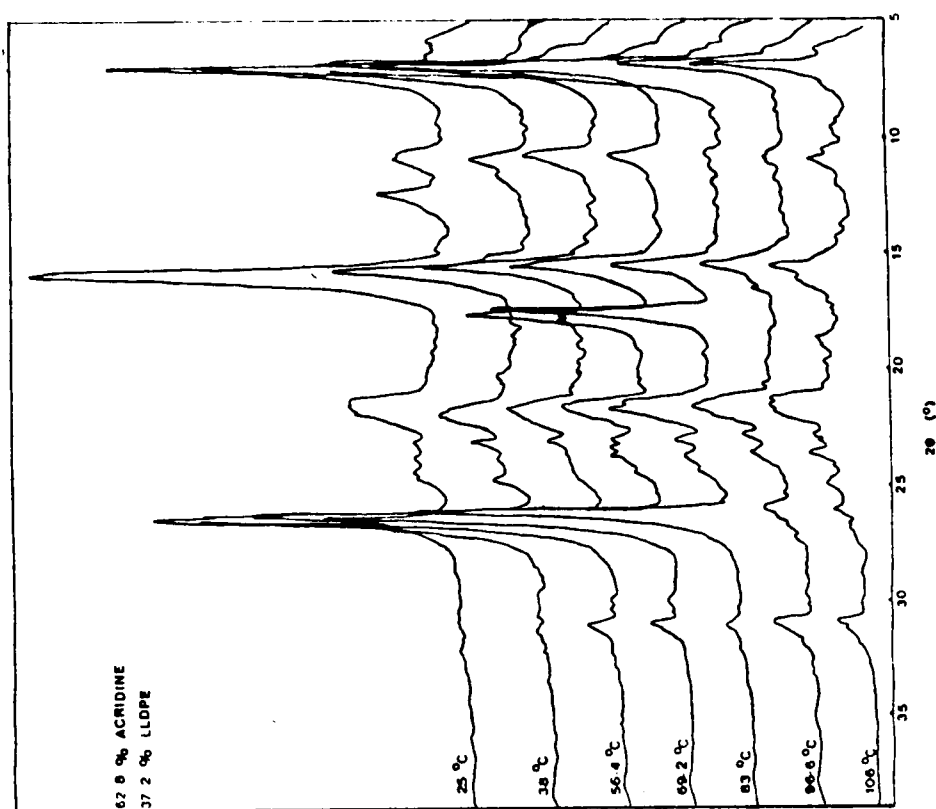


Figure 4.83. X-ray Study of the Composition 62.8% Acridine-37.8% LLDPE as a Function of Temperature. (1) 25°C (2) 38°C (3) 56.4°C (4) 69.2°C (5) 83°C (6) 96.6°C (7) 106°C.

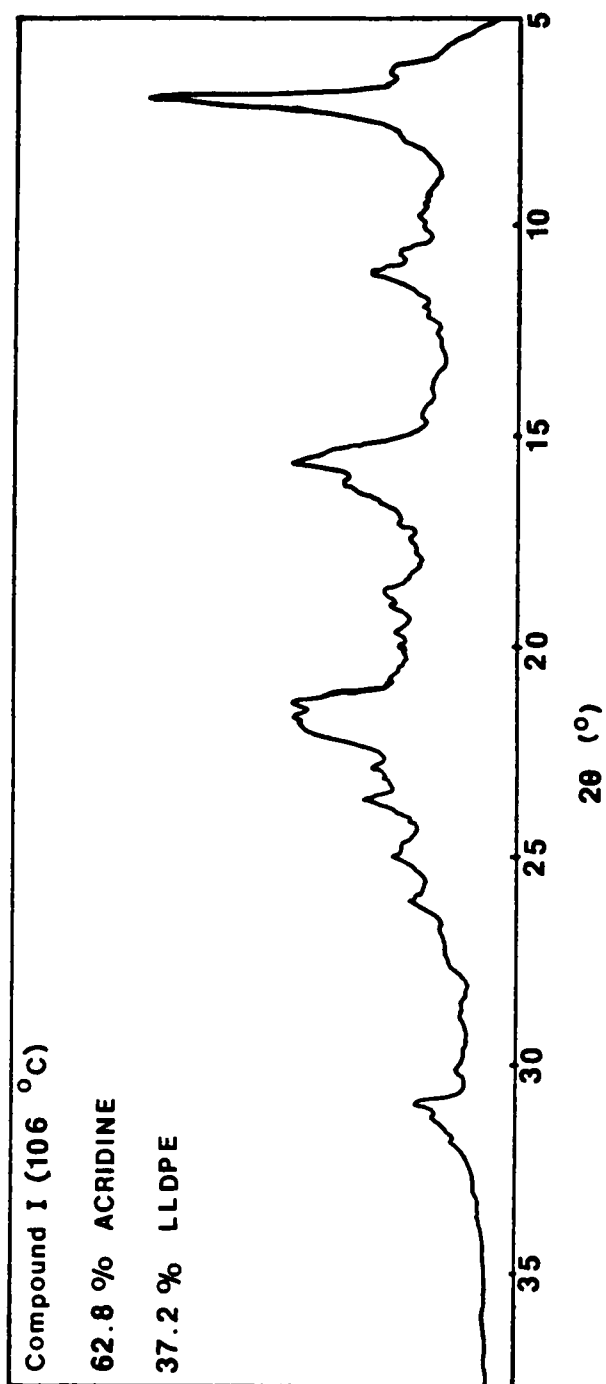


Figure 4.83. (Continued)

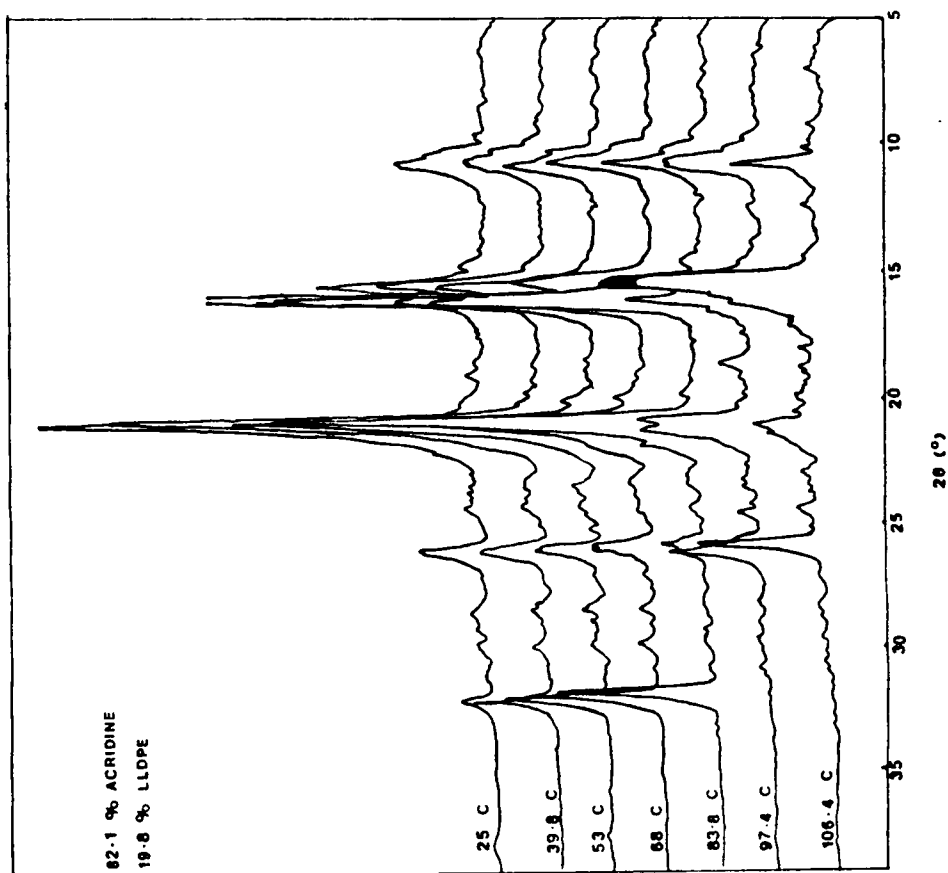


Figure 4.84. X-ray Study of the Composition 82.1% Acridine, 19.9% LLDPE as a Function of Temperature. (1) 25°C (2) 39.8°C (3) 53°C (4) 68°C (5) 83.8°C (6) 97.4°C (7) 106.4°C.

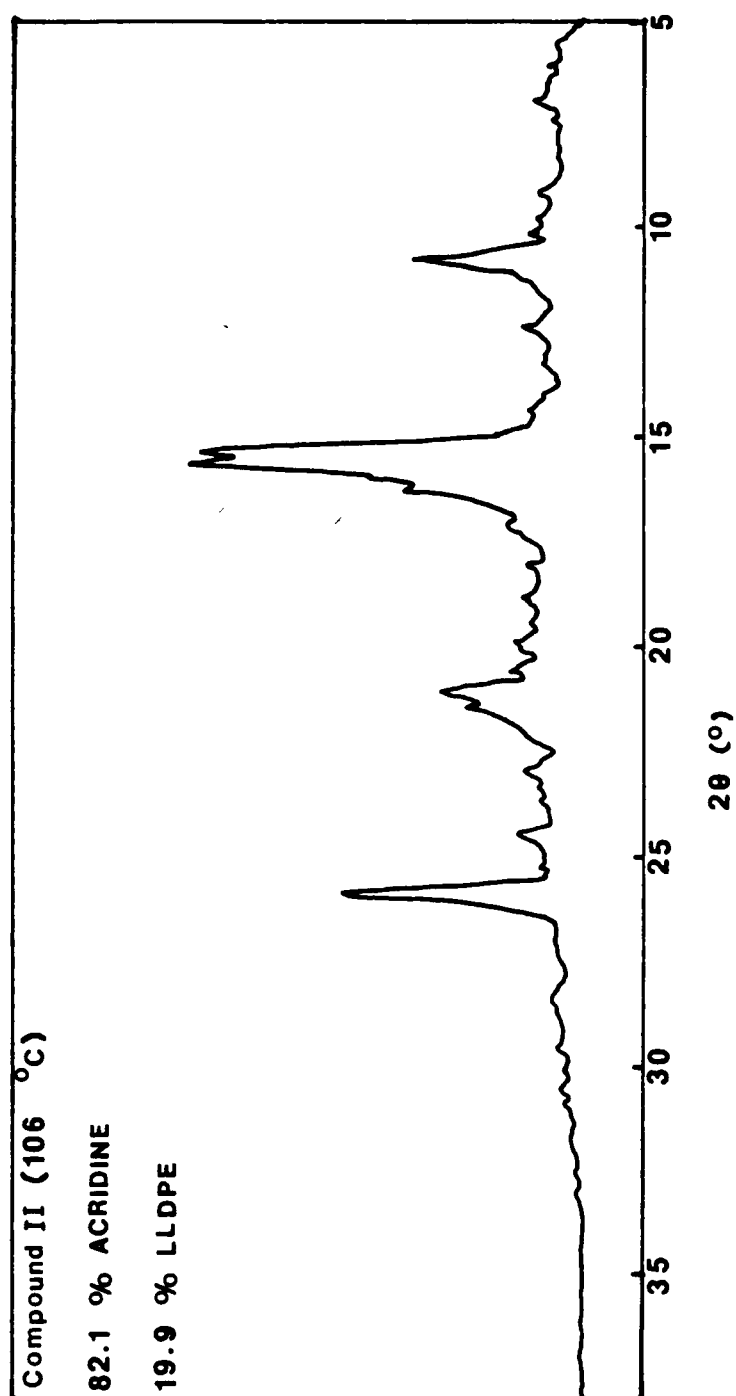


Figure 4.84. (Continued)

4.7.2 Polyethylene/Phenazine System

4.7.2.1 Thermal analysis. Powder of HDPE was prepared as described in section 3.3.4 and melted at 131°C. Phenazine crystals have a melting point at 177°C obtained from the differential scanning calorimetry (see Figure 4.85). Various compositions at HDPE and phenazine were prepared and melted. Their melt was held at 185°C for 15 minutes and cooled to 30°C at the rate of 10°C/min. These thermally treated compositions were melted at 10°C/min and their peak positions were used to construct the binary phase diagram of the HDPE/phenazine system (see Figure 4.86). There are two eutectic points at compositions of 12% phenazine-88% HDPE and 34% phenazine-66% HDPE located at 129°C and 128.5°C, respectively. There is a possibility of compound formation at the composition 23.5% phenazine-76.5% HDPE.

4.7.2.2 X-ray diffraction study. Phenazine has a monoclinic crystal structure with the unit cell parameters as follows: $a = 13.2 \text{ \AA}$, $b = 5.07 \text{ \AA}$, $c = 7.12 \text{ \AA}$ and $\beta = 108^\circ 55'$ (Wood and Williams, 1941; Herbstein and Schmidt, 1955a, 1955b). All diffraction angles and their corresponding d-spacings are given in Table 4.12. The X-ray diffraction pattern at a composition of 20.2% phenazine-79.8% HDPE is compared with the X-ray diffraction pattern of pure HDPE and pure phenazine in Figure 4.87. This particular composition shows four additional peaks at 2θ values equal to 24.2° , 27.2° , 31.1° and 33.5° . These peaks neither belong to polyethylene nor to

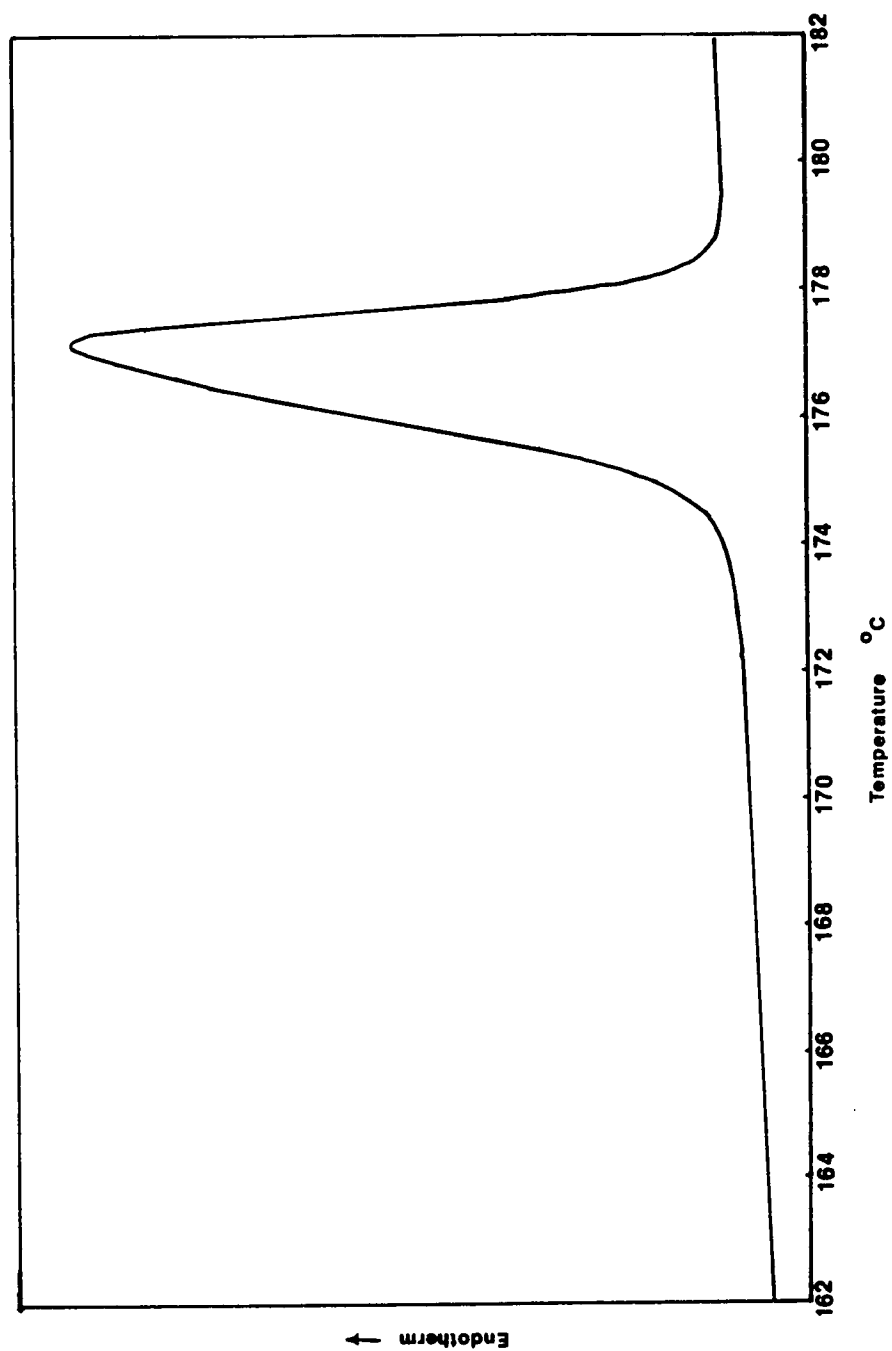


Figure 4.85. Melting Curve of Phenazine.

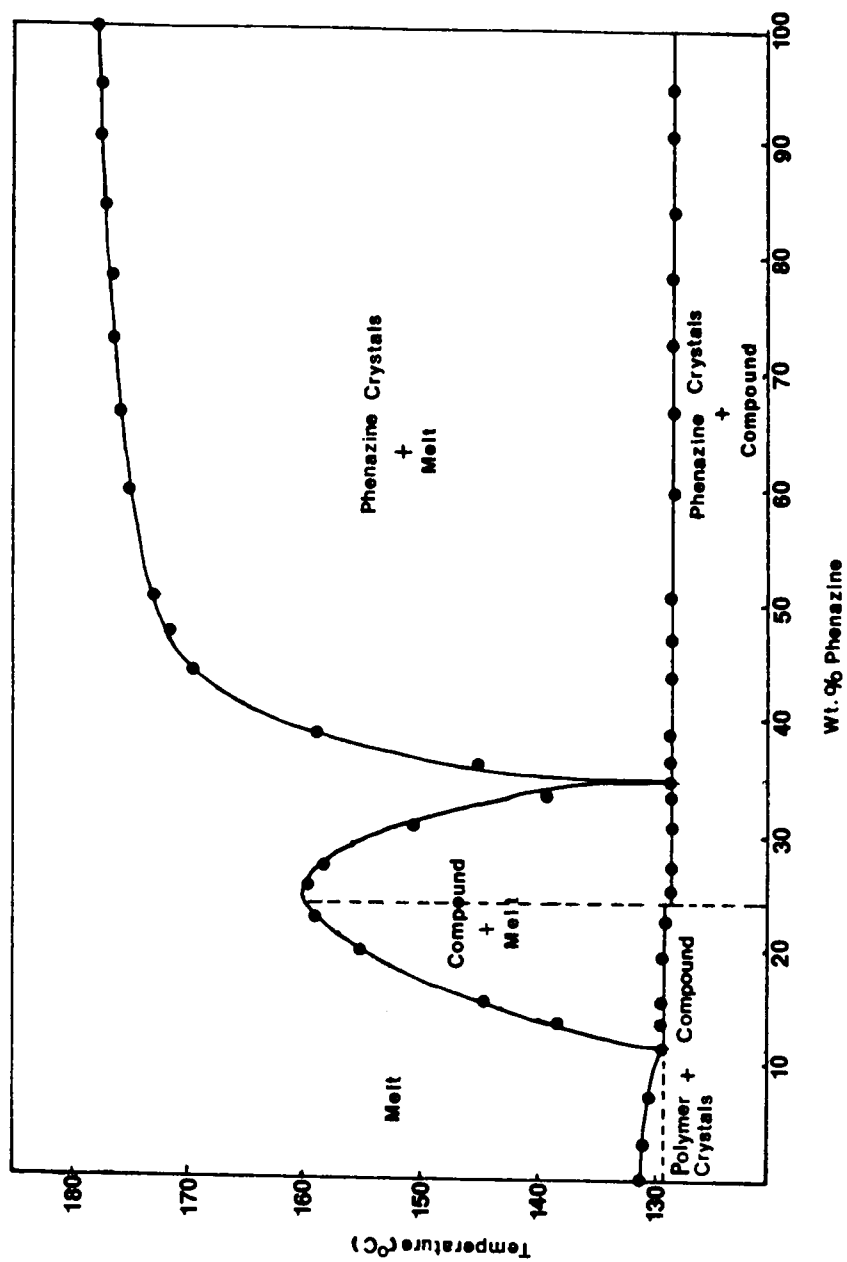


Figure 4.86. Phase Diagram of HDPE and Phenazine.

Table 4.12. Crystal Structure of Phenazine.

Phenazine:

Crystal Structure: Monoclinic

$$a = 13.2 \text{ \AA}$$

$$b = 5.07 \text{ \AA}$$

$$c = 7.12 \text{ \AA}$$

$$\beta = 108^\circ 55'$$

2θ values	$d \text{ \AA}$
13.0	6.81
14.0	6.33
15.6	5.68
15.8	5.61
25.3	3.52
31.9	2.80

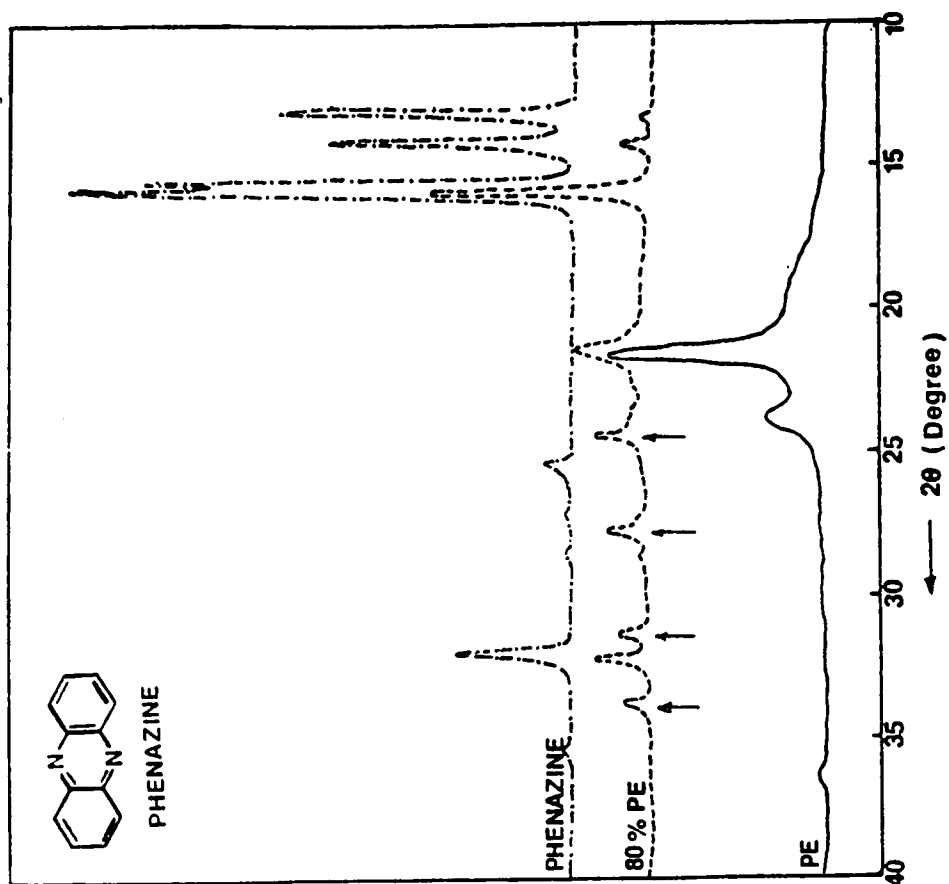


Figure 4.87. X-ray Diffraction Patterns of the HDPE/Phenazine System--(a) Pure Phenazine, (b) 80% HDPE, (c) Pure HDPE.

phenazine. Results obtained using differential scanning calorimetry and X-ray diffraction indicate the possibility of compound formation in this system.

4.7.3 Polyethylene with Other Aromatic Molecules

The binary phase diagrams of acridine/LLDPE and phenazine/HDPE were constructed using differential scanning calorimetry and X-ray diffractometry and presented in sections 4.7.1 and 4.7.2. Similar studies carried out with other systems including 9-bromoanthracene/LLDPE, 9-fluorenone/LLDPE, naphthalene/LLDPE, phenanthrene/HDPE, p-terphenyl/HDPE failed to show any possibility of compound formation. However, the system p-terphenyl/HDPE shows one eutectic (see Figure 4.88). Some of the contributing factors like shape of aromatic molecules, nucleating ability of polyethylene on aromatic compounds, difference between the melting points of two constituents, presence of amorphous phase of polyethylene and others which might be affecting the solidification of polyethylene and aromatic compounds and oriented growth in these systems will be discussed in the next chapter. The crystal structures of the aromatic compounds used in this study are presented in Appendix 1.

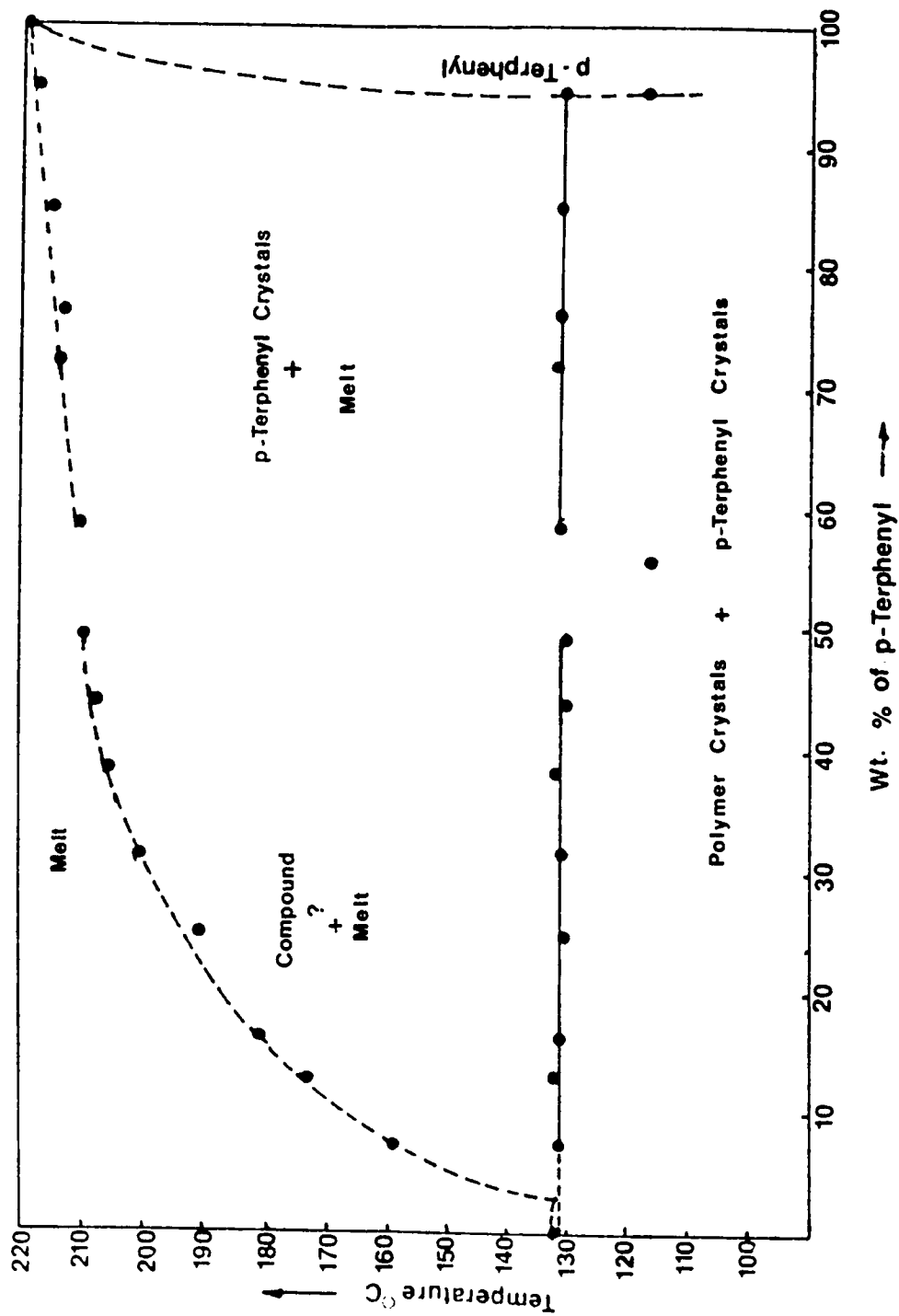


Figure 4.88. Phase Diagram of HDPE and p-Terphenyl.

CHAPTER 5

DISCUSSION

For many years it has been known that organic molecules are oriented in oriented polyethylene but the mechanism of orientation was not known. There were several suggestions made but no direct evidence was available. A systematic investigation of the orientation mechanism has been attempted here.

In recent dielectric relaxation studies carried out by Jang et al., (1982), it was found that a large fraction of molecules were immobilized by the orientation process. Since then attempts have been made to determine the possible locations and the possible operating mechanisms of orientation.

Dielectric relaxation studies of unoriented film, stretched film and extruded rods of linear low-density polyethylene containing polar aromatic molecules have been carried out to determine the locations of the immobilized aromatic molecules and the cause for this immobilization process. Use of extruded rod made it possible to acquire information about the fractions of molecules relaxing parallel and perpendicular to the orientation direction. It emerged from this study that these missing molecules are located on potential adsorption sites, such as the lateral surfaces of polyethylene crystals through possible orientation mechanisms such as surface adsorption or surface crystallization.

To investigate whether the molecules are crystallized or adsorbed preferentially on the surfaces of polyethylene crystals, spectroscopic and thermal techniques were used. These experiments revealed that the aromatic molecules are able to crystallize in the oriented polyethylene but not in unoriented polyethylene and it is quite likely that the aromatic crystals are growing epitaxially on the surfaces of the crystalline microfibrils of oriented polyethylene. It is apparent from these studies that specific surface adsorption related to the mechanism of epitaxial growth of microcrystals is the major orientation mechanism.

The studies then were concentrated on exploring the epitaxial crystallization mechanism in detail. There is a report in the literature by Wittmann and Lotz (1981a) on epitaxial crystallization of polyethylene on anthracene. Since anthracene and acridine molecules and crystals are very similar, it seemed likely that these linearly fused ring aromatics could function through a similar epitaxial crystallization mechanism. The studies carried out in this respect showed that polyethylene can grow epitaxially on acridine single crystals and acridine can grow on epitaxially grown polyethylene film. Hence this study provided the direct evidence that epitaxial crystallization is a major orientation mechanism. This study also showed that epitaxial crystallization occurs on both (110) and (100) planes of polyethylene (slip planes of polyethylene). Growth on (100) planes places the long axis of the molecule normal to the chain direction whereas growth on (110)

planes places the long axis parallel to the polymer chain direction. Hence combining these facts with the results of spectroscopic and dielectric relaxation studies the relative magnitudes of the (110) and (100) planes were calculated. This provided the first method to estimate the actual relative areas of competing slip planes.

At this stage the question arose as to whether the aromatic compounds and polyethylene can co-crystallize. Are there any new molecular states associated with these components? Is the oriented overgrowth related to eutectic solidification? To answer these questions the phase diagrams of aromatics and polyethylene were constructed. New states of molecular association have been found in some of the systems studied here. The existence of compound formation was verified with the help of high temperature x-ray studies. The results open the possibility of creating a new polymer composite with anisotropic properties.

Linear low-density polyethylene (LLDPE) was used in this work as a substrate material. LLDPE by itself is a non-polar material and polar aromatic molecules were introduced into it and their dielectric behavior studied. Before attempting a detailed study of aromatic molecules in oriented polyethelene and their orientation mechanism, it is important to understand the morphology of linear low-density polyethylene and its influence on dielectric behavior. The structure of substrate polyethylene is important since it governs the possible locations of aromatic molecules. In the following section the dielectric behavior of LLDPE is discussed. In

subsequent sections other studies already discussed in brief above will be considered in detail.

Linear low-density polyethylene is a copolymer of ethylene with a long chain alkene, typically octene, and is produced by heterogeneous catalysis. It is neither a linear polyethylene nor a typical branched polyethylene having a distribution of short and long chain branches. Unlike conventional low-density polyethylenes (LDPE), LLDPE has shorter branching with uniform length. It is known that short chain branching strongly influences crystallization ability whereas long chain branching affects long-range mobility. Study of LLDPE provided an opportunity to separate the influences of short and long chain branching on the dielectric behavior of branched polyethylenes.

5.1 Dielectric Relaxation Studies of LLDPE

Dielectric studies of polyethylenes have been conducted for several decades by many researchers (McCrum et al., 1967; Ashcraft and Boyd, 1976; Boyd and Yemni, 1979; Phillips, 1983) and the general trends are well known. Dielectric relaxation studies show three relaxation regimes (usually designated α , β , and γ in order of decreasing temperature). The α relaxation process is known to be associated with the crystalline phase and is sensitive to orientation effects (Phillips et al., 1971, 1972). The β relaxation process is definitely associated with the glass transition for low-density polyethylenes. It was recently shown to occur in linear

polyethylene (LPE) and is also associated with the glass transition for LPE (Boyd, 1984). The γ relaxation process was thought to be associated with both the crystalline and amorphous phases, but was recently shown by Sayre and Boyd (1978) to arise only from the amorphous phase. LDPE exhibits higher losses associated with amorphous phase relaxations (Mikhailov et al., 1957; Oaks and Robinson, 1954; Phillips et al., 1971).

Dielectric experimentation on polyethylenes has generally relied on the introduction of dipoles in the form of carbonyl or carboxylate groups or chlorine side atoms. Such groups perturb the crystalline state of polyethylene. The magnitudes of the three major loss peaks in polyethylenes are dependent on the number of active dipoles present. In this study, the absence of carbonyl groups provides an opportunity to investigate the influence of morphology on the dielectric behavior of LLDPE. The sources of dipoles in LLDPE are likely to differ from other polyethylenes since the chain ends may be of different character. Also, because of the catalytic system used, there is the possibility of residual transition metals and/or their complexes being dielectrically active. The dielectric spectra of LLDPE do not differ much from those of LDPE in any major way for unoriented specimens. Significant differences were observed when the material was oriented. The dielectric spectra contain important information on the location of the dipoles present and on the anisotropy of the different relaxation processes. Since infrared studies (FTIR) did not reveal the presence of polar

groups it is likely that dielectric losses arose from the presence of initiator fragments of some unknown structure. Small amounts of alumina with traces of transition metal catalysts such as titanium can be present.

5.1.1 The α Peak

The relative magnitude of the α loss peak differs considerably from that of slightly oxidized low-density polyethylene in that the relaxation is the dominant process. In copolymers of ethylene and carbon monoxide (Phillips et al., 1971), where the active group was clearly a carbonyl and capable of entering the crystal without severe distortion for the concentration present, the α loss was larger and proportional to the carbonyl content. The α loss in unoriented LLDPE is, however, slightly more prominent than normally observed for LDPE, perhaps a result of the somewhat higher crystallinity. The dielectric data of stretched LLDPE in Figure 4.15, page 112, show that the α loss peak has decreased in magnitude. This behavior is the opposite of that of low-density polyethylene in that orientation of a polymer in which the active groups are carbonyls (Phillips et al., 1971) produces an increase in the magnitude of the α loss process. This is because the dipole moment of the carbonyl group is normal to the chain direction. Hence introduction of oriented crystals in which the molecular chain is in the direction of stretching results in more dipoles being in the direction of the electric field than are normal to it and hence

normal to the stretch direction. Since the effect observed here is opposite, the dipoles must be predominantly in the chain direction.

Orientation of the LLDPE by stretching causes a decrease in the magnitude of the α loss peak, which must mean that either the dipole moments have a large component in the chain direction or they have been placed in an immobile location. Since extrusion tends to produce similar orientation the results from the extruded rods are of considerable importance as it is possible to obtain data both parallel and perpendicular to the orientation direction. It is readily apparent from Figures 4.18 (page 116) and 4.19 (page 117) that the magnitude of the α peak in the extrusion direction is almost double that normal to the extrusion direction. Enhancement of the α peak in the orientation direction is large for the extruded rod; however, the magnitude normal to the extrusion direction was the same as for the stretched sheet.

Figure 5.1 is a comparative plot of dielectric loss at 10 Hz of unoriented film, stretched film, extruded rod parallel to the extrusion direction and perpendicular to the extrusion direction. This figure shows that the α loss peak for the direction normal to the extrusion direction is of approximately the same magnitude as that of the stretched sheet. However, the α loss peak parallel to the extrusion direction has been enhanced considerably. It is, therefore, reasonable to conclude that the effect observed is largely due to orientation and not of immobilization of dipoles. Hence, it is obvious that the dipoles are oriented preferentially in

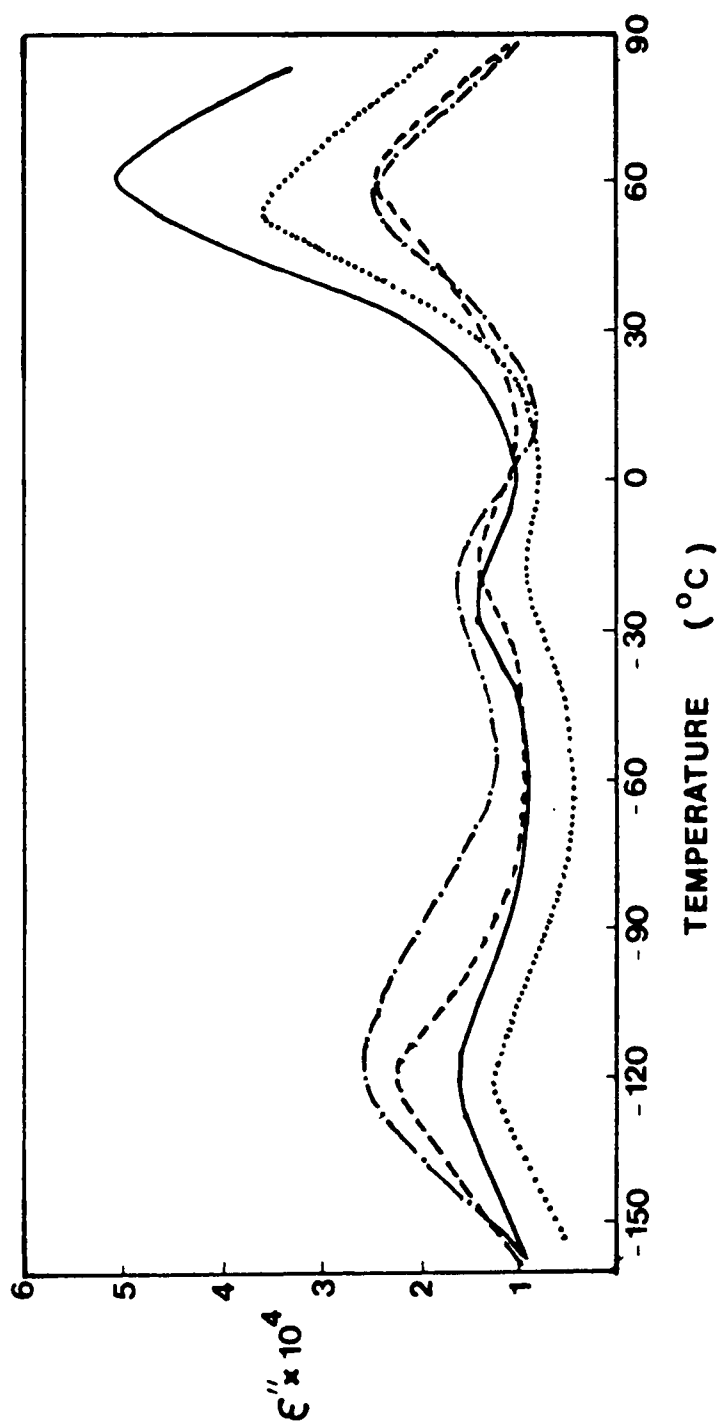


Figure 5.1. Comparative Plot of the Dielectric Loss at 10 Hz of LLDPE Specimens. (.....) Unoriented, (---) Oriented Sheet, (—) Extruded Rod, || to Extrusion Direction, (— · —) $\perp$ to Extrusion Direction.

the chain direction. This behavior is the opposite of that of carbonyl groups, which have their dipole moments perpendicular to the polymer chain. Orientation of crystals in that case results in the dipoles being preferentially oriented normal to the stretching direction. For dipoles oriented in the chain direction to relax, two possible mechanisms exist. First, if the dipoles are in the crystal, they could relax through translational motion of Mansfield-Boyd defects (Mansfield and Boyd, 1978) which have both rotational and translational motion. Second, the dipoles could be located at the fold surface. If indeed, they are caused by chain ends and associated with initiator fragments, then this could be a more likely mechanism. For such a mechanism to function, however, the transition metal, if present, would need to have a dipole inclined to the chain direction. The dipole could relax through a cooperative process involving a Mansfield-Boyd defect and the fold surface. The activation energy of the α process (~ 14.8 kcal/mole for unoriented and 17.0 kcal/mole for stretched sheet, Table 4.1, page 108) is lower than that observed in highly oxidized materials (24 to 30 kcal/mole by Ashcraft and Boyd (1976) and 26 kcal/mole by Boyd and Yemni (1979)). Also the temperature location of the α peak is, significantly higher than is normally observed (see Figure 5.2). This is a reflection of a change in the frequency factor of the relaxation and implies an intrinsically slower process.

The known contaminants in LLDPE are silica particles with traces of titanium. It seems possible that a chain end could be

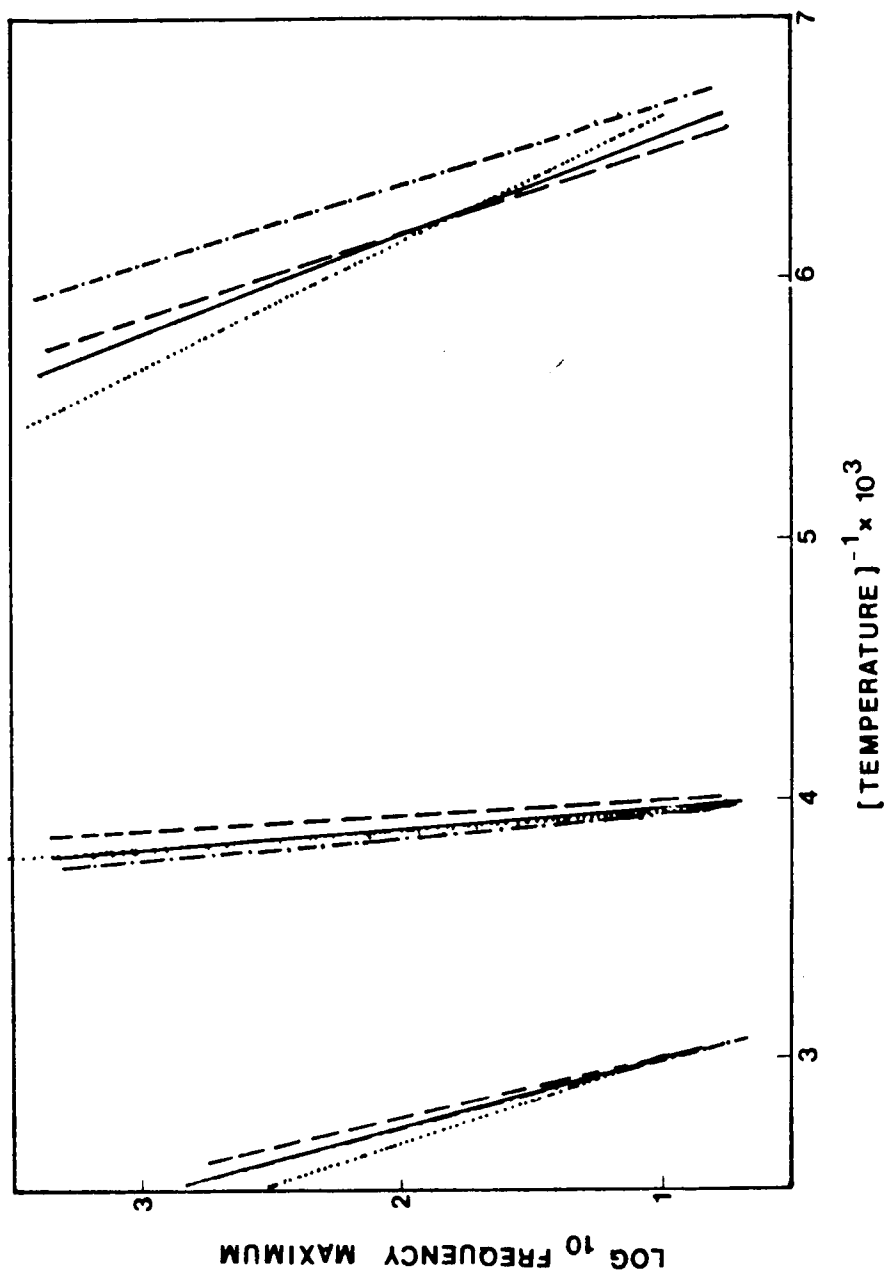


Figure 5.2. Arrhenius Plots of LLDPE Specimens for α , β and γ Relaxations. (.....) Unoriented, (---) Oriented Sheet, (—) Extruded Rod, (— · —) to Extrusion Direction, (— · —) $\perp$ to Extrusion Direction.

attached to a silica particle through a titanium atom. Lamellar thickening immediately following crystallization could tighten the chain, pulling the chain end into the fold surface and orienting it at the same time. The relaxation could, therefore, be due to interaction of the α process with an oriented chain end. This explanation can be tested with the help of a quantitative comparison of the dipolar concentration with the end group concentration. Data for the α process were analyzed using the Onsager equation (equation 4.6, page 147), producing the dipolar concentrations listed in Table 5.1. Such an analysis produces $N\mu^2$, where N is the number of dipoles per unit volume, and μ is the dipole moment. In order to estimate the likely range of N , calculations were performed for dipole moments of 1 and 5D. For the unoriented polymer, dipolar concentrations of 7.4×10^{19} and $2.9 \times 10^{18} / \text{cm}^3$ were obtained for 1 and 5D, respectively. Using the supplier's number-average molecular weight of 7723, the population of chain ends were calculated to be $1.4 \times 10^{20} / \text{cm}^3$. It is impossible to estimate the fraction of chain ends carrying transition-metal dipoles, however, it is clear from this analysis that the dipole and chain-end populations are comparable. Therefore, an explanation involving chain ends at the fold surface is quite reasonable.

The change in magnitude of the relaxation in the temperature plane can sometimes be misleading and it is instructive to estimate the magnitude ($\Delta\epsilon'$) of any relaxation process using Cole-Cole plots. Values of $\Delta\epsilon'$, i.e., $(\epsilon_R' - \epsilon_U')$ for each of the relaxation

Table 5.1. Dipole Populations (N) from $\Delta\epsilon'$ Values in Numbers/cm³ for the α Process.

	Unoriented	Stretched Sheet	Extruded Rod	
			" to Extrusion Direction	1 to Extrusion Direction
For a dipole moment of				
1 D	7.4×10^{19}	5.6×10^{19}	1.2×10^{20}	3.2×10^{19}
5 D	2.9×10^{18}	2.2×10^{18}	4.9×10^{18}	1.3×10^{18}

processes are obtained from the Cole-Cole plots and are tabulated in Table 4.2, page 111). Values of Cole-Cole parameters ($\bar{\beta}$) for each of the relaxation processes are also given in Table 4.2, page 111. It is possible to test the conclusion that the effects observed are largely due to orientation. The way to do this is to calculate $\Sigma \Delta \epsilon' = 2(\Delta \epsilon'_{\perp}) + \Delta \epsilon'_{\parallel}$ and compare the value with three times the value of $\Delta \epsilon'$ for unoriented material, i.e., $(\Delta \epsilon')_{\text{unoriented}}$. The value of $\Sigma \Delta \epsilon'$ for extruded rod of LLDPE for the α peak is 0.0353 whereas the value of $(\Delta \epsilon')_{\text{unoriented}}$ is 0.042. Hence the α process shows a decrease in $\Sigma \Delta \epsilon'$ of about 20%, which would be caused largely by immobilization of dipoles. The α process shows an increase in $\Delta \epsilon'$ in the extrusion direction caused by orientation. In studies of extruded rod of linear polyethylene (Boyd and Yemni, 1979), where the dipoles were carbonyl groups, the relaxation strength was increased in the opposite way, i.e., perpendicular to the extrusion direction. These analyses basically confirm the conclusion that the dipoles are quite different in origin.

5.1.2 The β Peak

The β process is the largest relaxation process in LDPE. It is usually regarded as symptomatic of the glass transition process. The β peak observed in LLDPE is very small and quite uncharacteristic of low-density polyethylene. Dielectric and mechanical relaxation studies (Willbourn, 1958; Tobolsky et al., 1961; Boyer, 1963, 1973; Davis and Eby, 1973) reported earlier in the literature had raised arguments on the location of the glass

transition of polyethylenes. Boyd (1984), analyzing mechanical relaxation data in the literature, has found that the β relaxation process is sensitive to the crystallinity of linear polyethylene. He suggested that the β relaxation is indeed the glass transition temperature of semicrystalline polyethylene.

In the study of oxidized polyethylene, (Ashcraft and Boyd, 1976) the active groups are quite large and could not fit into the polyethylene crystal, thereby producing a loss magnitude which was high and not proportional to the amorphous content. In the case of uniaxially stretched film, the β loss peak has increased somewhat from that of unoriented LLDPE. From the dielectric data of Figures 4.18 (page 116) and 4.19 (extruded rods, (page 117)), it is readily apparent that the magnitude of the β peak is larger in the direction perpendicular to the stretch direction. Although enhancement of the peak in the normal-to-stretch direction occurred in stretched sheets, the magnitude of the effect was not as large as observed in the direction perpendicular to the extrusion direction.

The β relaxation process is essentially conventional in its response to orientation effects in that both the stretched sheet and extruded specimens show an increased magnitude of the relaxation normal to the stretching direction. The β process is influenced considerably by orientation. The value of $\Sigma \Delta \epsilon'$, i.e., $2(\Delta \epsilon'_{\perp}) + \Delta \epsilon'_{\parallel}$ is equal to 0.166 for the process, a drop of almost 50% (compared to $3(\Delta \epsilon')_{\text{unoriented}} = 0.312$), indicating the immobilization of large numbers of dipoles. There is also some anisotropy in the Cole-Cole

parameter since the distribution is slightly narrower for the extrusion direction but considerably broader for the perpendicular direction. So although the process appears to show conventional behavior from a qualitative standpoint, the large fraction of immobilized dipoles is an important new development for the relaxation process.

5.1.3 The γ Peak

The γ peak is located near -120°C having a dielectric loss of 1.2×10^{-4} at 10 Hz in unoriented LLDPE which increases by almost 50% in magnitude when it is stretched. This change is undoubtedly due to the orientation of dipoles. In the case of solid-state extruded rods, it is apparent from Figures 4.18 and 4.19 (pages 116 and 117) that the magnitude of the γ peak is larger in the direction perpendicular to the extrusion direction. The γ process is conventional in its response to orientation in that both the stretched sheet and extruded specimens show an increase in the magnitude of the relaxation normal to the stretching direction. Of course, the γ relaxation process is influenced by the orientation, but not as much as the α and β processes. The γ process shows an orientation effect, but the value of $\Sigma\Delta\epsilon'$ (see Table 4.2, page 111) is unchanged within experimental error, showing a lack of dipole immobilization. In the work of Boyd and Yemni (1979) the γ process was scarcely affected by orientation.

The activation energy for the γ process calculated from the Arrhenius plot (see Figure 5.2) is in the range of 9 to 15 kcal/mole

for LLDPE whereas the activation energy for the γ relaxation in LDPE has been reported to be 10.8 to 16.8 kcal/mole by Ashcraft and Boyd (1976), 11 kcal/mole by Boyd and Yemni (1979) and Mikhailov (1957). Even though the dipoles in the sample are somewhat different in character from those reported earlier by others, the activation energies obtained here for the γ process are, nevertheless, close to those reported in the literature.

5.2 Dielectric Relaxation Studies of LLDPE Containing Aromatic Molecules

Although the dielectric behavior of polyethylenes has been well known for many years, there are relatively few studies of polyethylenes containing polar solutes. Dielectric relaxation is of considerable importance in probing polymer structure. Dielectric relaxation is based on the measurement of the polarization due to orientation of permanent dipoles induced in a polymer by an externally applied electric field. Polyethylene is a non-polar material but the presence of polar molecules would be expected to give rise to dielectric losses in particular regions of the frequency-temperature plane. The locations of the aromatic molecules in oriented polyethylene can be studied with the help of dielectric relaxation. The permanent dipoles of aromatic molecules would be expected to behave differently if they reorient in an oriented substrate. The number of dipoles participating in the relaxation processes of unoriented and oriented polyethylene can

give quantitative information regarding the fraction of molecules which is immobilized. If the molecules behave differently in unoriented and oriented polyethylene, their dielectric behavior would show the difference immediately. Dielectric relaxation studies here have concentrated on two aromatic compounds, namely acridine and 9-bromoanthracene.

Acridine is used in this study as representative of symmetrical fused ring compounds. From the earlier studies of Jang et al., (1982) and Thulstrup and Michl (1980), it is known that symmetrical fused ring compounds are able to orient in oriented polyethylene with their long axis aligned along the direction of orientation (i.e., with the chain axis of polyethylene). Acridine contains three linearly fused rings and differs from anthracene in the substitution of a nitrogen atom for a carbon-hydrogen pair in the central ring (despite this substitution planarity is retained). The replacement of carbon by nitrogen in an aromatic system may be expected to cause only a small perturbation of a system and thus a simple molecular-orbital treatment should be valid. The substitution of a nitrogen atom in the central fused ring induces a permanent dipole moment in a direction perpendicular to the long axis of the molecule and in the plane of the ring. Hence, acridine retains the planarity of a fused ring structure and at the same time the presence of a permanent dipole allows its behavior to be studied dielectrically.

Another compound used in the dielectric relaxation studies is 9-bromoanthracene. Both acridine and 9-bromoanthracene consist of three linearly fused rings but differ in their substitutions. 9-bromoanthracene has a bromine atom attached to the central fused ring. In 9-bromoanthracene a carbon-bromine pair is substituted for a carbon-hydrogen pair in the central fused ring whereas in acridine a nitrogen atom is substituted for a carbon-hydrogen pair in the central fused ring. In spite of the difference in molecular structure, these two molecules have their dipole moments in the same direction, i.e., in the direction perpendicular to the long axis of the molecule. The reason for this choice was to investigate the perturbing effect of a bromine atom on orientation. It is known from spectroscopic experiments that acridine molecules orient very well in oriented film and its orientation behavior in stretched film has been studied by Thulstrup and Michl (1980) whereas 9-bromoanthracene does not show orientation in oriented polyethylene. The effects of molecular size and shape on activation energies, relaxation magnitudes, peak temperatures and the loss magnitudes for both the solute molecules in polyethylene are discussed in this chapter.

The potential adsorption sites in linear low-density polyethylene can be investigated through the dielectric relaxation behavior of dipolar aromatic solutes in polyethylene. When dipolar organic solutes are added to polyethylene, we would expect the β and/or γ relaxation processes to be intensified if the molecules are

present in the amorphous phase. The locations of the peaks depend on the molecules dissolved in LLDPE. For both the solutes studied here, the magnitude and the location of the γ relaxation process is affected much more than the β and α processes. Since the γ relaxation process is usually regarded as local segmental motion of polymer chains in the amorphous region, changes in the peak position reflect changes in the onset of motion.

Activation energies obtained from Arrhenius plots ($\log f_{\max}$ vs. $1/T$) are an indication of how difficult it is for the molecules to reorient under an applied electrical field. The activation energy is dependent on the molecular size and shape. Larger molecules need to sweep out larger volumes, hence they have higher activation energies (Davies and Edward, 1967; Tay and Walker, 1975). Planar and flexible molecules are easier to reorient than larger molecules; hence, they have lower activation energies (Jang and Phillips, 1983). The dielectric relaxation processes are greatly dependent on the rotational volume (i.e., volume to be swept out) of solute molecules, the size and the shape of the molecules.

5.2.1 Acridine

Acridine is a rigid planar molecule having three linearly fused rings and differs from anthracene in the substitution of nitrogen atom for a carbon-hydrogen pair in the central ring. It has a dipole moment in the molecular plane and perpendicular to the long axis.

For unoriented LLDPE, the dielectric loss curves of a specimen containing 0.17% by weight of acridine are presented in Figure 4.36 (page 139). Clearly the β and γ processes increase in magnitude whereas the α process is unchanged. Data for the stretched film containing 0.183% acridine are presented in Figure 4.41 (page 145). It can be seen that the β and γ loss processes are reduced relative to the unstretched film, whereas the α peak is unaffected. The magnitudes and the locations of the γ and β processes are affected when the stretched film contains acridine molecules. The peak positions of the β and γ loss processes of LLDPE containing acridine are shifted which could mean that there might be plasticization of molecules in the amorphous phase. It is apparent that the magnitude of the γ loss process is affected more than that of the β process. Indeed, the relative magnitudes for stretched to unstretched film are 0.68 and 0.75 for the γ and β processes, respectively. The activation energy of the γ process of LLDPE containing acridine is very close to that of LLDPE, whereas the activation energy for the β process has decreased.

The use of solid-state extruded rod with acridine molecules permits the acquisition of dielectric data parallel and perpendicular to the orientation direction. Dielectric spectra are presented in Figure 4.46 (page 159) and 4.51 (page 167), where it is apparent that the magnitudes of the γ and β peaks have increased compared to LLDPE. For similar concentration of acridine molecules, the γ peak is increased by 67% for a specimen of extruded rod having

the electric field parallel to the extrusion direction, whereas it is increased by only 23% for a specimen of extruded rod having the electric field perpendicular to the extrusion direction. For the β peak, the increase in magnitude is 12% for a specimen having the electric field parallel to the extrusion direction and 7% for the direction perpendicular to it. Orientation of the polyethylene by stretching as well as by solid-state extrusion does not produce a proportional increase in the magnitude in the direction normal-to-orientation. This means that a large fraction of dipoles are placed in an immobile location and/or dipole moments have a component in the chain direction.

The number of molecules participating in relaxation processes calculated as described earlier are shown in Table 4.10. Only a fraction of the molecules dissolved in the polyethylene matrix were detected. As will be discussed later, this may be due to the orientation of acridine molecules, the formation of microcrystals, as the adsorption of the acridine molecules on the polyethylene crystallites, or even a combination of these processes.

It is most likely that the β process is associated with the motions of the bulk amorphous phase between the crystals in the fibrils and not with the interfibrillar amorphous phase since the oriented chains will require a high temperature for the onset of motion. This can be confirmed by Arrhenius plots of the β and γ processes which show that the activation energy is unchanged by orientation. From this, it is evident that the chances of oriented

amorphous phase in its glassy state associating with the aromatic molecules to give rise to a new molecular state are quite unlikely.

It is quite evident from the dielectric loss data that there are two temperature regions in which acridine molecules begin to reorient under the action of an electric field. The high temperature region (approximately -20°C) of these two is associated with the glass transition of the amorphous polyethylene. According to Boyer (1973) and Kumler and Boyer (1976) the glass transition of polyethylene lies between -50 to -80°C and that the β and γ relaxation processes are both reflections of it. Boyer has also shown using ethylene-propylene rubber (EPR) that organic molecules containing free radicals when added to polyethylene librate in this temperature range. The γ process as observed here is in the same temperature range and hence it should be a reflection of the lowest temperatures at which the solute molecules present in the amorphous phase have enough energy to allow them to rotate. This also indicates that molecules will not reorient until the glass transition temperature of polyethylene matrix is attained and the environment becomes flexible enough for them to move easily. It is quite likely that rotation of the molecules at low temperature in a more rigid, constrained environment is more difficult. Acridine is a planar molecule without any flexibility and certainly requires a flexible environment for motion. This can be possible only at higher temperature where the β process dominates. The number of molecules able to move and contribute to the dielectric relaxation

is proportional to the temperature. At higher temperatures, more molecules are free to move.

The loss in the intensity of the γ process with orientation is caused because a small fraction of acridine molecules is participating in the relaxation process. This also indicates that a fraction of the molecules are removed to an alternative site, and hence no longer able to relax in the γ region.

This shows that although a fraction of molecules remained in the amorphous phase of oriented polyethylene, a large fraction is no longer able to reorient and hence becomes immobilized by the orientation of polyethylene. This immobilization could arise from several possible causes:

1. aromatic molecules are adsorbed on the polyethylene crystal with a preferential orientation rendering them undetectable dielectrically;
2. immobilized molecules are present in the form of microcrystals which are grown epitaxially on the planes of polyethylene crystals exposed during yielding process (i.e., (110) and (100) planes) because of lattice matching and interaction of the polyethylene chain and the planar aromatic molecules;
3. immobilized molecules may be crystallizing randomly on the lateral surfaces of polyethylene crystals.

The most likely alternative site for the immobilized molecules is the lateral surfaces of the polyethylene crystals. If the change

in intensity of the γ process is a result of orientation, it should lead to the conclusion that adsorbed molecules are preferentially oriented with respect to the polyethylene crystals. It will produce the observed orientational effects for acridine molecules provided that the adsorption sites are anisotropic in shape and have a major axis parallel to the molecular axis of the polymer chain.

The γ relaxation process observed here occurs in the amorphous state. The loss in magnitude of the process may be caused by molecules that would otherwise be in the γ -amorphous region, crystallizing on alternative sites. These alternate sites are most likely polymer crystal surfaces, where reorientation of the solute molecules could not occur unless the melting point were approached. Indeed, thermal analysis of the oriented LLDPE containing acridine molecules shows this behavior. In oriented specimens (stretched or extruded) containing acridine molecules, the melting point of the acridine crystals can be discerned (in spite of it being very close to the melting point of LLDPE) as is the phase transformation of acridine crystals (see Figures 4.29 (page 130) and 4.35 (page 138)). Hence the supposition of acridine molecules crystallizing is confirmed by thermal analysis. This also explains why a fraction of the molecules in oriented specimens are not detected in dielectric relaxation studies.

The values of the relaxation magnitudes ($\Delta\epsilon'$) were determined using the Williams' plots and are presented in Table 4.6 (page 153). The way to check for immobilization or orientation of the dipoles

dissolved in polyethylene is to calculate $\Sigma\Delta\epsilon' = 2(\Delta\epsilon'_\perp) + \Delta\epsilon'_\parallel$ for extruded LLDPE, and compare the value with three times the value of $(\Delta\epsilon')_{\text{unoriented}}$. The γ process shows an increase in $\Delta\epsilon'$ in the extrusion direction caused by orientation and a decrease in $\Sigma\Delta\epsilon'$ of about 20%, which would be caused largely by immobilization of dipoles. The β process is also affected by orientation. It shows a decrease in $\Sigma\Delta\epsilon'$ of about 50%, which could also be caused by immobilization of dipoles.

The relaxation magnitudes ($\Delta\epsilon'$) shows that the β and γ processes are affected by orientation. At the same time, the β and γ processes are reflections of the amorphous phase in polyethylene. The orientation of polyethylene also produces the oriented amorphous phase. This raises the question whether the population of aromatic molecules present in the oriented amorphous phase are oriented or not. For this reason the orientation of aromatic molecules in oriented amorphous phase needs to be checked. Experiments carried out in this context with the help of crosslinked ethylene-propylene rubber (EPR) revealed that the dichroic ratio of acridine molecules does not increase with the concentration of acridine. Since dichroic ratio is a measure of orientation, the lack of change in it indicates that the aromatic molecules present in the amorphous phase are unoriented. Hence the possibility of molecules being oriented in amorphous phase above the glass transition temperature does not exist. Dielectric experimentation has shown that the aromatic molecules present in oriented amorphous phase (below the glass

transition temperature) are oriented. Hence, it is clear that the aromatic molecules in oriented amorphous phase behave differently above and below the glass transition temperature. The β process shows an increase in $\Delta\epsilon'$ in the direction perpendicular to the extrusion direction but the major effect lies in the comparison of $\Sigma\Delta\epsilon'$ with $3(\Delta\epsilon')_{\text{unoriented}}$. The $\Sigma\Delta\epsilon'$ is decreased by almost 50%, indicating the immobilization of dipoles and subsequently relocation of these dipoles. These immobilized dipoles (molecules) are most likely crystallized on the polyethylene crystals surfaces which are exposed during yielding process. The relaxation magnitudes ($\Delta\epsilon'$) of acridine molecules are presented in Table 5.2. From the comparison of $\Sigma\Delta\epsilon'$ and $3(\Delta\epsilon')_{\text{unoriented}}$, it is possible to separate out the orientation and immobilization effects. Both the γ and β processes show an increased $\Delta\epsilon'$ in the extrusion direction of 20% compared to that in the perpendicular direction. Here, the main effect lies in the β process, in which the $\Sigma\Delta\epsilon'$ shows a decrease of about 83%. This shows that acridine molecules are immobilized and are not able to participate in the dielectric relaxation. This raises the question as to what are the possible sites which makes molecules undetectable dielectrically. The most obvious site would be the crystal surfaces and planes exposed during the yielding of the polymer. These exposed planes would provide the sites for solute molecules to crystallize. In polyethylene, the planes exposed during yielding are (110) and (100).

Table 5.2. Relaxation Magnitudes ($\Delta\epsilon'$) for Acridine from Williams' Equation.

	Unoriented	Stretched Sheet	Extruded Rod	
			" to Extrusion Direction	⊥ to Extrusion Direction
β	0.031	0.0042	0.0061	0.0048
γ	0.0087	0.0023	0.0075	0.0057

$3 (\Delta\epsilon') \text{ unoriented}$		$2 (\Delta\epsilon'_\perp) + \Delta\epsilon'_\parallel$
β	0.093	0.0157
γ	0.0261	0.0189

5.2.2 9-Bromoanthracene

Each solute molecule, being different in shape, size, dipole moment and orientability, may show different dielectric behavior when dissolved in oriented polyethylene. To study the orientation behavior of aromatic molecules in polyethylene it is necessary to compare the dielectric data of polyethylene containing solute molecules having different behavior, i.e., those molecules which are able to orient and those which are not. It is known from spectroscopic studies that acridine molecules are able to orient in oriented polyethylene whereas 9-bromoanthracene molecules do not show orientation in oriented polyethylene. The dielectric behavior of polyethylene containing acridine molecules was discussed in the previous section and the dielectric behavior of polyethylene containing 9-bromoanthracene will be discussed in this section.

The activation energy of the γ process in the present case, being about 25 kcal/mole, is considerably larger than that of LLDPE (approximately 10 kcal/mole). This result indicates that the activation energy is related to the volume of solute molecules. About 50% of the dissolved molecules are not detected by the dielectric relaxation. 9-Bromoanthracene is a large molecule, therefore, the volume to be swept out for orientation (reorientation volume) is comparatively larger if the mechanism involves spinning about the long axis. A possible explanation for the high activation energy is that the molecule has a bromine atom projecting out of the rigid planar aromatic rings, which causes more hindrance to

rotation; moreover, the volume that needs to be swept out during rotation is relatively large. For the same reason it becomes difficult for 9-bromoanthracene molecules to reorient when the substrate polyethylene is oriented. Because of the presence of the bulkier bromine atom, it becomes more difficult for the molecules to relocate on the lateral surfaces of the polymer crystals.

The relaxation magnitudes ($\Delta\epsilon'$) are obtained by constructing Williams' plots and are presented in Table 4.9 (page 161) along with the values of $\Sigma\Delta\epsilon'$ and $3(\Delta\epsilon')_{\text{unoriented}}$. For the γ process, the values of $\Sigma\Delta\epsilon'$ and $3(\Delta\epsilon')_{\text{unoriented}}$ are comparable within the experimental error, whereas for the β process there is a decrease in $\Sigma\Delta\epsilon'$ value by about 20% due to immobilization of dipoles. The relaxation magnitudes ($\Delta\epsilon'$) were also obtained for 9-bromoanthracene by constructing the Williams' plots and obtained values are tabulated in Table 5.3 with the values of $\Sigma\Delta\epsilon'$ and $3(\Delta\epsilon')_{\text{unoriented}}$. Thus it is possible to see the effect due to 9-bromoanthracene molecules on the relaxation magnitudes. The $\Sigma\Delta\epsilon'$ of the β process shows a decrease of 9% whereas in the case of acridine, for almost similar concentration, the decrease was 83%. This indicates very clearly that most of the 9-bromoanthracene molecules present in oriented polyethylene are not relocated to an alternative site, such as the lateral surfaces of polymer crystals. It also demonstrates that the fraction of 9-bromoanthracene molecules participating in relaxation processes in unoriented and extruded rod of LLDPE are similar, hence the chances of relocating these molecules to possible

Table 5.3. Relaxation Magnitudes ($\Delta\epsilon'$) for 9-Bromoanthracene from Williams' Equation.

	Extruded Rod		
	Unoriented	" to Extrusion Direction	" to Extrusion Direction
β	0.04	0.037	0.0415
γ	0.0103	0.0076	0.0097

$3 (\Delta\epsilon')$ unoriented $2 (\Delta\epsilon'_I) + \Delta\epsilon'_II$		
β	0.120	0.1095
γ	0.031	0.027

alternative sites are negligible. Similar values of $\Sigma\Delta\epsilon'$ and $3(\Delta\epsilon')_{\text{unoriented}}$ of 9-bromoanthracene suggest that the number of dipoles participating in the relaxation processes are unaffected by the orientation process. The values of $\Sigma\Delta\epsilon'$ and $3(\Delta\epsilon')_{\text{unoriented}}$ of 9-bromoanthracene are very close which is indicative of the fact that most of the 9-bromoanthracene molecules failed to relocate on orientation of polyethylene.

This study with the aid of 9-bromoanthracene demonstrates that similarly shaped large molecules having dipole moments in the same direction have different dielectric behavior when some geometrical asymmetry is introduced.

5.3 Orientation Mechanisms

The phenomenon of orientation of anisotropically shaped aromatic molecules by oriented polyethylene has been known for sometime. It is generally accepted that complete orientation is never achieved and that there are oriented and unoriented fractions present. Obviously, the unoriented molecules must be found in the amorphous regions of semicrystalline polyethylene; however, a controversy exists regarding the location of the oriented molecules. Yogeve and co-workers (1969, 1973, 1977, 1978) suggested that these molecules are present in the polyethylene crystals. The orientation mechanism must involve the polyethylene crystals in some way but the possibility of aromatic molecules being present inside the polyethylene crystals was ruled out (Jang et al., 1982).

A surface adsorption mechanism was proposed by Konwerska-Hrabowska et al. (1973, 1978, 1981). Based on the similar zig-zag pattern of host (polyethylene) and guest (aromatic solutes) molecules and also the experimental results, they proposed that the solute molecules are adsorbed on the surface of polyethylene.

As described in the previous section, acridine molecules are present in the amorphous phase as evidenced by the presence of the γ and β loss processes. The γ process is caused by the libration of the solute molecules at a temperature where the polymer chain becomes flexible on the scale of local segmental motion in the amorphous phase. For a similar concentration, the presence of γ loss process of reduced magnitude in oriented film showed that although a fraction of molecules remained in the amorphous phase of the oriented polymer, a large fraction of acridine molecules were no longer able to reorient and hence were immobilized by the orientation process. Similar behavior was also observed by Jang et al. (1982) when 1-bromonaphthalene was dissolved in oriented polyethylene. The study carried out using extruded rod also revealed that a large fraction of dipoles are immobilized. This behavior can be caused by strong surface adsorption or surface crystallization. These possible mechanisms were tested with the help of other techniques.

Earlier work on this subject has concentrated on dichroic ratios from ultraviolet and infrared spectroscopy. Such studies have been restricted to low solute concentrations in order to study

isolated molecules and have shown that the dichroic ratios of solute molecules rarely approach those of the polyethylene. When extended to higher concentrations, infrared studies of the 956 cm^{-1} band of acridine, typical of the long axis of the molecule, show a dichroic ratio which increases with concentration (see Figure 4.30, page 132). This result could indicate a better orientation of individual molecules or an increasing fraction of oriented molecules if a two-state model is assumed. In the latter case, two realistic possibilities exist which are (1) an increasingly large fraction of the surface area of polyethylene crystals is being covered with adsorbed oriented molecules or (2) solute crystals are growing epitaxially on the surface of the polymer crystals. A concentration of solute molecules even less than 0.1% is sufficient to provide monolayer coverage of the polyethylene crystal surfaces. This has been worked out using the adsorption model for crystal surfaces (Phillips, 1982). In the present case, the concentration of acridine molecules is a few percent and it was demonstrated that dichroic ratio increased with concentration. If aromatic molecules are crystallizing randomly on the lateral surfaces of polyethylene crystals, then dichroic ratio will not increase with the concentration, but that is not the case here. Hence, this possibility is eliminated. This means that the dichroic ratios of acridine molecules increase even after the monolayer coverage of polyethylene crystal surfaces. In other words, orientation of aromatic molecules occurs not only at the monolayer stage but also way beyond monolayer

coverage. This could be possible only if an oriented phase was produced. The most likely phase would be acridine crystals formed on polyethylene crystal surfaces in an epitaxial manner. At this stage, it is necessary to test whether the aromatic molecules are able to associate in oriented polyethylene or not, using ultraviolet spectroscopy. Ultraviolet spectra are sensitive to association, becoming smeared when microcrystals are formed. For unstretched spherulitic polyethylene, the spectra are sharp and well resolved even for relatively high solute concentrations of acridine whereas for stretched sheets, they become smeared for concentrations in excess of 0.15% by weight of acridine. This leads to the obvious conclusion that acridine molecules are able to associate and probably crystallize in oriented polyethylene yet remain isolated in the spherulitic polymer. In a similar ultraviolet spectroscopic study of 9-bromoanthracene the spectra are sharp and well resolved even up to 3.5% concentration in stretched film. Because of the bulkier bromine atom sticking out of a plane fused ring structure, 9-bromoanthracene does not behave like a rod. The presence of the bromine atom makes this molecule behave differently from other fused ring molecules which is reflected in its having different orientation behavior. Apart from this, it is evident from the spectroscopic study that 9-bromoanthracene molecules do not associate in oriented polyethylene as do acridine molecules. This also explains why these two molecules behave differently in dielectric relaxation studies.

When aromatic molecules such as acridine are dissolved in oriented LLDPE, the aromatic crystals and polyethylene crystals are separate entities with a preferred interface for crystal growth. The only common property between them is the orientation of the molecules, which should be maintained until the melting temperature of polyethylene or of the aromatic crystal is approached. A clear resolution of the mechanism between the alternatives of epitaxial crystallization and associated solute adsorption would be the detection of solute crystals using a conventional technique such as differential scanning calorimetry. Acridine shows two transitions (a melting point and a crystal transformation), the crystal transformation of acridine being from the monoclinic to the orthorhombic crystal form. The melting point of acridine is close to that of polyethylene, however, the crystal transformation has a much larger latent heat and is easily detected. Oriented polymer shows the crystal transformation and a hint of acridine melting (see Figure 4.29, page 130). The use of extruded rod polyethylene, which is known to orient molecules better than the stretched polymer produces very clear evidence of crystal transformation and even the melting of the acridine crystals can be discerned very close to the main polyethylene peak.

There are, therefore, several pieces of information consistent with orientation of acridine through the growth of crystals on the surfaces of polyethylene microfibrillar crystals.

Since the molecules are fixed here with respect to the polyethylene crystals, obviously, their dipoles are fixed and hence this fact will be reflected as a loss in the number of molecules being detected through conventional dielectric relaxation processes. Hence the earlier supposition that solute molecules are orienting through the growth of crystals on polyethylene crystals must be true. There is a report on crystal growth of polyethylene on anthracene crystals through epitaxial crystallization (Wittmann and Lotz, 1981a). Since anthracene and acridine molecules are very similar in their molecular structure and the arrangement of molecules in their crystal structure, it is quite possible that they are functioning through an epitaxial crystallization mechanism.

Earlier in the literature, epitaxial crystallization on to various substrates has been reported (Fischer, 1958; Williams, 1950, 1959, 1967; Fischer and Williams, 1966; Koutsky, 1966; Geil, 1960; Carr et al., 1970). These above mentioned references deal with systematic investigations of epitaxial crystallization on inorganic substrates. Recently, the epitaxy of polymers on crystals of organic compounds has been considered (Rickert et al., 1978; Wittmann and Manley, 1977, 1978; Wittmann and Lotz, 1981a, 1981b). Several studies of epitaxial growth of polymers on foreign crystal substrates have been reported by Wunderlich (1973). The condition for epitaxial growth of polyethylene as well as for many other polymers is lattice matching (Mauritz et al., 1973). Hence, epitaxial growth of polyethylene on aromatic substrates will occur

only on certain growth planes and is highly specific in nature. Polyethylene is known to crystallize epitaxially onto crystals of homologous series of (1) condensed aromatic hydrocarbons like naphthalene, anthracene, phenanthrene and (2) linear polyphenyls like biphenyl, p-terphenyl and quaterphenyl (Wittmann and Lotz, 1981a). Polyethylene crystallizes epitaxially on single crystals of fused ring aromatic compounds and the growth planes of polyethylene were found to be (100) or (110).

In the case studied here, all the results from spectroscopic and thermal analysis are consistent with the epitaxial growth of acridine microcrystals on the surfaces of the microfibrils of oriented polyethylene. Why should this be? The reason for this lies in the fact that the anthracene molecule is structurally very similar to acridine and is known to be oriented effectively by stretched polyethylene (Thulstrup and Michl, 1980). Anthracene serves as an excellent nucleating agent for polyethylene and it has been shown (Wittmann and Lotz, 1981a) to function as such through an epitaxial growth mechanism. In their study, a very thin film of polyethylene was obtained on glass slide by drying a dilute solution in p-xylene, thin crystals of aromatics were then deposited on the dried polyethylene film, and the polyethylene film was then melted and recrystallized. The growth occurs through deposition of polyethylene molecules on the (001) face of anthracene single crystals because of lattice matching. Aromatic molecules exhibiting crystal packing similar to that of anthracene in the (001) plane

also serve as nucleating agents. This phenomenon was shown to occur because the spacing in the (001) plane is determined by the stacking of the aromatic fused rings resulting in a constant molecular spacing despite major changes in molecular structure. Since anthracene and acridine both consist of three linearly fused rings and differ only in the substitution of a nitrogen atom for a carbon-hydrogen pair in the central ring (planarity of the molecule is being retained) it would be a reasonable supposition that the two molecules should behave in a similar manner. The study referred to above considered only the large (100) faces of the polyethylene crystals produced by the match with anthracene.

The work carried out with acridine in a similar fashion produces epitaxial growth of polyethylene on the (001) faces of single crystals of acridine. The polyethylene reflections in Figure 4.71 (page 194) correspond to a superposition of two diffraction patterns rotated by an angle of ca. 56° . This angle of 56° corresponds in fact to the angle made by $[110]$ and $[\bar{1}\bar{1}0]$ directions in the ab plane of acridine, i.e., in the contact plane with polyethylene. The polyethylene molecules are oriented parallel to the $[110]$ and $[\bar{1}\bar{1}0]$ directions of the acridine crystal. The 110 inter-row distance of acridine molecule is $5.298 \text{ \AA}$ which is close to the b -axis repeat distance of $4.94 \text{ \AA}$ for the polyethylene provides the lattice matching required for the epitaxial crystallization. In the present case, lattice mismatch for epitaxy was found to be -6.7% . Hence, in this case, the polyethylene chain axis lies

parallel to the acridine surface and the contact plane of the polyethylene with the substrate is (100), and the growth occurs through deposition of polyethylene molecules on the (001) face of acridine crystals because of the lattice matching.

In the present case of epitaxy of polyethylene on acridine, the lattice mismatch (ca. -6.7%) obtained is well within the accepted limits of epitaxy ($\Delta < \pm 15\%$). As mentioned earlier, only certain faces of the crystals are favored for the epitaxial growth, and the growth plane for polyethylene crystals is the (100) plane.

The above mentioned experiments were carried out for polyethylene crystallized on the solution grown single crystal of acridine. The thickness of the single crystals were in the range of 0.002 to 0.007 inches. During the crystallization process of polyethylene on a single crystal of acridine, polyethylene was crystallized on top as well as sides of the crystal. It was possible to obtain the polyethylene films from the sides and top of the crystal. The polyethylene films recovered from the sides and top have different orientations. The polyethylene films recovered from the top and sides of the single crystal of acridine, have (100) and (110) orientations, respectively. Thus, it was possible to obtain polyethylene films having different orientations. This made it possible to study the reverse epitaxy (i.e., acridine on polyethylene) for the two different planes believed to be involved in the epitaxial crystallization process.

When the linear low-density polyethylene is oriented, the incoming aromatic molecules (either in the form of vapor or concentrated solutions in chloroform) crystallize on the polyethylene microfibrillar crystals and assume their orientation. Now the polyethylene crystals become the substrate and the aromatic molecules are growing substances. Again, the growing conditions, crystallization mechanism and resultant growing surfaces should apply here since the dichroic ratio of aromatic molecules continues to increase as a function of their concentration (i.e., way beyond the monolayer coverage).

For investigating this aspect in further detail the reverse epitaxy, i.e., epitaxial growth of acridine on polyethylene, was studied. This corresponded to the case of depositing acridine on the oriented films. For the same purpose, the thin films of polyethylene, which was melted and recrystallized on the single crystal of acridine, was recovered by detaching the films from the sides and top of the single crystal of acridine under vacuum. After ensuring the removal of the original acridine, acridine was vapor deposited onto the thin film. The film recovered from the top of the acridine crystal and having vapor-deposited acridine on it, shows the same behavior as observed earlier, i.e., (100) plane of polyethylene becomes the substrate plane and acridine grows on this plane with (001) being the contact plane of acridine. The films recovered from the sides of crystal were treated in an identical manner. Patterns obtained by depositing the crystals from

the vapor phase give better diffraction patterns than solution grown crystals. In this case, the contact plane of polyethylene with acridine is no longer (100) but is (110). This phenomenon occurs because the aromatic fused rings are stacked vertically with their long axes perpendicular to the (001) plane. Hence, the acridine molecules in their (110) plane are arranged in such a way that their long axes remains perpendicular to the (001) surfaces. This (110) plane of acridine is in contact with the (110) plane of polyethylene in such a way that the polyethylene chain axis lies parallel to the long axes of the acridine molecules. In the present case of epitaxy of acridine on the polyethylene film, the lattice mismatch for epitaxy was found to be 3.4%.

The polyethylene chain axis (c-axis) has a repeat distance of 2.54 Å and the average width of the flat benzene rings of the acridine molecule along the long axis is 2.43 Å which provides the zigzag pattern of the guest and host molecules. It is demonstrated by Lamotte and co-workers (1972, 1974) from energy calculations that this kind of zigzag pattern is one of the most stable forms of arrangement. The fact that epitaxy was discovered for (110) planes of polyethylene with (110) planes of acridine, provides evidence that (110) planes of polyethylene are slip planes. It is also known that (110) planes of polyethylene are essential for epitaxial growth of p-terphenyl (Wittmann and Lotz, 1981a) and for sodium chloride (Fischer, 1958). It is likely that the results presented here provide solid evidence for (110) planes being the dominant slip

planes of bulk polyethylene. Figure 5.3 shows a schematic diagram of the arrangement of polyethylene crystal planes and acridine crystal planes involved in epitaxial crystallization.

The fact that acridine microcrystals could be detected for oriented polyethylene but not for spherulitic polyethylene suggests that there are certain planes exposed during the yielding process and that they provide the site for acridine crystals to grow. It is generally accepted that the growth planes (Hoffman et al., 1972) in polyethylene single crystals are (110), however, conventional crystals resulting from bulk growth show (001) being the fold surfaces and (010) being the lateral surfaces. The uneven fold surface, although a potential adsorption site (but irregular in nature), would not produce epitaxial growth. The predominant exposed surfaces would be the (010) planes which do not produce the required lattice match. The ends of the lamellae would be (110) planes and could serve as sites for epitaxial growth, however, they would correspond to a minute fraction of available lamellar surface producing, at best, an undetectably low fraction of acridine microcrystals. When polyethylene is drawn or extruded, the spherulitic lamellar crystals are believed to be destroyed by a shearing process (see Figure 2.9, page 35) and reconstituted into microfibrils. The exposed surfaces of the microfibrils should be the slip planes. In single crystals of polyethylene the slip planes are known to be (110) and in the bulk (100) have been identified (Young and Bowden, 1974). Although it has never been demonstrated that the slip planes

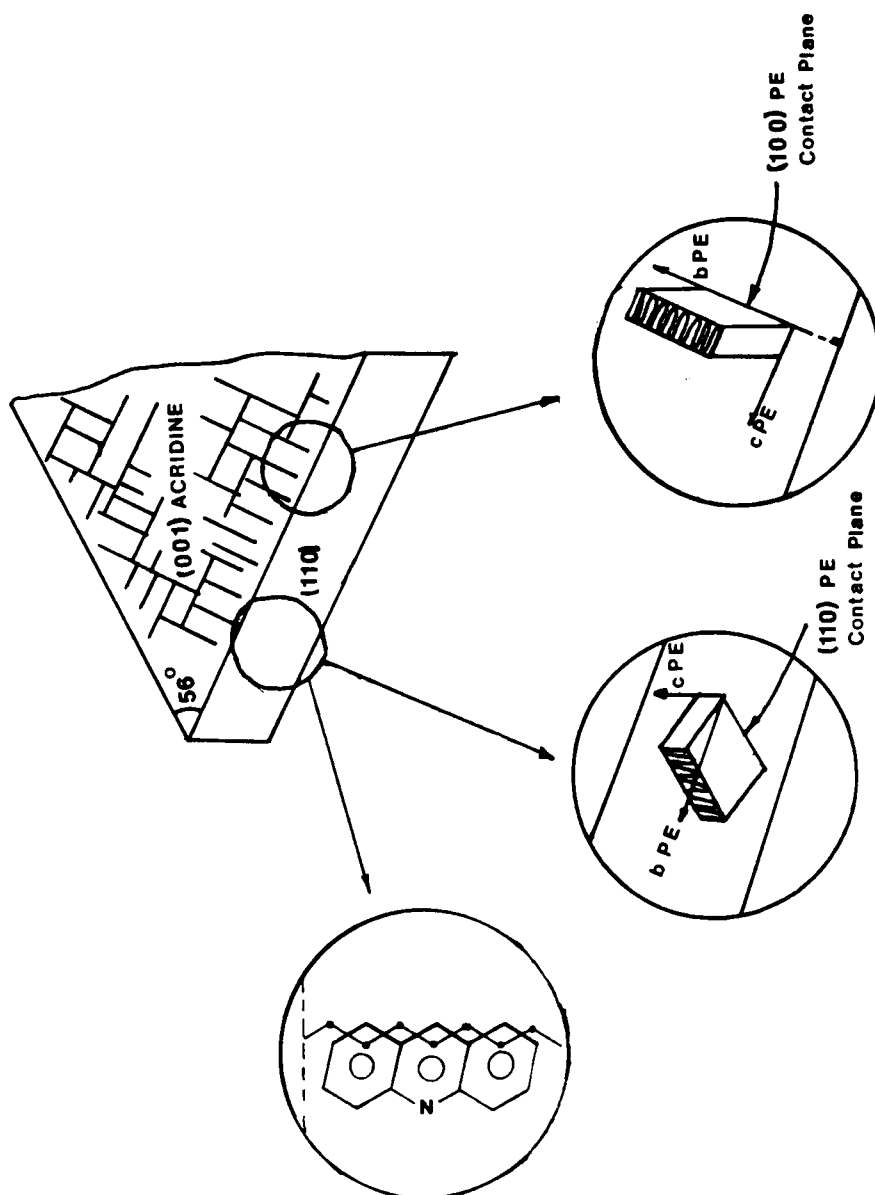


Figure 5.3. Schematic Diagram of the Arrangement of Polyethylene Crystal Planes and Acridine Crystal Planes Involved in Epitaxial Crystallization.

of bulk polyethylene can be (110), such an assumption would not be unreasonable. In a recent study carried out by Boon (1984), it was observed that (110) planes are the slip planes in bulk polyethylene. Shearing in other directions would require breaking of carbon-carbon bonds.

When the (110) planes of polyethylene are in contact with the {110} acridine planes, the acridine molecules lie with their long axis along the polyethylene chain axis and hence the dipole moment of the acridine molecule is perpendicular to the chain axis. When the (100) planes of polyethylene are in contact with the (001) faces of acridine, the molecules lie with their long axes perpendicular to the chain axis and hence the dipole moment of acridine is along the chain axis. At this stage, it is advisable to correlate this fact with the dielectric studies. In the dielectric relaxation studies of LLDPE containing acridine, it appeared that the dipole moment could have a component in the chain direction. In that situation, the dipole moment of the acridine molecule is in the chain direction of the polyethylene crystal and the long axis of acridine is perpendicular to the chain axis of polyethylene. It is known that (100) planes of polyethylene are exposed during the yielding process and the possibility of acridine molecules crystallizing on these planes cannot be ruled out. Now the most likely case is that the long axis of the molecule is aligned with the stretching direction (i.e., C-axis of polyethylene) hence the dipole moment of acridine should be in the direction perpendicular to the molecular chain direction.

This will happen only if (110) or similarly exposed planes are in contact with acridine molecules in such a way that they align themselves in the chain direction. It is possible that a small fraction of (100) slip planes are exposed during stretching compared to (110) planes. But there remains a possibility that acridine molecules are crystallizing on the (100) planes, thus immobilizing a fraction of dipoles in the chain direction. If both the planes, i.e., (100) and (110) planes, are exposed during the yielding process, then it raises the question of what are their relative fractions. There is no quantitative study in the literature on this aspect. To carry out this analysis, the dichroic ratios of the polyethylene crystalline and amorphous phases and that of acridine are used along with the fraction of molecules detected dielectrically.

Acridine molecules are present in the amorphous phase and on the exposed crystal planes of polyethylene (i.e., (100) and (110) planes). Hence it can be given as follows:

$$V_{\text{amorphous}} + V_{110} + V_{100} = 1 \quad (5.1)$$

Where $V_{\text{amorphous}}$ represents the fraction of molecules in the amorphous phase which would be the fraction obtained from dielectric relaxation studies. This fraction can be calculated using the ratio of $(2\Delta\epsilon'_{\perp} + \Delta\epsilon'_{\parallel})/3(\Delta\epsilon')_{\text{unoriented}}$, integrated over the β and γ relaxation processes. This fraction is 0.56 for the case of acridine. V_{110} and V_{100} represent the fractions of acridine

molecules on the (110) and (100) planes exposed during the yielding process, respectively.

Knowing the dichroic ratios of the crystalline and amorphous phases of polyethylene and the dichroic ratios of acridine we can set up another equation

$$\Delta_{\text{acridine}} = V_{110} (\Delta_{\text{PE}}) + V_{100} (-\Delta_{\text{PE}}) + \Delta_{\text{amorphous}} \quad (5.2)$$

Where Δ_{acridine} is the dichroic ratio of acridine at a particular concentration in the stretched film. V_{110} and V_{100} are the fractions of (110) and (100) planes exposed. Δ_{PE} is the dichroic ratio of the polyethylene crystals and $\Delta_{\text{amorphous}}$ is the dichroic ratio of the amorphous phase.

By solving these two equations simultaneously, one can obtain the fractions of (110) and (100) planes. For 500% stretched film, the percentage of (110) planes exposed is 80.3% and the percentage of (100) planes exposed is 19.7%. It has been known for some time that both the (110) and (100) planes are exposed during yield but this analysis provides the first estimate of the actual relative areas of each plane. Hence, in the system LLDPE-acridine, both (100) and (110) planes of polyethylene play an important role in epitaxial crystallization.

It is shown here that polyethylene molecules are able to crystallize epitaxially on acridine and acridine molecules are able to crystallize epitaxially on (110) and (100) planes of polyethylene.

The broader question can be raised on whether the effect observed is solely due to adventitious lattice matching of the two components or whether the solute molecules are trying to enter the polyethylene crystals. Is it just oriented overgrowth on the substrate surface under controlled environment or does there exist a favorable interaction between the solute molecules and the polyethylene chain? Are these components wanting to co-crystallize? The question can be answered by having the phase diagram over the entire range of composition of both components.

Low molecular weight materials play a major role in altering various properties of polymeric materials when they are used as additives. Such additives are plasticizers, ultraviolet absorbers, antioxidants, fire retardants and others. In spite of their technological interest and scientific importance little attention has so far been paid to systems of polymer and low molecular weight crystalline additives, their structure and properties.

Aromatic molecules can be introduced into polymers in two ways (1) by diffusion into the solid polymer and (2) by blending in melt. There are a large number of articles in the literature on diffusion of aromatic molecules into stretched polyethylene where the molecules can become as highly oriented as the polymer crystals themselves. Direct blending of the polymer and aromatic molecules has received little attention until recently. After comelting of polymer with solute molecules, the molten solution is then quenched or cooled slowly to room temperature and melting endotherms of these

thermally treated samples are used to construct the binary phase diagram. These phase diagrams are helpful in understanding the interaction of polyethylene and organic compound over the entire range of composition.

Recently, the preparation and properties of binary eutectic systems in which at least one of the components is a polymer have received some interest. Some of the well studied systems of polymer and low molecular weight organic compound are: polyethylene and 1,2,4,5-tetrachlorobenzene (Smith and Pennings, 1974), polyethylene and phenanthrene (Ke, 1961), polyethylene and 1,3,5-tribromobenzene (Hodge et al.; 1982) poly(ϵ -caprolactone)-trioxane (Wittmann and Manley, 1977a) poly(ethylene oxide)-trioxane (Wittmann and Manley, 1977b). In most of the above systems the melting point of the polymer was depressed by a few degrees centigrade. One of the necessary conditions for a binary eutectic system is that the melting temperatures of the pure components should not differ appreciably (Smith and Pennings, 1974). This condition is satisfied by polyethylene with a number of organic solute molecules. The in-situ solid-state polymerization of organic molecules on the surface of polymer fibrils offers a possible means of creating a novel type of polymer composite. The system of polyethylene and 1,3,5-tribromobenzene displays both eutectic solidification and oriented growth of the polymer crystals on freshly grown 1,3,5-tribromobenzene needle-like crystals. The polyethylene component of the eutectic assumes a habit in which lamellae are highly oriented

with the chains in the (110) contact plane parallel to the tribromobenzene needle axis. This well defined orientation is most probably based on the epitaxial relationship between polymer and organic compound. Hence, it is obvious that eutectic solidification is very closely related to epitaxial crystallization.

The phase diagram of acridine and LLDPE shows the existence of two different compound crystals, one at 50% acridine-50% LLDPE and the other at 84% acridine-16% LLDPE. Compound crystals of the LLDPE/acridine system produce X-ray diffraction patterns totally different from those of either homogeneous component. X-ray diffraction patterns were also obtained as a function of temperature. These patterns show that there are two totally different crystal structures at the above mentioned compositions. The X-ray diffraction patterns which correspond solely to compound I and compound II are shown in Figures 4.83 and 4.84, (pages 215 and 217) respectively. Since the X-ray diffraction patterns of compound I and compound II are totally different, their molecular organization must be different. These patterns provide solid evidence of a new class of polymer blend which could have different structure and properties. There are few reports in the literature on the existence of co-crystallization in polymer-low-molecular weight organic compound systems. Amongst them are: polyurethane and phenanthrene (Moisya and Semenvich, 1970), polycarbonate and aryl-substituted dye (Dulmage et al., 1978), cellulose acetate fibers and azo dyes (Chaudhuri, 1981) and polyethylene with urea (Yokoyama and

Monobe, 1983). In the work carried out by Dulmage et al. (1978), the crystalline aggregate resulted from crystallization involving polymer and dye. This crystalline complex of the polymer and the dye formed an aggregate as a separate phase having useful electrophotographic applications. Moisy and Semenovitch (1970) proposed two-or-one dimensional ordering of the quasi-crystal by phenanthrene in polyurethane. They also proposed that the necessary condition for the formation of such ordering should be the proximity of crystallographic parameters common to the crystallized substances, a statement itself which can be considered as another way of saying epitaxy.

In the system LLDPE/acridine the phase changes as a function of temperature were revealed by the high temperature X-ray study. As the temperature increases, the orientation of the molecules also changes. It can be seen from the high temperature X-ray data that some of the peaks which are strong at room temperature become less intense at higher temperatures. It is also possible that the molecules are reorganizing within the compound crystals. The phase diagram of phenazine and HDPE also shows the compound crystal formation.

These systems also provide examples of polymer and low molecular weight crystallizable solvent mixtures in which eutectic solidification occurs. It is known from the experiment of epitaxial crystallization that oriented growth of polymer occurs on single crystals of acridine resulting in a highly anisotropic film.

In the crystallization of eutectic polymeric systems the behavior of the polymer cannot be simple because the mobility of macromolecules is important and has to be taken into consideration. The movements of the polymer chains are limited to changes in conformation and it is to be expected that relaxation of the chains plays an important role in the simultaneous crystallization process of the polymer and the organic compounds. The limited mobility of the segments of the macromolecules and the entanglements in such concentrated polymer solutions make the solidification process more complex than it may appear.

In addition to entanglements in the polymer melt and concentrated solutions, there is a possibility of forming metastable folded chain crystals, connected by tie molecules, which grow normal to the face with lowest surface energy. Also the amorphous phase in the semicrystalline polymers gives rise to specific problems in the simultaneous crystallization of a polymer and a low molecular weight organic compound.

Apart from this, it is possible to create a totally new class of material. For example, polymerization of p-terphenyl crystals produces poly(p-phenylene) which is a conductive polymer. Doping of poly(p-phenylene) with AsF_5 increases the conductivity of polymer by 14 times (Schaklette et al., 1979). Variation of dopant (AsF_5) concentration allows the conductivity to be adjusted within a broad range. There is a possibility that polymerization of terphenyl crystals in the presence of AsF_5 will produce poly(p-phenylene)

crystals within the polyethylene film and might produce better electrical and optical properties than those produced by other means.

CHAPTER 6

CONCLUSIONS

Preferred orientation of solute molecules in oriented polyethylene has been known for several years. The mechanism of orientation of solute molecules present in oriented linear low-density polyethylene has been studied here. It constitutes the first detailed study of the mechanism of orientation of aromatic molecules in oriented polyethylene.

Conclusions relating to the orientation mechanisms are as follows:

1. Dielectric relaxation studies have shown that large fractions of the molecules cannot relax and are immobilized.
2. The immobilized molecules are located on the lateral surfaces of the polyethylene microfibrils.
3. The molecules, which are present in the oriented amorphous phase of polyethylene, are oriented only below the glass transition temperature.
4. Different shaped molecules behave differently in oriented polyethylene and the factors which are responsible for their orientation are the planarity of the molecules and the presence of side groups or atoms attached to the condensed fused rings.
5. All spectroscopic and thermal analytical data are

consistent with the epitaxial growth of acridine microcrystals on the surfaces of the crystalline microfibrils of oriented polyethylene.

6. Specific surface adsorption related to the mechanism of epitaxial growth of microcrystals is likely to be the major orienting mechanism for symmetrical fused ring aromatic compounds when present in low concentrations.
7. Polyethylene can grow epitaxially on a single crystal of acridine on the (001) and (110) planes producing polyethylene films having (100) and (110) orientations. Acridine can grow epitaxially on the (110) and (100) planes of polyethylene.
8. The analysis performed in this study provided the first estimate of the relative amounts of (110) and (100) planes of polyethylene exposed during the yielding process by slip processes.
9. The phase diagrams constructed over the entire range of composition of both components revealed that epitaxial crystallization observed in this study is not just due to adventitious lattice matching of the two components but solute molecules are trying to enter the polyethylene crystals. This is because the components are trying to form a compound which is the stable species determined by the phase diagram. The systems acridine/LLDPE and

phenazine/HDPE showed the existence of new molecular compounds.

10. The existence of the two compounds formed in the LLDPE/acridine system were confirmed using high temperature X-ray diffraction studies. The molecules of both the components are able to organize within the compound crystals to give totally different X-ray diffraction patterns of each compound at higher temperatures.

CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

1. To explore the interactions of polyethylene and aromatic molecules in detail, their phase diagrams can be constructed and the systems which demonstrate compound formation can be explored in further detail. Such a compound introduces a totally new class of polymer blend which could have special optical/electrical properties because of the molecular organization within the compound crystals having highly anisotropic properties due to oriented crystallization. Crystal structures of the compounds and their morphologies can be studied. Then selected optical and electrical studies could be performed for appropriate blends.
2. Polymerization of p-terphenyl crystals produces poly(p-phenylene) which is a conductive polymer. Polymerization of p-terphenyl or similar aromatic molecules within the polyethylene film might be possible. This could generate a new route for synthesis of polymers with special properties.
3. Polyethylene forms a ternary solution with isotactic polypropylenes and certain aromatic solvents. Their blending could be of interest because specific deficiencies such as low melting point (of PE) and weak

impact strength (of PP) can be improved. The presence of aromatic molecules would lower the melting points of polymer blend with the reduction of melt viscosity due to the solute molecules which would make processing favorable from an economical point of view. At the same time such a blend would provide better properties as there is going to be anisotropy of solute molecules.

4. It is known that (110) and (100) planes (slip planes) of polyethylene are exposed during the drawing process. A systematic investigation can be carried out to estimate their relative areas as a function of draw ratio by the method used in this study.
5. The structures of the compound crystals should be determined to learn the ground rules covering compound formation in the systems.

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APPENDIX

APPENDIX

CRYSTAL STRUCTURES OF SOME AROMATIC COMPOUNDS

(a) Phenanthrene:

Crystal Structure: Monoclinic

$$a = 8.46 \text{ \AA}$$

$$b = 6.16 \text{ \AA}$$

$$c = 9.47 \text{ \AA}$$

$$\beta = 97^{\circ}7'$$

(b) Pyrene:

Crystal Structure: Monoclinic

$$a = 13.649 \text{ \AA}$$

$$b = 9.256 \text{ \AA}$$

$$c = 8.470 \text{ \AA}$$

$$\beta = 100^{\circ}28'$$

(c) p-Terphenyl:

Crystal Structure: Monoclinic

$$a = 8.08 \text{ \AA}$$

$$b = 5.60 \text{ \AA}$$

$$c = 13.59 \text{ \AA}$$

$$\beta = 91^{\circ}9'$$

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