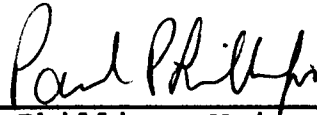


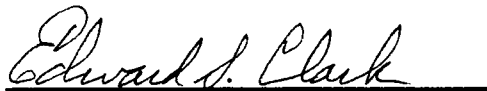
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ENTHALPY RELAXATION PROCESSES
NEAR THE GLASS TRANSITION TEMPERATURE
OF POLY(ETHYLENE TEREPHTHALATE)

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Trishna Ray-Chaudhuri

August 1988

Dedicated to
Mom and Dad

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ABSTRACT

This study attempted to correlate the changes observed in thermal properties with the dielectric properties of poly(ethylene terephthalate) PET glasses. It was of particular interest to examine the effect of annealing below the glass transition temperature (T_g). Several amorphous PET film samples were annealed at various temperatures below the glass transition (70°C). The dielectric spectra showed significant changes in the relaxation occurring in the annealed samples. In addition, volumetric studies of the annealed glasses showed changes in specific volume. In differential scanning calorimetry studies the absorbed thermal energy in the transition interval of annealed PET paralleled the enthalpy relaxation occurring during the annealing process. The spherulite size on crystallization decreased following annealing in the subglass region, as observed by small angle light scattering (SALS). This phenomenon is attributed to an increase in nucleation density. The excess amount of enthalpy and free volume quenched into the glassy systems decreased with sub- T_g annealing, thus bringing the system closer to equilibrium.

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1. INTRODUCTION

There is considerable interest in the structural and property changes that occur in glassy and partially glassy polymers upon annealing below the glass transition temperature (T_g).¹ This aging or time-dependent behavior is often a direct result of the nonequilibrium nature of the glassy state. The phenomenon has been observed in many types of polymer systems containing glassy regions such as purely glassy polymers,²⁻⁴ semicrystalline polymers,⁵ polymeric network glasses⁶⁻⁸ and block copolymers.^{1,9,10} An understanding of this phenomenon is important due to the fact that material performance must be predictable to insure compliance with the design specifications of a product throughout its anticipated service life. Research efforts have stressed two approaches: (1) experimental studies of this phenomenon in various glassy polymer systems,⁴ and (2) development of a quantitative theory capable of predicting aging behavior for a variety of polymer materials under different conditions.¹¹

The aging behavior of glassy polymers (known also as nonequilibrium behavior, enthalpy or volume recovery (relaxation)) results from the inherent kinetic nature of the glass transition. As a polymer molecule is cooled in a normal process from the melt through the glass transition into the glassy state there is a rapid decrease in molecular

mobility which is observed as a sudden increase in viscosity and modulus as the transition temperature is approached. The polymer molecules are not, in fact, able to reach their equilibrium conformation and packing with respect to temperature. As the temperature is further decreased the molecules are essentially "frozen" into a nonequilibrium state of higher energy and volume relative to the corresponding equilibrium state at that same temperature. Since the polymer molecules are in a nonequilibrium state there exists a thermodynamic potential or driving force for them to approach equilibrium by undergoing further packing and/or conformational rearrangement. Although the molecular mobility is decreased drastically in the glassy region compared to the rubbery region, a finite mobility remains allowing the molecules to approach closer to the equilibrium state.

In this type of polymer system two of the measurable thermodynamic state functions, enthalpy and volume, have been found to decrease with sub-T_g annealing time (at a fixed temperature) as the excess enthalpy and volume originally quenched into the system decrease. These changes have been related to changes in the physical and mechanical properties of polymer systems. It has been shown that there is an increase in density,³ tensile and flexural yield stress, and elastic modulus accompanied by a decrease in impact strength, fracture energy, ultimate elongation, and

creep rate.¹² A transition from ductile behavior to brittle fracture can occur.⁶

Dielectric methods have been used extensively to study the relaxation behavior of many polymeric materials.¹³⁻¹⁹ By varying temperature and frequency, one can separate the activation energy and the volume contributions from the activation enthalpy.²⁰

This study attempts to correlate the changes observed in the thermal properties with the dielectric properties of poly(ethylene terephthalate) (PET) glasses in order to gain insight into the mechanisms of annealing below the glass transition temperature, T_g . In addition volume changes were determined, the annealed glasses showing a definite change in the spectrum. Variations in the magnitudes of the relaxation processes and their relaxation time distributions will be discussed in the context of the molecular scale of the changes induced by annealing.

2. LITERATURE REVIEW

2.1. Enthalpy Relaxation

Dielectric methods have been used extensively to study the relaxation behavior of many polymeric materials.^{13-16,18-21} By varying temperature and frequency, one can separate the activation energy and the volume contributions from the activation enthalpy.²² It is of interest to study the limiting effects of pressure on the glass transition temperature, T_g .^{18,19,23,24} Other investigators have attempted to correlate the changes observed in thermal behavior with the dielectric behavior of glasses in order to gain some insight into the implications of the annealing studies.

The influence of annealing processes on the thermal behavior of organic glasses in the glass-transition interval has been investigated and analyzed quantitatively.⁴ In her paper on enthalpy relaxation, Petrie⁴ provided a rationalization and consistent experimental response to observations in glassy polymers. Glasses exhibited excess free energy, annealing a glassy sample producing an enthalpy peak and an increased glass transition temperature T_g when analyzed using differential scanning calorimetry (DSC). DSC studies revealed only an endotherm upon cooling. The influence of the annealing process on the thermal behavior was also analyzed.

The absorption of thermal energy was viewed as a kinetic effect. Petrie⁴ showed that it was not necessary to postulate a first order process, because an abrupt change in enthalpy is a necessary condition for a first order process, but not a sufficient one.

The absorption of thermal energy around T_g paralleled the extent of molecular relaxation that had taken place during the annealing period. Petrie⁴ showed that the enthalpy approach to equilibrium can be followed with differential scanning calorimetry. Analysis of the absorption of thermal energy in the transition interval during the heating cycle of an annealed glass suggested that the amount of free energy absorbed could be accounted for on the basis of the kinetics of the glass transition, and thus paralleled the enthalpy relaxation occurring during annealing. Petrie's studies indicated that the time required for the enthalpy to relax to equilibrium values is extremely long. The enthalpy measured from the DSC peak during the transition is related to the enthalpy relaxation process. With longer annealing periods, more recovery occurred with an increase in the transition endotherm.

To gain further understanding of the modes of molecular motion which contribute to the ductility and the toughness of glassy polymers, and the factors that influence such molecular mobility, a study was conducted to determine the effect of excess volume in glassy poly(ethylene

terephthalate). The mode of failure was observed in tensile tests and on the associated level of molecular motion.¹² The results of tensile stress-strain studies of annealed glassy PET film indicated that there is a relationship between the mode of failure and the level of trapped free volume in the polymer. Further modes of molecular motion in addition to those involved in the subsidiary relaxation processes appeared to contribute to the ductility and toughness of glassy polymers. The dynamic mechanical studies of annealed PET suggested that among the modes of motion that are significant to the ductile behavior of glassy polymers are those that involve limited segmental mobility associated with the glass transition phenomenon.

The dynamic mechanical properties of two glassy polymers, atactic polystyrene and poly(ethylene terephthalate), have been studied as a function of excess enthalpy during isothermal annealing at selected temperatures below their respective glass transition temperatures.²⁵ Glassy polymers (prepared from crystalline as well as noncrystallizable polymers) showed changes in modulus which paralleled the extent of enthalpy relaxation occurring during the annealing period as a result of the nonequilibrium nature of the glassy state. The modulus therefore increased with time and approached a limiting value that increased with decreasing temperature. These results suggested that the observed changes in the dynamic

mechanical moduli were associated with changes in the excess thermodynamic properties of the polymeric glasses, and not with structure formation (other than the normal liquid-like packing of the chain segments). The physical properties for corresponding equilibrium glassy states could therefore, be determined for crystallizable polymers without interference from structure formation.

From FTIR (Fourier transform infrared) spectroscopy samples of annealed PET, at temperatures well below the glass transition have shown a process of volume recovery.²⁶ Spectra obtained after annealing for times to and beyond the onset of embrittlement (as judged from mechanical response) indicated that several distinct changes in band intensities occur during this time interval. Spectroscopic results for times longer than that required for embrittlement suggested an increase in motions associated with in-plane vibrations located in, and near, the aromatic portions of the chains, as well as a decrease in out-of-plane vibrations. The overall results suggested that this method has potential for evaluating fast, as well as slow, recovery processes.

Adam and Gibbs suggested that the glass transition temperature T_g is a true second order transition and not due to kinetic effects. This is a fundamental difference between their theory and the later theories of Petrie et al.⁴ in which it was not necessary to assume a first or second order transition. Petrie et al.⁴ saw T_g as

a kinetic phenomena, while Adam and Gibbs²⁷ did not believe that T_g was due to kinetic effects. Both theories assumed that kinetics is dominant in determining the position of the observed T_g at lower temperatures (the more time required to reach equilibrium). Each theory capably explained the observed phenomena such as heating rate dependence, annealing time, annealing temperature and also the enthalpic relaxation toward equilibrium.

DeBolt et al.²⁸ developed a method for the determination of the kinetic parameters controlling structural relaxation in the glass transition region from data acquired during heating or cooling. Structural relaxation was described in terms of kinetic parameters such as relaxation times and activation energies. The following empirical expression was developed for the equilibrium relaxation function:

$$\phi_e(t - t_1) = \exp(-((t - t_1)/\tau_{oe})^\beta)$$

where τ_{oe} = characteristic relaxation time
 β = constant $0 \leq \beta \leq 1$

DeBolt²⁸ also showed that the heating rate data for a glass of known thermal history could be analyzed to yield a set of fundamental kinetic parameters for the structural relaxation of the property monitored in an experiment.

O'Reilly²⁹ suggested that there were two processes occurring during the relaxation process, volume and enthalpy recovery. Volume recovery corresponded to the free volume,

while enthalpy recovery was related to the molecular configurations. In the study it was attempted to separate effects of free volume change and effects resulting from conformational change since relaxation change is affected by both phenomena.

Roe³⁰ found that the glass transition temperature may result from a metastable equilibrium present when a glassy polymer is brought to a temperature moderately below its T_g and undergoes a slow relaxation toward a limiting structure. In this study two observations seemed to suggest that 1). the limiting state might not be an equilibrium state or 2). the relaxation times for different properties may be quite different. This suggested that either the T_g is not an equilibrium state or the different relaxation times for various properties reflect different moments of the relaxation time distribution. There were two types of observations which seemed to suggest that the limiting state might not be an equilibrium state. The first relates to the thermal density fluctuation observable with small-angle x-ray scattering. The second limiting annealed state was reported in an early work by Kovacs³¹ on volume relaxation of poly (vinyl acetate).

The physics of slow relaxation processes in glass-forming liquids are being studied extensively. Substantial progress has been made on the phenomenological understanding of the thermodynamic recovery process by Moynihan et al.³²

Kovacs et al.³³ studied the thermodynamic recovery process by introducing a distribution of relaxation times superimposed on the nonlinear dependence of relaxation time with the change of structure. Their basic differential equations are close to the same nonlinear equation with distributed order parameters. Moynihan (M model) used the Kohlrausch-Williams-Watts relaxation function³⁴, while Kovacs, Aklonis, Hutchinson, and Ramos³³ (KAHR model) used a double box-shaped distribution of relaxation times. The variations in density fluctuations at various stages of recovery were implied in the solution of the differential equation, but the relaxation spectrum was assumed to remain unchanged throughout the recovery process. Both used the formulae of Tool³⁵ or Narayanaswamy³⁶ for the temperature and structure dependence of the relaxation spectra, which were reduced to an Arrhenius type dependence with a very large activation energy along the equilibrium liquidus line.

A question which remains unanswered is the relationship between the dielectric or viscoelastic relaxation time and the volume or enthalpy relaxation(recovery) time extrapolated to equilibrium. Kovacs, Stratton and Ferry³⁷ have shown that the viscoelastic and volumetric data near T_g do not coincide with the curve calculated from data obtained at higher temperatures. Sasabe and Moynihan³⁸ have also shown that

the extrapolation of dielectric data from high temperature does not coincide with the enthalpic data near T_g . The work of Matsuoka et al.³⁹ has shown that the basic distribution of the recovery times can be assumed to be about the same as the relaxation spectrum and also, that the relaxation and the recovery times do coincide near the glass temperature.

2.2. Literature Review of Poly(ethylene terephthalate)

Poly(ethylene terephthalate) has served as an important model for studying relaxation processes in semicrystalline polymers.^{17,24,40-43} PET can be quenched into the completely amorphous state as well as isothermally crystallized allowing direct measurement of the effect of crystallinity on relaxations. PET shows two relaxation processes, one designated α_a and the other β .

The α_a relaxation is the glass transition (disappearance of long-range segmental motion with lowering temperature) in the completely amorphous material or in the amorphous fraction in semicrystalline specimens. The α_a relaxation is quite sensitive to the presence of the crystalline fraction in that it is much broader in the frequency domain and shifted to higher temperature isochronally in crystalline samples. Isochronally the β relaxation occurs at lower temperatures than the α_a process. This relaxation was thought to take place largely

in the amorphous phase and therefore is considered a "subglass transition" process. The β relaxation was insensitive to morphology, having almost the same characteristics (other than strength or intensity) in completely amorphous materials as in semicrystalline ones. This was consistent with the molecular motions associated with it being of shorter range character than those for the α_a process, although the assignment of the β relaxation as a purely amorphous one has been tested by extrapolation of relaxation strength vs. density to 100% crystallinity. Ishida et al.⁴¹ concluded after the extrapolation of their β -process strength that the process did not disappear at 100% crystallinity. They proposed that a third component between the crystal and amorphous phases was present and contributed to the β process. PET does not crystallize to high crystallinity so that the extrapolation was quite lengthy. In recent times, it has been found that the extrapolation is even more complicated by the uncertainty of the density of the crystal phase in PET. A number of various crystal density values have been reported ⁴⁴⁻⁴⁷, but Wunderlich's⁴⁸ determination is the most accurate.

The work of Coburn and Boyd²⁴ reported specimens of crystallinity higher than available in previous relaxation experiments in studying several different issues. It is known that the glass-rubber relaxation in PET and other semicrystalline polymers is seriously perturbed

kinematically by immobilization of amorphous chains through their attachments to the crystals. This results in a much broader relaxation time distribution and some change in the location of the relaxation center, as described before.

From the relaxation studies performed by Coburn et al.²⁴, the following conclusions were made. The distribution of relaxation times for the α_a process is quite dependent on crystallinity and the β process is quite insensitive to crystallinity, as seen by the width parameters. The α_a process is narrow and skewed to high frequencies in amorphous PET and is broad and symmetric in semicrystalline PET. The β process was broad and symmetric for both amorphous and semicrystalline PET. The central relaxation times followed a WLF behavior for the α_a process and Arrhenius behavior for the β process.

The morphological origin of the β process has been a point of dispute. Some investigators⁴⁰ have concluded that the β process occurs in the amorphous phase; others have indicated that the process occurs in both amorphous and crystalline phases.^{49,50} The β process by Coburn et al.²⁴ was found to originate exclusively in the amorphous phase. This was evidenced by plots of relaxation strength versus density which extrapolated to zero for both α_a and β processes at approximately 1.495 g/cm^3 , and based on the knowledge that the α_a process is the glass-rubber transition which occurs entirely in the amorphous phase. Also, these

plots supported the value of 1.495 g/cm^3 reported by Killian⁴⁵ as the density of 100 percent crystallized PET.

Experimental evidence supporting a composite origin to the β process has been seen in curves of relaxation strength⁴¹ or loss peak height⁵⁰ versus crystallinity extrapolated from data of relatively low crystallinities to 100 percent crystallinity. These plots have shown that the α_a process data extrapolates to zero at 100 percent crystallinity while the β process data extrapolates to zero at crystallinities well above 100 percent. This result has led to conclusions that the α_a process originates in the amorphous phase and the β process must occur in both phases. One reason for this conclusion was that the crystallinities were calculated from density measurements of 1.455 g/cm^3 ,⁴⁴ which was a much lower value than that of Killian.⁴⁵ A second reason is the linear fit to the relaxation strength or loss peak height for the α_a process versus crystallinity plot tends to neglect the effect of changes in the correlation factor on the relaxation strength. The linear fit was only possible because the crystallinity range available in these investigations was much lower than the range used by Coburn et al.²⁴

This is an important answered question which deals with the β relaxation origination. Now that the origin of the process is fairly clear, by performing more dielectric relaxation studies on amorphous PET (annealed below its

glass transition temperature), it is possible to determine if relaxations are occurring within the β -process.

3. THEORETICAL BACKGROUND

3.1. Static Dielectric Theory

Static dielectric theory has been well developed and detailed information can be found in many standard references.^{13,51-54} A review of the basic concepts and equations of dielectric spectroscopy will be discussed here.

The capacitance of a system consisting of two conductors is:

$$C = \frac{Q}{V_{12}} = \frac{q_f + q_b}{V_{12}} \quad 3.1$$

where Q is the total charge on the conductors and V_{12} is the difference in electrical potential between the two conductors. The total charge consists of the free charge q_f , which creates the macroscopic field between the conductors, plus the bond charge q_b , which balances the "structural" charge caused by the induced polarization in the material.

For a parallel plate capacitor in a vacuum (neglecting the edge effects) the capacitance, C , is simply

$$C = A/4\pi d \quad 3.2$$

where A is the surface area of the plates and d is the displacement between the plates.

When a constant voltage is applied across the two electrodes of a parallel plate capacitor separated by insulating material, the charges in the atoms and molecules

of the insulating material are displaced. The positive charges are displaced toward the negative plate, and the negative charges toward the positive plate, and each atom or molecule has a net separation of charges. These atoms or molecules are polarized.

The presence of the insulator increases the charges on the capacitor plates. The ratio of the charges in the capacitor plates with or without the insulator is defined as the (relative) dielectric constant ϵ of the insulator material. In two conductors separated by an insulator, the electron density at the surface of the conductor increases with the dielectric constant ϵ of the insulation material, and more power is dissipated in the high frequency transmission of electric energy in the conductor; this phenomenon is known as the skin effect.

3.1.1. Electrical Fields

The applied electrical field E_0 , between the plates of an empty capacitor is produced by charges on the conducting plates provided by an externally applied field.

The macroscopic electric field, E , inside a dielectric consists of contributions from the applied electric field and a depolarization field, E_1 , resulting from induced polarization opposing the applied electric field. The local electric field E_{local} , which acts at the site of an atom is

significantly different from the macroscopic electric field and is given fundamentally as:

$$E_{\text{local}} = E_0 + \sum \frac{3(P-r_1)r_1-r_1^2P}{r_i^2} \quad 3.3$$

Lorentz (1909) developed an expression for the local electric field in a uniformly polarized medium in terms of the macroscopic electric field and the polarization P , defined as the dipole moment per unit volume. This expression given below is known as the Lorentz relation:

$$E_{\text{local}} = E + \frac{4\pi P}{3} \quad 3.4$$

3.1.2. Polarization

The polarization in a dielectric can be separated into several contributions: electronic, atomic, ionic, dipolar (orientational), and interfacial (Maxwell-Wagner). The electronic contribution is due to the displacement of the electron shell relative to the nucleus in the atoms of the dielectric. Atomic contributions are caused by changes in the displacement of atoms, which have permanent bond moments, relative to each other. The ionic contribution is due to the displacement of charged ions with respect to oppositely charged ions. Ionic polarization does not generally occur in polymer dielectrics where the atomic bonding is predominantly covalent. The dipolar contribution is due to changes in the net orientation of molecules, or functional groups, that possess permanent electric dipole

moments. The interfacial contribution is due to accumulation of charge at structural interfaces in dielectrics possessing two or more distinct phases.

The dielectric constant of an isotropic dielectric can be defined in terms of the macroscopic electric field and the polarization as:

$$\epsilon = 1 + \frac{4\pi P}{E} \quad 3.5$$

3.1.3. Clausius-Mosotti Relation

Electronic and atomic polarization show dispersions at very high frequencies (optical and infrared, respectively). The polarization and in turn the dielectric constant at high frequencies or at very low temperatures is entirely due to electronic (and atomic) polarization. This polarization at low fields is simply proportional to the local electric field.

$$P_e = \sum N_i \alpha_i E_{\text{local}} \quad 3.6$$

Substituting the Lorentz relation eqn. 3.4 for the local field:

$$P_e = (\sum N_i \alpha_i) (E + 4\pi P_e / 3) \quad 3.7$$

eqn. 3.5 and 3.7 can be rearranged to obtain:

$$(\epsilon_u - 1) / (\epsilon_u + 2) = (4\pi / 3) \sum N_i \alpha_i \quad 3.8$$

substituting the definitions:

$$p = N_4 / 3\pi\alpha \quad \sum N_i = N/V = (N/M)d \quad 3.9$$

into eqn. 3.8 yields

$$(\epsilon_u - 1)/(\epsilon_u + 2) = pd/M \quad 3.10$$

The above equation 3.10 is the expression known as the Clausius-Mosotti relation and is applicable to dielectrics where the electronic and atomic polarization is the only source of polarization.

3.1.4. Debye Theory for Static Permittivity

At low frequencies or at high temperatures, the total polarization is due to contributions from electronic, atomic and dipolar polarizations and is expressed by:

$$P = N/V\langle\mu\rangle + (N/V)\alpha E_{\text{local}} \quad 3.11$$

When the electric field energy is much lower than the thermal energy the average dipole moment, $\langle\mu\rangle$, assuming a Boltzmann distribution, can be given as:

$$\langle\mu\rangle = (\mu^2/3kT)E_{\text{local}} \quad 3.12$$

substituting eqns. 3.4, 3.5 and 3.12 into eqn. 3.11 yields:

$$\frac{(\epsilon_r - 1)}{(\epsilon_r + 2)} = \frac{4\pi N}{3V} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad 3.13$$

This equation is known as the Debye equation for static permittivity. The static dielectric constant ϵ_r comprises contributions from all orientation processes is related to the actual dipole moment of a molecule in the above equation.

Onsager⁵⁵ gave the first derivation of the static dielectric constant for a condensed phase of dipolar molecules. The derivation introduced the important factor known as the Reaction field. This arises due to the polarization of the medium surrounding a molecule by the molecule itself, and this additional polarization reacts back on the molecule. The Onsager theory applies only to systems of rigid molecules where there is no orientation correlation between the individual molecules.

Onsager relation is: μ_o is the dipole moment of the molecule.

$$\mu_o^2 = \frac{3kT}{4\pi N} \frac{2\epsilon_r + \epsilon_u}{3\epsilon_r} \left[\frac{3}{\epsilon_u + 2} \right]^2 (\epsilon_r - \epsilon_u) \quad 3.14$$

Examples of the application of the Onsager equation are given by Smyth.⁵¹ As is seen from the Onsager model the molecules are not considered to have correlations in orientations. Thus eqn. 3.14 applies only to systems of rigid nonassociating molecules, and as a result cannot be applied to a condensed phase of polymer molecules.

Kirkwood⁵⁶ developed a theory of the static dielectric constant which took into account the hindered rotations of the dipoles. Kirkwood generalized the Onsager equation obtaining the following results:

$$\frac{(\epsilon_r - 1)(3\epsilon_r + 1)M}{g\epsilon_r d} = \frac{4\pi N}{3V} \left(\alpha + \frac{g\mu^2}{3kT} \right) \quad 3.15$$

$$\text{where:} \quad g = 1 + \sum \sum \langle \cos \gamma_{ij} \rangle \quad 3.16$$

where $(\cos \gamma_{ij})$ is the Boltzmann average of the cosine of

the angle between the i and j th dipoles. Rearranging eqn. 3.15 and solving for the strength of the relaxation process yields:

$$(\epsilon_r - \epsilon_u) = \frac{3\epsilon_r}{(2\epsilon_r + \epsilon_u)} (\epsilon_u + 2)^2 4\pi N g \mu_o^2 \quad 3.17$$

The correlation factor g , is a useful quantitative source of information about the effect of the crystal phase on the relaxation processes in the amorphous phase. For a system of unconstrained isolated dipoles, the correlation factor is one. If the dipoles are not sufficiently isolated and a parallel orientation is favored then the correlation factor is greater than one. If however, the dipoles are sufficiently displaced from each other, direct intra- and inter-molecular interactions would be negligible. If the dipoles are spatially restricted or the energies between different orientational sites are different, then the correlation factor is less than one and temperature dependent. This behavior can result from restrictions induced by the crystal phase on the chains in the amorphous phase.

3.1.5. Lamellar Bounds Model

The correlation factor can be obtained with useful accuracy from the Kirkwood-Onsager equation if the dipole number density, the dipole moment, the relaxed and unrelaxed

dielectric constants are known and if the dielectric is a homogeneous single phase system.

Semi-crystalline polymers have two phases and often the subglass and the glass relaxation processes are attributed to reorientation mechanisms in the amorphous phase and not in both phases in the composite dielectric. This indicates that the relaxed dielectric constant of the amorphous phase which is a result of both electronic and reorientational polarization is much higher than the dielectric constant of the crystalline phase which is a result of only electronic polarization. Because of the nonconformity of the two phases, the best approach for analysis is to consider the amorphous phase separately and to assign appropriate dielectric constants to this phase. Then the Kirkwood-Onsager equation can be used on the amorphous phase to obtain the correlation factor.

The bulk dielectric constant only can be measured. The problem then becomes one of determining the separate phase dielectric constants. The unrelaxed amorphous and the crystalline phase dielectric constants, both resulting from electronic polarization only, can be obtained from the bulk unrelaxed dielectric constant using the Clausius-Mosotti equation (eqn. 3.10). The relaxed amorphous phase dielectric constant can be extracted from the relaxed bulk dielectric constant, using upper and lower bound mixing equations, and the crystalline phase dielectric constant.

The simplest set of mixing equations are based on geometric models of parallel arrangement (uniform electric field) and series arrangement (uniform displacement field) of the phases as illustrated in Figure 1. The upper and lower bounds set for this model are:

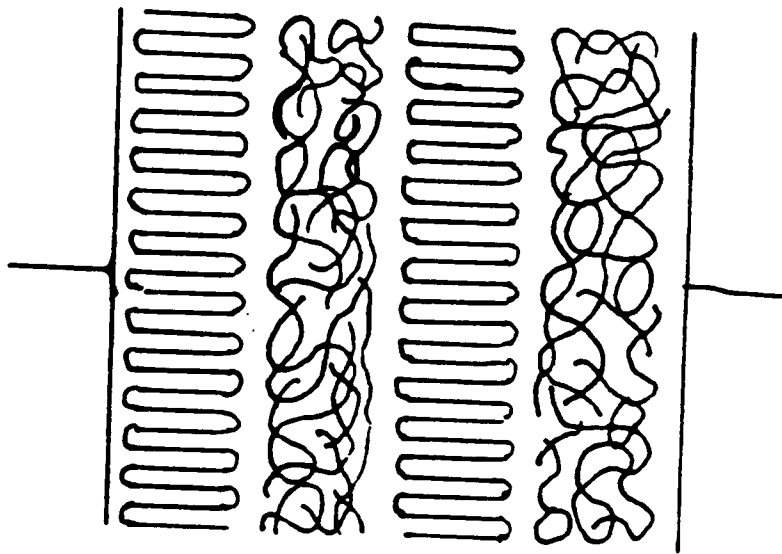
$$\begin{aligned}\epsilon_u &= V_1\epsilon_1 + V_2\epsilon_2 \\ \frac{1}{\epsilon_l} &= \frac{V_1}{\epsilon_1} + \frac{V_2}{\epsilon_2}\end{aligned}\quad 3.18$$

where v, ϵ are the volume fraction and dielectric constant respectively. Subscripts u and l denote the upper and lower bounds, respectively, and subscripts 1 and 2 denote the amorphous and crystalline phases, respectively.

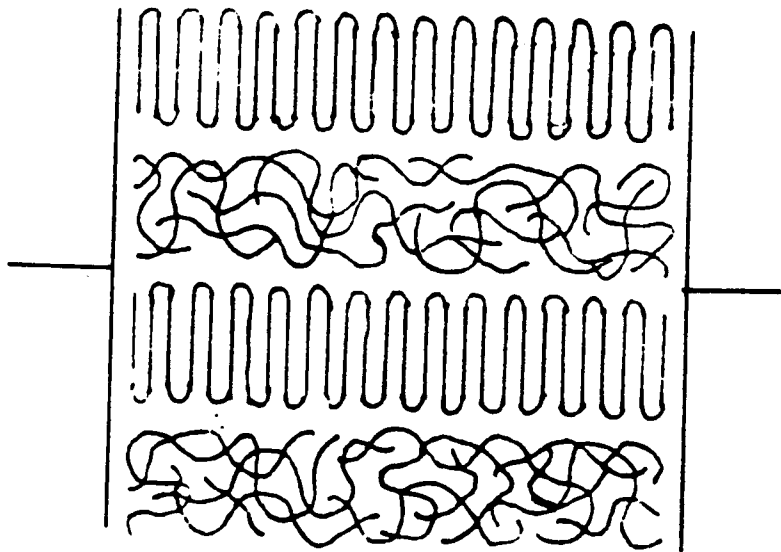
3.2. Dynamic Relaxation Theory

The dielectric relaxation theory developed to this point has been concerned only with the static case of dielectric relaxation theory where the dipoles in the dielectric are in equilibrium with the applied field. The dynamic case, where there is an observable lag in the attainment of equilibrium is discussed in this section.

Relaxation is generally defined as the lag in the response of a system to changes in the externally applied force. This force may be mechanical (stress field) or electrical (electrical field). Dielectric relaxation is the exponential decay with time of the polarization in a



.



b

FIGURE 1: Series (a). and parallel (b). arrangement of a two phase system.

dielectric when an externally applied electric field is removed.

3.2.1. Debye Theory (SRT)

The time dependent displacement electric field, $D(t) = \epsilon E(t)$ can be written as

$$D(t) = \epsilon_u E(t) + \int_{-\infty}^t E(v) f(t - v) dv \quad 3.21$$

where $f(t)$ is an exponential decay function based on a single relaxation time having the form $f(t) \propto \exp(-t/\tau)$. Taking the derivative of both sides of equation 3.21 and rearranging results in the following :

$$\tau \frac{d}{dt} (D(t) - \epsilon_u E(t)) + (D(t) - \epsilon_u E(t)) = \tau f(0) E(t) \quad 3.22$$

Applying the boundary conditions: $\tau f(0) = \epsilon_r - \epsilon_u$ when $E(t) = \text{constant}$. Equation 3.22 reduces to:

$$\tau \frac{d}{dt} (D(t) - \epsilon_u E(t)) + (D(t) - \epsilon_u E(t)) = (\epsilon_r - \epsilon_u) E(t) \quad 3.23$$

For the case, $E(t) = E_0 \exp(i\omega t)$, eqn. 3.23 reduces to:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{1 + i\omega\tau} \quad 3.24$$

separating into real and imaginary parts:

$$\epsilon' = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{(1 + \omega^2\tau^2)} \quad 3.25$$

$$\epsilon'' = \frac{(\epsilon_r - \epsilon_u) \omega\tau}{(1 + \omega^2\tau^2)} \quad 3.26$$

These equations are known as the Pellat-Debye equations.⁵⁷ As seen in Figure 2, most of the relaxation process occurs over a two decade frequency range. The maximum loss is:

$$\epsilon''_{\max} = 1/2(\epsilon_r - \epsilon_u) \quad 3.27$$

and occurs when: $\omega_{\max} = 1/\tau \quad 3.28$

Combining equations 3.25) and 3.26 by eliminating $\omega\tau$ gives:

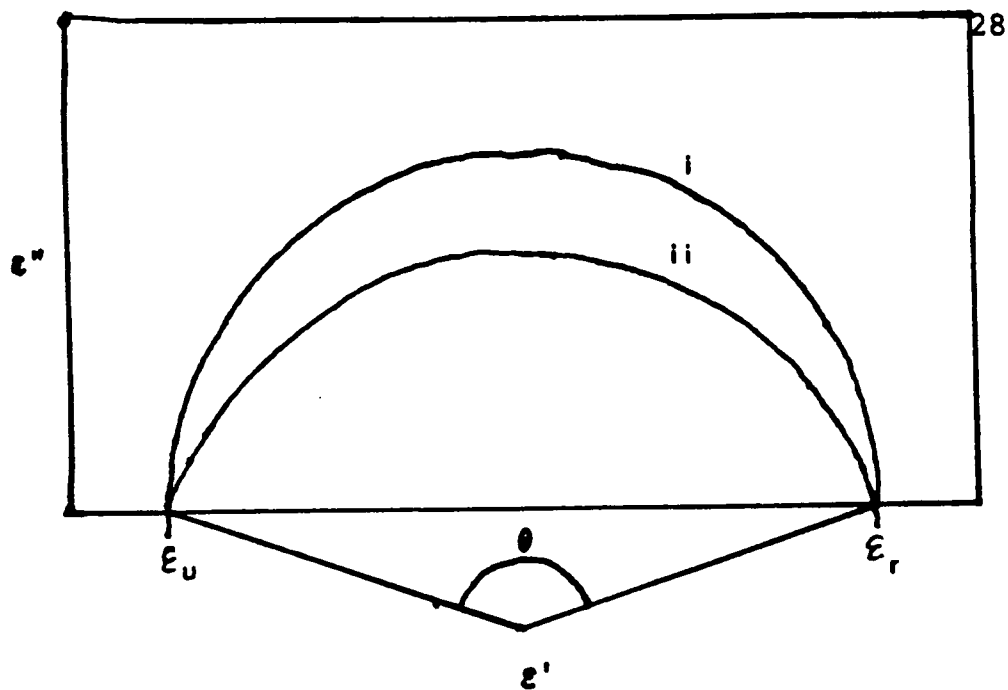
$$(\epsilon' - (\frac{\epsilon_r - \epsilon_u}{2}))^2 + (\epsilon'')^2 = (\frac{\epsilon_r - \epsilon_u}{2})^2 \quad 3.29$$

This equation is a circle when ϵ'' is plotted against ϵ' (Figure 2) with the center on the ϵ' -axis at $((\epsilon_r - \epsilon_u)/2.0)$ and with a radius of $(\epsilon_r - \epsilon_u)/2$. ϵ_u and ϵ_r are determined by the ϵ' -axis intercepts of the circle.

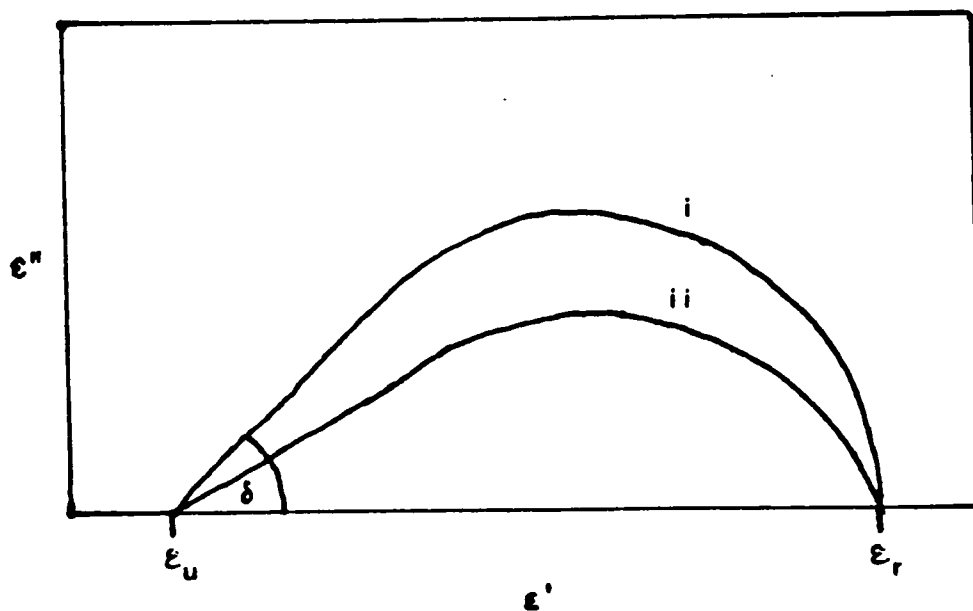
The plot of the imaginary versus real parts of a complex function is known as an Argand plot. When applied to the complex dielectric constant, the plot has become known as the Cole-Cole plot regardless of the function used to fit the data. The SRT model represents dipolar relaxation in many simple liquids fairly well, but relaxation in polymers usually occurs over a wider frequency range and the maximum loss is much lower (Figure 3). Therefore these equations have to be modified to take into account the distribution of relaxation times present in the dielectric relaxation data of a polymer.

3.2.2. Semi-Empirical Equations

The approach used by Debye for a single relaxation time can be expanded to include a distribution of relaxation

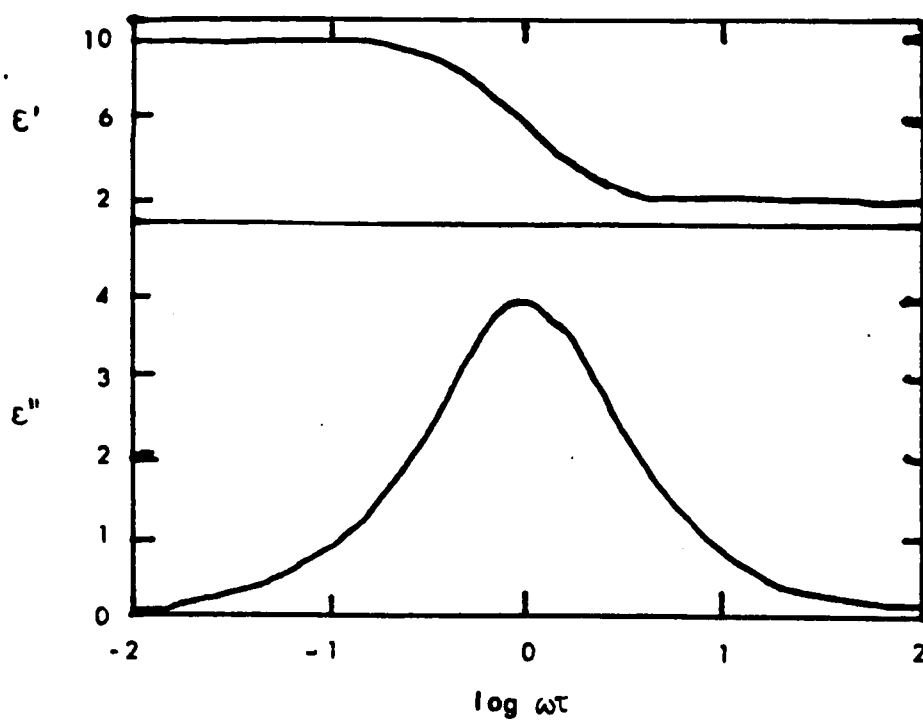


a.

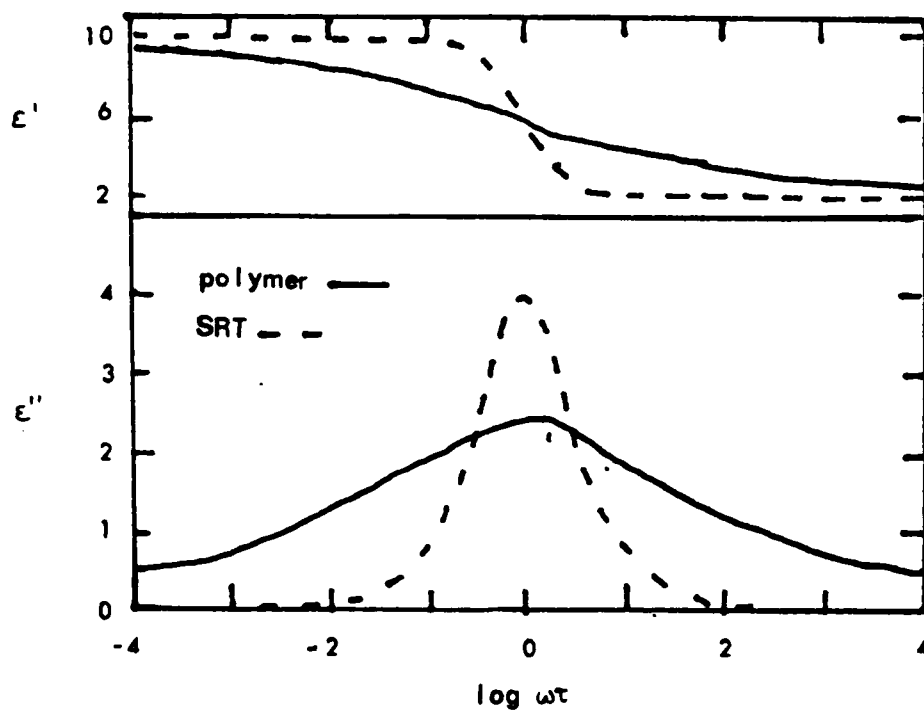


b.

FIGURE 2: Cole-Cole plots of the dielectric loss versus dielectric constant. (a). i) SRT; ii) Cole-Cole, and (b). i) Cole-Davidson; ii) Havriliak-Negami.



a.



b

FIGURE 3: Schematic representation for the dielectric constant and loss. (a). Single Relaxation Time (b). Typical Polymer.

times.¹³ A more common approach is to modify the Debye equations with empirical parameters.

The Cole-Cole function⁵⁸ modifies the Debye equation by incorporating the empirical parameter α into the denominator in the following manner:

$$\epsilon^* = \epsilon_u + (\epsilon_r - \epsilon_u) / (1 + (i\omega\tau_0)^\alpha) \quad 3.30$$

Separating into real and imaginary parts:

$$\epsilon' = \epsilon_u + \frac{(1 + (\omega\tau_0)^\alpha) \cos(\alpha\pi/2) (\epsilon_r - \epsilon_u)}{(1 + 2(\omega\tau_0)^\alpha \cos(\alpha\pi/2) + (\omega\tau_0)^{2\alpha}} \quad 3.31$$

$$\epsilon'' = \frac{(\omega\tau_0)^\alpha \sin(\alpha\pi/2) (\epsilon_r - \epsilon_u)}{1 + 2(\omega\tau_0)^\alpha \cos(\alpha\pi/2) + (\omega\tau_0)^{2\alpha}} \quad 3.32$$

The empirical parameter α varies between zero and one and provides for symmetric broadening of the dielectric constant and loss. When $\alpha = 1$ this case reduces to the SRT model and lower values of α produce broader relaxation time spectra.

The maximum loss occurs when $\omega\tau_0 = 1$ and is given by:

$$\epsilon''_{\max} = 1/2(\epsilon_r - \epsilon_u) \frac{\sin(\alpha\pi/2)}{(1 + \cos(\alpha\pi/2))} \quad 3.33$$

The parameter τ_0 can be considered to be a mean relaxation time. Combination of eqn. 3.30 and 3.31 by eliminating $\omega\tau_0$ gives:

$$\begin{aligned} & (\epsilon' - (\epsilon_r + \epsilon_u)/2)^2 + (\epsilon'' + (\epsilon_r - \epsilon_u) \cot(\alpha\pi/2))^2 \\ & = (1/2(\epsilon_r - \epsilon_u) \operatorname{cosec}(\alpha\pi/2))^2 \end{aligned} \quad 3.34$$

If ϵ'' is plotted against ϵ' , eqn.(34) leads to a circle with the center at $((\epsilon_r + \epsilon_u)/2, -(\epsilon_r - \epsilon_u)/2 \cot(\alpha\pi/2))$ and radius $(\epsilon_r - \epsilon_u) \operatorname{cosec}(\alpha\pi/2)$. The resulting diagram is a Cole-Cole plot, and is schematically shown in Figure 2. The

values of ϵ_u and ϵ_r are obtained from smaller and larger intercepts, respectively, on the ϵ' -axis. The parameter α is determined from the angle $\theta = \alpha\pi/2$.

The Davidson-Cole function⁵⁸ modifies the Debye equation by incorporating the empirical parameter β into the denominator in the following manner:

$$\epsilon^* = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{(1 + i\omega\tau)^\beta} \quad 3.35$$

Separating into real and imaginary parts:

$$\epsilon' = \epsilon_u + (\epsilon_r - \epsilon_u)(\cos\phi)^\beta \cos\beta\phi \quad 3.36$$

$$\epsilon'' = (\epsilon_r - \epsilon_u)(\cos\phi)^\beta \sin\beta\phi \quad 3.37$$

$$\text{where:} \quad \tan - \phi = \omega\tau \quad 3.38$$

The empirical parameter β varies between zero and one, results in assymmetrical broadening.

The maximum in the loss occurs at

$$\omega\tau = \tan \left(\pi/2 \cdot 1/(1+\beta) \right) \quad 3.39$$

The low frequency end of the argand plot is circular, while the high frequency end is skewed (Figure 3). ϵ_u and ϵ_r are determined by the angle δ .

The Havriliak-Negami equation⁵⁹ is a generalized function which allows for both symmetric and asymmetric broadening. This equation is given as:

$$\epsilon^* = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{(1 + (i\omega\tau)^\alpha)^\beta} \quad 3.40$$

A Cole-Cole plot of this equation is illustrated in Figure 2

3.3. Theories of the Glass Transition

The relaxation in a dilute solution of a polymer primarily involves conformational changes by rotation about main-chain bonds. Bond rotation is hindered by the potential energy barriers and therefore is a thermally activated process dependent on the chain stiffness. In the case of relaxation in a bulk amorphous phase, where the molecules are packed closely together, the above process requires also the cooperative motion of segments of several neighboring chains. The cause of these local structural changes are the intermolecular van der Waal forces which are related to the cohesive energy density.

When the temperature is lowered the cooperative motion slows down quickly, until a temperature is attained where relaxation cannot be detected within the time scales (minutes to days) usually used. This temperature is the glass transition temperature T_g measured by "static" scanning techniques such as dilatometry.

As seen in Figure 4 the slight reduction in T_g at slower scanning rates, corresponds with the molecular mechanism as described above. By usual scanning techniques it is quite evident that the glass transition is a kinetic phenomenon.

The Williams-Landel-Ferry (WLF) theory⁶¹ is a semi-empirical free-volume theory which has been successful in

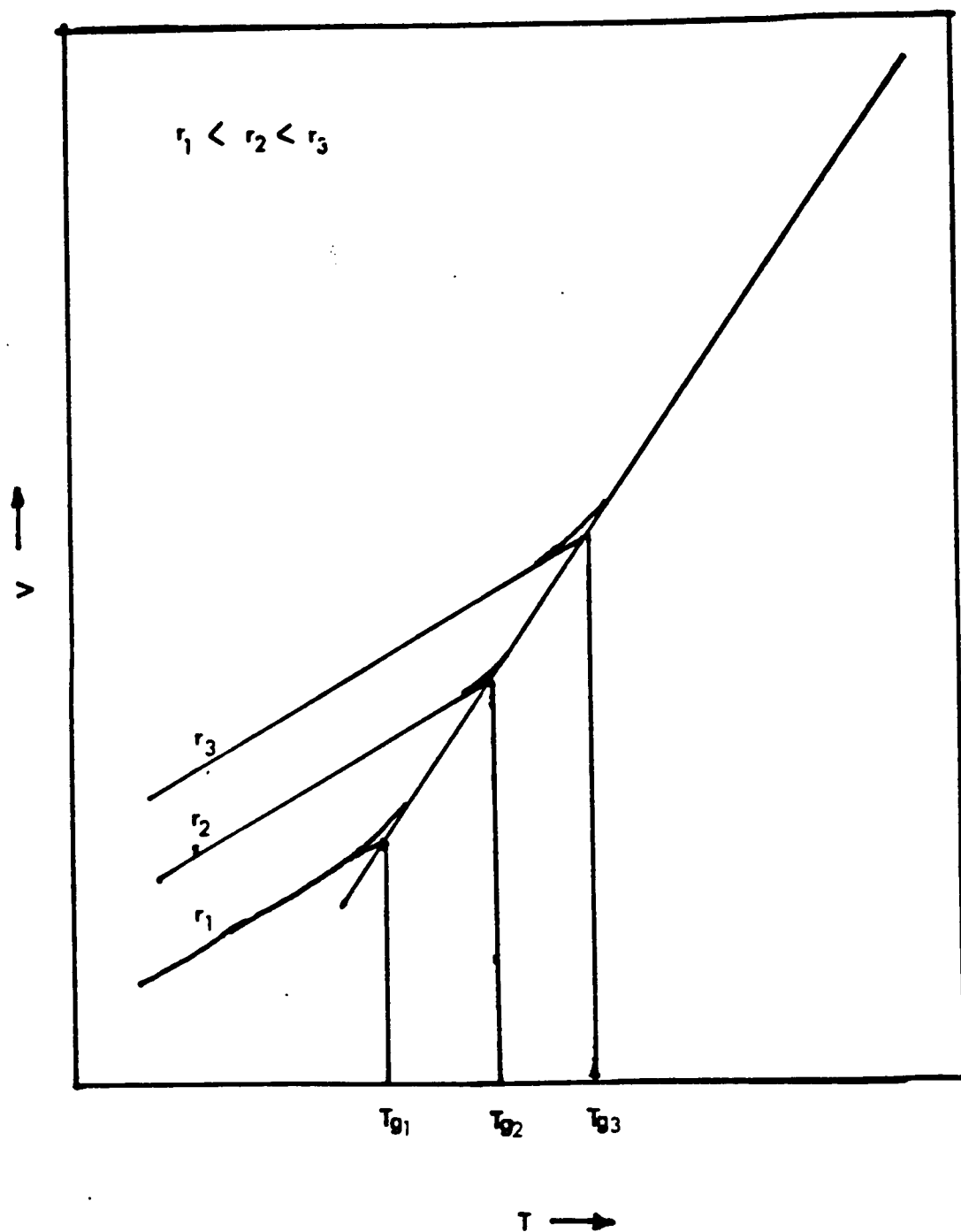


FIGURE 4: Schematic illustration of the variation of the glass transition temperature with cooling rate.⁶²

relating time and temperature, at least over the range from T_g to $T_g + 100^\circ\text{C}$. It is usually represented by this form

$$\log a_T = \frac{-c_1(T - T_g)}{(c_2 + T - T_g)} \quad 3.41$$

where $a_T = \tau(T)/\tau(T_g)$ is the ratio of the relaxation time at a given temperature T to that at T_g . The function $a_T(T)$ reflects the temperature dependence of a segmental friction coefficient or mobility on which the rates of all configurational rearrangements depend, and is important in describing the physical properties of a polymer system.⁶¹ The empirical constants c_1 and c_2 may vary somewhat with specific polymer, but are usually close to the universal values $c_1 = 17.44$ and $c_2 = 51.6^\circ\text{K}$.

It can be seen that equation 3.41 predicts infinite $\log a_T$ at some temperature T_∞ given by

$$T_\infty = T_g - c_2 \quad 3.42$$

Williams et al.⁶¹ suggested the following relationship for the empirical constants dependence of viscosity arising largely from its dependence on free volume.

$$\begin{aligned} c_1 &= 1/(2.303fg) \\ c_2 &= fg/\alpha_f \end{aligned} \quad 3.43$$

Here, fg is the fractional free volume at T_g , and α_f is the relative free volume expansion. Comparison of equation 43 with the "universal" variables c_1 and c_2 yield $fg = 0.025$ and $\alpha_f = 4.8 \times 10^{-4}^\circ\text{K}^{-1}$. The fractional free volume is known to be the fraction of the bulk volume not actually

occupied by the polymer chains, but fg is not well defined. The coefficient α_f is approximated by α , the difference between the thermal expansion coefficients above and below the T_g .

The relaxation time τ of an SRT system (or the mean relaxation time of a Cole-Cole function) can be related to the angular frequency ω_m and frequency ν_m of the applied electric field at the loss peak by:

$$\tau = 1/\omega_m = 1/2\pi \nu_m \quad 3.44$$

Hence,

$$\log a_T = \log(\tau(T)/\tau(T_g)) = \log(\nu_m(T)/\nu_m(T_g)) \quad 3.45$$

Substitution of equations 3.42 and 3.45 into eqn. 3.41 yields:

$$\log \nu_m(T) = \log g + c_1 - (c_1 c_2)/(T - T_\infty) \quad 3.46$$

where $\nu_m(T_g)$ is ν_g . At very high temperatures, the peak loss frequency is represented by ν_o :

$$\nu_m(T \rightarrow \infty) = \nu_o \quad 3.47$$

Thus, at very high temperatures $(T - T_\infty)^{-1} \rightarrow 0$ eqn.(46) goes to

$$c_1 = \log(\nu_o/\nu_g) \quad 3.48$$

Hence at temperature T

$$\log \nu_m(T) = \log \nu_o - c_1 c_2/(T - T_\infty) \quad 3.49$$

An empirical expression having the same form as this equation has been used to describe the temperature dependence of viscosity and in fact is the basis of the WLF equation.⁶¹ This expression also allows the effect of

pressure to be incorporated by a simple application of free volume theory.

From equation 3.49 a plot of the logarithm of the dielectric loss peak frequency against $(T - T_{\infty})$ should be linear with a slope of $(-c_1 c_2)$ with an intercept of $\log \nu_0$. The parameter T_{∞} may be found from experimental ν_m vs. T data by iterating for T_{∞} such that the linearity is optimized.

Gibbs and DiMarzio⁶³ have proposed a quasilattice theory based on statistical mechanics which avoids the entropy problem⁶⁴ by a second-order thermodynamic transition occurring at a temperature T_2 estimated to be about 50°C below T_g ; values of T_2 and T_{∞} almost coincide. Because of this transition, the configurational entropy remains zero below T_2 , rather than obtaining negative values. The rapid increase in relaxation times on cooling near T_g is contributed to the lack of configuration available.

Based on the Gibbs-DiMarzio⁶³ statistical mechanical theory, Adams and Gibbs²⁷ developed a molecular-kinetic theory dealing with the temperature variation of the size of the cooperatively rearranging region in glass-forming liquids, which was shown to be a function of the configurational entropy. The Adams and Gibbs theory results in eqn. 50 which is similar to the empirical WLF equation presented in eqn. 41. Although the constants could

be related to molecular parameters instead of being fitted empirically to the data.

Unfortunately, there are no independent estimates of these molecular parameters available, but comparison with experimental data yields reasonable values.

$$\log a_T = -a_1(T - T_g)/(a_2 + T - T_g) \quad 3.50$$

$$a_1 = 2.303 \mu S^* / (k C_p T_g (T_g/T_2))$$

$$a_2 = T_g \ln(T_g/T_2) / (1 + \ln(T_g/T_2))$$

where μ is the hindrance-free enthalpy per mole and S^* is the critical configurational entropy.

Within the free volume theories is the assumption that the glass transition occurs at a constant fractional free volume, a polymer being considered to vitrify when f is reduced (by cooling, or by application of pressure, etc.) to a critical value f_g . On the otherhand, Goldstein⁶⁵ has claimed on the basis of a comparison of the reported values of the terms (dT_g/dP) , $(\Delta\beta/\Delta\alpha)$ and $(T_g V \Delta\alpha/\Delta C_p)$ for several polymers, that the glass transition occurs under either an iso-enthalpic or an iso-entropic condition rather than an iso-free-volume condition. Sasabe and Saito⁶⁶ have produced data to support Goldstein's results. However, Havlicek et al.⁶⁷ have recently obtained molecular parameters from the Gibbs DiMarzio theory for several polymers, their results indicated that the fractional free volume is more nearly constant at T_g than the configurational entropy (S_{cg}) or the product ($S_{cg}T_g$).

Based on the usual assumption of free volume theories that the relaxation time is a function of the free volume alone. Ferry and Stratton¹²¹ derived an expression for the effect of pressure on the relaxation time.

$$\begin{aligned}\log a_p &= \log(\tau(P)/\tau(P_0)) \\ &= b_1(P - P_0)/b_2 - (P - P_0)\end{aligned}\quad 3.51$$

where f_0 is the fractional free volume at the reference pressure P_0 , and $\beta_f = \beta$ is the free volume compressibility. The expression is only valid to the extent that β_f is independent of pressure, and moreover is limited to the (T,P) range where the fractional free volume $f \leq 0.08$.

3.4. Small Angle Light Scattering Studies of Unoriented Bulk Polymers

The most commonly observed SALS pattern for unoriented polymers is due to spherulites, which may be interpreted in terms of the scattering by anisotropic spheres (Stein and Rhodes;⁶⁷ Stein⁶⁸). The anisotropic spheres consist of a four-leaf clover type crossed-polaroid (H_V) pattern and a parallel-polarization having two-fold symmetry. The H_V pattern exhibits an interesting maximum occurring at an angle inversely related to the spherulite size. Other studies have been concerned with the changes in spherulite size accompanying crystallization.

Experimental efforts have been concerned with the quantitative comparison of theory with observed scattering

patterns. Such studies have been reported by Baba⁶⁹ for PET crystallization and by Stein et al.⁶⁸ for the melting of polyethylene and for i-PS/a-PS blends. It was found that scattering intensities depend upon the number, size, degree of crystallinity and perfection of spherulite in a manner useful for sample characterization.

3.4.1. General Theory

A model of ideal homogeneous anisotropic spherulites in an isotropic medium was proposed by Stein and Rhodes (1960). The light scattering pattern from these spherulites was calculated by the amplitude method based on the equation derived by Guinier¹¹⁷:

$$A_1 = K(M_1 \cdot O) \cos \{k(r_1 \cdot s)\} \quad 3.52$$

A_1 is the amplitude of scattering by the i th volume element of the system; K is a proportionality constant; M_1 is the induced dipole in the i th volume element of a distance r_1 from the origin; O is a unit vector perpendicular to the scattered light beam and along the polarization direction; s is equal to $s_0 - s'$, where s_0 is a unit vector in the direction of scattered light beam; k is the wave number $2\pi/\lambda$

For systems of known geometry, the overall intensity, I , can be obtained by integrating A_1 over all elements of the system to obtain an expression for the total amplitude and squaring A . In the case of scattering from a uniform

sphere, the total amplitude is expressed in terms of the general integral:

$$A = \Sigma A_i = K \int_{r=0}^R \int_{\Omega=0}^{\pi} \int_{\alpha=0}^{\pi} (M \cdot O) \cos(k(r \cdot s)) r^2 \sin \alpha d\Omega dr d\alpha \quad 3.52$$

where r , α and Ω are the polar coordinates, the origin being taken as the center of the sphere.

Stein and Rhodes⁶⁷ calculated the scattering pattern for spherulites, the sample being placed between a polarizer and an analyzer. A schematic diagram is shown in Figure 5. Based on the integral given in eqn. 3.52 and assuming that the spherulite is surrounded by an isotropic uniform medium of polarizability α_s , the expressions for V_V and H_V are given by

$$I_{VV} = K' v_o^2 (3/U^3) ((\alpha_t - \alpha_s)(2\sin U - U\cos U - S_1 U) + (\alpha - \alpha_s)(S_1 U - \sin U) + (\alpha_t - \alpha_r) \cos^2(\theta/2) \cos^2 \mu (4\sin U - U\cos U - 3S_1 U))^2$$

eqn. 3.53

and eqn. 3.54.

$$I_{HV} = K' v_o^2 (3/U^3)^2 ((\alpha_t - \alpha_r) \cos^2(\theta/2) \sin \mu - \cos \mu (4\sin U - U\cos U - 3S_1 U))^2$$

where K' is the proportionality constant; v_o is the scattering volume of the spherulites; α_t and α_r is the tangential and radial polarizabilities of the spherulites respectively; θ and μ are the scattered and azimuthal angles

shown in Figure 5. S_1 is the integral defined by

$$S_1 U = \int_0^U (\sin x/x) dx \quad 3.55$$

U is the form factor given by

$$U = (4\pi R/\lambda) \sin(\theta/2) \quad 3.56$$

where R is the mean spherulite radius and λ is the wavelength in the polymer sample.

I_{VV} contains three terms, in which the last term arises from the anisotropic characteristics of the spherulite and is dependent upon μ . The first two terms depend upon the difference between the polarizabilities of spherulites and that of the surrounding medium and are independent of μ . The experimental result⁷¹ shows that the V_V scattering is strongly oriented along the polarization direction. This indicates that the last term of I_{VV} dominates the intensity and the first two terms are negligible. Thus the anisotropy of the spherulite is the major cause of the low-angle light scattering in this case. From Figure 5 it can be seen that I_{HV} arise entirely from the anisotropy of the spherulite and depends strongly on the azimuthal angle μ .

The calculated light intensity contours for H_V scattering by an anisotropic sphere are shown in Figure 5. It is apparent that H_V scattering has a maximum intensity at $\theta = 45^\circ$ from the experimental results (Stein and Keane⁷¹) and the theoretical calculations (Stein and Rhodes⁶⁷). The

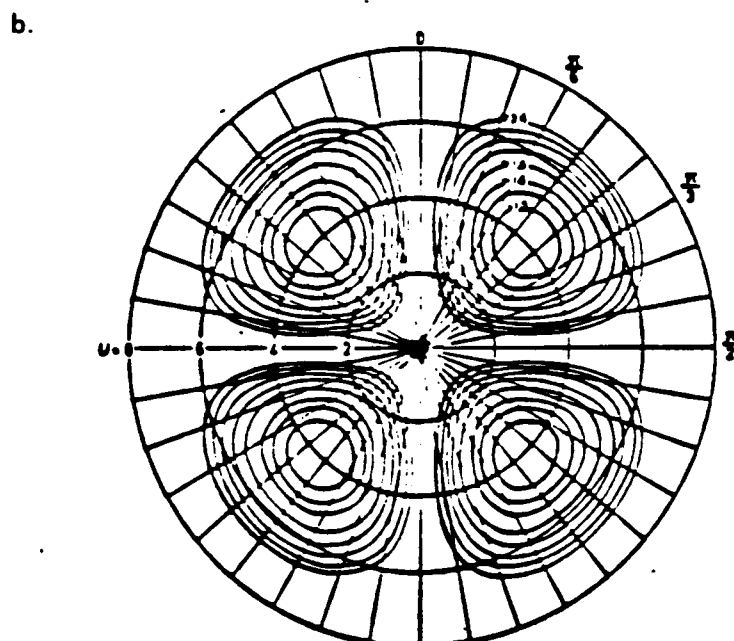
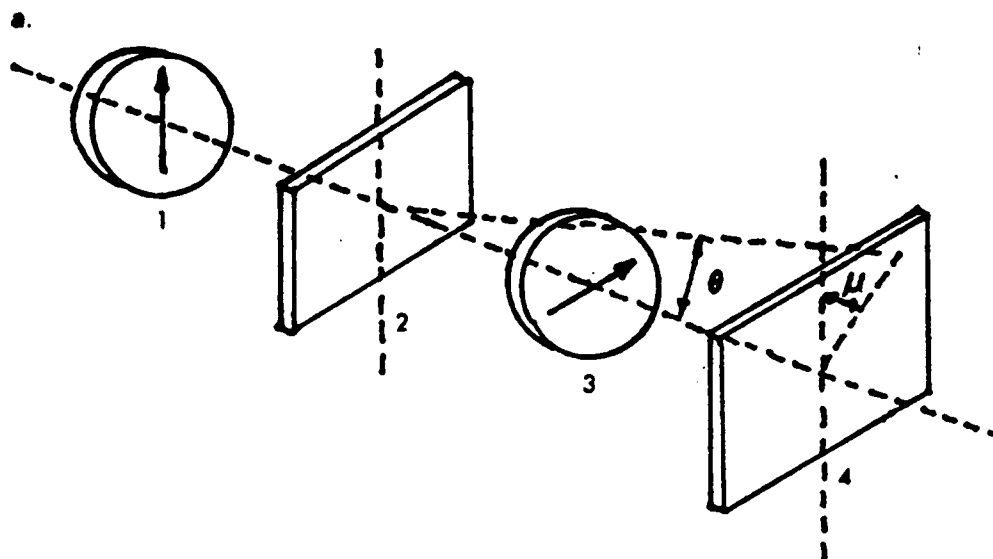


FIGURE 5: (a). The coordinate system for H_V and V_V scattering from anisotropic spheres. (1). Polarizer; (2). Sample; (3). Analyzer; (4). Screen. (b). Calculated light intensity contours for H_V scattering by an anisotropic space.

intensity is zero at $U = 0$ and $U = \infty$. The position of maximum intensity is found at $U = 4.1$ as well as $\theta = 45^\circ$.

The effect of the distribution of spherulite sizes on the scattering pattern has been examined by Stein et al. and Keijzers et al.¹¹⁸ by numerically summing equations of Gaussian and other distributions. The result is that the intensity becomes more uniform as the distribution broadens. This causes a problem in the determination of the position of maximum intensity in the scattering pattern. Recently Crist et al.¹¹⁹ did further studies and found by calculations of scattering profiles from a wide variety of distributions fail to demonstrate that the light scattering profile should be related to the spherulite distribution. But it was found to have a strong dependence of scattering power on spherulite size. Though exceptions were noted for the case of certain bimodal distributions.

Using eqn. 3.56 and assigning $U = 4.1$ as well as the value of θ_m based on maximum intensity criteria, the mean spherulite size R can be calculated using the following equation;

$$R = \frac{4.1\lambda}{4\pi\sin(\theta_m/2)} \quad 3.57$$

where λ and θ_m are the wavelength and scattering angle in the polymer.

Experimentally, the scattering $\theta_{m,a}$ in air, rather than θ_m , is measured. Therefore, it is more convenient to

express the average spherulite size in terms of $\theta_{m,a}$ and λ_a , Snell's Law of refraction.

$$\frac{\sin \theta_{m,a}}{\sin \theta} = \frac{n}{n_a} = n, \quad 3.58$$

and $\lambda = \lambda_a / n$,

where n_a and n are refractive indices in air and in the crystalline region of the polymer, respectively.

So the average spherulite size in terms of $\theta_{m,a}$ and λ_a gives:

$$\bar{R} = \frac{4.1 \lambda_a}{4\pi \cdot n \sin(1/2 \arcsin(1/n \sin \theta_{m,a}))} \quad 3.59$$

after approximation, eqn. 3.59 leads to

$$\bar{R} = \frac{4.1 \lambda_a}{4\pi \sin(\theta_{m,a}/2)} \quad 3.60$$

3.4.2. Light Scattering by Imperfect Spherulites

It has been previously shown that for a perfect spherulitic system there is no intensity present in the H_V scattering pattern. However, in a real system, there is considerable intensity observed in the center of the H_V pattern. There are several factors which may contribute to this intensity: 1. Imperfections in optical polarizers which allow a very small part of the direct beam through the crossed polarizers. 2. The anisotropic character of the amorphous region within or outside the spherulites, which is considered as an isotropic uniform medium in a perfect system. 3. Impingement of spherulites which causes the

polarizability resulting from random orientation fluctuation of crystallites in the spherulites (Stein and Wilson⁷²).

An alternative approach used to obtain the light scattering intensity by squaring before summing is given by eqn. 3.61.

$$I = \sum \sum A_i A_j = K^2 \int \int (M_1 \cdot O)(M_j \cdot O) \cos K(r_1 \cdot s) dr_1 dr_j \quad 3.61$$

The definitions of all the symbols in the above equation are the same as for those of eqn. 3.51.

The fluctuations in polarizability may arise from fluctuations in the density or the orientation of anisotropic materials. A general consideration for the combination of these two fluctuations has been proposed by Goldstein and Michalik,⁷³ a more detailed expression having derived by Stein and Wilson.⁷²

Two correlation functions, $\gamma(r)$ defines a correlation function for fluctuation in average polarizability

$$\gamma(r) = \langle n_i n_j \rangle_r / \langle n^2 \rangle_{av} \quad 3.62$$

where $\langle n_i n_j \rangle_r$ represents the average polarizability of overall pairs of elements at constant scalar separation r , $\langle n^2 \rangle_{av}$ being the mean square fluctuation in average polarizability.

A similar correlation function $\psi(r)$ for fluctuations in the magnitude of the anisotropy is expressed as

$$\psi(r) = (\Delta_i \Delta_j)_r / (\Delta^2)_{av} \quad 3.63$$

Using this fluctuation concept and some mathematical manipulation, the H_V scattering pattern for random orientation of crystallites leads to this expression.

$$I'_{H_V} = \int_0^{\infty} (1/15)K\delta^2 f(r)\mu(r)(\sin(hr)/hr)r^2dr \quad 3.64$$

where δ is the mean anisotropy in polarizability and $h = 4\pi\sin(\Theta/2)/\lambda$; $f(r)$ and $\mu(r)$ are two spherically symmetric correlation functions for elements separated by a distance r , and are expressed as follows:¹¹⁸

$$f(r) = x\exp(-r^2/b^2) + (1 - x)\exp(-r^2/c^2) \quad 3.65$$

$$\text{and} \quad \mu(r) = 1 + (\langle n^2 \rangle / \alpha^2) \sigma(r) \quad 3.66$$

where b and c characteristic correlation distances and x is a factor between zero and unity, $\langle n^2 \rangle$ is the mean-square polarizability function ($n_i = \alpha_i - \alpha$), in which α is the polarizability of the sample, and $\sigma(r)$ is the density correlation function.

Substituting equations 3.65 and 3.66 into 3.64 and integrating from zero to infinity, I'_{H_V} leads to the following expression

$$I'_{H_V} = 1/15K\delta^2 [(xb^3\sqrt{\pi}/4\exp(-h^2b^2/4) + (1-x)c^3\sqrt{\pi}/4\exp(-h^2c^2/4))] \quad 3.67$$

At the center of light scattering pattern $h = 0$, I_{H_V} can be expressed as

$$I'_{H_V} = (h=0 \text{ or } \Theta=0) = (\sqrt{\pi}/60)K\delta^2 [xb^3 + (1-x)c^3] \quad 3.68$$

3.5. Polymer Crystallization

It has been recognized for many years that polymer molecules possess the ability to crystallize. The extent to which this occurs varies with the type of polymer and its molecular microstructure. The main characteristic of crystalline polymers that distinguishes them from most other crystalline solids is that they are usually only semi-crystalline. The degree of crystallinity, the size and arrangement of the crystallites in a semi-crystalline polymer have a profound effect upon the physical and mechanical properties of the polymer. In order to explain these properties, full understanding of these crystalline regions are necessary.

On cooling a dilute solution of a semi-crystalline polymer, lamellar single crystals are formed. (see Figure 6) Polyethylene molecules were shown to form single crystals from dilute solution by Keller.⁷⁴ Based on electron diffraction experiments molecules were found to be normal to the lamellae. Keller concluded that polymer molecules in the crystals are folded back and forth on themselves. This theory has also been supported by similar observations of Fisher⁷⁵ and Till⁷⁶.

These polymers can also be crystallized from the melt by cooling below the melting point. Melt-crystallized

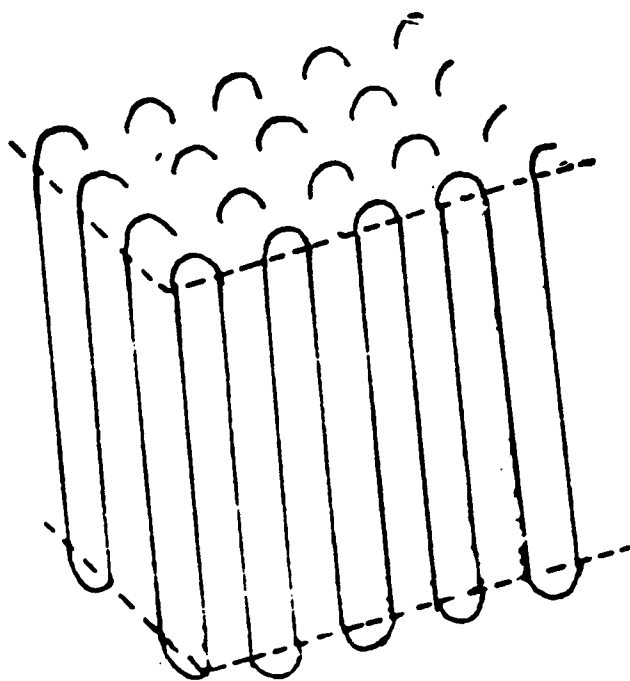


FIGURE 6: A typical lamellar single crystal in polymers.

polymers usually form spherulites (other objects such as axialites are found under certain conditions) which consist essentially of lamellae radiating outward from a central point. Spherulites usually initiate at a heterogeneity, and subsequently grow such that their radii increase linearly with time, until they approach impingement with other spherulites. They grow as three-dimensional objects, the lamellae branching frequently.

The lamellae which form the spherulites in a melt-crystallized polymer are quite similar to the single crystals obtained from dilute solution. Based on the analysis of optical extinction patterns and micro-beam x-ray data, it is known that the c-axis (chain direction) of the polymer is perpendicular to the radius of the spherulite and hence to the crystal lamellae. Usually the length of the chains are at least two orders of magnitude larger than the lamellar thickness and therefore sort of chain folding is generally believed to occur. The structure of the chain fold is still a matter of some controversy and is discussed in detail in a later section. The folds lie on the large surfaces of the lamellae. Whatever the nature of the folds, they introduce some strain into the polymer chain. Therefore the surface free energy (σ_e) is much higher than that of the other surfaces (σ). Hoffman et al.⁷⁷ have pointed out that in contrast to crystals of small molecules which grow most rapidly on their highest energy surfaces,

polymer crystals do not grow at all on their fold surfaces. In both cases the origin of this high surface energy is quite different.

Melt crystallized polymers do possess some features quite different from those crystallized from dilute solution. These features are due to the extensive interpenetration of the coiled amorphous molecules in the melt, in contrast to their separation in very dilute solution. Consequently melt-crystallized polymers have been shown to possess a considerable number of inter-crystalline and inter-lamellae links, formed by crystallization of one molecule on two or more lamellae. This results in entanglements which prevent the attainment of 100% crystallinity; even after crystallizing for extended periods an amorphous component can be detected by several techniques such as calorimetry, dilatometry and dielectric spectroscopy. The extent of this "residual" amorphous component increases with molecular weight and varies widely with different polymers.

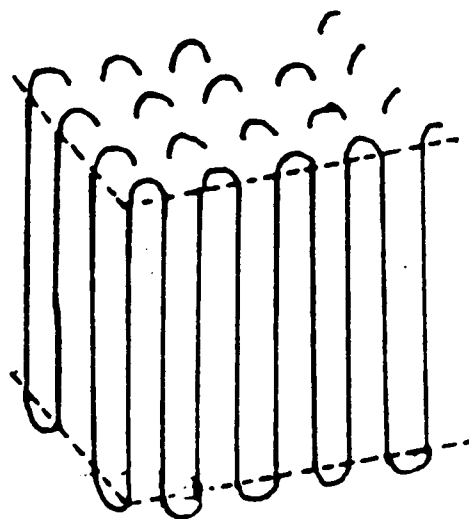
Therefore a two-phase system exists, containing crystalline and amorphous components coexisting over a wide range of temperature (which violates the phase rule). The explanation that Hoffman et al.⁷⁷ gave is the phase rule is not applicable to this system since it is not at equilibrium.

3.6. Fold Surfaces

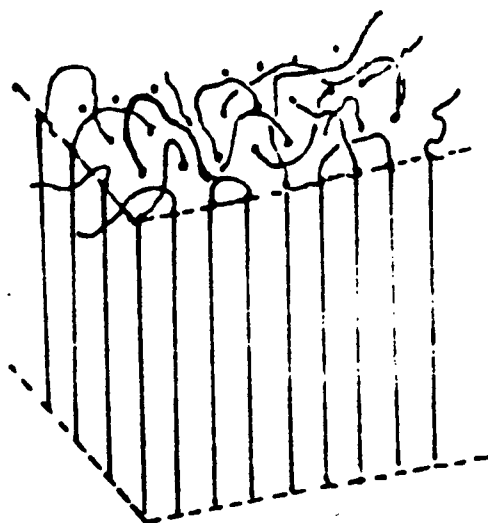
3.6.1. Nature of the Fold Surface

There has been considerable controversy about the nature of the fold surface structure. One model which explains the fold structure is the adjacent re-entry (AR) model, suggested by Keller.⁷⁴ While the other extreme model with irregular re-entry was proposed by Flory,⁷⁸ and is commonly known as the "switchboard model". (Figure 7) This model was formulated on the basis of space limitations at the crystal-liquid interface and the density defect nature of single crystals. In this model it was believed that folding exists but that the molecule reenters the crystal somewhat randomly and in a non-adjacent manner. The fold surface is very rough with loops of various lengths due to the random reentry, entanglements, etc.. Mandelkern's⁷⁹ interzonal model is quite similar to the "switchboard" model, though in this model the outermost amorphous region is sandwiched (interzonal) before passing into the ordered crystalline state of the crystal.

In the AR model there are short, uniform and tight folds resulting in a folded surface. Only possible defects are the ends of molecules which might form as short length flexible rod (or cilia) above the folded surface or else fold back into the crystal. In the case of single crystals formed from mixtures of deuterated and normal hydrogenated



a



b

FIGURE 7: Schematic representations of (a). the adjacent re-entry model and (b). "switchboard model".

polyethylene chains, Bank and Krimm⁸⁰ were able to show through a detailed analysis of infrared spectra that the predominant type of folding involves re-entry of the emergent stem into an adjacent position on the crystal face. The existence of intercrystalline and lamellar links show that non-adjacent re-entry (NAR) must occur to some extent in melt crystallized polymers. The researchers at the National Bureau of Standards (NBS) have been the major contributors and supporters of the AR model. The researchers accept the mode of folding as "predominantly AR" with a probability of AR (p_{ar}) less than unity. Usually $p_{ar} = 0.6-0.8$ is claimed.

3.6.2. Arguments About the Fold Surface Structure

A summary of the issues which are the most controversial on the nature of fold surfaces are given as follows: Density, Neutron Scattering and Mobility in the crystallizing melt.

Density: It is well established that polymer single crystals have densities below the x-ray value, which are determined from the unit cell dimensions. The switchboard model implies the defect is attributed to the amorphous zone arising mostly from nonadjacent re-entry on a large scale. In the adjacent re-entry model the density defect is related to surface roughness in the form of long loose folds ("loops").

Neutron scattering is an experimental tool which is based on elastic scattering of isotropically distinct guest molecules introduced in a host matrix. Since neutrons are scattered by nuclei, a proton scatters very differently from a deuteron.

Thus, it is possible to study "solid solutions" of an isotropically labelled molecule in a chemically very similar matrix. As the angular range of investigation is varied, information on size, shape and trajectory of a single polymer molecule can be obtained. Small angle neutron scattering at very low angles gives the radius of gyration of the tagged molecules. After crystallization, melt grown crystals had a reduction of about 10% in their radius of gyration. It has been suggested that the conformation of the molecule undergoes only minor adjustments as it goes from the molten to the crystalline state. From this observation, the supporters of the switchboard model (Flory and Yoon)⁸¹ claimed that adjacent reentry is mostly or entirely absent for the stems that are in the crystal. While on the other hand, Hoffman⁸² explained the liquid-like radius of gyration in semi-crystalline polymers as a result of the tie molecules and multiple nucleation of a molecule at distant points on the same lamella, even though a considerable fraction of stems in the crystal exhibit adjacent reentry.

Mobility in the Crystallizing Melt: Yoon and Flory⁸¹ contended that the rates of molecular disentanglements were not high enough to allow adjacent reentry folding. While, Klein and Ball⁸³ and DiMarzio⁸⁴ pointed out that reptation increases the expected rates of rearrangements so that at least short sequences of adjacent reentry should be possible. Reptation is a process first proposed by de Gennes^{85,86} and involves the motion of a polymer molecule along its length.

3.7. The Lauritzen-Hoffman Kinetic Nucleation Theory

The model used is shown in Figure 8 where a , b , l are width, thickness and height of the surface nucleus respectively. The height " l " is fixed at a specified undercooling, L is the crystal width, σ and σ_e are the lateral and fold surface free energies. The surface nucleus grows along the " g " direction, however the measured growth is in the " G " direction. When stems and $\nu_f = \nu - 1$ folds have been formed from the free energy of formation is (ignore chain end effects)

$$\Phi_\nu = 2bl\sigma + 2\nu_f ab\sigma_e - \nu abL\Delta f \quad 3.69$$

for large ν the equation becomes

$$\Phi_\nu = 2bl\sigma + \nu ab(2\sigma_e - L\Delta f) \quad 3.70$$

The surface nucleus is believed to start from a polymer segment or a set of segments, from a solution or undercooled melt, attaching itself to the crystal surface, then coming

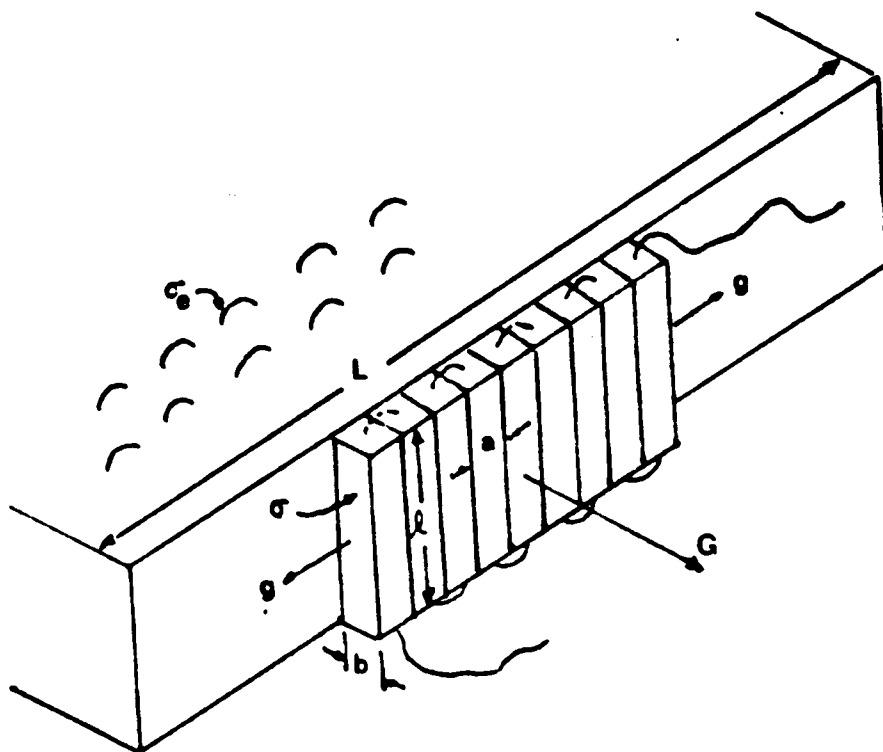


FIGURE 8: Idealized schematic model for polymer lamellar crystal growth. (from Hoffman et al.⁷⁷).

into crystallographic register with the substrate forming the stem at a cost of $2b\sigma$. The molecule then folds back on itself and starts to crystallize adjacent to the first stem. The adjacent position is the most probable site for re-entry after folding, since attachment on a non-adjacent position will add a large extra term $2b\sigma$. As this act is repeated, a surface nucleus begins to approach the region of stability as it spreads in the direction "g". The surface nucleus goes through a maximum in its free energy of formation at or near the first stem ($\nu=1$) and then gradually approaches the region of stability as it increases in size. (Figure 9)

Therefore a set of rate processes can be connected by rates of forward and backward reactions between the states $\nu = 0$ and $\nu = 1$ are A_0 and B , respectively. This corresponds in general to a nucleation controlled process where a large barrier results from the creation of new surfaces which must first be overcome to initiate the nucleus. With subsequent steps leading to the stable region.

3.7.1. Total Flux

The net flow of polymer from sites in the liquid ($\nu = 0$) to the first stem of polymer in the nucleus ($\nu = 1$) of a new layer of polymer crystals is designated as "S".

$$S = N_0 A_0 - N_1 A_1 \quad 3.71$$

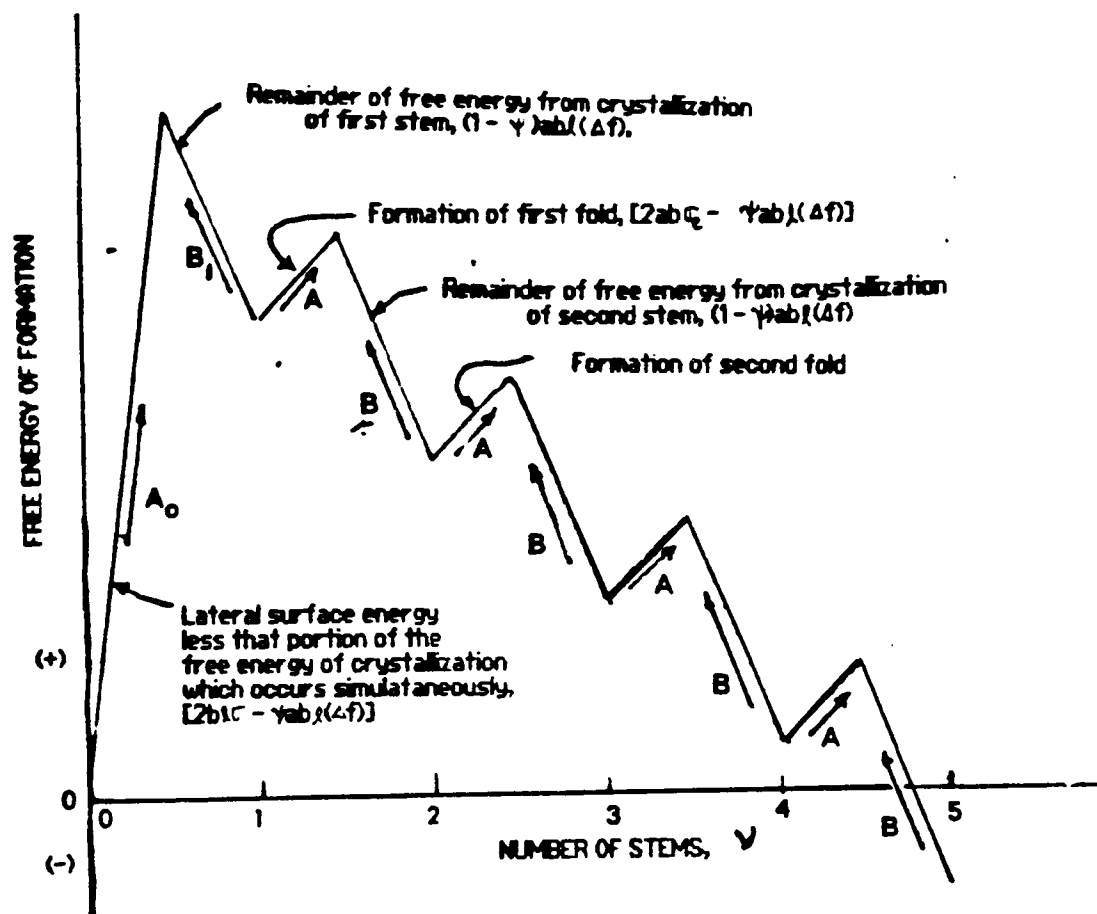


FIGURE 9: Free energy of formation of a chain folded surface nucleus.

N_0 and N_1 are the occupation numbers for $\nu = 0$ and $\nu = 1$ respectively. The net rate of formation of nuclei of length "l" is,

$$S(l) = \beta N_0 \exp\{[-2bl\sigma + \psi ab l(\Delta f)]/kT\} \\ \times [1 - \exp\{[-ab l(\Delta f) - 2ab\sigma_e]/kT\}] \quad 3.72$$

β is the retardation factor which accounts for retardations to molecular motions resulting from the fact that polymer molecules must be transferred to the site of crystallization. ψ is a fraction of the free energy of fusion appropriated to the activation free energy of the forward reaction. The value of ψ may then be related to whether or not the polymer molecule is physically absorbed on the surface prior to crystallographic attachment onto the substrate. The total flux (S_T) is found by summing the above equation by all possible values of "l". Also, assuming that possible values of l are increments of the monomer repeat length l_n , the summation can be replaced by the integral:

$$S_T = (1/l_n) \int_{2\sigma_e/\Delta f}^{\infty} S(l) dl \quad 3.73 \\ = N(\beta/l_n) p \exp(2ab\sigma_e \psi/kT) \times \exp[-4b\sigma\sigma_e/\Delta f kT]$$

where $p = kT/(2b\sigma - ab(\Delta f)) - kT/(2b\sigma + (1-\psi)ab(\Delta f))$

3.7.2. Initial Lamellar Thickness

The average value of l is defined as the initial lamellar thickness l_g^* and is calculated from the flux according to

$$l_g^* = (1/l_n) \int_{2\sigma e/\Delta f}^{\infty} lS(l)dl / (1/l_n) \int_{2\sigma e/\Delta f}^{\infty} S(l)dl \quad 3.74$$

after integrating

$$l_g^* = \frac{2\sigma e}{\Delta f} + \frac{kT}{2b\sigma} + \frac{[2 + (1-2\psi)a(\Delta f)]/2\sigma}{(1-a(\Delta f)\psi/2\sigma)[1+a(\Delta f)(1-\psi)/2\sigma]} \quad 3.75$$

The last term in the previous equation is dl , the additional thickness required for the crystal to grow at a finite rate.

When $\psi = 1$.

$$l = \frac{kT}{2b\sigma} \times \frac{(4\sigma/a) - \Delta f}{(2\sigma/a) - \Delta f} \quad 3.76$$

From the denominator in the above equation and the fact that $(h_f)(T)/T_m^0$ that l becomes infinite at the critical undercooling

$$T_c = 2\sigma T_m^0 / \Delta h_f \quad 3.77$$

this is referred to as the δl catastrophe. At the other extreme when $\psi = 0$ there is no δl catastrophe and l_g falls continuously with temperature. The value of ψ may be related to whether or not the polymer molecule is physically absorbed on the surface prior to the actual crystallographic attachment. The condition where $\psi = 1$ corresponds to the state where the polymer molecule goes directly from the undercooled melt onto the surface without an intermediate

state. On the otherhand, if the polymer molecule is physically adsorbed onto the surface prior to the crystallographic attachment, the lateral surface energy will be incurred first. Thus crystallographic attachment leading to free energy of fusion will to values below one. The conditions of $\psi = 0$ and $\psi = 1$ are extremes and in the case $0 < \psi < 1$ is expected in real polymers.

3.7.3. Retardation Factor

The retardation factor (β) accounts for retardations to molecular motion resulting from the fact that polymer molecules must be transported to the site of crystallization. This factor contains effects resulting from viscosity and surface transport (expressed as events per second). When polymer solutions are at low temperatures or very high undercoolings, they become very viscous and the retardations may control the flux. β can be considered to be the jump rate for local motion,

$$\beta = (kT/h)J_1 \exp[-U^*/R(T-T_\infty)] \quad 3.78$$

The factor $\exp[-U^*/R(T-T_\infty)]$ is the temperature dependence of the segmental jump rate in polymers. Values of U^* and T_∞ can be obtained from the temperature dependence of bulk fluididity. Generally these are quite close to the "universal" values, U^* is 10-15% of 4.1 kcal/mol and T_∞ usually 5-10°K of being 50°K below T_g . However, considerably lower values of both these parameters often fit

the data better, and are claimed to be normally applicable to the crystallization process. It was suggested that this due to crystallization occurring from an adsorbed layer of macromolecules rather than directly from the bulk amorphous region ($\psi < 1$ case). Using empirical values of U^* and T_∞ which are lower than the universal values, will give a better linear fit for the kinetic data of some polymers. This procedure involves assuming a set of values U^* and T_∞ and then fitting $\ln G + U^*/R(T-T_\infty)$ to a linear relation in $1/T/(\Delta T)f$. This method is very similar to the one suggested by Suzuki and Kovacs⁸⁷ in which the transport parameters are analyzed on the basis of the WLF equation.

The term J_1 is inserted into equation 3.78 to allow for any barriers not accounted for by the exponential term. When compared to the exponential term the temperature dependence of J_1 is small. Generally J_1 will act as a pre-exponential factor that simply reduces to β .

3.7.4. Free Energy of Fusion

The free energy of fusion in the expression for total flux G_f is the driving force for crystallization

Near the melting point:

$$\begin{aligned} G_f &= h_f - T \Delta S_f = h_f - T(\Delta h_f)/T_m^0 \\ &= h_f (1 - T_m/T_m^0) \end{aligned} \quad 3.79$$

h_f is the heat of fusion per unit volume at the equilibrium melting point T_m^0 , ΔS_f is the corresponding entropy of fusion.

However, at large undercoolings the above approximation becomes increasingly in error. It is necessary to use a correction factor f :

$$f = \left(h_f(\Delta T)/T_m^0 \right) f \quad 3.80$$

The form of the correction factor given by Hoffman and Weeks¹²⁰ is:

$$G_f = 2T/(T_m^0 + T) \quad 3.81$$

The factor f is almost one at low undercoolings, but decreases G_f considerably at high undercoolings. The source of f is the reduction in the heat of fusion with decreasing temperature.

3.7.5. Growth Rates, Regime I, II and III

The growth rates associated with the model by Lauritzen and Hoffman depend on some function of the product of the net surface nucleation rate and the layer thickness. Polymer crystals can grow in three regimes denoted as I, II and III.

The growth rate regime I is considered to be controlled by nucleation. This regime can be described ideally as a nucleus formed on the growing face and then a strip immediately grows and adds a layer on the face (Figure 10). The linear growth rate G in this regime is proportional to

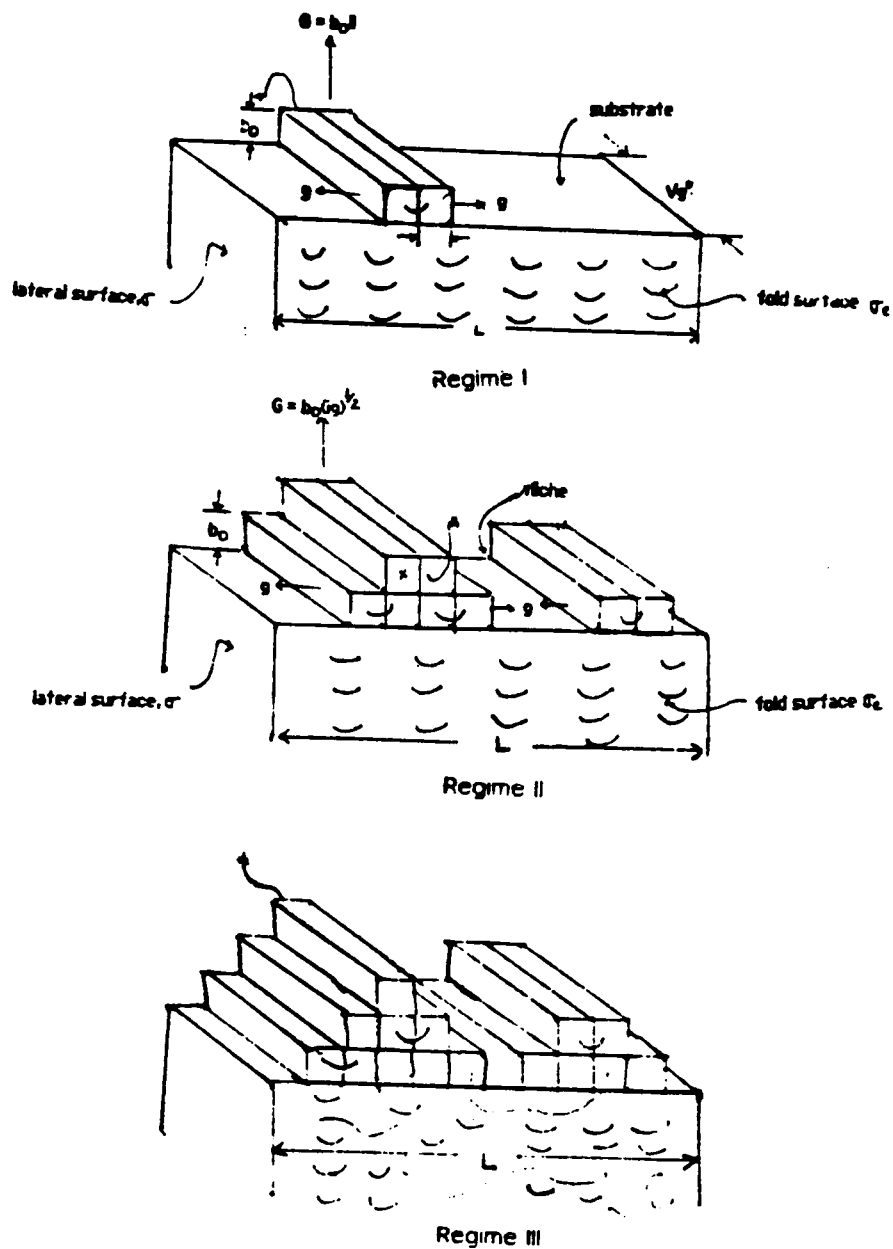


FIGURE 10: Regime I, Regime II and Regime III crystallization (schematic).

the length of the face and is given as:

$$G_I = bil = bL S_T / aN \quad 3.82$$

where b is the layer thickness, L is the substrate length, N is avogadro's number and i is the net surface nucleation rate. Substituting equation 3.72 into equation 3.82 gives:

$$G = G_0 \exp[-U^*/R(T-T_\infty)] \exp[-4\sigma\sigma_e/(\Delta f)kT] \quad 3.83$$

For Regime I, where

$$G_0(I) = n_s(kT/h)J_1 \exp(2ab\sigma_e\psi/kT) \quad 3.84$$

is the pre-exponential factor containing all factors that are not strongly dependent on temperature.

In regime II, multiple nuclei are formed on the face and the linear growth rate is proportional to the geometric mean of the nucleation rate and the strip growth rate

$$G_{II} = b(ig)^{1/2} = b(S_T g/aN)^{1/2} \quad 3.85$$

can be expressed as

$$G = G_0 \exp[U^*/R(T-T_\infty)] \exp(-2b\sigma\sigma_e/(\Delta f)kT) \quad 3.86$$

where

$$G_0 = b(kT/h)J_1 \exp[ab\sigma_e(2\psi - 1)/kT] \quad 3.87$$

The ratio of G_0 values of regimes I and II is

$$G_0(I)/G_0(II) = n_s \exp(ab\sigma_e/kT) \quad 3.88$$

$$G_0(I) \gg G_0(II)$$

In Regime III the growth rate is proportional to nucleation rate just as in regime I. However, in regime III nucleation is so rapid that nuclei are formed on even partially grown strips. In this regime niche separation

eventually approaches the molecular width "a". The growth rate for regime III is

$$G_{III} = biL' = bin_s a = bLS_T/aN \quad 3.89$$

where L' is the effective substrate length and n_s is the mean number of stems that are laid down in the niche adjacent to the newly nucleated stem.

The linear growth rate is

$$G_{(III)} = G_{O(III)} [-U^*/R(T-T_\infty)] \exp[-4b\sigma_e/(\Delta f)kT] \quad 3.90$$

$$G_{O(III)} = b[(kT/h)n_s'](2ab\sigma_e/kT) \quad 3.91$$

3.7.6. Limitations to the Lauritzen-Hoffman Nucleation Theory

The Lauritzen-Hoffman theory, and all other kinetic theories, imply sharp chain folding with adjacent re-entry. This is not an intrinsic characteristic of the theory, but is an assumption required in order to make the model analytically attractive. The theory does not include the effects of a departure from the adjacent re-entry. In the case of extended chain crystallization, (few or no folds), LH theory is inadequate because of the lack of adjacent re-entry and a large number of folded stems.

Another major limitation of LH theory is the constant fold period. In the LH theory it is assumed that a fold plane once nucleated will grow with a constant fold period. This has been questioned by Frank and Tosi,⁸⁸ Price⁸⁹ and

Lauritzen and Passaglia⁹⁰ and found to be too strict an assumption. The theory postulated by Lauritzen and Passaglia⁹⁰ takes all possible fold periods into account but fails since it predicts that $\bar{l}$ increases catastrophically as T reaches to a high critical undercooling.

4. EXPERIMENTAL TECHNIQUES

4.1. Equipment

Dielectric measurements (at one atmosphere pressure) were made using a system consisting of a signal generator and detector, a capacitance bridge, a dielectric cell and container, and a temperature monitor and controller. A schematic of this system is shown in Figure 11.

4.1.1. Capacitance Bridge

The capacitance and conductance measurements were made using a General Radio 1620 Precision Capacitance Bridge. The precision capacitance bridge is a transformer ratio arm bridge. The sample arm is configured in a three terminal unknown mode. This mode excludes ground lead capacitances from the measurements. The standard arm of the bridge consisted of calibrated internal standards and has a capacitance range of $10^{-19} \text{ F} < C_X < 10^{-7} \text{ F}$ and a conductance range of $10^{-16} \text{ Mhos} < G_X < 10^{-5} \text{ Mhos}$. The bridge was designed to operate over a frequency range from 10 hz to 100 khz.

The measurements of capacitance, particularly when of high accuracy is made by a null method which uses some form of basic ratio bridge. (see Figure 12) The capacitance of the unknown is C_X (polymer) is balanced by a calibrated variable standard capacitor, C_N , or by a fixed standard

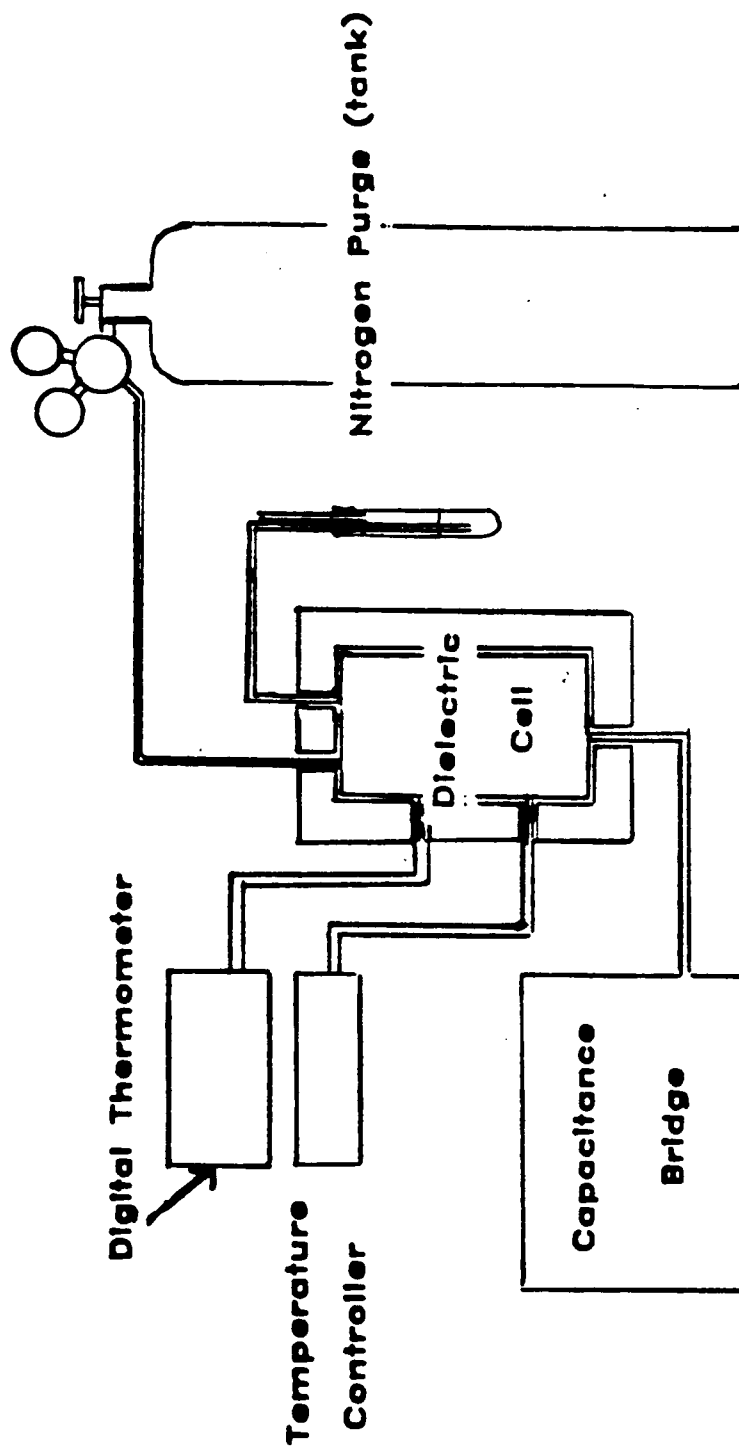


FIGURE 11: Dielectric data acquisition system.

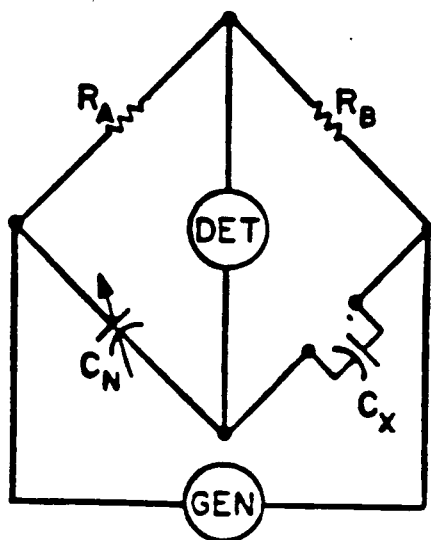


FIGURE 12: Basic ratio bridge.

capacitor and variable ratio such as R_A or R_B . Such bridges with resistive ratio arms and with calibrated variable capacitor or resistors can be used over a wide range of capacitance and frequency.

4.1.2. Parallel Plate Capacitor

The dielectric cell used in this study was originally designed by Coburn⁹¹ as a three-terminal parallel plate capacitor to measure sample capacitance and conductance as seen in Figure 13. The parallel plate capacitor consisted of a central brass disc surrounded by three concentric brass rings. The central disc served as a low electrode and the middle concentric ring as the air capacitor electrode. 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. Air gaps 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.

The temperature of the sample was measured by a copper-constantan thermocouple placed in the inner concentric ring through a hole in the bottom disc. Top brass disc was aligned parallel to the coplanar surface of the central disc

DIELECTRIC CELL

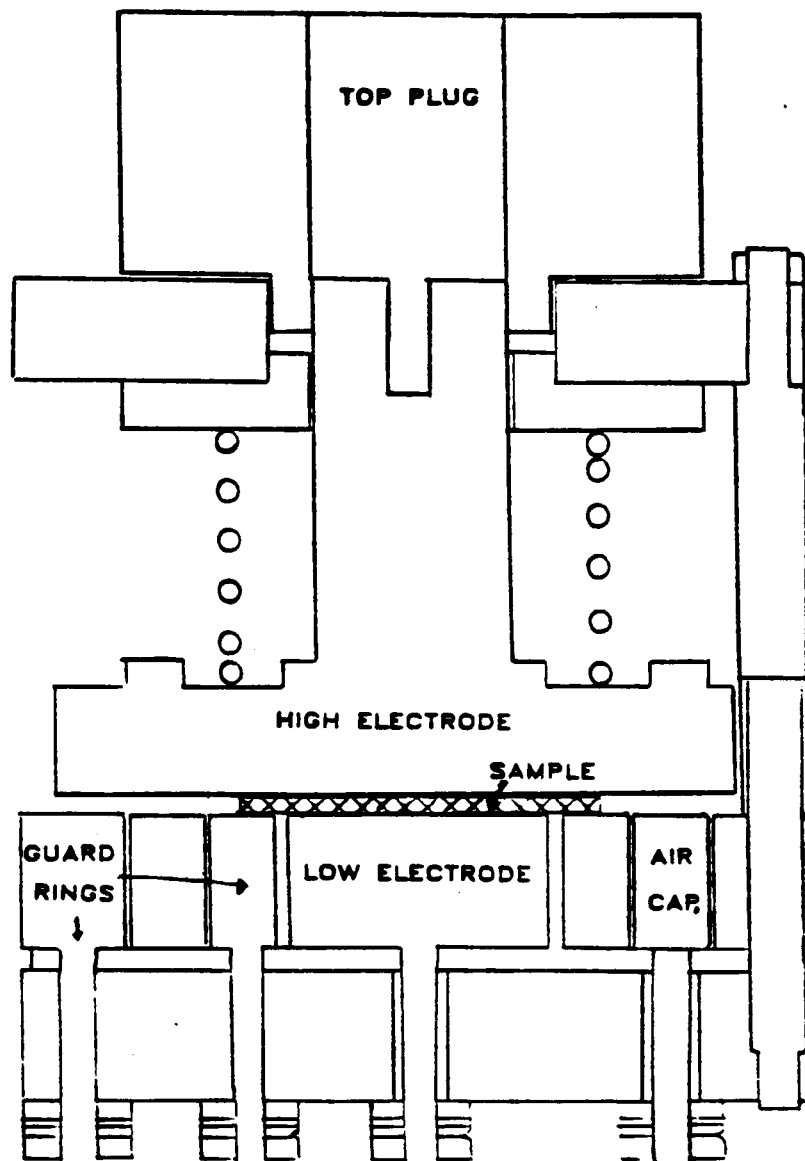


FIGURE 13: Parallel plate capacitor (side view).

and three concentric rings with the help of three brass columns. This top brass electrode served as a high electrode for both the sample and air capacitor. Pyrex sheets were used to electrically insulate the electrode since they have excellent thermal stability over the entire range of experimentation.

A distinct feature of the above cell design is the fact that the actual value of the air-filled area capacitance at any temperature can be converted (after a correction for area expansion of the electrode) to the distance between the plates and therefore to the sample thickness. This provides a convenient and extremely sensitive way to measure the linear thermal expansion of solid specimens. For completely amorphous materials that become fluid, measurements of thermal expansion above T_g become quite inaccurate.

The specimens to be used were coated with gold deposited by evaporation in a vacuum sputterer. The coated diameter on the lower side slightly exceeded that of the active center electrode so that the active area is to be determined by the coating rather than by the diameter. A correction of the sample area was made on the base of the linear thermal expansional isotropy.

4.2. Data Reduction

4.2.1. Offset Corrections

The first step in reducing the data was to correct the measured conductance for offset. D.C. conductivity becomes significant at lower frequencies and higher temperatures. A plot of $\log(\text{frequency})$ versus $\log(\text{conductance})$ was constructed at each temperature. At each temperature the low-frequency conductance data was extrapolated to zero frequency and the zero-frequency data was obtained. For low temperatures the value of the d.c. conductivity was very small and at the higher temperatures the d.c. conductivity was quite significant. The value of the d.c. conductivity calculated at any given temperature was subtracted from the bridge conductance data. This method minimized errors due to d.c. conductivity.

4.2.2. Dielectric Constant and Loss

From the signal generator a sine-wave signal was generated and applied to the parallel plate capacitor given by:

$$V(t) = V_0 \exp(i\omega t) \quad 4.1$$

The corresponding current had a component in-phase (resistive) and a component 90° out-of-phase (capacitive) with the applied field and can be shown by the vector plot

in Figure 14(a).

$$I(t) = \frac{d(q(t))}{dt} = \frac{d(C^*V(t))}{dt} \quad 4.2$$

Applying equation 4.1 for the voltage equation 4.2 yields:

$$\begin{aligned} I(t) &= i\omega\epsilon^*C_0V(t) \\ &= i\omega(\epsilon' - i\epsilon'')C_0V(t) \\ &= i\omega\epsilon'C_0V(t) + \omega\epsilon''C_0V(t) \end{aligned} \quad 4.3$$

The capacitance bridge measured the parallel equivalent parameters C_x and $G_x (= 1/R_x)$. A schematic of the parallel equivalent circuit for the dielectric is shown in Figure 14(b). The equivalent circuit equation is given by:

$$Y_p = 1/R_p + i\omega C_p \quad 4.4$$

Applying Ohm's law results in:

$$I(t) = Y_pV(t) = 1/R_pV(t) + i\omega C_pV(t) \quad 4.5$$

By equating the real and imaginary parts of equation 4.3 and equation 4.5 results in:

$$\epsilon' = \frac{C_p}{C_0} \quad \epsilon'' = \frac{G_p}{\omega C_0} \quad 4.6$$

These equations were used to calculate the dielectric constant and loss from the sample capacitance and conductance.

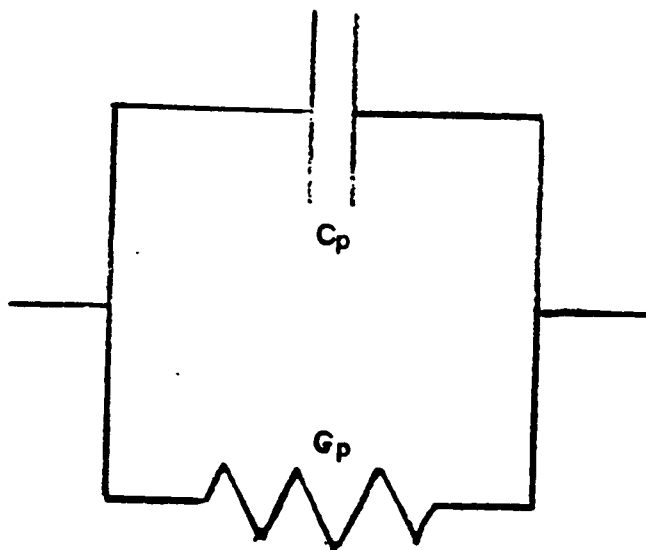
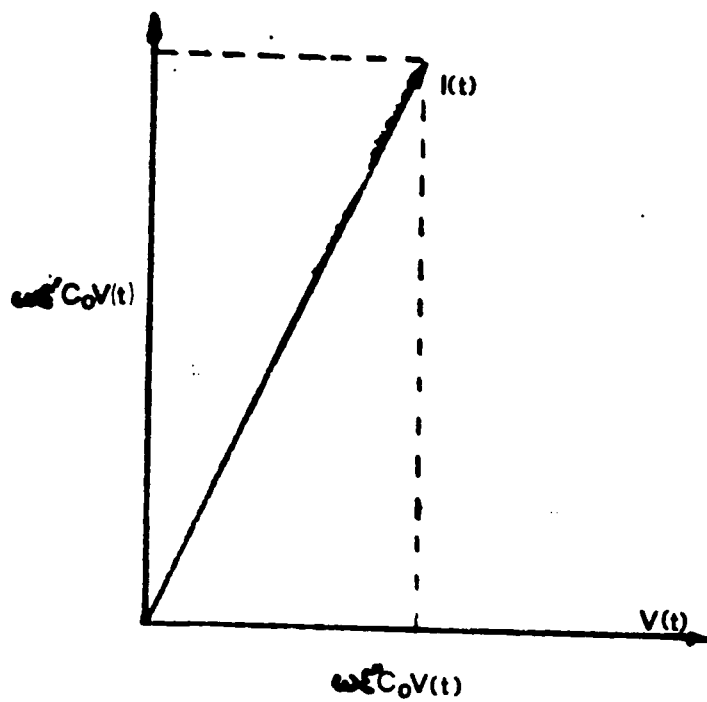


FIGURE 14: (a). Current-voltage diagram. (b). Parallel equivalent circuit.

4.2.3. Temperature Dependence of C_o

The design of the parallel plate capacitor allowed for the determination of the displacement of the plates, C_o in equation 4.2.6 was corrected for the thermal expansion effects of the samples studied prior to calculation of the dielectric constant and loss.

Displacement of the air capacitor plates were calculated from:

$$d_A(T) = \frac{A_A(T)\epsilon_o}{C_{XA}(T)} \quad 4.7$$

where $A_A(T)$, $d_A(T)$ and $C_{XA}(T)$ were the area displacement and capacitance measured at 10.5 khz of the air capacitor at temperature T , respectively. Displacement of the sample capacitor was equal to the displacement of the air capacitor. Therefore, the thickness of the sample at 25°C was given as:

$$\frac{L(t)}{L(25^\circ\text{C})} = \frac{d(T)}{d(25^\circ\text{C})} = \frac{A_A(T)}{A_A(25^\circ\text{C})} \frac{C_{XA}(25^\circ\text{C})}{C_{XA}(T)} \quad 4.8$$

Since the plates of the air capacitor were made of brass, the term $A_A(T)/A_A(25^\circ\text{C})$ was calculated from the normalized thickness of brass as a function of temperature given in section 4.5. The empty cell capacitance was given by:

$$C_o(T) = \frac{A_S(T)\epsilon_o}{d_S(T)} \quad 4.9$$

$A_S(T)$, the area of the sample capacitor, was determined by the area within the gap in the gold plating on the

sample, and $d_s(T)$, the displacement of the sample capacitor, was determined by the sample thickness. Therefore, the temperature dependence of $C_o(T)$ was related to the thermal expansion of the sample in the following manner.

$$C_o(T) = \frac{A_s(25^\circ\text{C})}{d_s(25^\circ\text{C})} \frac{((L(T)/L(25^\circ\text{C}))^2 \epsilon_o)}{((L(T)/L(25^\circ\text{C})))} \quad 4.10$$

$$C_o(T) = C_o(25^\circ\text{C}) (L(T)/L(25^\circ\text{C}))$$

Equation 4.9 was used with equation 4.7 to calculate the temperature dependent empty cell capacitance for use in equation 4.6.

4.3. Experimental Procedure

Amorphous PET samples were studied over a temperature range from -160°C to 130°C . The parallel plate capacitor was placed in a brass container and heating tape was wrapped around the brass container which was then sealed, wrapped in fiberglass and placed into a dewar.

The container was continuously purged with dry nitrogen gas, to keep moisture from condensing on the capacitor, while being cooled to liquid nitrogen temperatures at a rate approximately $1^\circ\text{C}/\text{min}$. The capacitor was heated and the temperature was stabilized manually by a variac connected to the electrical tape. The dielectric measurements were made during the heating cycle of the run.

4.4. Sample Preparation

The glassy polymer studied in this thesis was poly(ethylene terephthalate), which was obtained from Pacur Inc. (produced by Eastman Chemical Products). Information which was provided by Pacur indicated that the amorphous films had a number average molecular weight of 26,000 grams/mole.

Amorphous PET film samples were annealed at various temperatures just below the glass transition temperature 70°C. For the annealing cycles at selected temperatures below the glass transition temperature, the films were supported inside a stoppered glass test tube with teflon tape and aluminum foil. A thermocouple was attached to the films to obtain the accurate temperature of annealing. The tubes were suspended in a water bath maintained at constant temperatures to within $\pm 0.2^\circ\text{C}$.

4.5. Sample Characterization

The instrument used to check for the enthalpy relaxation measurements was the Perkin-Elmer DSC-7. The temperature scale was calibrated using the melting transition of indium. Both the temperature and energy-input calibrations were checked frequently using the melting transition of indium. Normally, the scanning rate used throughout these studies were 10°C/min. In addition small

angle x-ray scattering was performed to determine if there was any increase in orientation or crystallinity of the annealed samples.

Densities were determined using a density gradient column made from sodium bromide and water with a range of 1.30 gram/cc to 1.45 gram/cc. The technique used for preparing the density gradient column is described in the ASTM D 1505(128) standard.

Dilatometric information was obtained for all the samples. The normalized thickness of the samples as a function of temperature was given in section 4.2.3 in equation 4.8. The samples were considered to be isotropic and the specific volume of the samples was calculated from the normalized thickness with the equation:

$$v(T) = ((L(T)/L(25^{\circ}\text{C}))^3 v(25^{\circ}\text{C}) \quad 4.11$$

To obtain accurate specific volume data, the normalized surface area of the air capacitor's low lead electrode, $A_A(T)/A_A(25^{\circ}\text{C})$ in equation 4.8 needs to be known over the entire temperature range of interest. The normalized surface area was defined in terms of the normalized thickness of brass.

$$A_A(T)/A_A(25^{\circ}\text{C}) = (L_{br}(T)/L_{br}(25^{\circ}\text{C}))^2 \quad 4.12$$

The normalized thickness of brass as a function of temperature was calculated from the equation below, derived from a vycor standard as a sample, as done by Coburn (1984).

$$L_{br}(T)/L_{br}(25^{\circ}\text{C}) = 0.999574 + 1.77297 \times 10^{-5}T(^{\circ}\text{C}) + 1.967307 \times 10^{-8}T^2(^{\circ}\text{C}^{-2}) \quad 4.13$$

In addition, small angle light scattering (SALS) experiments were performed on the samples at different crystallization temperatures. These experiments made it possible to determine if there was any change in the size of the spherulites on annealing below the glass transition temperature.

5. RESULTS

5.1 Sample Characterization

5.1.1 Thermal Properties

In this study amorphous PET films were annealed below the glass transition temperature and analyzed thermally using differential scanning calorimetry (DSC). The influence of annealing processes of organic glasses in the glass transition interval was first investigated and analyzed quantitatively by Petrie.²⁵ The glasses studied here exhibited excess free energy; annealing these samples produced an enthalpy peak and an increased glass transition temperature (T_g) when analyzed by DSC, as shown in figure 15

Figure 15 shows an increase in the endotherm peaks as a function of annealing temperature and annealing time. The annealing time effect is shown by the scans of samples annealed at 68°C at annealing times of 1, 24 and 48 hours. The sample annealed for only one hour has a much smaller enthalpy peak than the sample annealed for 48 hours. This is due to the fact that the sample annealed for one hour did not have enough time for the molecular chains to relax.

The annealing temperature played a very important role in the thermal behavior, in comparison to the unannealed. As the annealing temperature approached the glass transition temperature, there was an increase in the magnitude of the peak. The sample annealed at 68°C for 48 hours produced the

largest endotherm peak, because the sample absorbed the most energy. Thus the annealed sample had most of its molecular relaxation taking place during the annealing process.

However, at lower annealing temperatures from the glass transition temperature, not as much effect was observed on annealing as compared to the unannealed sample. This indicated that the molecular chains did not have as much energy to relax as the samples annealed closer to the glass transition temperature.

In Figure 15 there is a distinctive shift in the glass transition temperature with increasing annealing temperature and time. As seen in these scans there is a general increase in the glass transition temperature with an increase in annealing temperature. This can be related to the fact that as the system was annealed, chain relaxation took place and this, in turn, reduced the volume of the system. Generally, when reducing the volume of the system, the glass transition temperature increases. This indicates the system needs more energy to go through such a transition.

The absorption of thermal energy can be viewed as a kinetic effect. The energy absorption near T_g paralleled the extent of molecular relaxation that had taken place during the annealing period. The absorption of thermal energy in the transition interval of an annealed PET sample

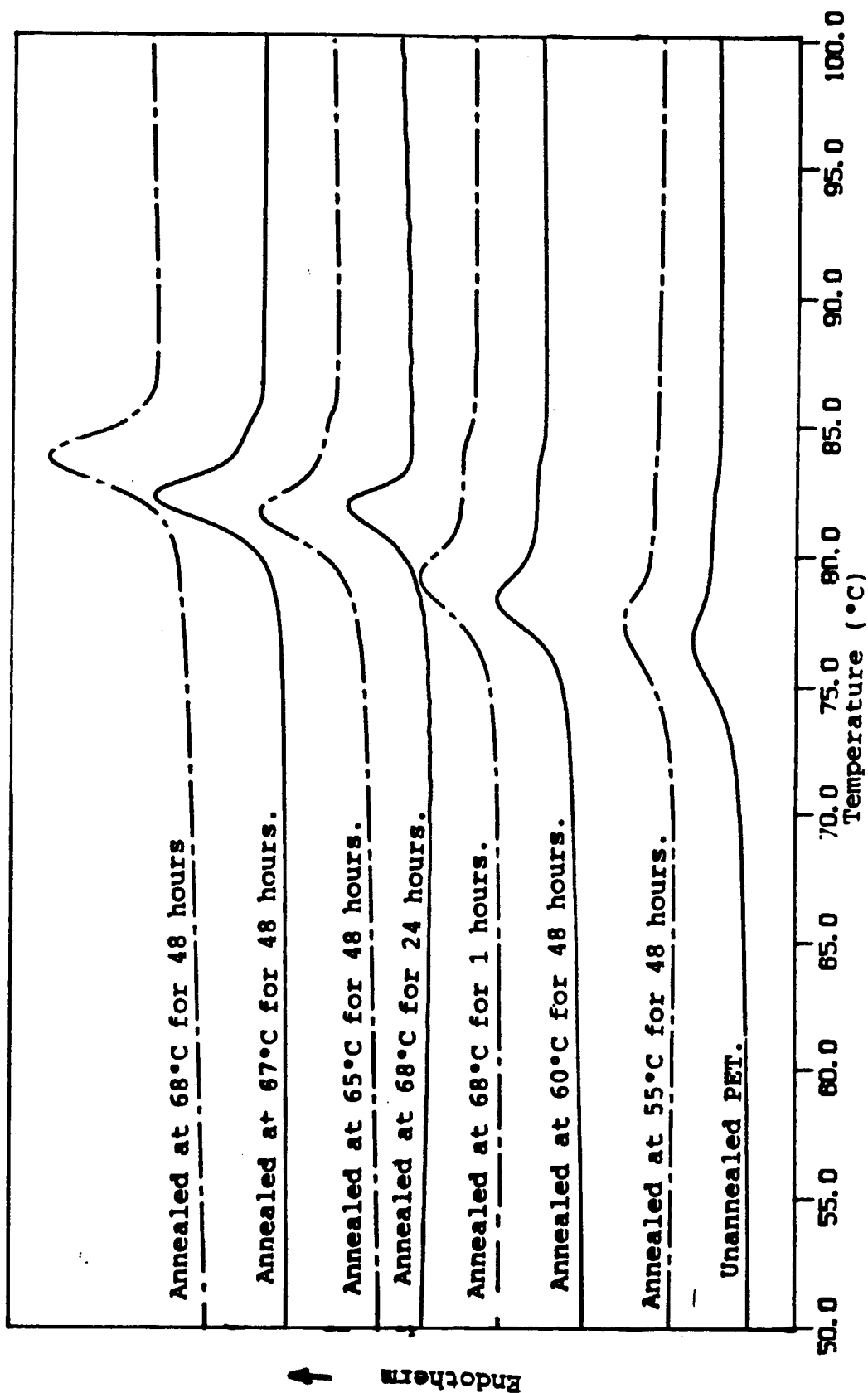


FIGURE 15: Enthalpy relaxation of amorphous PET at different annealing conditions shown by DSC scans.

suggested that the free energy absorbed could be accounted for on the basis of the kinetics of the glass transition.

Thus the absorbed energy parallels the enthalpy relaxation occurring during annealing. The enthalpy measured from the DSC peak during the transition was related to the enthalpy relaxation process. With longer annealing periods, more thermal recovery occurred with an increase in the transition endotherm.

5.1.2 Specific Volume Determination

The specific volumes was calculated as a function of temperature from the air capacitance data obtained concurrently with the capacitance and conductance data. The data is shown in Figure 16.

Figure 16 shows that the annealing temperature of the sample approached the glass transition temperature, and that the sample had a much smaller specific volume. This is shown by the sample annealed at 68°C for 48 hours. During the annealing process the molecular chains relaxed and thus the volume of the system decreased. As the temperature of the annealing was lowered, the samples did not show a decrease in the specific volume (free volume) as in the samples annealed at higher temperatures. The general trend is illustrated in Figure 16.

From these plots as the glass transition temperature of each sample was determined by fitting the linear regression

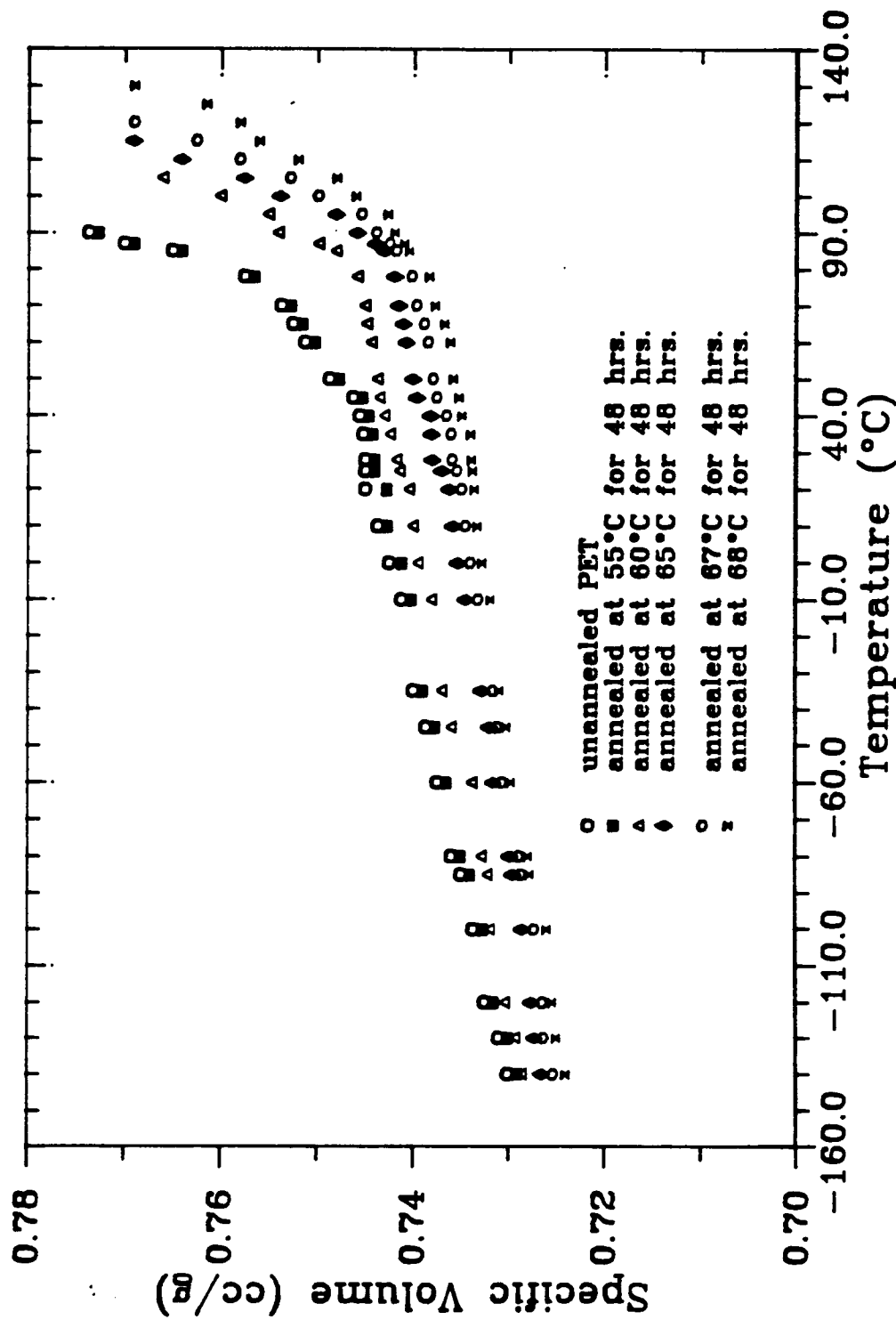


FIGURE 16: Temperature dependence of specific volume of the unannealed and annealed samples of PET.

of two lines with their intersection at the glass transition temperature (T_g). As the sample annealing temperature increased the glass transition temperature of the sample increased. The sample annealed at 68°C for 48 hours had a significant increase in T_g as compared to the unannealed sample as seen previously in the DSC scans. In section 6.3.1. a table of the glass transition temperatures are shown.

Densities were measured at 25°C using the density gradient column of sodium bromide and water. The density of the samples used in this study were utilized in determining specific volumes of the samples as explained in section 4.5. The amorphous PET density can be measured directly and its value of 1.335 g/cc is within one percent of what Mehta et. al.⁹² obtained.

5.2. Dielectric Data

5.2.1. Dielectric Constant and Loss

The dielectric data were obtained directly from the bridge, and consisted of capacitance (C) and conductance (G) values at different frequencies (ν) and temperature (T). The capacitance and conductance were respectively converted into the dielectric constant (ϵ') and dielectric loss (ϵ'') by using equations 4.2.6a and 4.2.6b.

5.2.2. Residual D.C. (direct current) Conductivity

D.C. conductivity is quite apparent at lower frequencies and higher temperatures and a correction is necessary. The following method was utilized in the correction for the d.c. conductivity. The low-frequency conductance data at each temperature were extrapolated to zero frequency and thus the zero-frequency conductance was obtained. At the lower temperatures the value of the d.c. conductivity was very small while at higher temperatures the d.c. conductivity was significant. At any given temperature the value of the d.c. conductivity was calculated and subtracted from the bridge conductance data. This procedure helped to minimize errors due to the d.c. conductivity picked up during the experiments. (Figure 17)

5.2.3. Cole-Cole Parameters

The single relaxation time (SRT) model represents an ideal system where all the relaxation processes have the same relaxation time τ . This model produces the following simple relationship between the complex dielectric constant and the applied field:

$$\epsilon^* = \epsilon_u + (\epsilon_R - \epsilon_u) / [1 + i\omega\tau] \quad (5.1).$$

The model represents dipolar relaxation in many simple liquids fairly well, but polymers usually have much broader

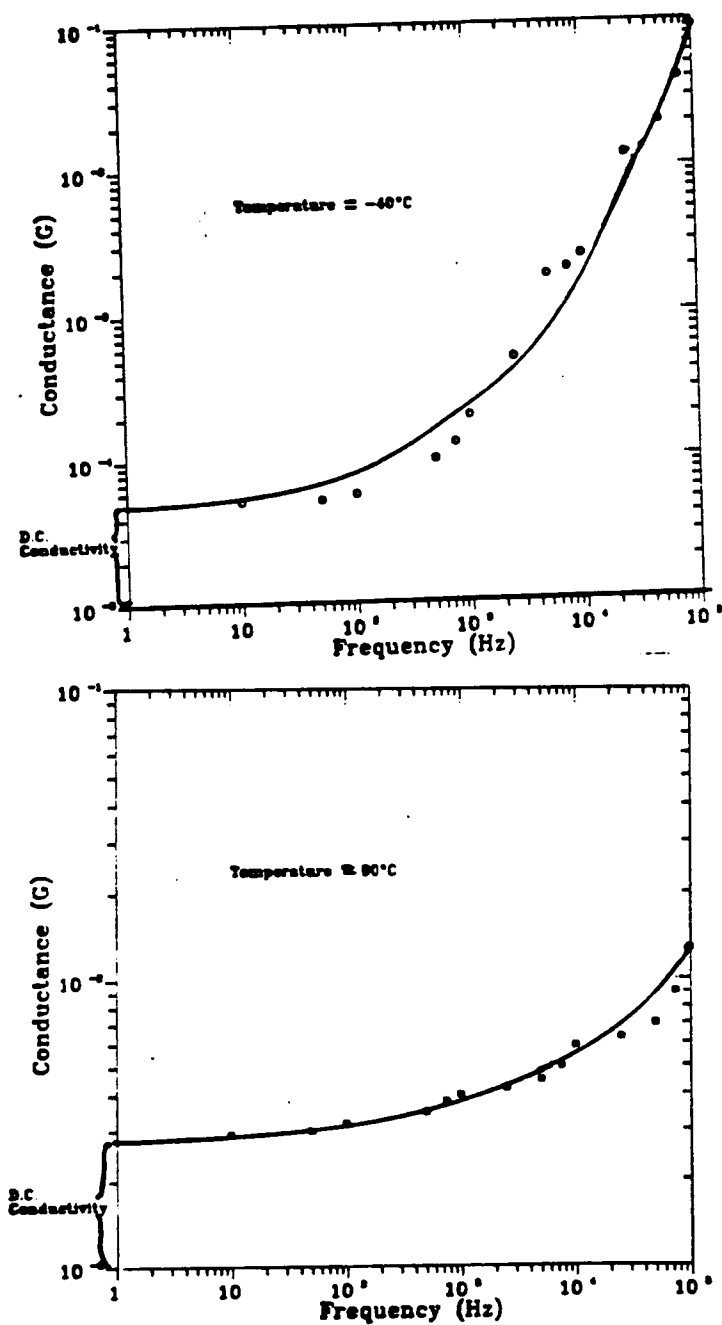


FIGURE 17: Determination of d.c. conductivity at different temperatures.

relaxations. Thus, this equation has to be modified to take into account the distribution of relaxation times present in dielectric data of a polymer. This is usually done using empirical functions of the type described below. The Cole-Cole function⁵⁸ modified the above equation by the introduction of the parameter β .

$$\epsilon^* = \epsilon_u + (\epsilon_R - \epsilon_u) / [1 + (i\omega\tau)^\beta] \quad (5.2).$$

The Cole-Cole parameter β takes values $0 < \beta < 1$. β is a measure of the width of a symmetric function. Cole-Cole plots are generated at isothermal conditions. 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 β of about 1% was due to the scatter in the data points.

At isothermal conditions and low frequencies, the dipoles on the polymer chains orient in phase in the direction of the applied field, hence ϵ' is called the relaxed dielectric constant, ϵ_R . While at the same temperature, but at high frequencies, the dipoles are not able to follow immediately the rapidly alternating field. The dielectric constant acquires a lower value and is called the unrelaxed dielectric constant, ϵ_u . At both ϵ_R and ϵ_u the dielectric loss is negligible. The difference between ϵ_R and ϵ_u is called the relaxation magnitude (or strength). A

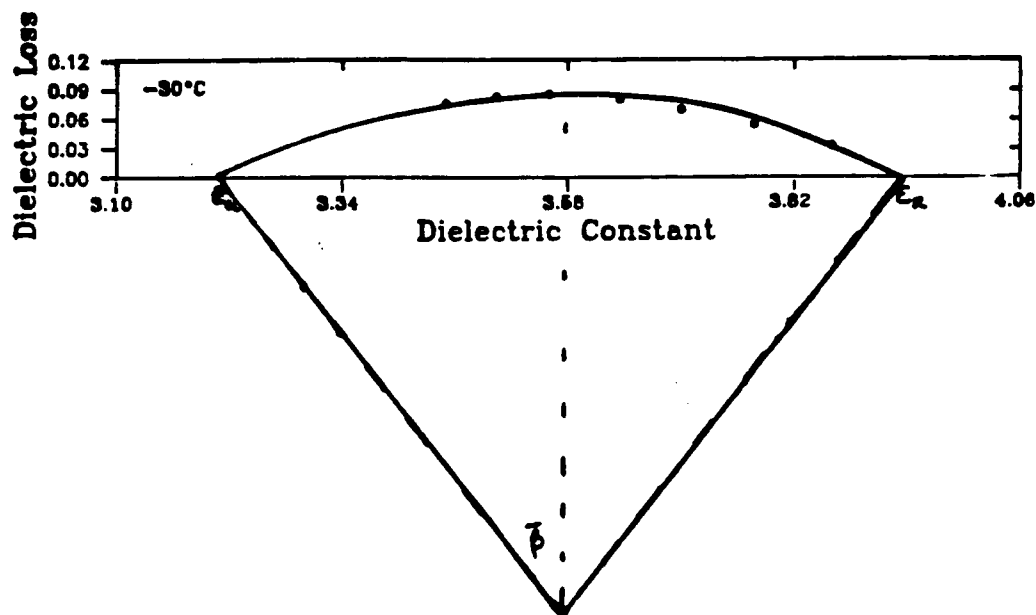
sample calculation of the Cole-Cole parameter is shown in Figure 18.

5.3. Dielectric Relaxation Studies of Unannealed (PET) Poly(ethylene terephthalate)

Figure 19 and figure 20 shows the dielectric constant and loss of amorphous PET as a function of temperature at several frequencies. There are two loss peaks at 100°C and -50°C and are labeled α and β respectively. Figure 19 shows that at a frequency of 100Hz the α loss peak occurs near 100°C and the β peak occurs near -50°C. Similar results were obtained by Reddish⁹³ and Coburn.⁹¹ The rising loss above 140°C at low frequencies was shown by Reddish to be due to a superposition of a d.c. conductivity and Maxwell-Wagner process.

Reddish showed that the α process was due to the micro-brownian motions of the chain, in the amorphous regions, and was associated with the glass-transition temperature. This result has been confirmed by many authors. The principal evidence is that the magnitude ($\epsilon_R - \epsilon_U$) of the α -relaxation decreases with increased degree of crystallinity.

The activation energies of each loss process can be estimated from Arrhenius plots of the logarithm of applied frequency vs. the reciprocal of the absolute temperature of maximum loss. Figure 21 is the Arrhenius plot of the amorphous unannealed PET, obtained from dielectric data of



$$\text{Radius} = \frac{(\epsilon_R - \epsilon_u)}{2} \csc \frac{\beta\pi}{2}$$

β is the Cole-Cole Parameter.

First determine the radius of the depressed circle obtained from the plot of dielectric loss versus dielectric constant (Cole-Cole plot). The relaxed dielectric constant (ϵ_R) and the unrelaxed dielectric constant (ϵ_u) is obtained where the circle intersects the x-axis. By solving the above equation, the β Cole-Cole parameter can be determined.

Figure 18: A sample calculation for determining the Cole-Cole parameter from a Cole-Cole plot.

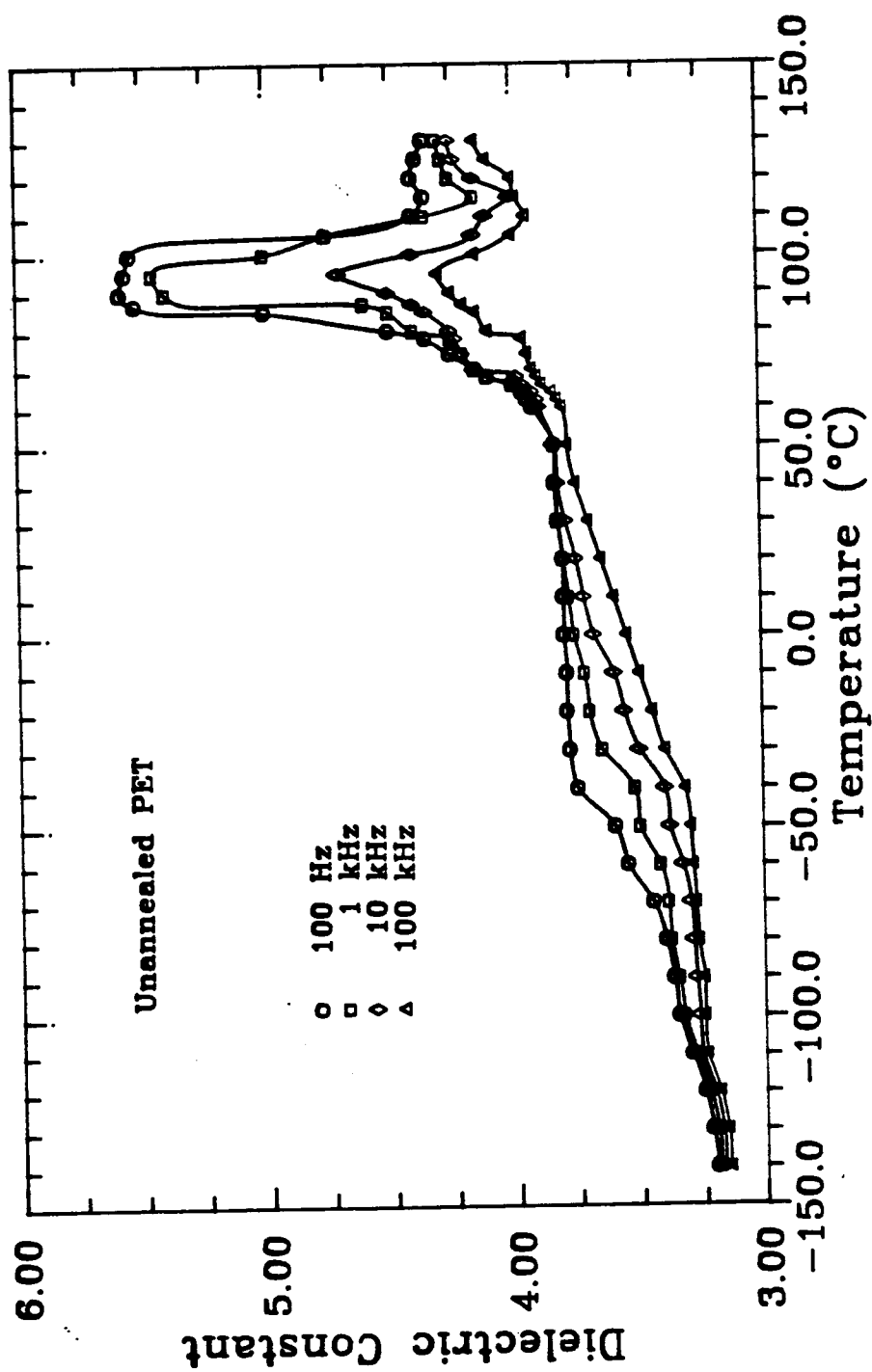


FIGURE 19: Dielectric constant versus temperature for the unannealed PET sample.

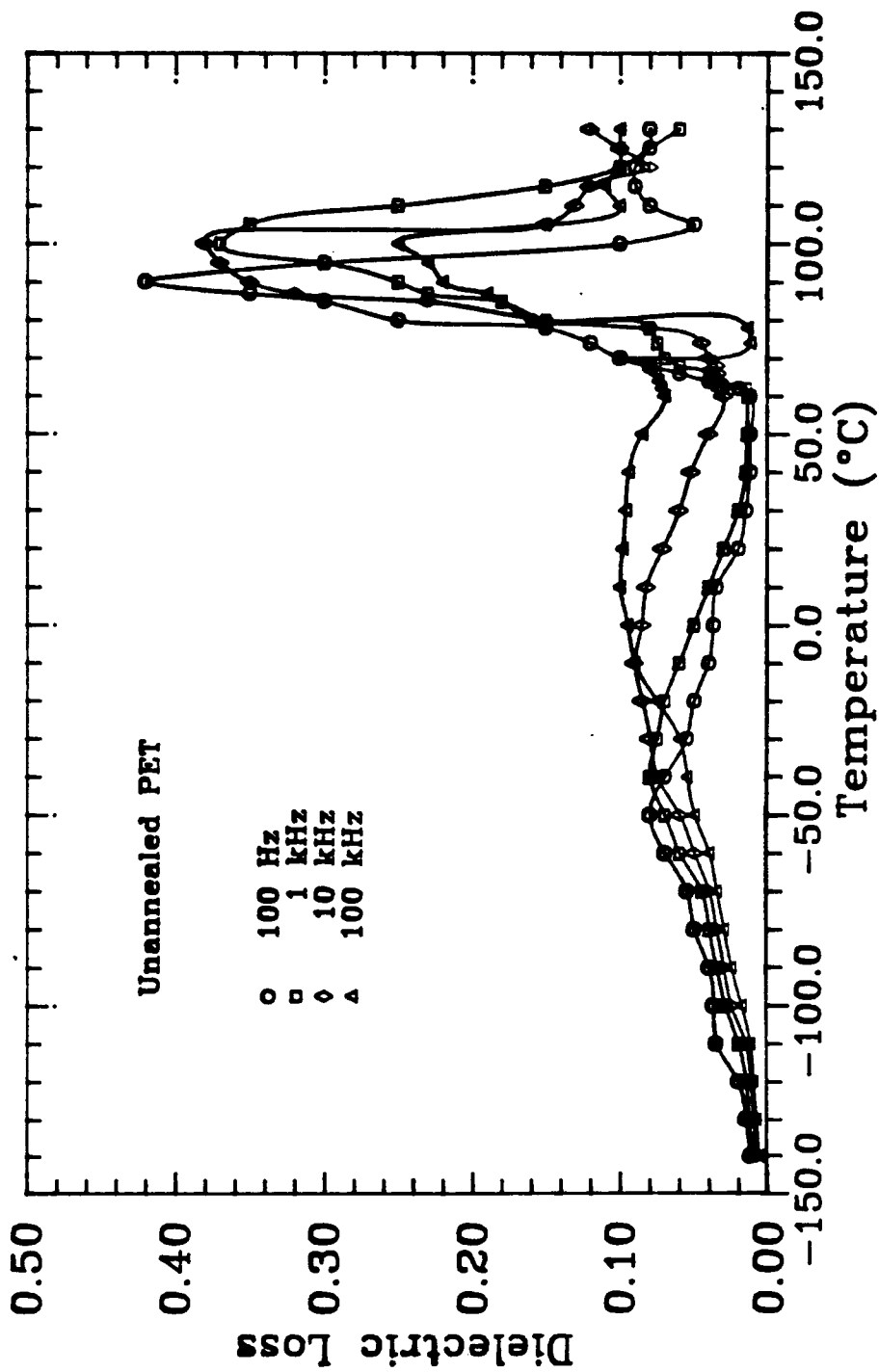


FIGURE 20: Dielectric loss versus temperature for the unannealed PET sample.

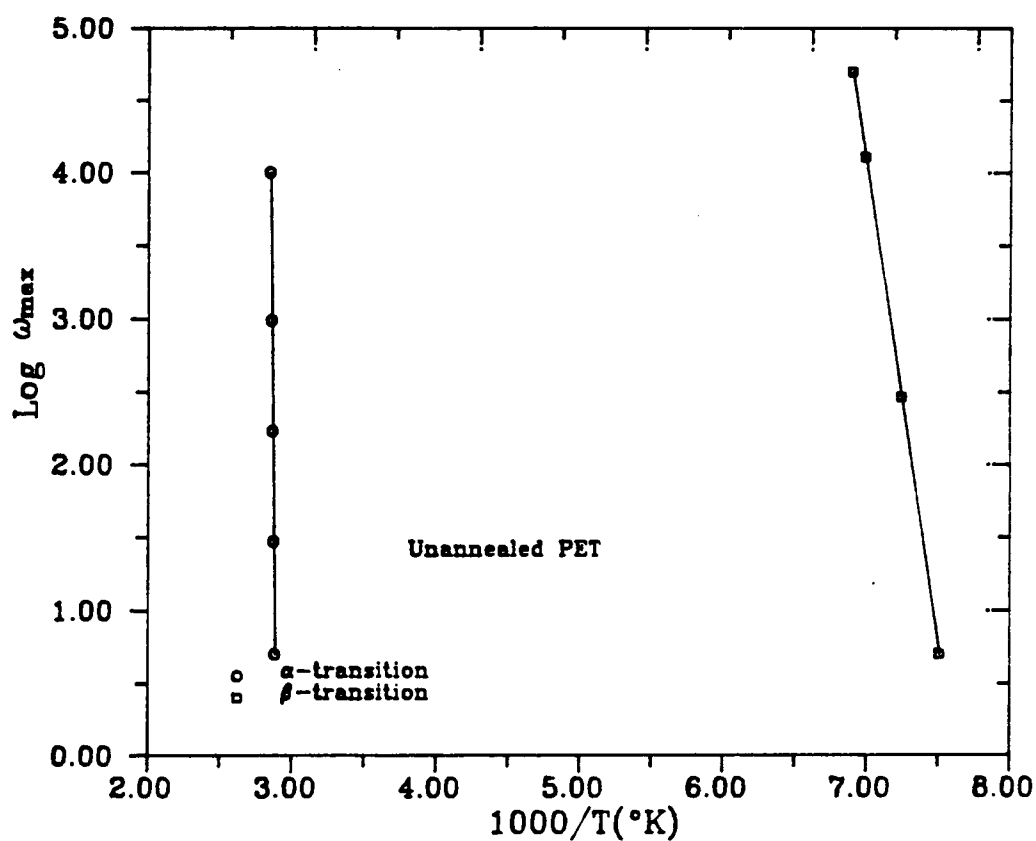


FIGURE 21: Plot of Log $\omega_{\max}$ vs. 1000/T(°K) for the α and β transition peaks of the unannealed sample. The activation energy of each transition peak.

figure 20. The α relaxation has an activation energy of 184.0 kcal/mol determined from the slope of the plot. The value reported by Illers and Breur,⁴² was $H_{\alpha} = 184$ kcal/mol for both the mechanical and dielectric α -relaxation in amorphous PET. The β -relaxation has an activation energy of 12.7 kcal/mol which is similar to $H_{\beta} = 12.9$ kcal/mol reported by Illers and Breur.⁴² Activation energies for the α and β relaxation processes are presented in Table I.

Cole-Cole plots have been generated for the α and β transitions (figure 22 and 23, respectively). The plots were obtained by interpolating the data in figure 19 and 20. The relaxation magnitude ($\Delta\epsilon'$) and Cole-Cole parameters obtained from the Cole-Cole plots for the α and β relaxation processes are listed in Tables II and III.

5.4. Dielectric Relaxation Studies of PET Samples Annealed below the T_g

This study attempted to correlate the changes observed in thermal properties shown in section 5.1.1 with dielectric properties of PET glasses. It was of particular interest to examine the implications of annealing below T_g . Several amorphous PET film samples were annealed at 55°C, 60°C, 65°C, 67°C and 68°C for 48 hours (below the glass transition of 70°C).

Figure 24 and 25 shows the dielectric constant and dielectric loss of the annealed PET sample (which was

Table I Activation Energy of the α and β transition peak.

<u>Sample</u>	<u>α - peak</u> kcal/mole	<u>β - peak</u> kcal/mole
Unannealed PET	184.12	12.92
Annealed at 55°C for 48 hrs.	180.00	12.77
Annealed at 60°C for 48 hrs.	165.20	12.30
Annealed at 65°C for 48 hrs.	158.30	12.15
Annealed at 67°C for 48 hrs.	120.15	11.82
Annealed at 68°C for 48 hrs.	108.72	11.62

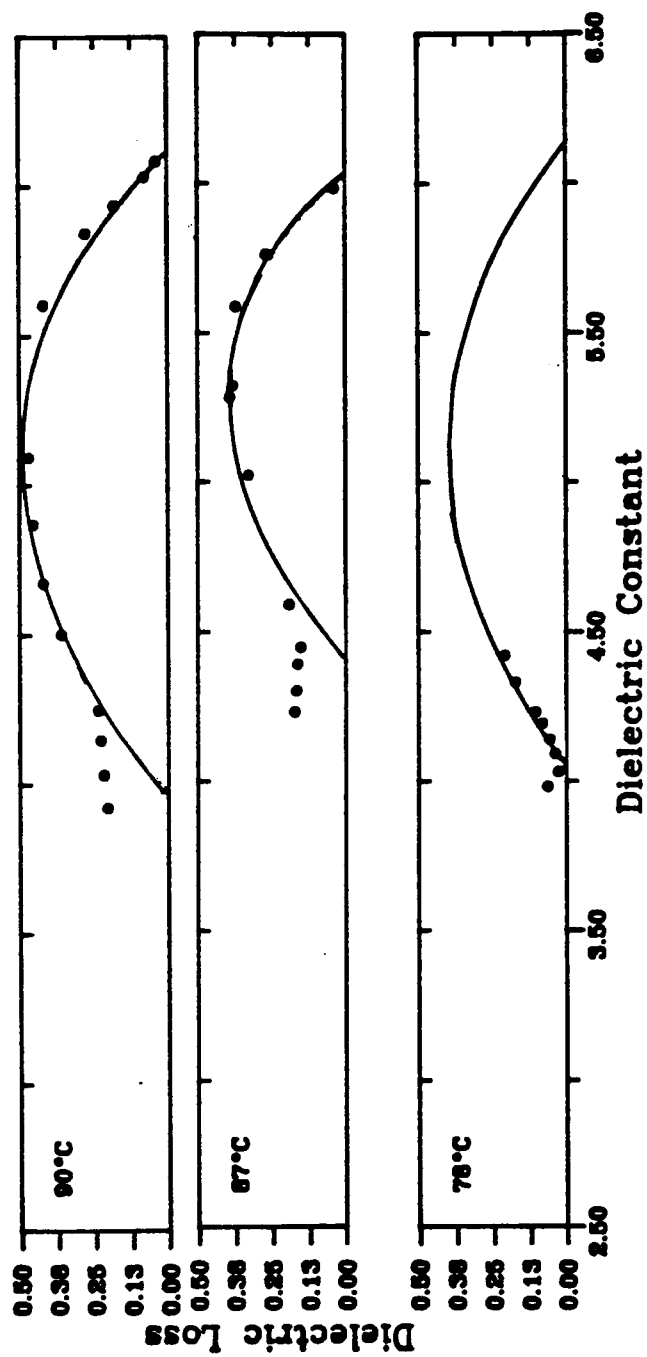


FIGURE 22: Cole-Cole plots the α -transition peak of the unannealed sample.

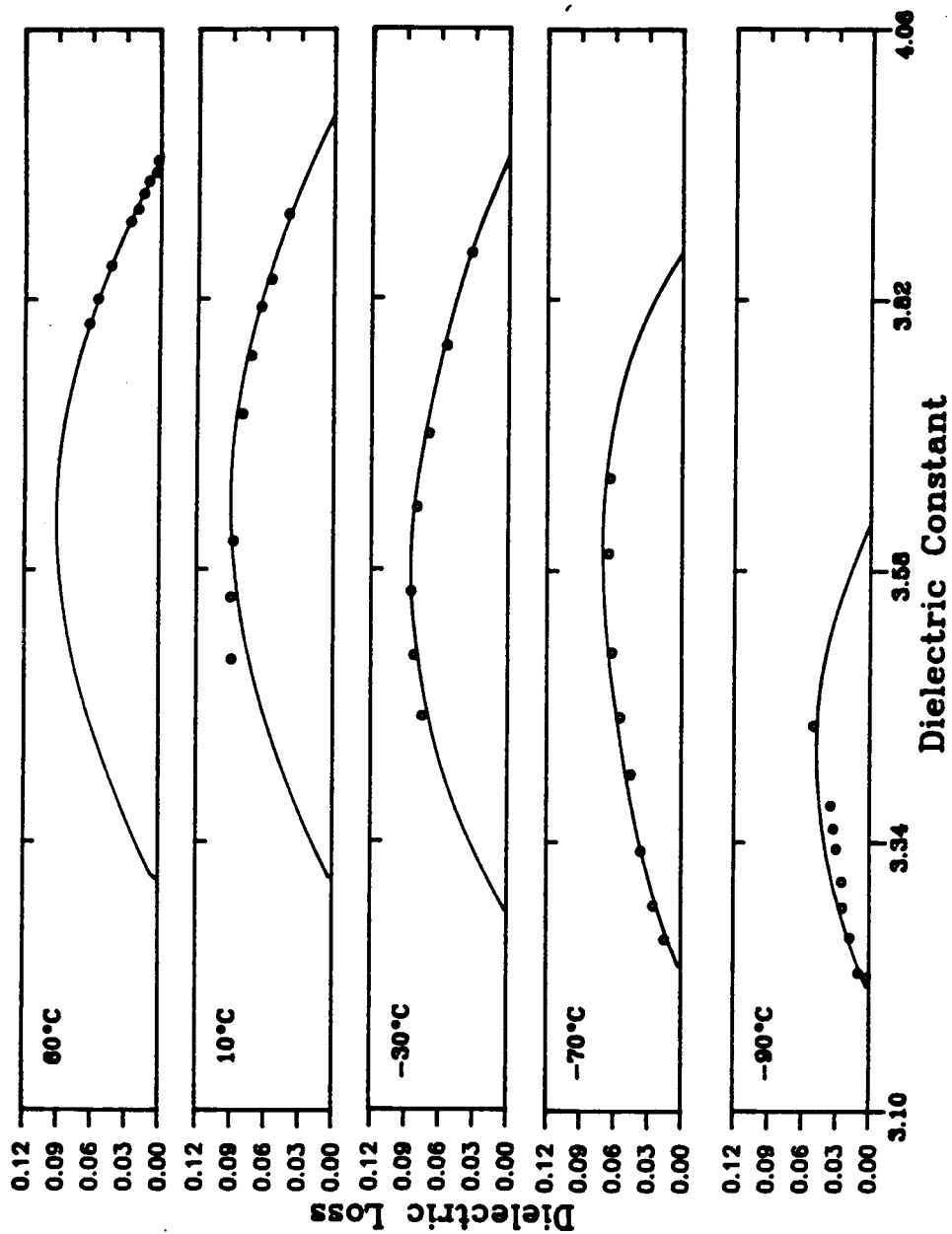


FIGURE 23: Cole-Cole plots of the β -transition peak of the unannealed sample.

Table II: Relaxation Magnitude and Cole-Cole Parameters of the α -transition.

<u>Sample</u>	<u>T (°C)</u>	<u>Relaxation Magnitude</u>	<u>$\tilde{\beta}$</u>
Unannealed	78.0	2.12	0.52
	87.0	1.80	0.53
	90.0	2.12	0.55
Annealed	78.0	2.14	0.52
at 55.0°C	87.0	1.92	0.48
for 48 hrs.	90.0	2.12	0.54
Annealed	78.0	2.10	0.50
at 60.0°C	87.0	1.92	0.49
for 48 hrs.	90.0	2.14	0.54
Annealed	78.0	2.04	0.50
at 65.0°C	87.0	1.92	0.48
for 48 hrs.	90.0	2.14	0.52
Annealed	86.0	0.98	0.41
at 67°C	96.0	0.93	0.40
for 48 hrs.	105.0	0.95	0.39
Annealed	86.0	1.10	0.42
at 68.0°C	96.0	0.96	0.41
for 48 hrs.	105.0	0.94	0.40

Table III: Relaxation Magnitude and Cole-Cole Parameters of the β -transition.

<u>Sample</u>	<u>T (°C)</u>	<u>Relaxation Magnitude</u>	<u>β</u>
Unannealed	-90.0	0.41	0.030
	-70.0	0.57	0.032
	-30.0	0.68	0.034
	10.0	0.69	0.036
	60.0	0.72	0.038
Annealed at 55.0°C for 48 hrs.	-90.0	0.44	0.032
	-70.0	0.60	0.034
	-30.0	0.65	0.035
	10.0	0.63	0.036
	60.0	0.65	0.039
Annealed at 60.0°C for 48 hrs.	-90.0	0.48	0.033
	-70.0	0.61	0.0332
	-30.0	0.63	0.035
	10.0	0.62	0.036
	60.0	0.66	0.038
Annealed at 65.0°C for 48 hrs.	-90.0	0.35	0.031
	-70.0	0.52	0.032
	-30.0	0.58	0.036
	10.0	0.61	0.037
	60.0	0.66	0.039
Annealed at 67.0°C for 48 hrs.	-95.0	0.34	0.029
	-51.0	0.48	0.0309
	-20.0	0.55	0.032
	15.0	0.57	0.033
	56.0	0.61	0.034
Annealed at 68.0°C for 48 hrs.	-95.0	0.33	0.026
	-51.0	0.49	0.031
	-20.0	0.51	0.032
	15.0	0.54	0.033
	56.0	0.61	0.0335

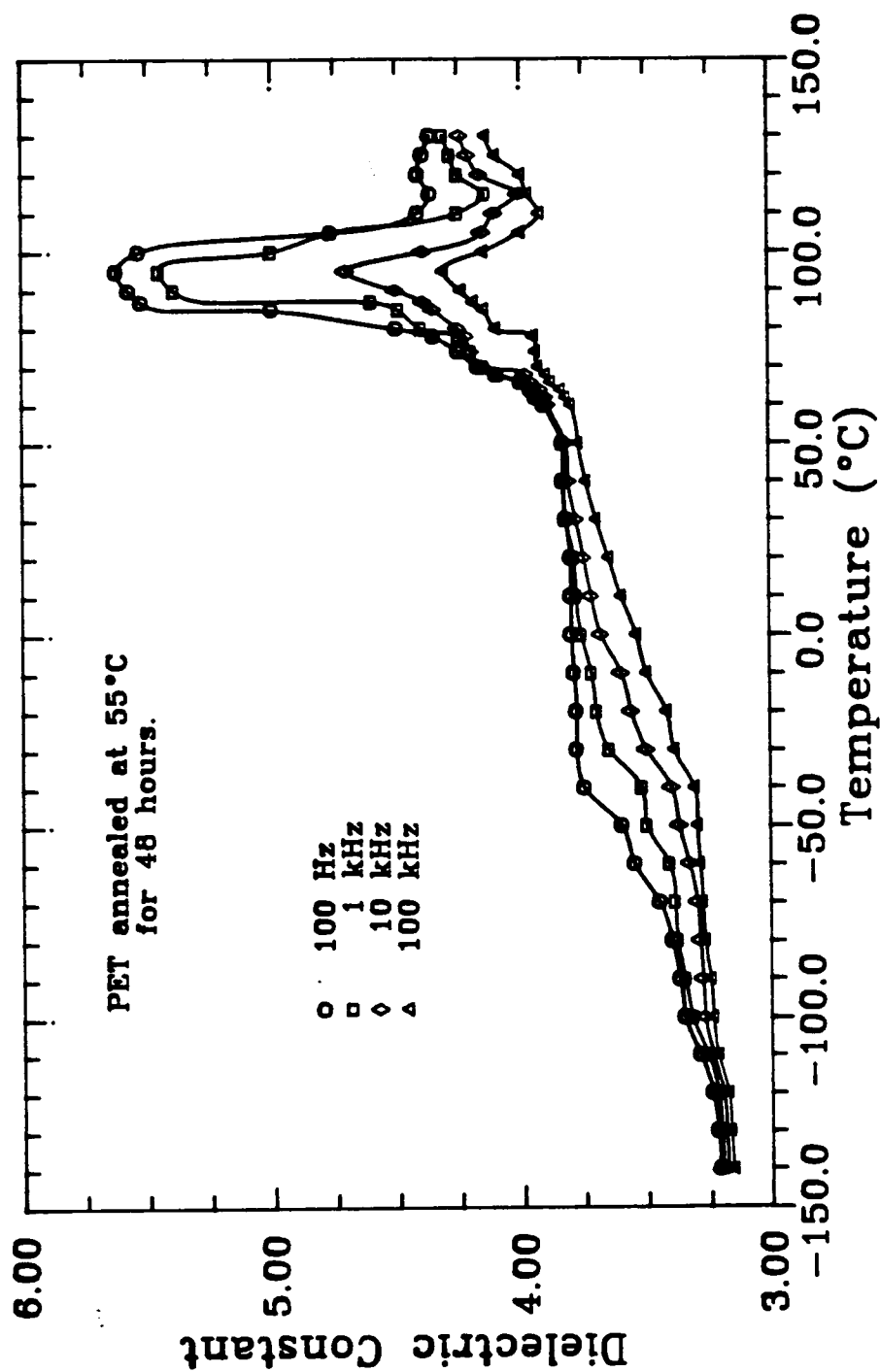


FIGURE 24: Dielectric constant versus temperature for PET annealed at 55°C for 48 hours.

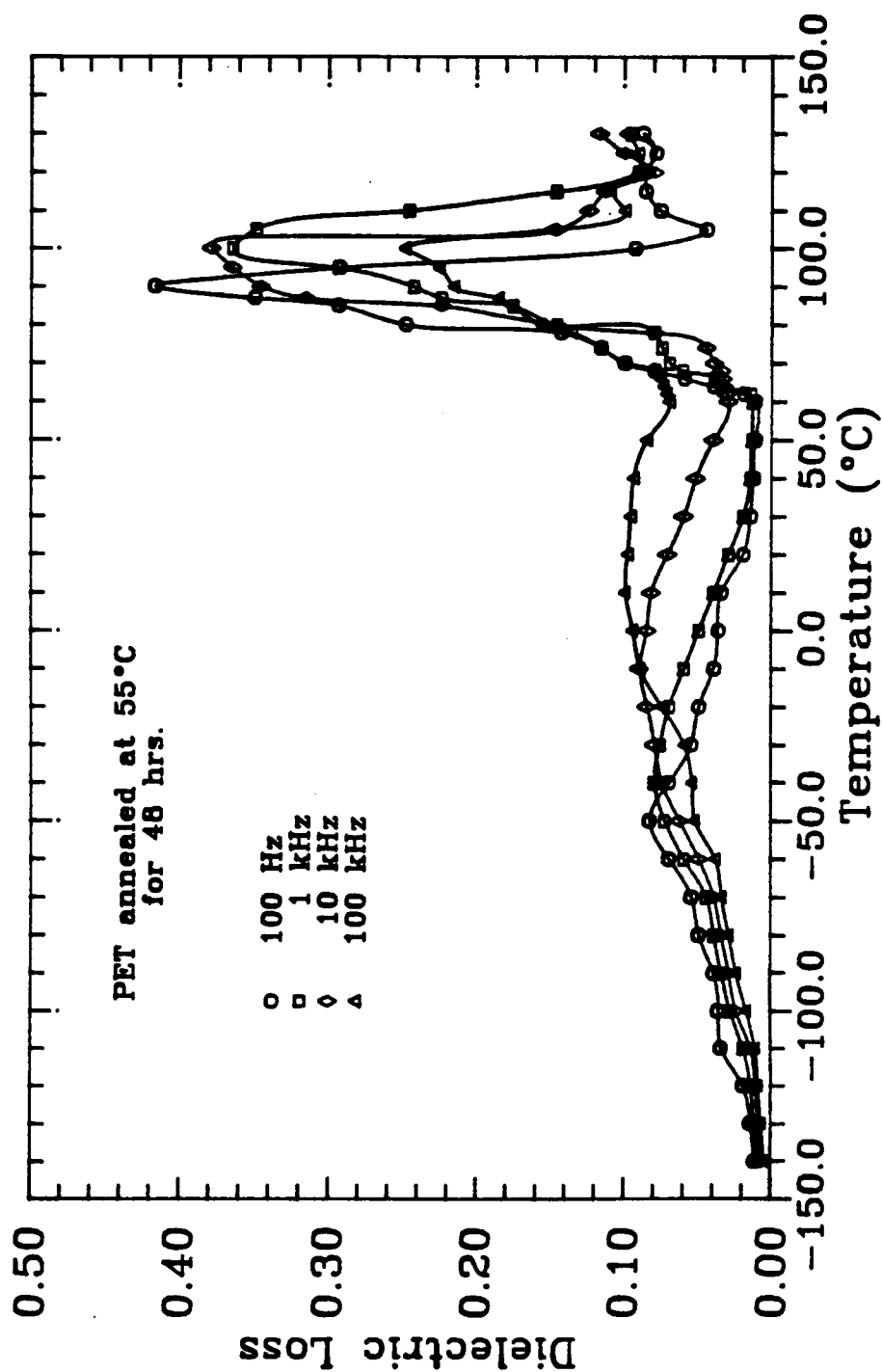


FIGURE 25: Dielectric loss versus temperature for PET annealed at 55°C for 48 hours.

annealed at 55°C for 48 hrs.) as a function of temperature only decade frequencies being plotted. Data were taken at 14 frequencies for all samples ranging from 10Hz to 100kHz. The plots show that there is very little change due to annealing the sample at 55°C for 48 hours. This may be due to the fact that the glassy system (polymer) has not received enough thermal energy to show significant change in the dielectric spectrum (relaxation at the transition peaks). Figure 26 shows the Arrhenius plots of the α and β peaks of the sample annealed at 55°C and in Table I the activation energy has been tabulated with little difference from the unannealed sample. Figure 27 and 28 show the Cole-Cole plots of the α and β transition peaks and the Cole-Cole parameters are shown in Table II and III.

Figures 29 and 30 shows the dielectric constant and loss plotted against temperature for the sample annealed at 60°C for 48 hours. The plots are similar to the unannealed sample, though there are some minor differences, which can be seen by the tabulated values of the activation energy of the transition peaks in Table I. Figure 31 shows the Arrhenius plot of $\log \max$ versus $1000/T(^{\circ}\text{K})$ from which the activation energy was obtained from the slope of the plots. Figures 32 and 33 show the Cole-Cole plots of the α and β relaxation peaks. There is not much difference between the Cole-Cole plots of the unannealed and the sample annealed at 60°C for 48 hours.

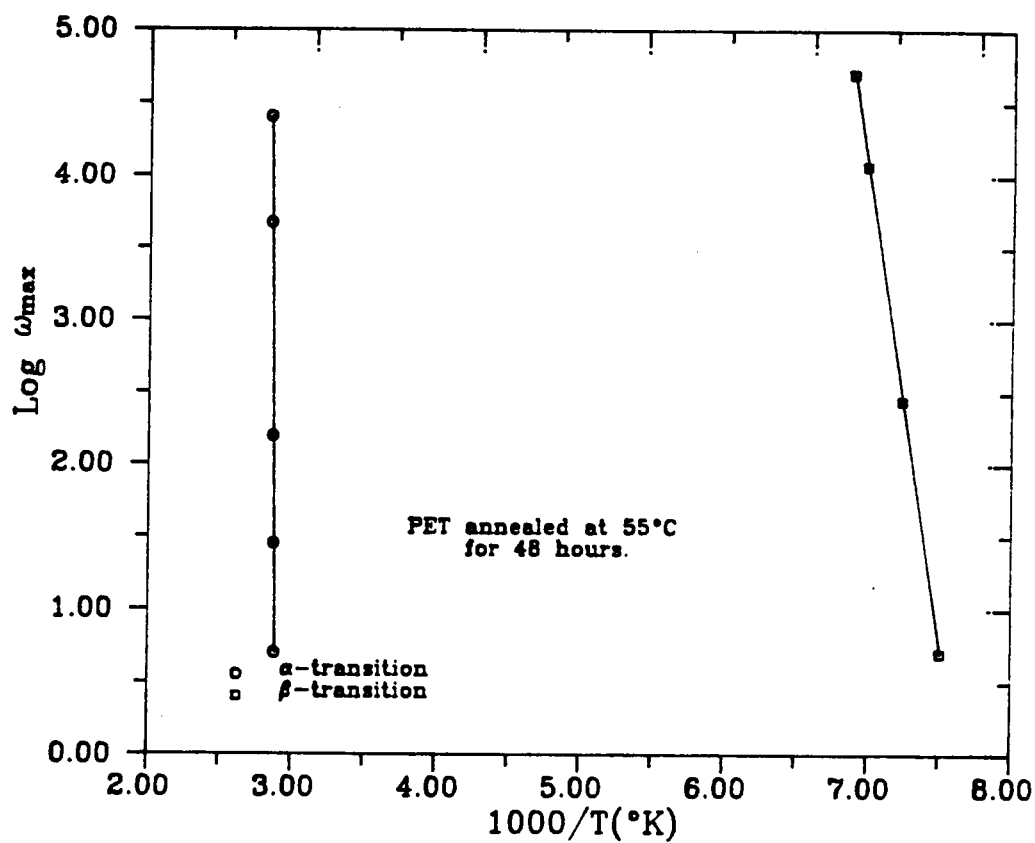


FIGURE 26: Plot of $\text{Log } \omega_{\text{max}}$ vs. $1000/T(^{\circ}\text{K})$ for the α and β transition peaks of the sample annealed at 55°C for 48 hours.

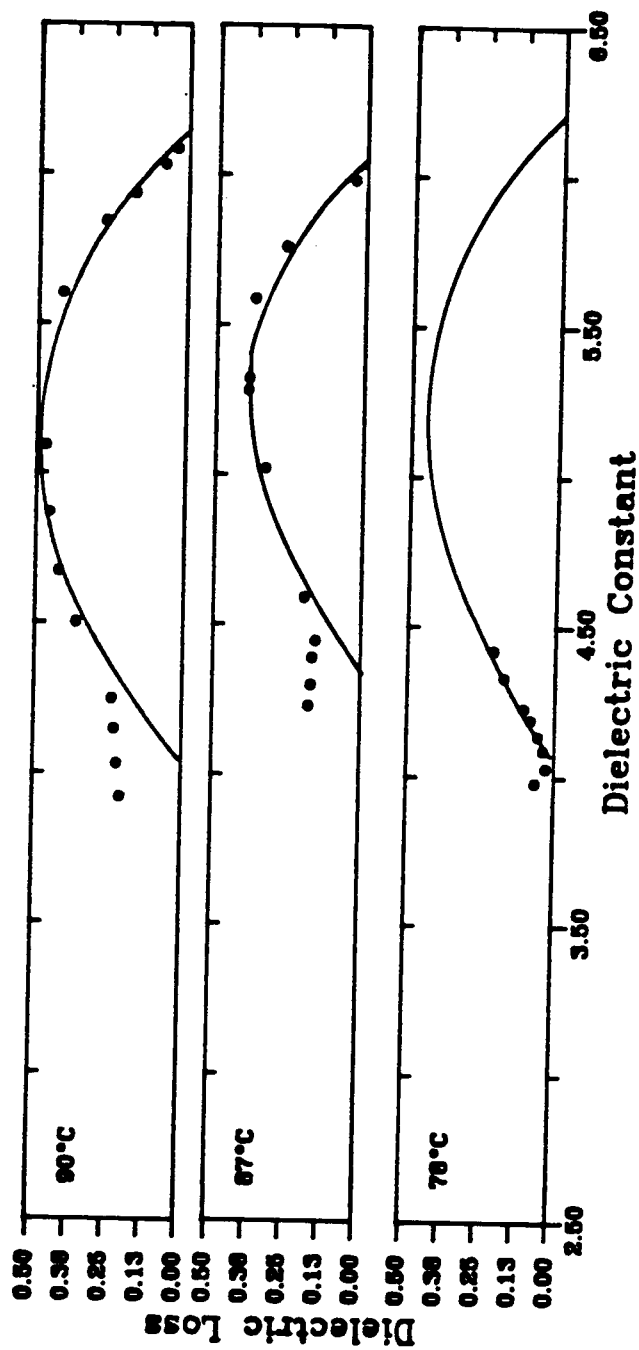


FIGURE 27: Cole-Cole plots of the α -transition peak of the sample annealed at 55°C for 48 hours.

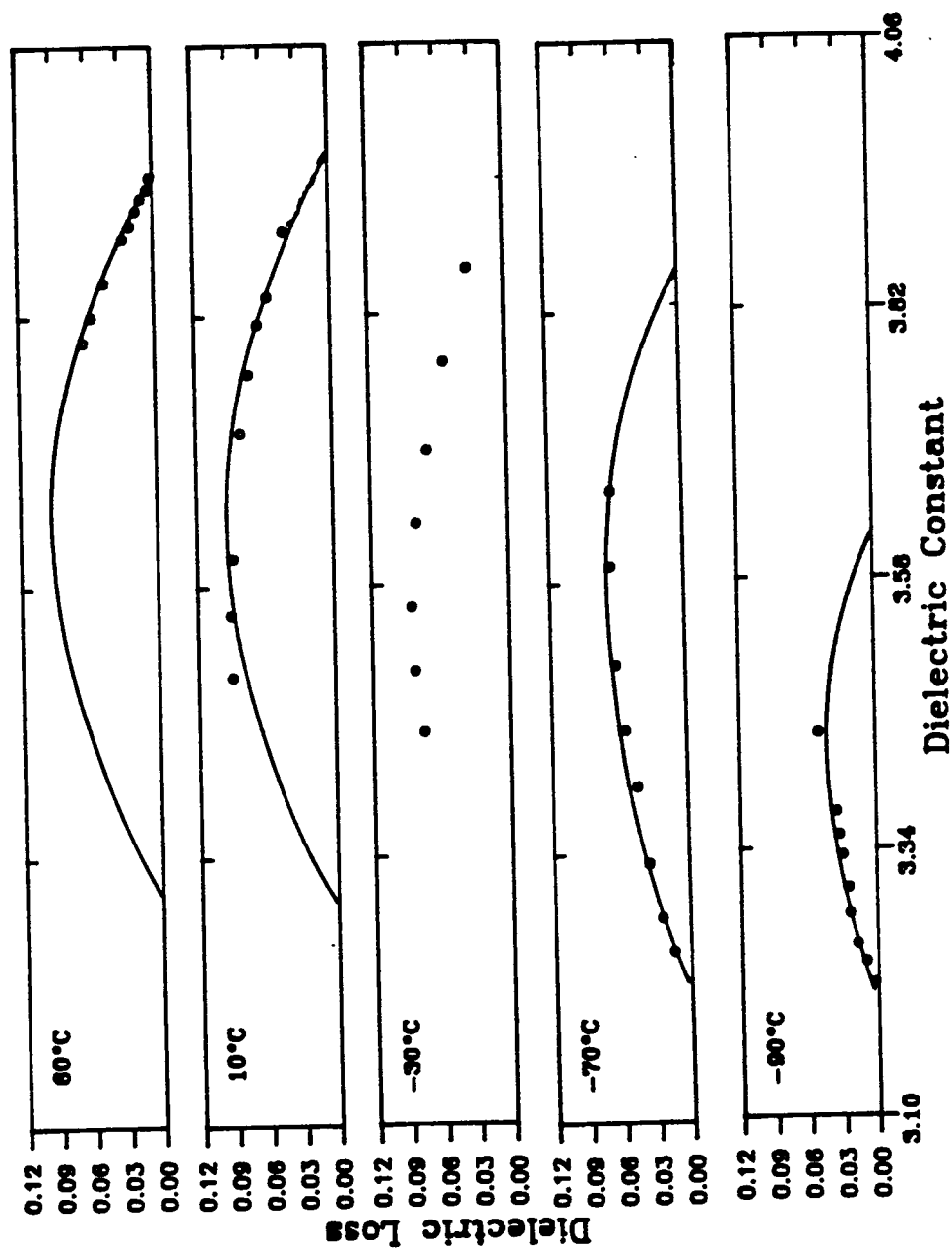


FIGURE 28: Cole-Cole plots of the β -transition peak of the sample annealed at 55°C for 48 hours.

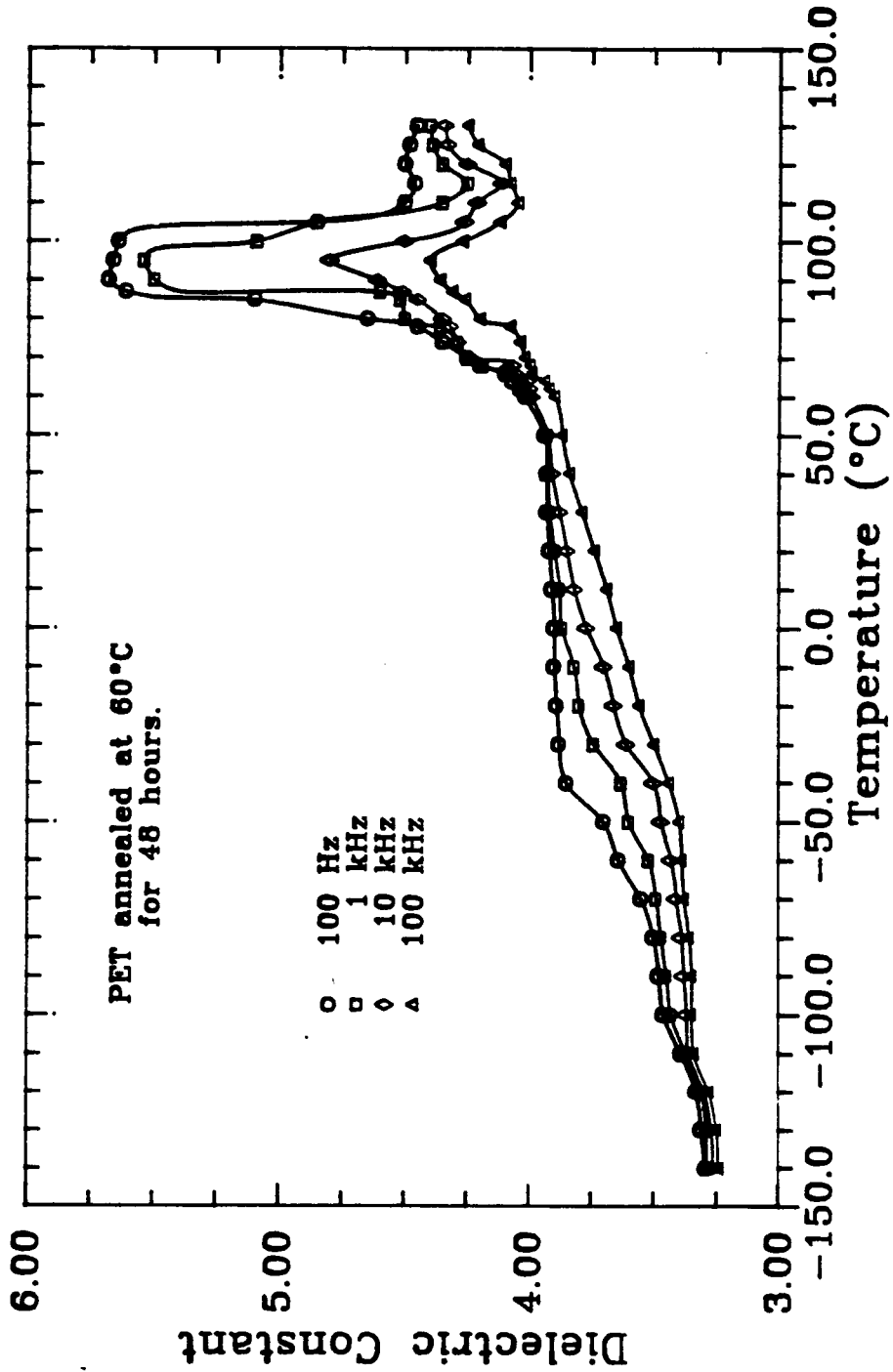


FIGURE 29: Dielectric constant versus temperature for PET annealed at 60°C for 48 hours.

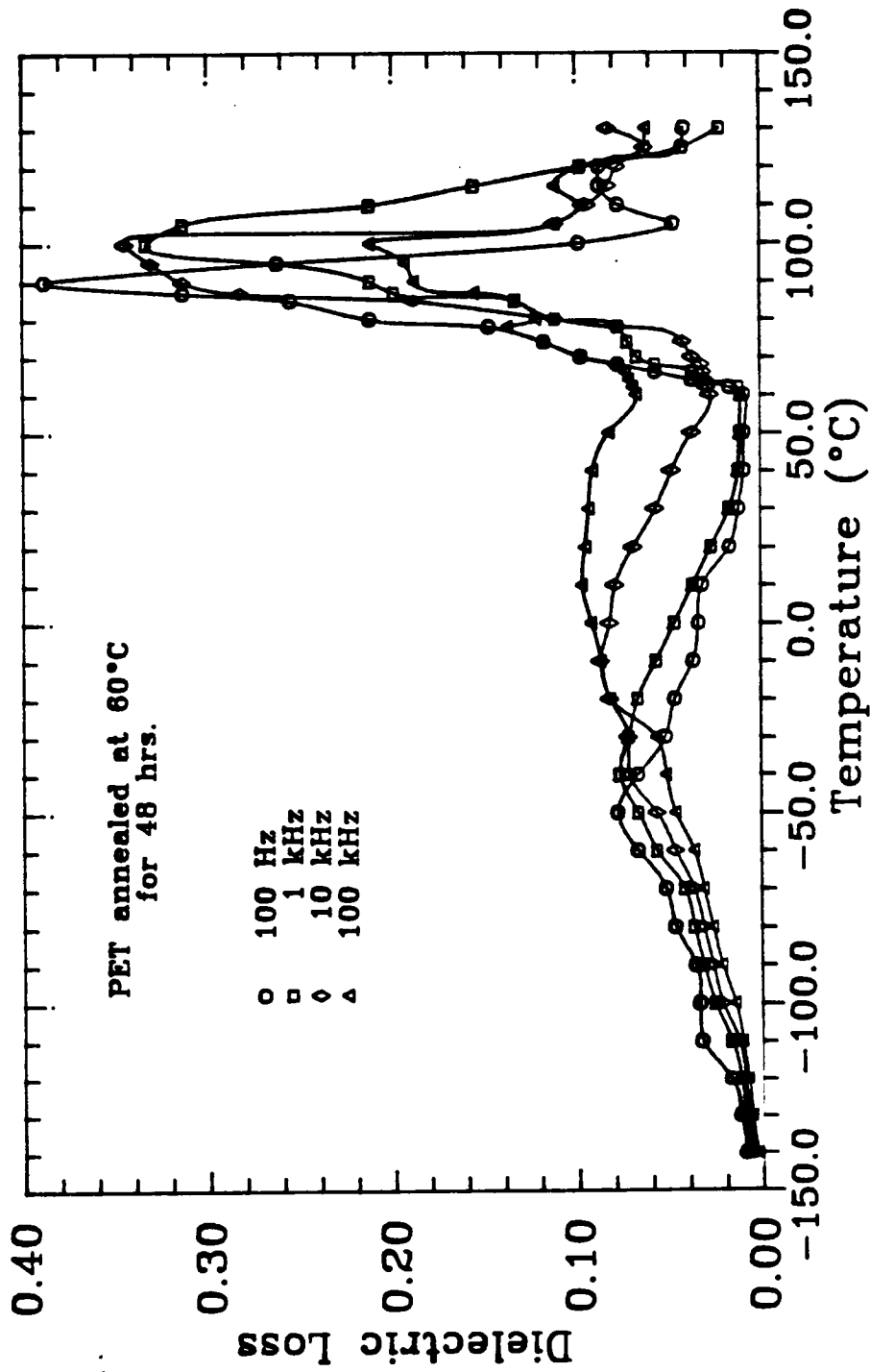


FIGURE 30: Dielectric loss versus temperature for PET annealed at 60°C for 48 hours.

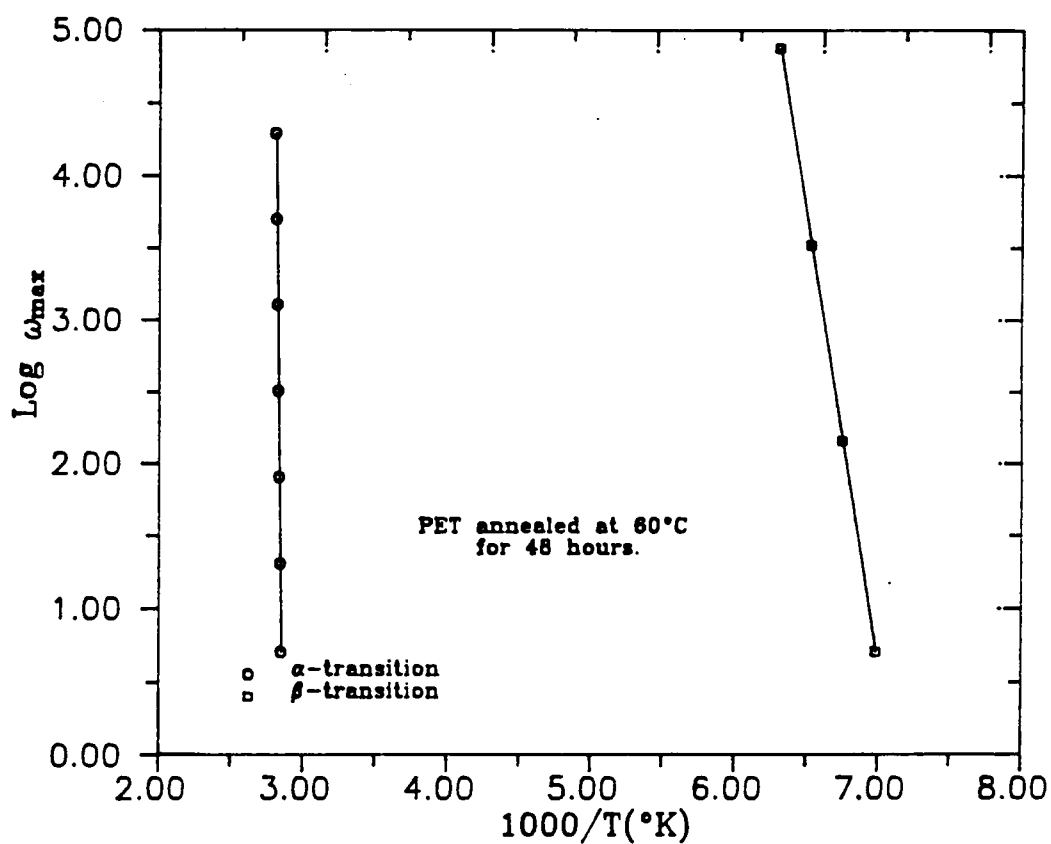


FIGURE 31: Plot of $\text{Log } \omega_{\max}$ vs. $1000/T(^{\circ}\text{K})$ for the α and β transition peaks of the sample annealed at 60°C for 48 hours.

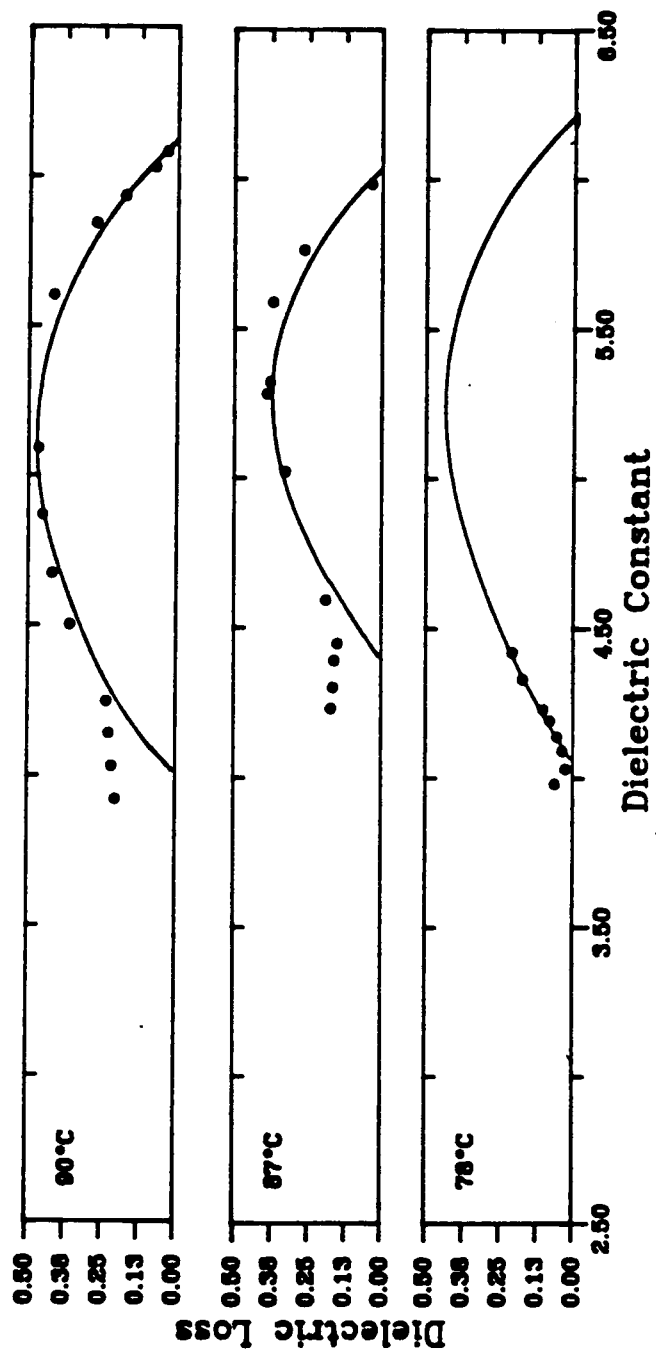


FIGURE 32: Cole-Cole plots of the α -transition peak of the sample annealed at 60°C for 48 hours.

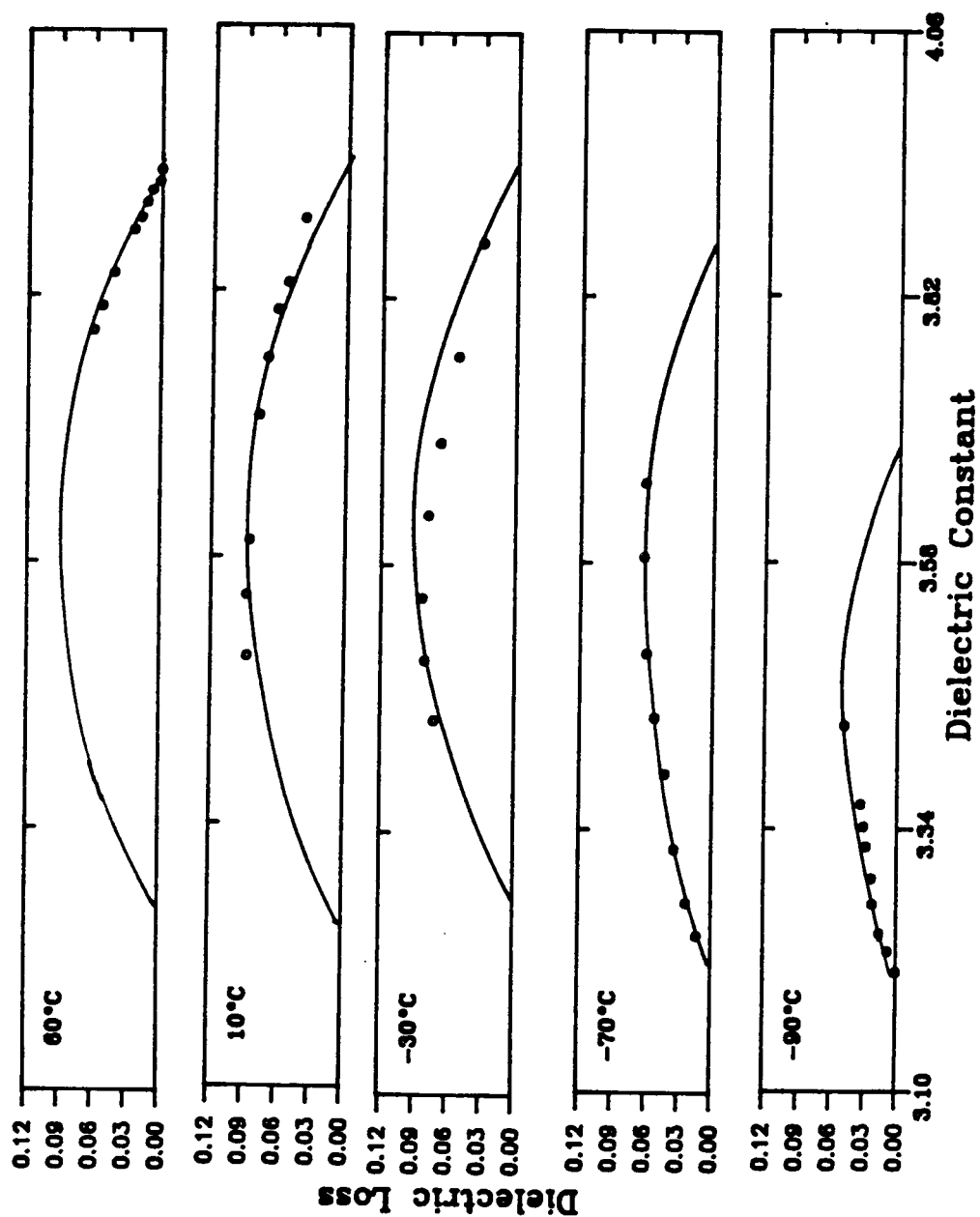


FIGURE 33: Cole-Cole plots of the β -transition peak of the sample annealed at 60°C for 48 hours.

In Figures 34 and 35 show the dielectric constant and loss versus temperature respectively, for the sample annealed at 65°C for 48 hours. In comparison to the unannealed sample there is an indication of some relaxation occurring. The value of the activation energy has decreased significantly with the higher annealing temperature. Figure 36 shows the Arrhenius plot of the α and β transition peaks and the tabulated values of the activation energies are shown in Table I. The Cole-Cole plots are shown in figures 37 and 38 of the α and β transition peaks and Cole-Cole parameters are shown in Table II.

Figure 39 and 40 are plots of the dielectric constant and loss versus temperature for the sample annealed at 67°C for 48 hours. Within the annealed sample relaxation has taken place and is seen in the significant decrease of the α and β transition peaks. The relaxation can be accounted for on the basis of the kinetics of the glass transition. During the annealing cycle the excess energy and excess volume in the PET glasses approached the equilibrium state. Thus, the enthalpy relaxation occurring during annealing is similar to the relaxation occurring in the dielectric spectroscopy.

Figure 41 shows the Arrhenius plots of the α and β transition peaks of the sample annealed at 67°C. The tabulated values of the activation energy is shown in Table I. The figures 42 and 43 are the Cole-Cole plots of

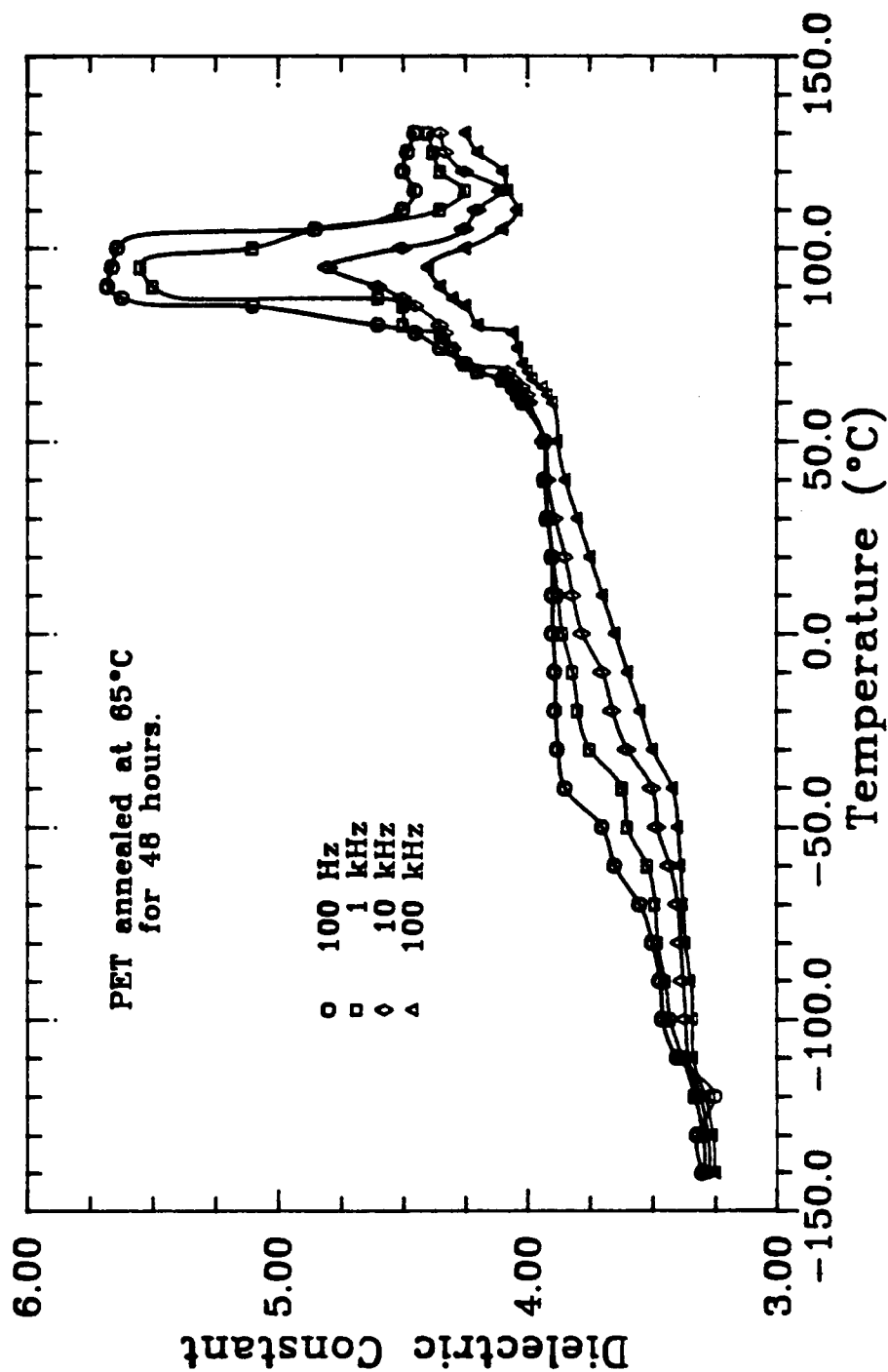


FIGURE 34: Dielectric constant versus temperature for PET annealed at 65°C for 48 hours.

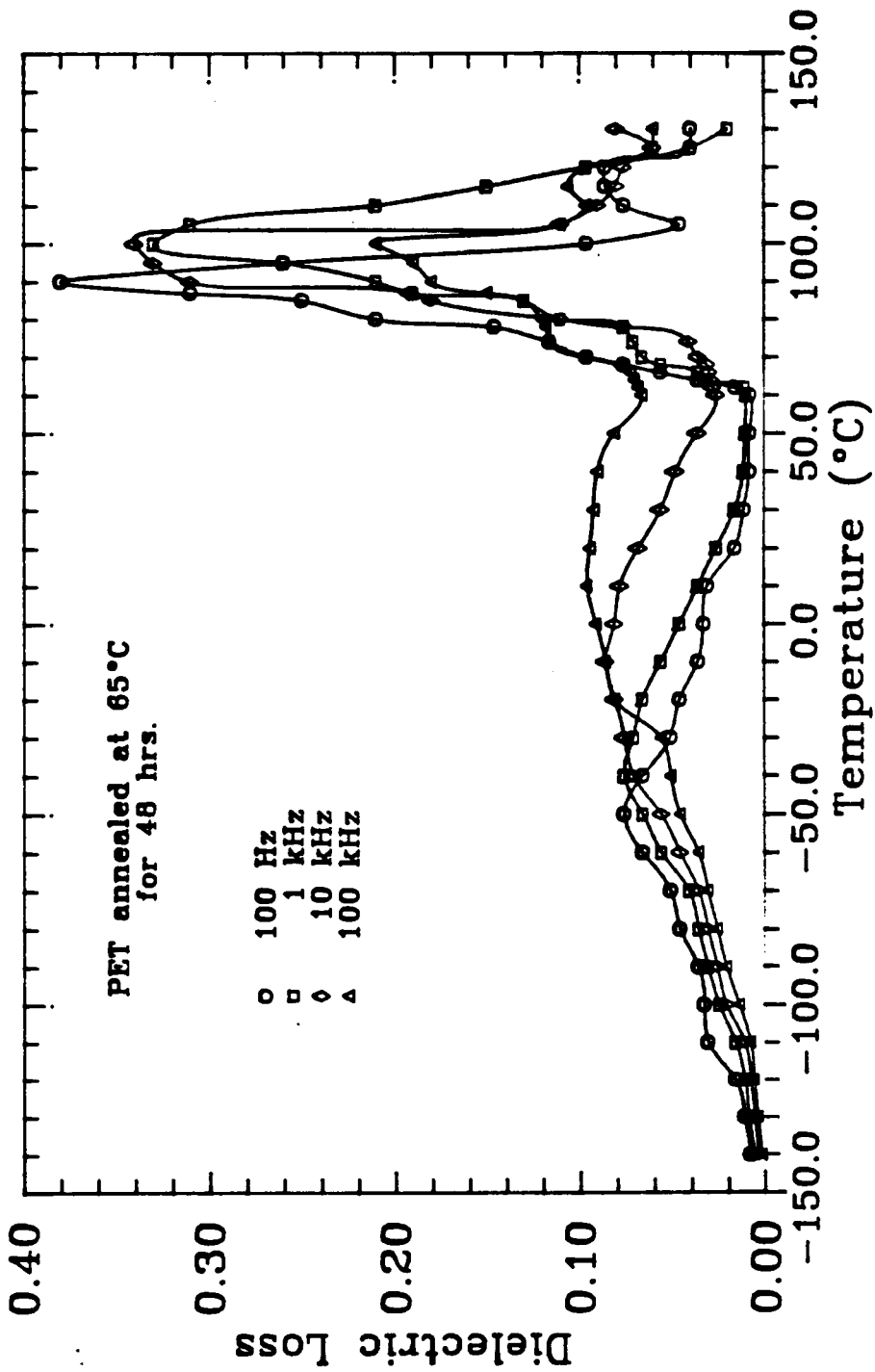


FIGURE 35: Dielectric loss versus temperature for PET annealed at 65°C for 48 hours.

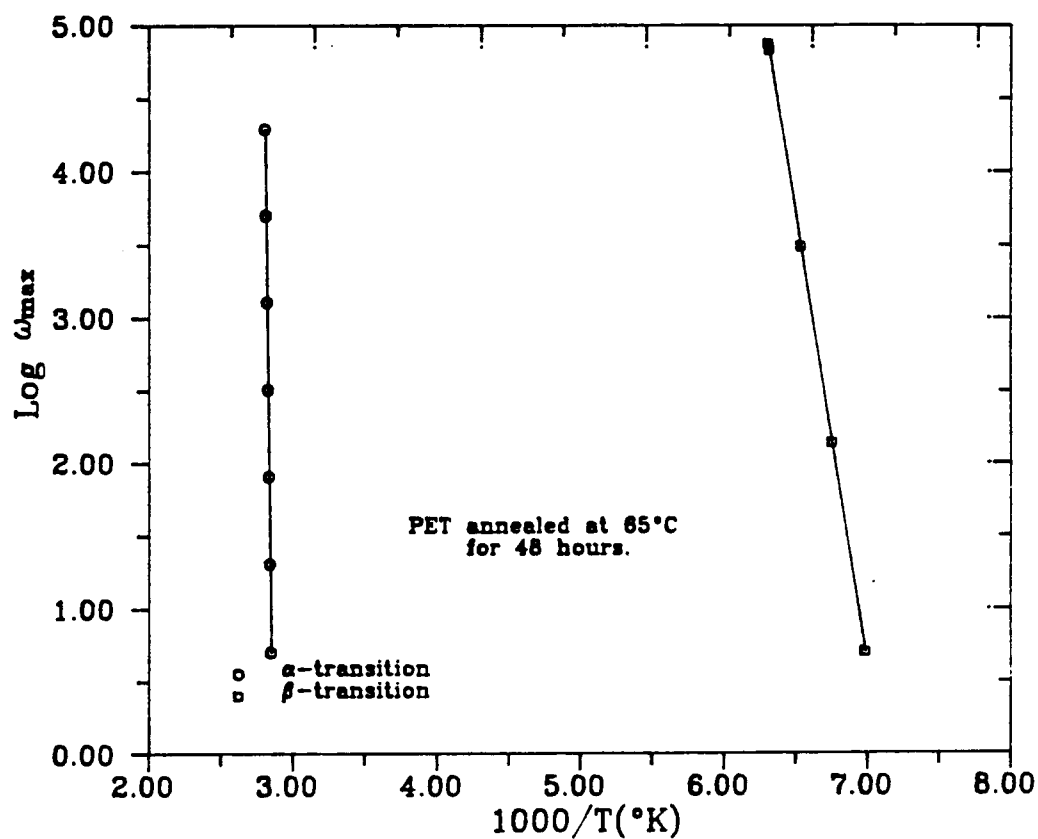


FIGURE 36: Plot of $\text{Log } \omega_{\max}$ vs. $1000/T(^{\circ}\text{K})$ for the α and β transition peaks of the sample annealed at 65°C for 48 hours.

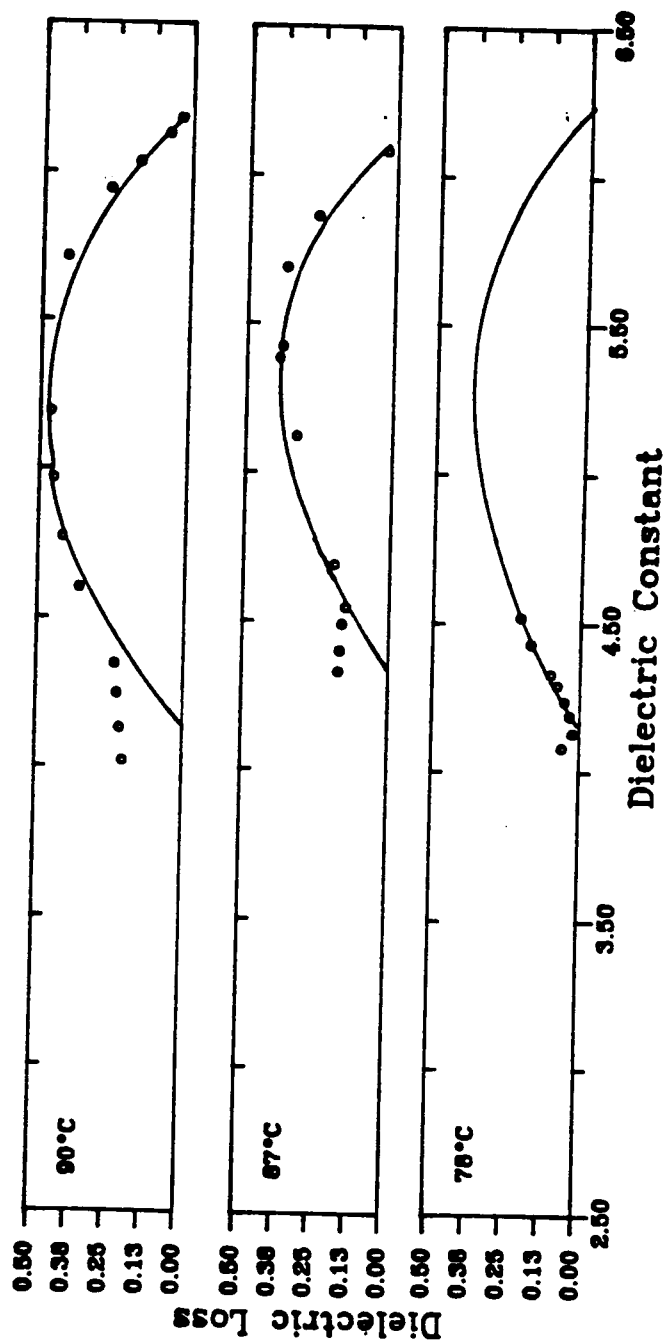


FIGURE 37: Cole-Cole plots of the α -transition peak of the sample annealed at 65°C for 48 hours.

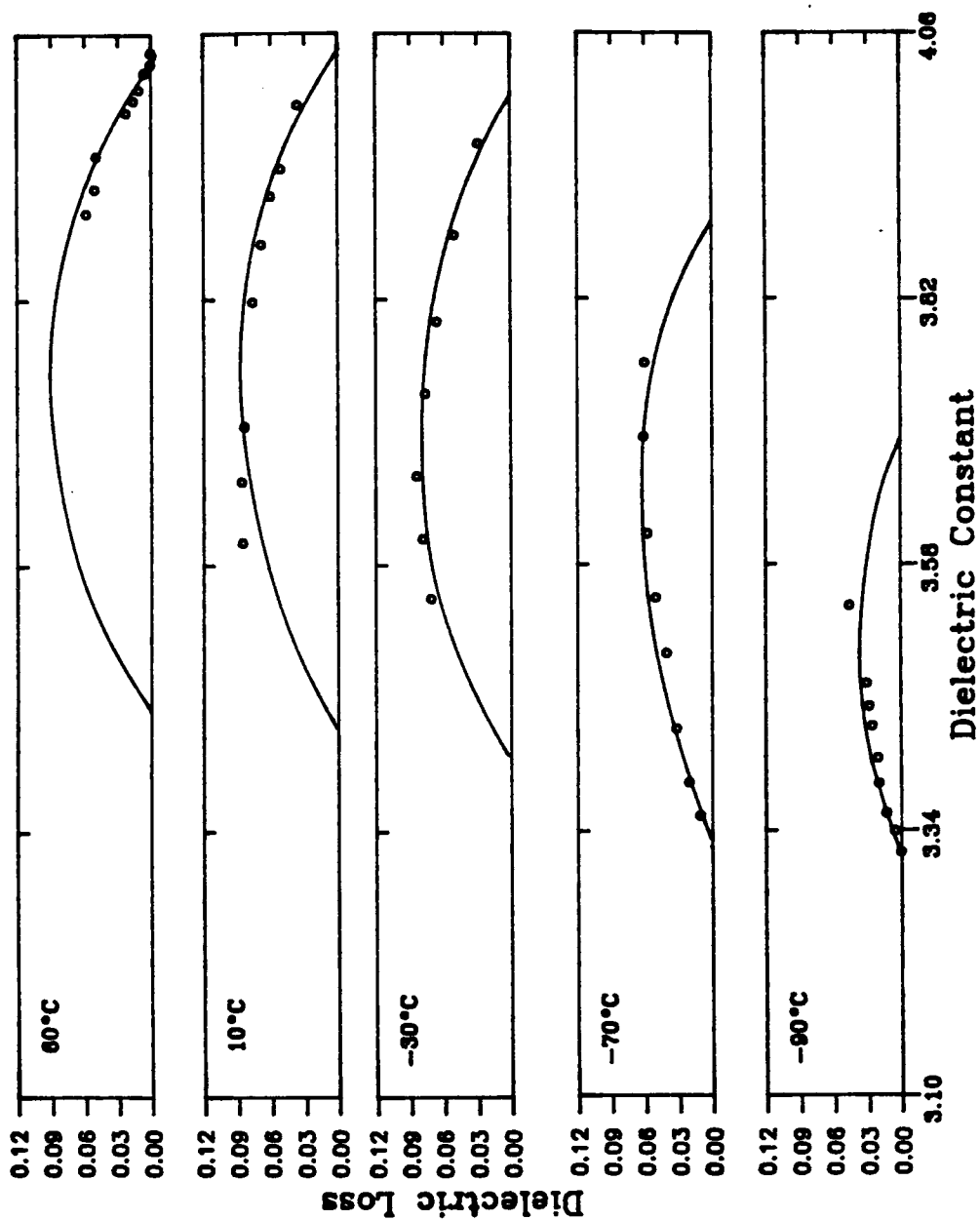


FIGURE 38: Cole-Cole plots of the β -transition peak of the sample annealed at 65°C for 48 hours.

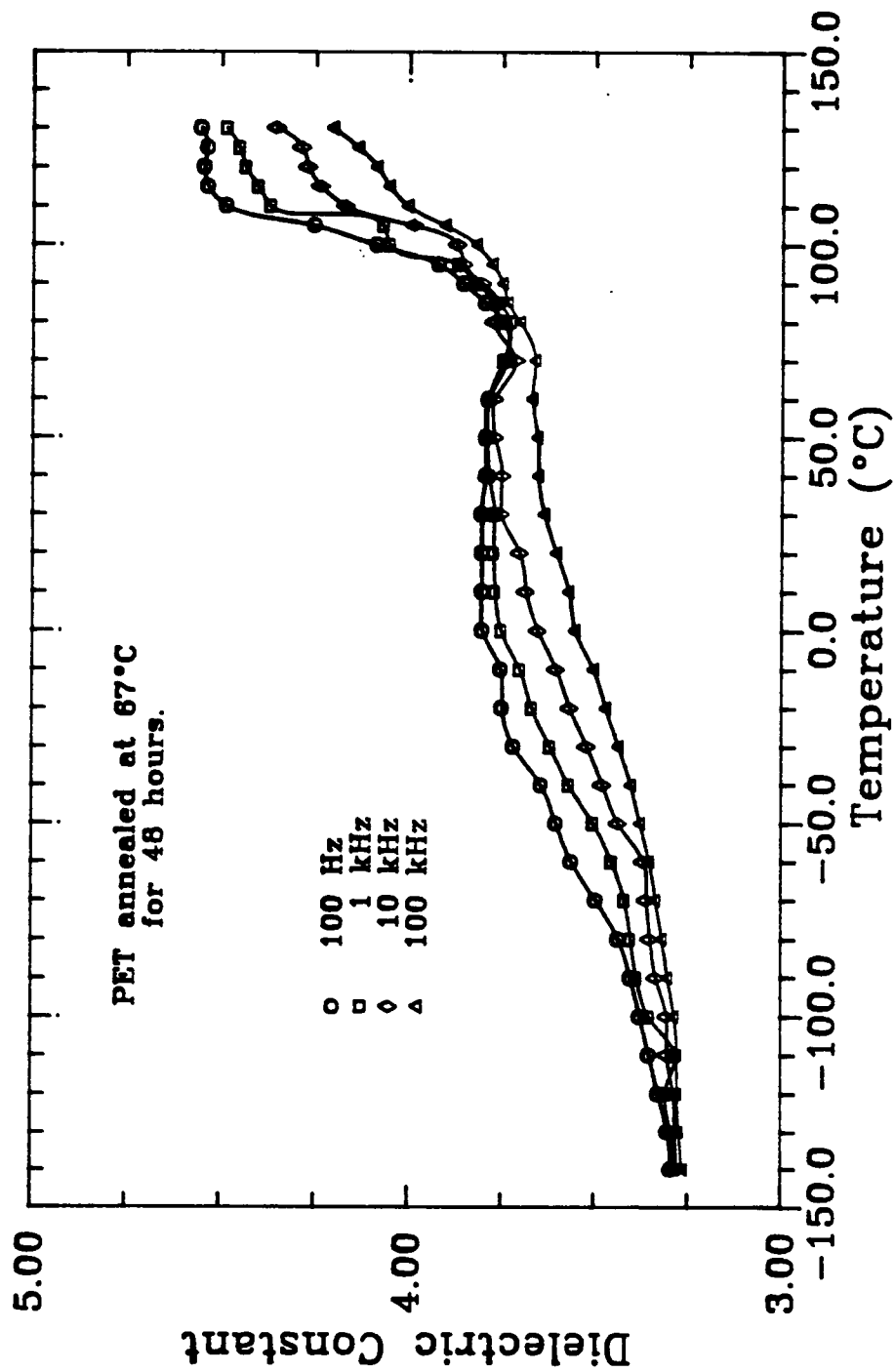


FIGURE 39: Dielectric constant versus temperature for PET annealed at 67°C for 48 hours.

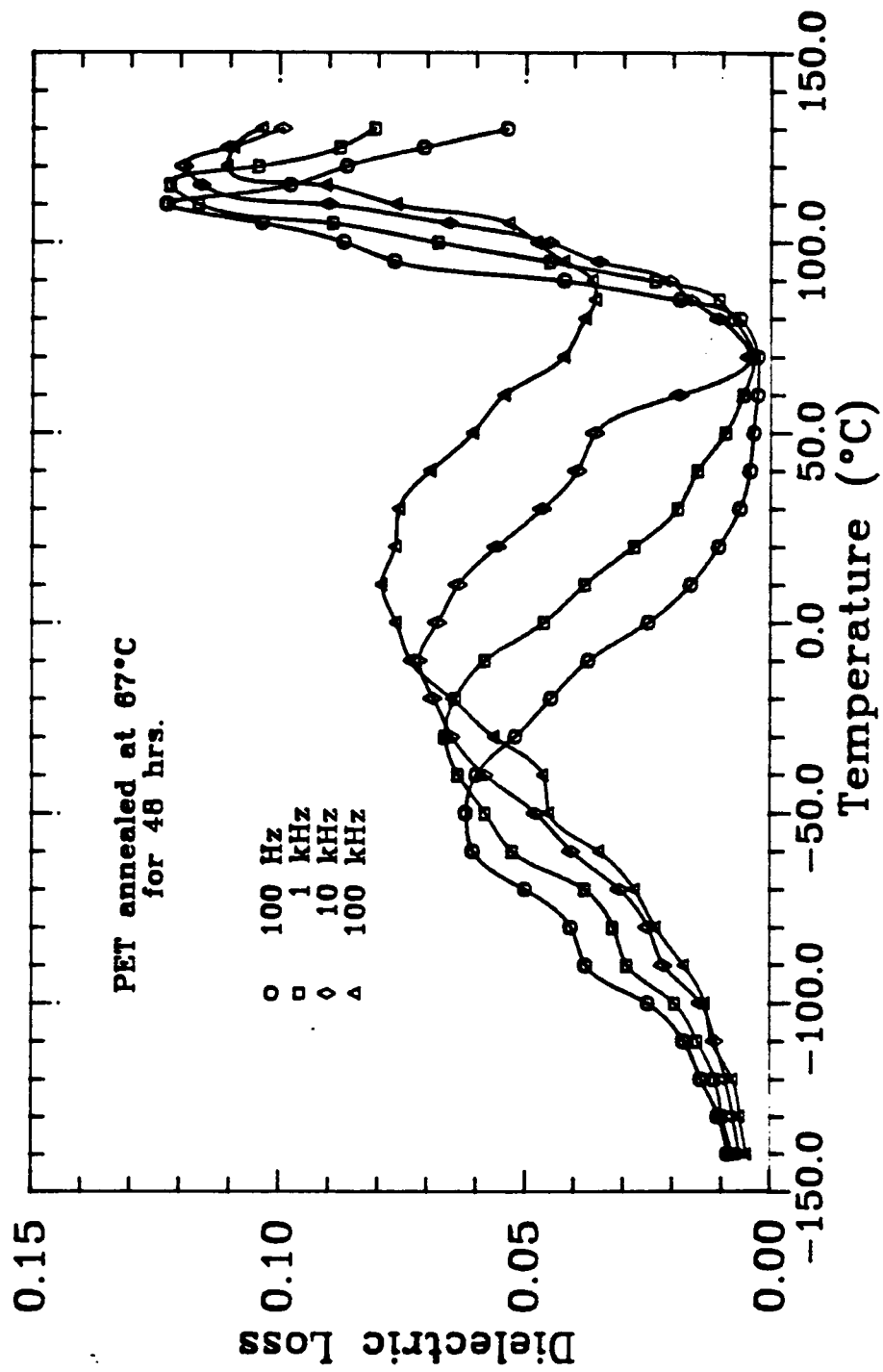


FIGURE 40: Dielectric loss versus temperature for PET annealed at 67°C for 48 hours.

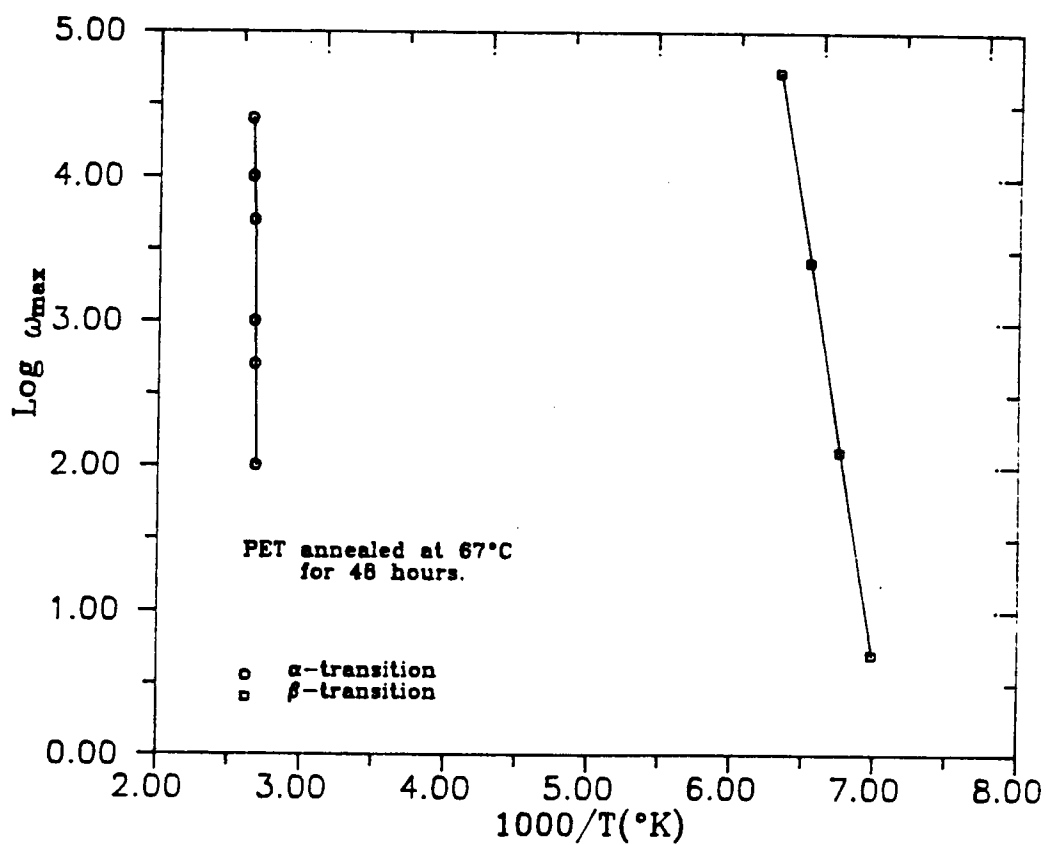


FIGURE 41: Plot of $\text{Log } \omega_{\max}$ vs. $1000/T(^{\circ}\text{K})$ for the α and β transition peaks of the sample annealed at 67°C for 48 hours.

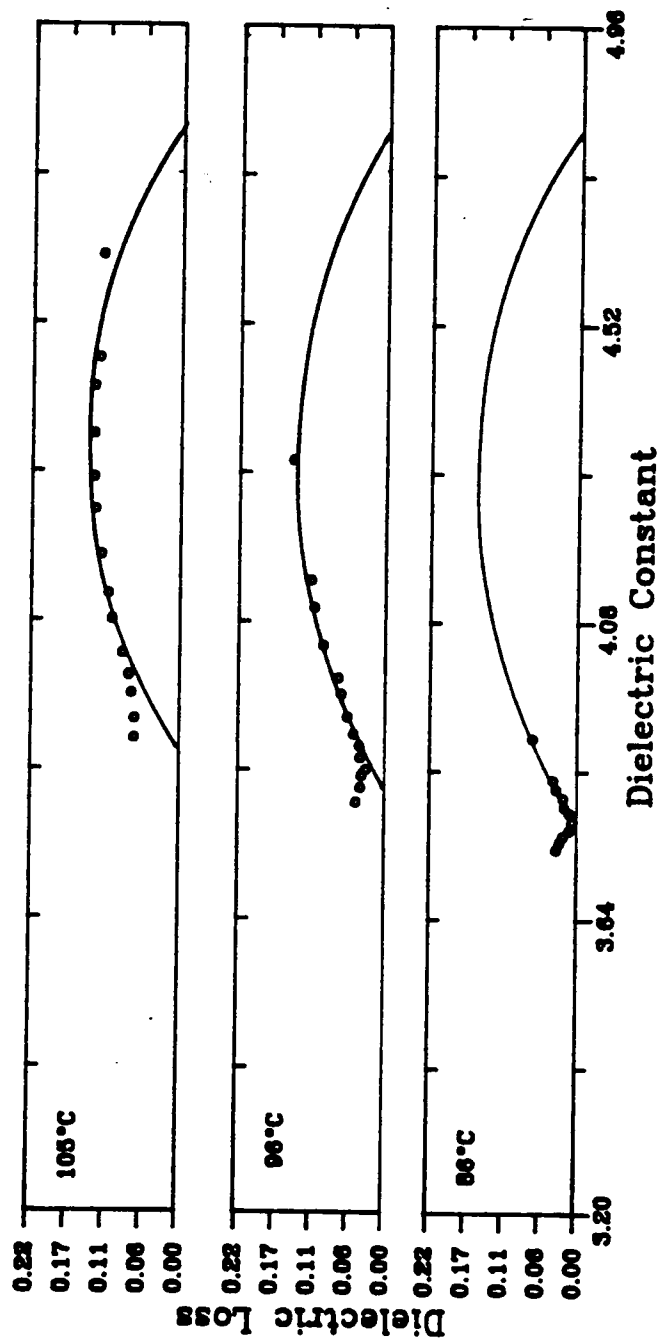


FIGURE 42: Cole-Cole plots of the α -transition peak of the sample annealed at 67°C for 48 hours.

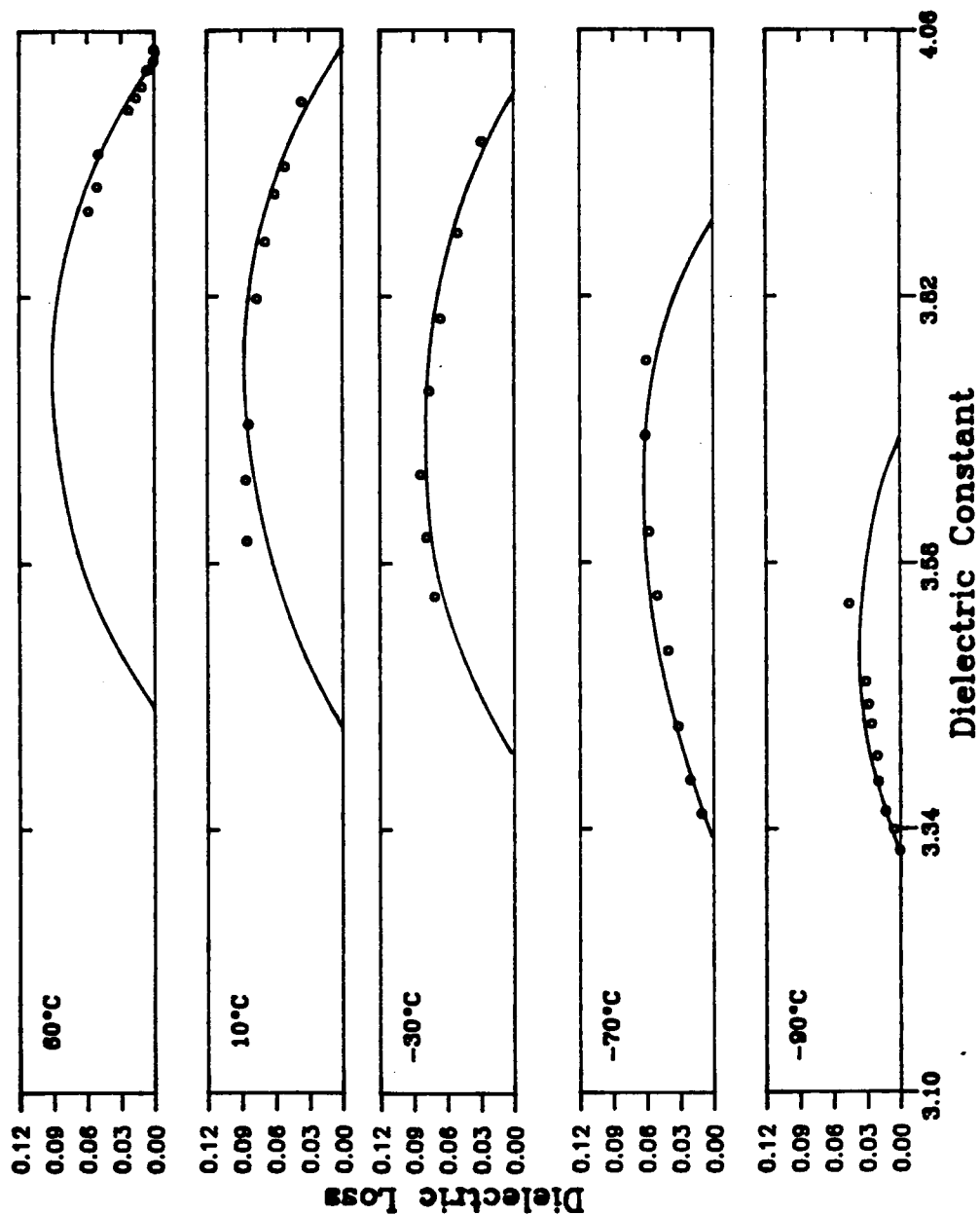


FIGURE 43: Cole-Cole plots of the β -transition peak of the sample annealed at 67°C for 48 hours

the α and β transition peaks. These plots show that relaxation taking place within the PET glass system is evident at the annealing temperature of 67°C.

In figures 44 and 45 the dielectric constant and dielectric loss versus temperature are shown for the sample annealed at 68°C for 48 hours. The plots are similar to the dielectric spectra obtained for the sample annealed at 67°C. Figure 46 is an Arrhenius plot of both the α and the β transition peaks. The activation energies values are slightly lower than those of the sample annealed at 67°C. The Cole-Cole plots are shown in figures 47 and 48 for the α and β transition peaks and are similar to the sample annealed at 67°C.

5.5. Crystallization Studies

5.5.1. Wide Angle X-ray Diffraction

Wide angle x-ray diffraction (WAXD) 2θ scans were obtained for each sample to determine if any samples had crystallized during the annealing process. Figure 49 shows a comparison plot between unannealed and annealed sample at 68°C (for 48hrs.) 2θ scans. As can be seen there is no evidence of crystallization having taken place in the annealed sample of 68°C. Though there is a slight narrowing of the amorphous peak in the annealed sample. This is due to the fact that a decrease in free volume has taken place on annealing of the sample. Figures 50 and 51 shows the 2θ

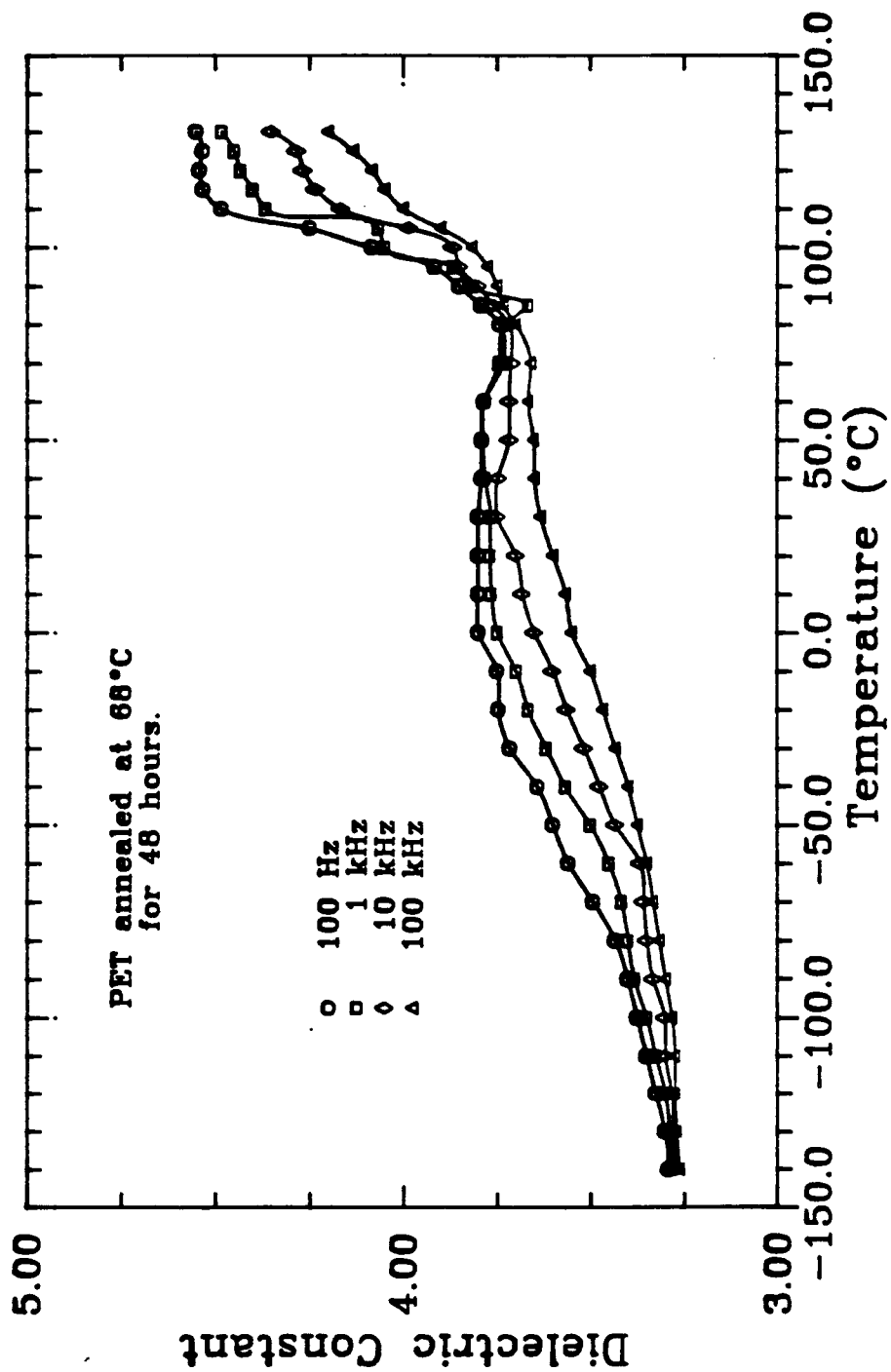


FIGURE 44: Dielectric constant versus temperature for PET annealed at 68°C for 48 hours.

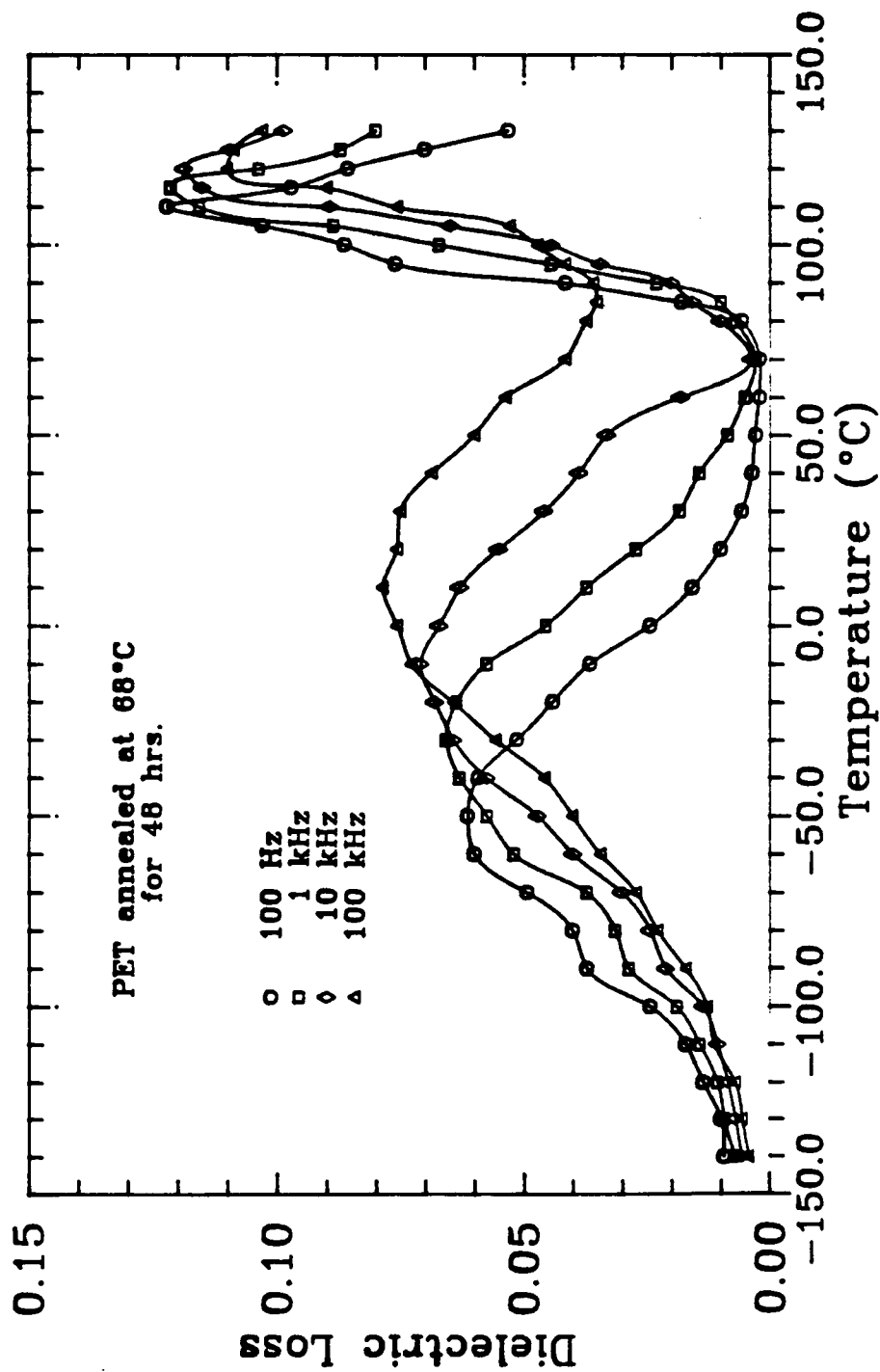


FIGURE 45: Dielectric loss versus temperature for PET annealed at 68°C for 48 hours.

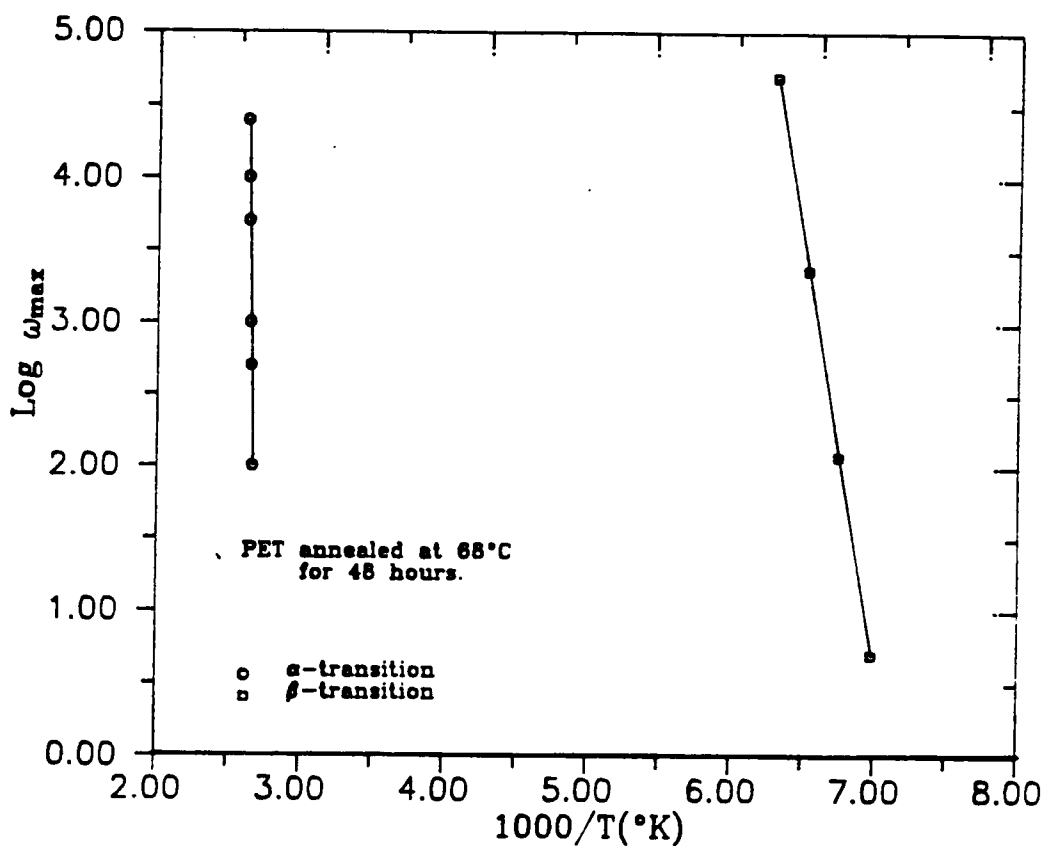


FIGURE 46: Plot of $\text{Log } \omega_{\max}$ vs. $1000/T(^{\circ}\text{K})$ for the α and β transition peaks of the sample annealed at 68°C for 48 hours.

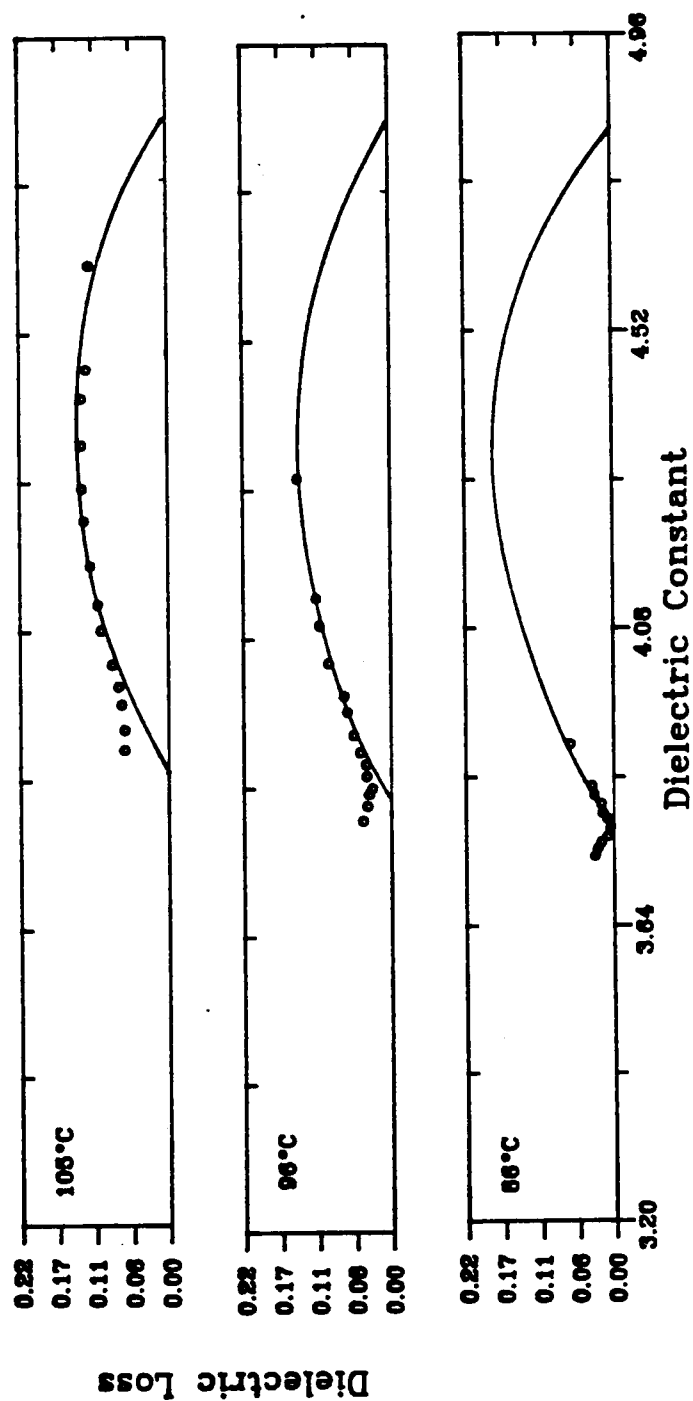


FIGURE 47: Cole-Cole plots of the α -transition peak of the sample annealed at 68°C for 48 hours.

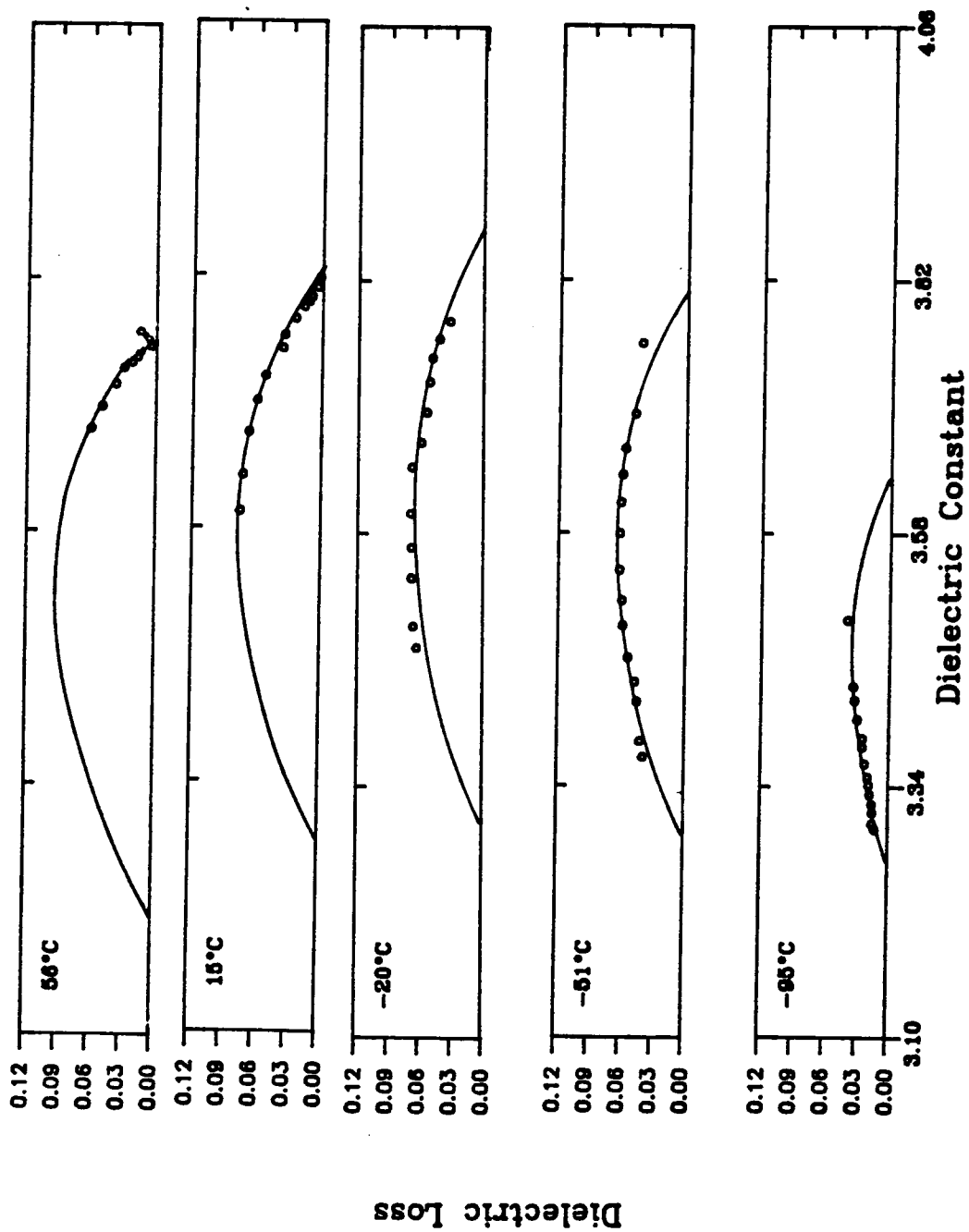


FIGURE 48: Cole-Cole plots of the β -transition peak of the sample annealed at 68°C for 48 hours.

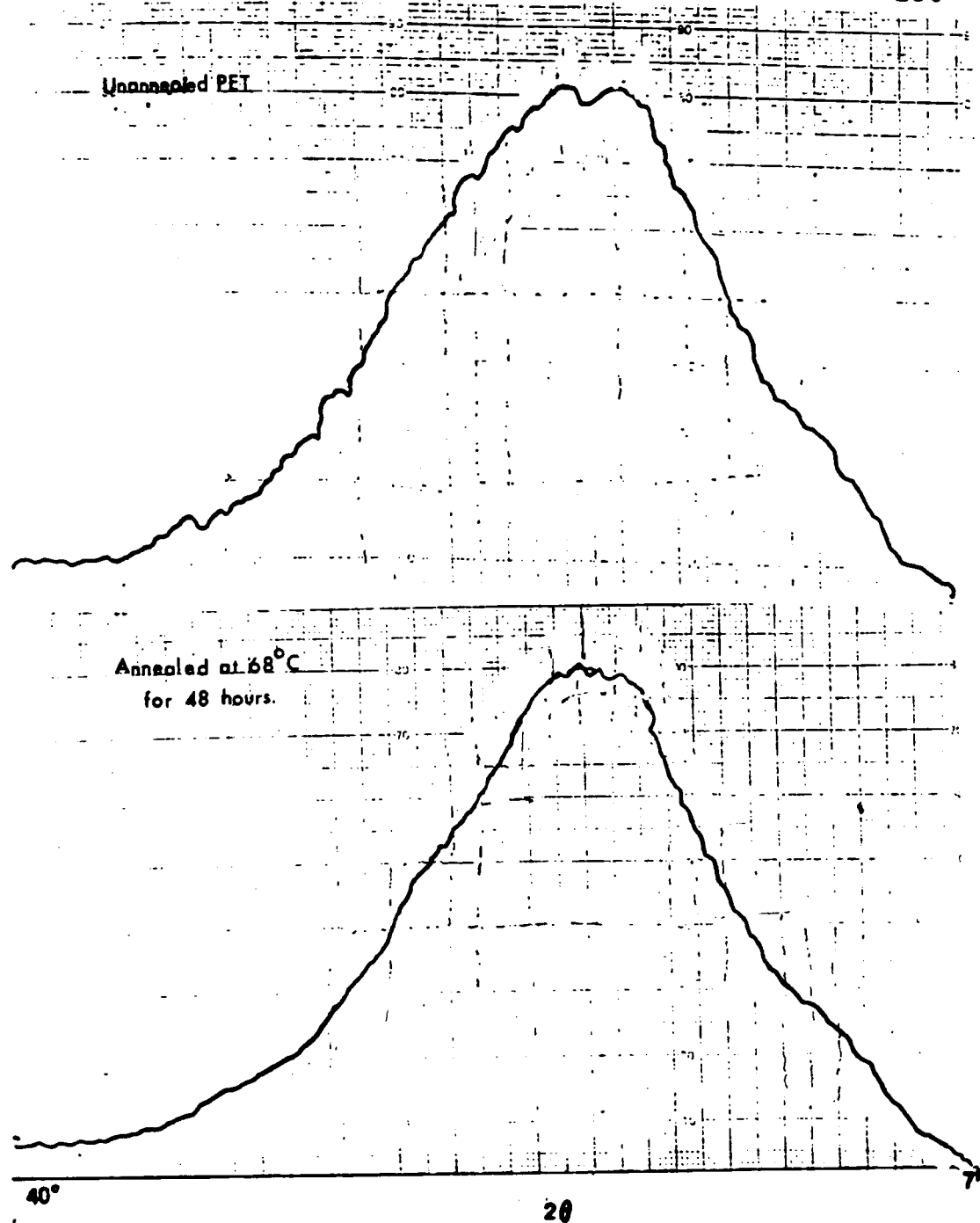


FIGURE 49: A comparison of the wide angle x-ray diffraction (WAXD) 2θ scan of the unannealed sample and annealed sample at 68°C .

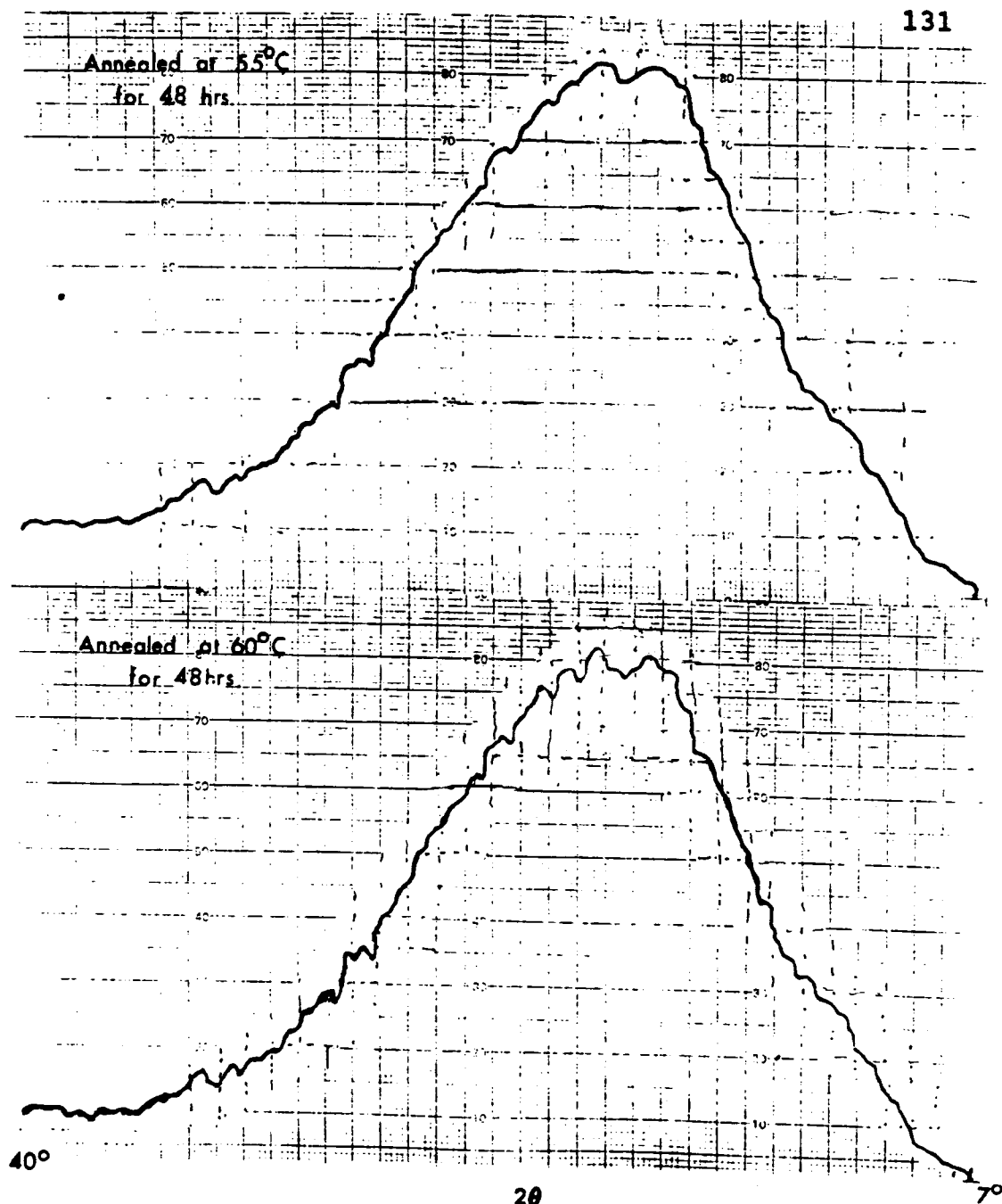


FIGURE 50: A comparison of the wide angle x-ray diffraction (WAXD) 2θ scan of the annealed sample at 55°C and 60°C .

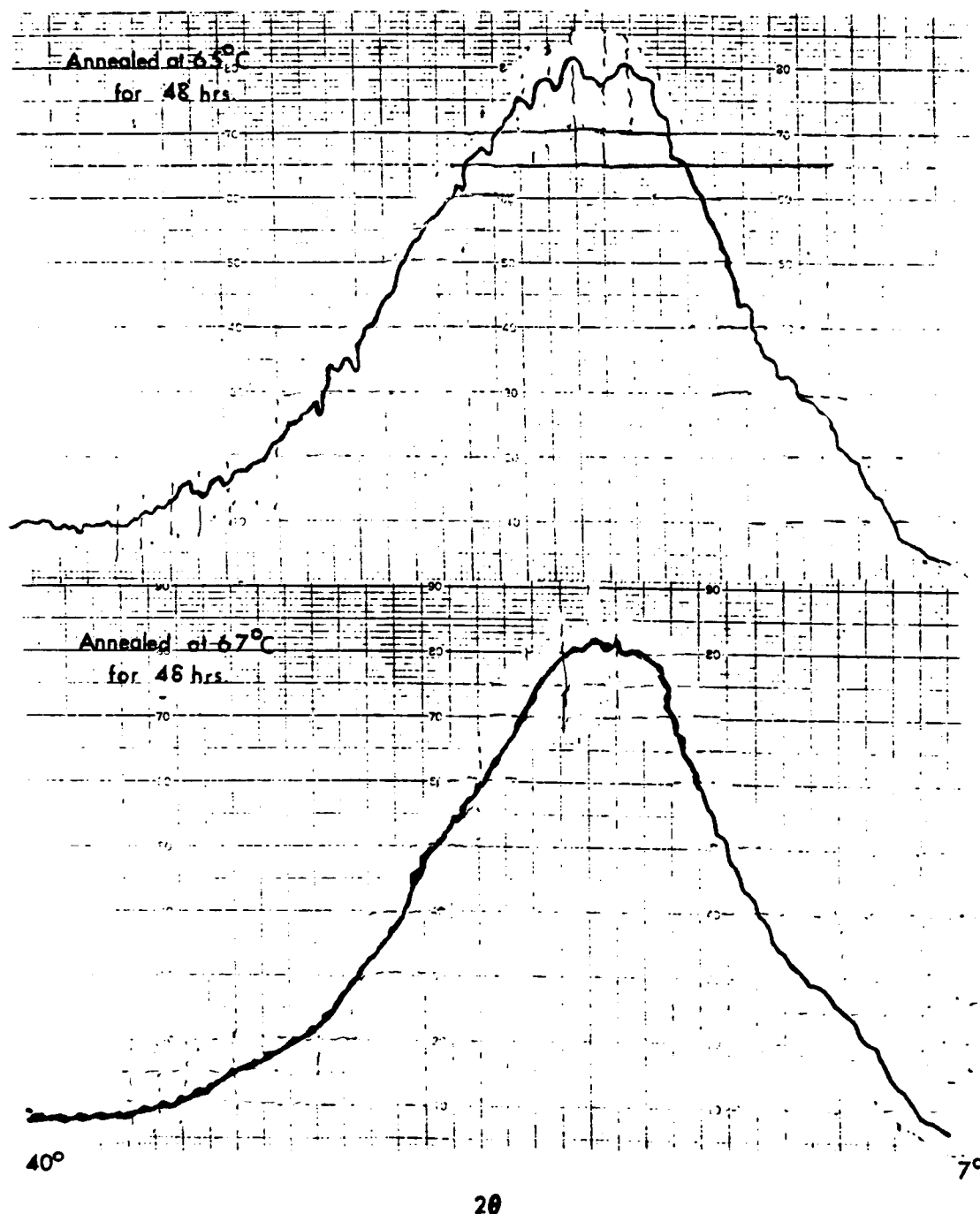


FIGURE 51: A comparison of the wide angle x-ray diffraction (WAXD) 2θ scan of the annealed sample at 65°C and 67°C.

scans of the other samples used in this study, and just as in the annealed 68°C sample there is no evidence of crystallization taking place during the annealing process. This is very important in that the amorphous system has only undergone molecular relaxation, but crystallization has not taken place during the annealing of the sample.

5.5.2. Small-Angle Light Scattering

Small-angle light scattering (SALS) experiments were performed on the PET samples which were crystallized at 120°C. Each sample (unannealed and annealed) was placed in a hot stage and crystallized at 120°C. (Temperature was increased at a rate of 10°C/minute). The spherulite radius size was determined by SALS. Figure 52 shows a plot of the spherulite radius size vs. annealing temperature; as seen in the figure, the spherulite size decreases with an increase of annealing temperature.

It is impractical to obtain the nucleation density as a function of time using laser light scattering methods, but the influence can be investigated by determining the maximum spherulite radius size. The maximum spherulite radii are obtained from the light scattering patterns.

The number of nuclei per unit volume (N) (in other words, the nucleation density) and the spherulite radius size are correlated with each other by the expression

$$\frac{4}{3} (\pi R_{\max}^3 N) = x \qquad 5.3$$

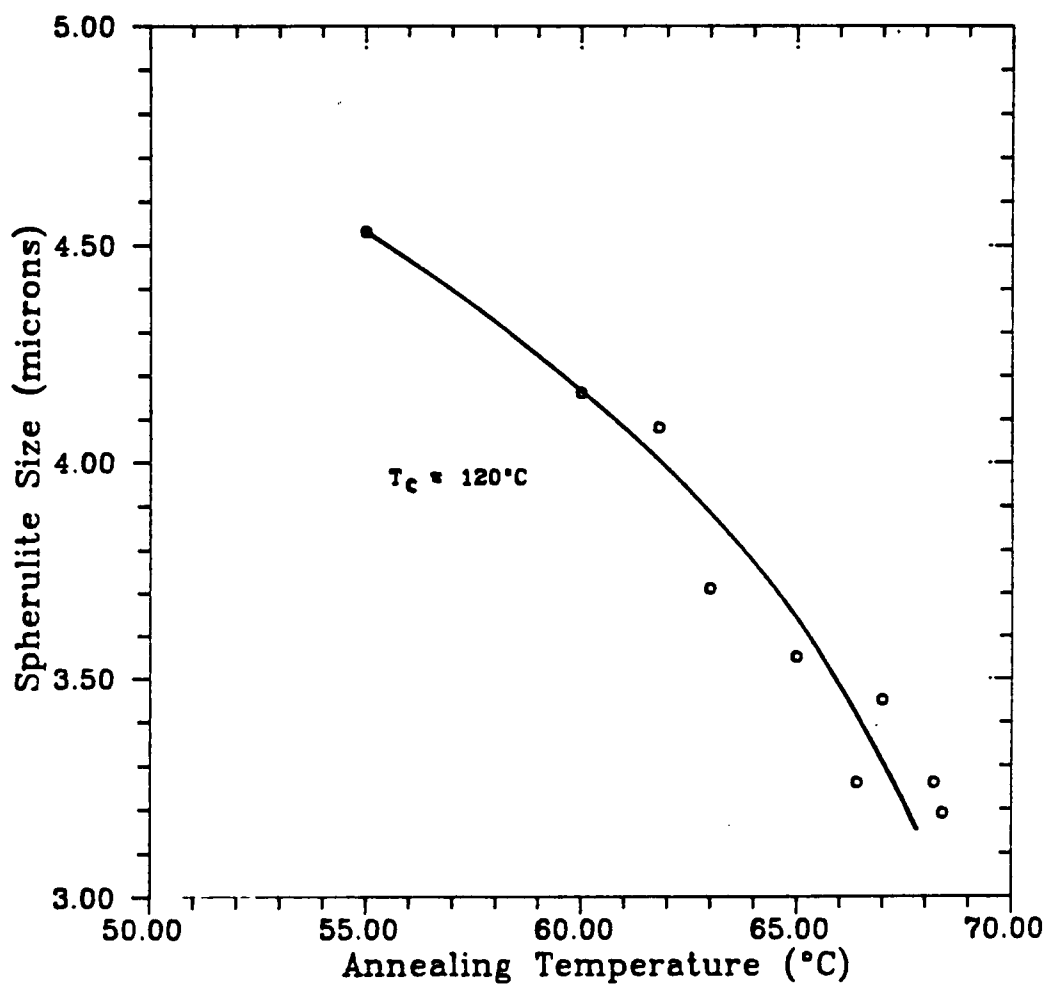


FIGURE 52: The spherulite size vs. the annealing temperature of the sample, before being crystallized.

where $x \approx 1$.

Since the degree of dispersity and the packing are unknown, x actually cannot be calculated. Keijzers¹¹⁸ assumed x equaled unity in the completely crystallized samples.

Figure 53 shows a plot of the nucleation density vs. the annealing temperature. As seen in the plot, nucleation increases with the annealing temperature. Therefore, as the annealing temperature is increased the nucleation sites increase with a decrease in spherulite size.

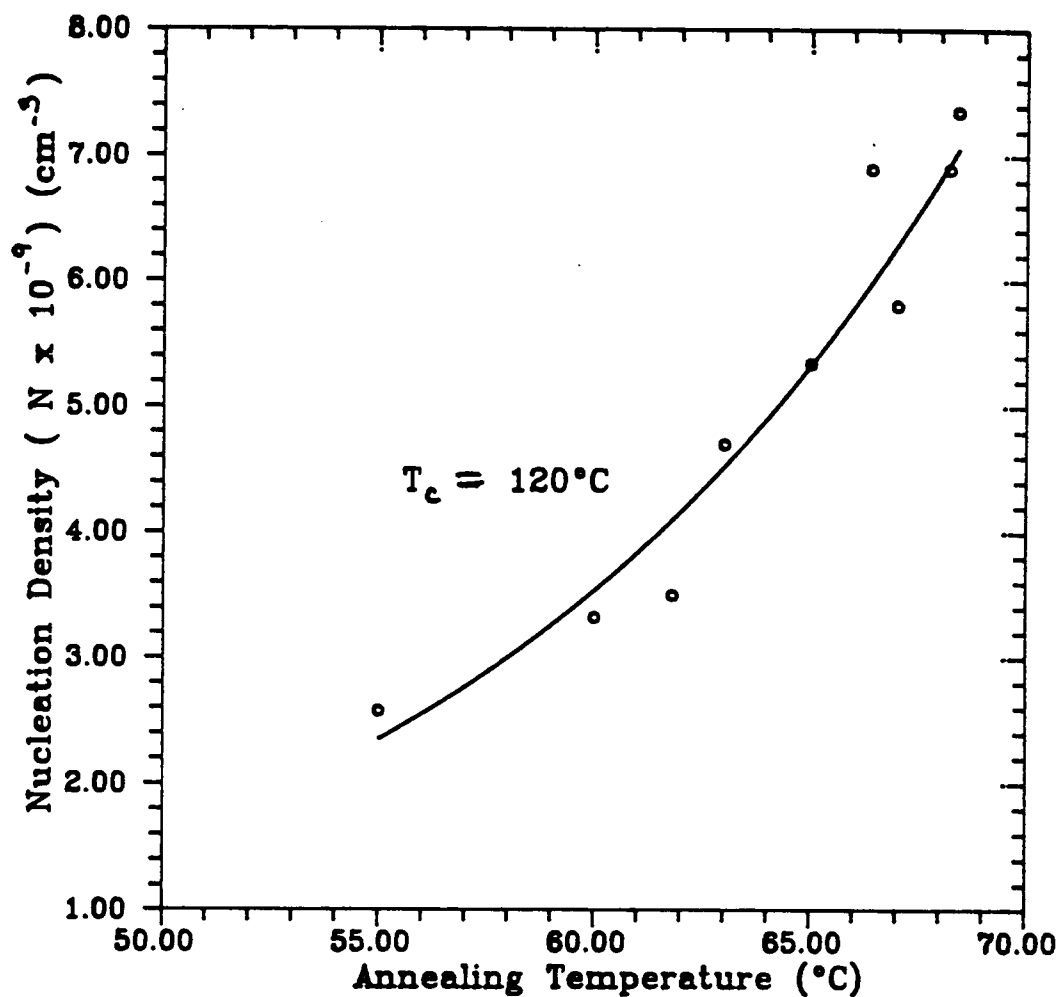


FIGURE 53: Plot of the nucleation density vs. the annealing temperature of the sample before being crystallized at 120°C .

6. DISCUSSION

There has been much interest in the influence of annealing processes on the thermal behavior of poly(ethylene terephthalate) in the glass transition region. Several techniques have been used to examine the extent of enthalpy relaxation occurring within the PET system. There have been several suggestions of specific volume change but no direct quantitative measurements.²⁵ This study attempted to correlate the changes observed in the thermal and volumetric properties with the dielectric properties of PET glasses in order to gain further insight into the mechanism of annealing below the glass transition temperature.

Poly(ethylene terephthalate) serves as an important model for studying relaxation processes in semicrystalline polymers.^{24,40-43,95} PET can be quenched into the completely amorphous state and can be isothermally annealed at temperatures below the glass transition allowing direct measurement of the effect of annealing on relaxations, as seen in this study. Isothermal crystallization allows direct measurement of the effect of crystallinity on relaxations taking place in the amorphous state. PET shows two relaxation processes, one designated α and the other β .

6.1. Thermal Properties

The influence of annealing processes on organic glasses in the glass transition was first investigated and analyzed quantitatively by Petrie.²⁵ The PET glasses (samples) used in this study exhibited excess free energy; annealing these samples produced an enthalpy peak and an increased T_g when analyzed by differential scanning calorimetry (DSC), as shown in Figure 15 (section 5). This is similar to the results Petrie obtained in her study of annealing PET glasses below the glass transition temperature. In her paper on enthalpy relaxation of PET and polystyrene, Petrie provided a rationalization and consistent experimental response to observations in glassy polymers.⁴

The absorption of thermal energy was viewed as a kinetic effect. Petrie showed that it was not necessary to postulate a first order process, because an abrupt change in enthalpy is a necessary condition for a first order process, but not a sufficient one.

Because of the kinetic aspects associated with the transformation of a melt to a glass in the glass transition temperature interval, the glassy states of materials prepared under normal cooling conditions have excess enthalpy and volume relative to those of the corresponding equilibrium glassy states that can be achieved through slow

cooling or annealing regimes.^{37,95-97} For glasses with excess thermodynamic properties, there is a thermodynamic potential for the properties to approach those of the equilibrium state, i.e., decrease with time, the rate of decrease being determined by the level of molecular or segmental mobility in the glassy state. Thus the changes in local order to be anticipated as a result of the approach of the glass toward its corresponding equilibrium glassy state during an annealing regime are those associated with a densification of the liquid-like packing.

The absorption of thermal energy around T_g paralleled the extent of molecular relaxation that had occurred during the annealing period. Petrie showed that the enthalpy approach to equilibrium can be followed with differential scanning calorimetry as in this study. Analysis of the absorption of thermal energy in the transition interval during the heating cycle of an annealed glass suggests that the amount of free energy could be accounted for on the basis of the kinetics of the glass transition. This parallels the enthalpy relaxation occurring during annealing. This study as well as Petrie's studies indicated that the time required for the enthalpy to relax to equilibrium values is extremely long. The enthalpy measured from the DSC peak during the transition is related to the

enthalpy relaxation process. With longer annealing periods, more recovery occurred with an increase in the transition endotherm.

6.2. Dielectric Relaxation Studies of PET

It was of particular interest to examine the implications of annealing below the glass transition temperature. Several amorphous PET film samples were annealed at various temperatures below the glass transition (70°C). Dielectric studies of poly(ethylene terephthalate) have been conducted for several years by many researchers^{24,25,97} and the trends are well known. Dielectric relaxation studies of PET show generally two relaxation regimes (usually designated α and β in order of decreasing temperature).

The α process is caused by large scale micro-Brownian motion characteristics of the glass-rubber transition in the amorphous phase of the polymer. This has been shown by mechanical relaxation data⁴³ where the shear modulus (at 1 Hz) for amorphous samples drops asymptotically toward zero at approximately 80°C. The shear modulus of semicrystalline PET exhibits a relaxation at 80°C but does not drop asymptotically toward zero until reaching 260°C, (the melting point of the polymer). The position of the α process is directly related to the position of the dilatometric glass transition (Figure 16, section 5).

The magnitude, location and breadth of the α relaxation in PET are a function of the degree of crystallinity. Ishida and others⁴¹ found that the magnitude ($\epsilon_R - \epsilon_U$) of the dielectric α -relaxation decreased with increased degree of crystallinity for PET. They showed that the α process in 5% crystalline PET is far smaller than that obtained for the 51% crystalline. This result indicated that the α relaxation occurs in the non-crystalline phase of the polymer, sample since ($\epsilon_R - \epsilon_U$) is proportional to the number of relaxing species per unit volume. A similar result was obtained by Saito⁹⁸ who studied specimens of PET with different crystallinities obtained by crystallizing at different degrees of undercooling.

Saito and Nakajima⁹⁹ found that the magnitude ($\epsilon_R - \epsilon_U$) of the dielectric α relaxation in amorphous PET increased in the usual manner with decreasing temperature to 75°C. Below this temperature ($\epsilon_R - \epsilon_U$) decreased rapidly and reached half of its maximum value near 68°C. This effect is known as the "dielectric transition" and has been seen by Saito in polybutyl methacrylate, amorphous and crystalline polycyclohexabutane, polyacrylonitrile and polyvinylidene chloride. The dielectric transition temperature was defined as the temperature at which ($\epsilon_R - \epsilon_U$) reached half its maximum value. It was found that the critical temperature was near the dilatometric glass-transition in all of the polymers above.^{98,99,17} Saito⁹⁸ considered the dielectric transition

an equilibrium phenomenon due either to a 'freezing in' of dipoles or a sudden change in the relative arrangement of the polar groups in the polymer. The result is a net cancellation and hence a sudden reduction in $(\epsilon_R - \epsilon_U)$ as the temperature is reduced. Ishida and Yamafuji¹⁰⁰ proposed an order-disorder theory to explain this effect.

Recently it was shown that the β process originates in the amorphous phase²⁴ of PET clarifying an uncertainty in the literature.

6.2.1. Dielectric Spectroscopy Analysis

Dielectric experimentation on amorphous samples annealed below the glass transition was performed. In this study an attempt is being made to correlate the changes observed in the thermal properties with the dielectric properties of PET glasses. The influence of annealing below the T_g on dielectric properties as the annealing temperature was approached was evident in this study as shown in Figure 15 in section 5. The dielectric spectrum showed significant relaxation occurring in the annealed samples (Figure 54). Figure 54 is a comparison plot between the unannealed PET sample and the PET sample annealed at 68°C for 48 hours. During the annealing cycle the excess energy and the excess volume in the PET glasses approach the equilibrium state. This relaxation can be accounted for on the basis of the kinetics of the glass transition. Thus, the enthalpy

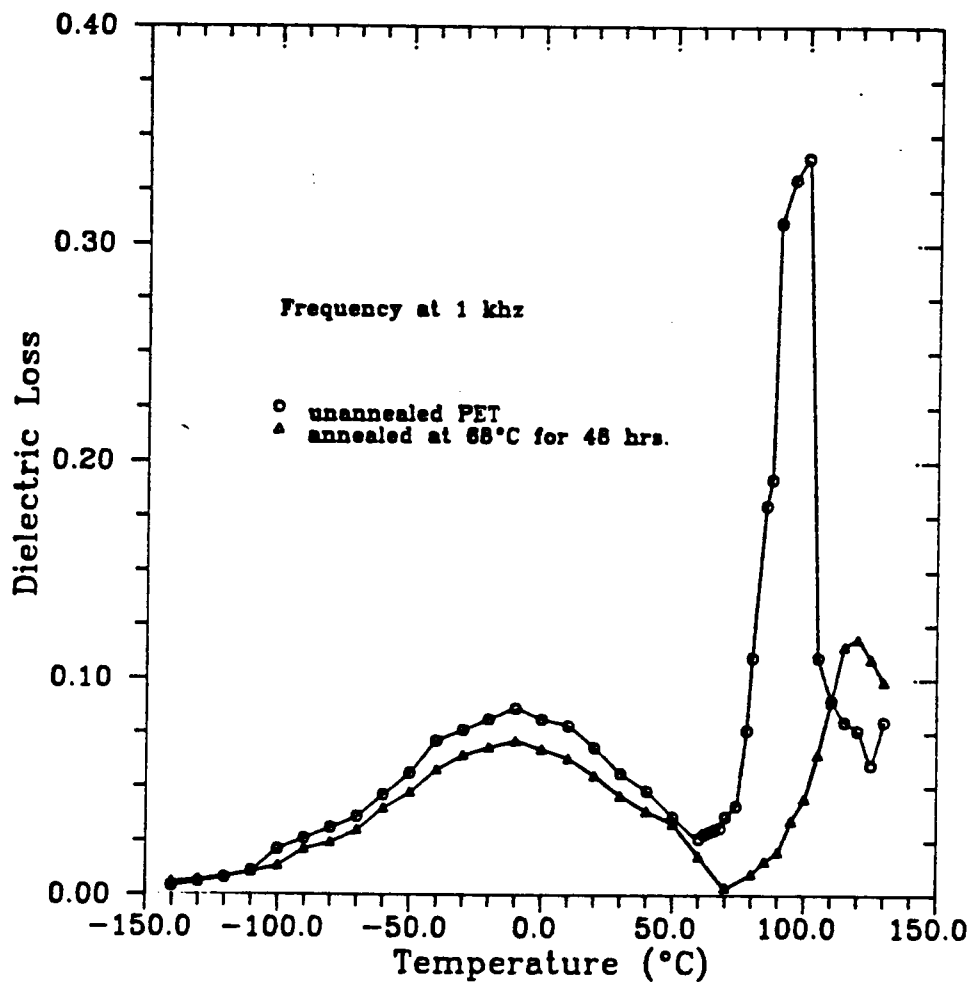


FIGURE 54: A comparison plot of the dielectric loss vs. temperature of the unannealed PET and annealed (48 hours) sample at 68°C.

relaxation occurring during annealing is similar to the relaxation occurring in dielectric spectroscopy.

As shown in Table I (section 5), the activation energy of the α and β transition peaks decreased with increasing annealing temperatures. Table I shows a drastic decrease in the activation energy of the α transition peak. Figures 55 and 56 are comparison plots of $\text{Log } \omega_{\text{max}}$ versus $1000/T(^{\circ}\text{K})$ of the unannealed and annealed amorphous samples (for the α transition peak). From the slopes of these lines the activation energy was obtained. These plots are essentially Arrhenius plots.

The magnitude, location and breadth of the α relaxation in PET are a function of the degree of crystallinity and also the manner in which a particular degree of crystallinity is obtained. From this study the breadth, location and magnitude of the α relaxation is not due mainly to the crystallinity of the samples. Each of the samples were amorphous initially. After annealing each a sample wide angle x-ray diffraction 2θ scan was run to check for crystallinity taking place during the annealing process. (see section 6.5 for further discussion). Each 2θ scan showed that crystallization did not take place, but a slight narrowing of the amorphous peaks did occur due to the dissipation of free volume in the annealed system. During the dielectric experiments the samples crystallized at about 100°C where the α -transition peak occurred.

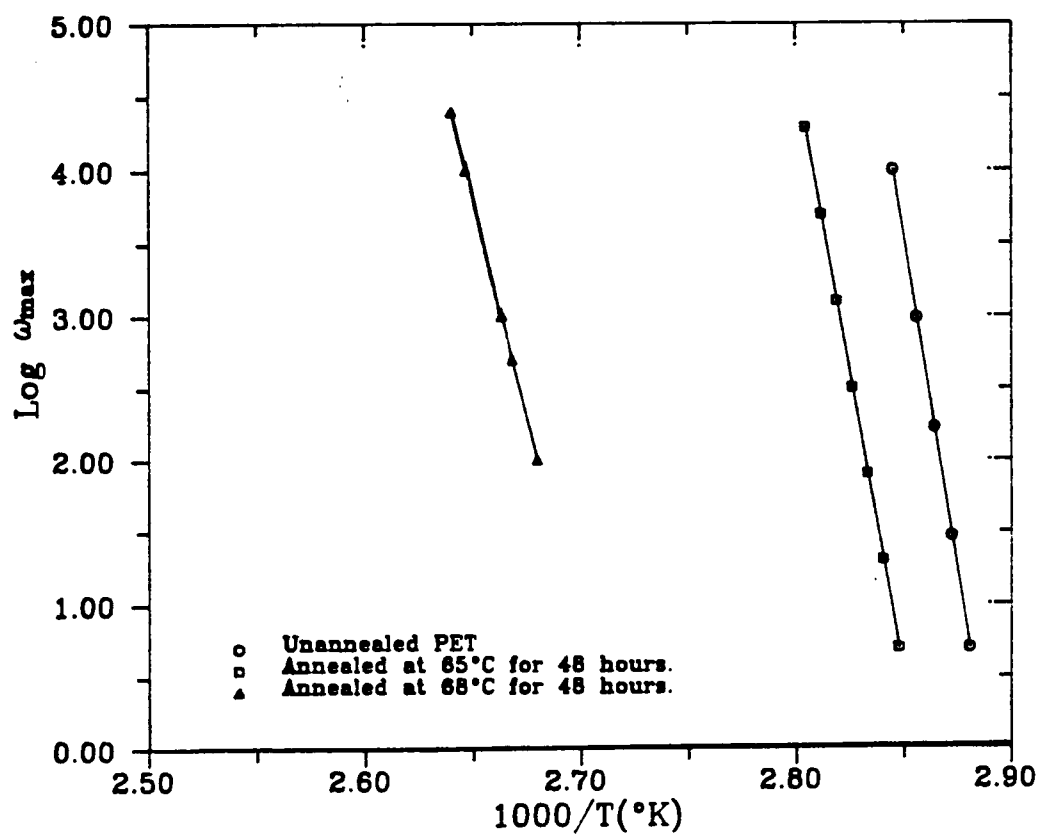


FIGURE 55: Plot of $\text{Log } \omega_{\text{max}}$ vs. $1000/T(^{\circ}\text{K})$ of unannealed, 65°C and 68°C annealed samples. The slope of these lines give the activation energy of the α peak.

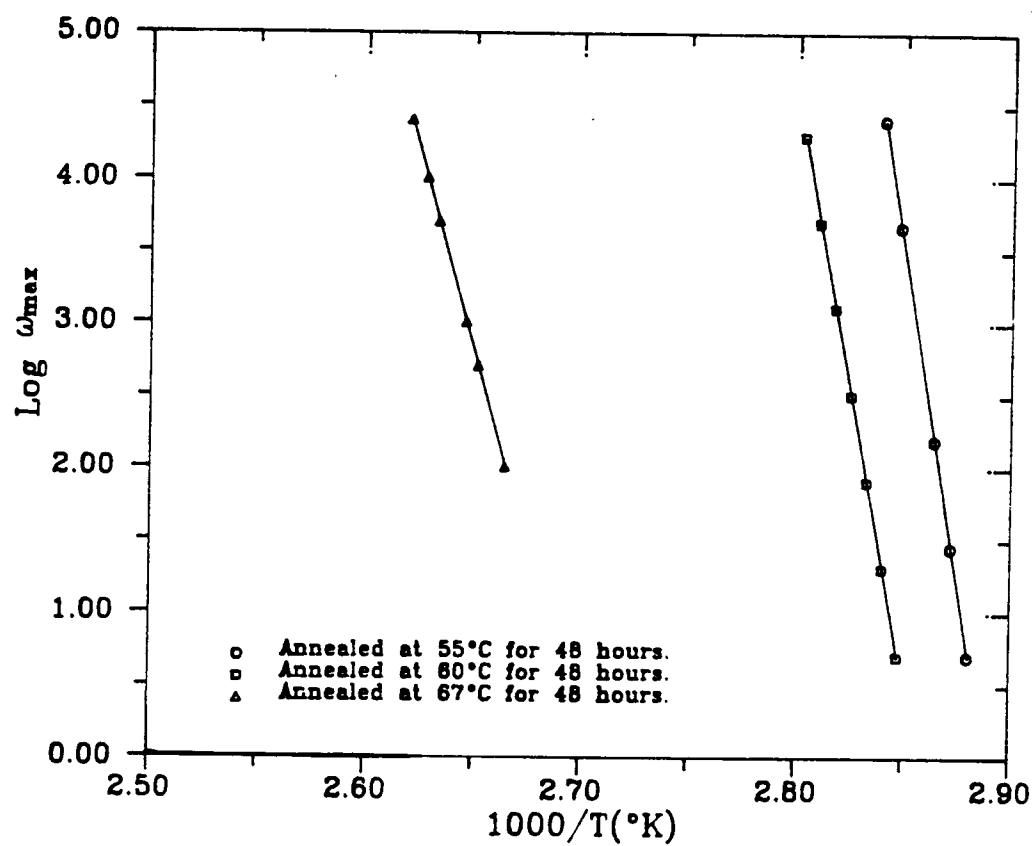


FIGURE 56: Plot of $\text{Log } \omega_{\max}$ vs. $1000/T(^{\circ}\text{K})$ of the 55°C, 60°C and 67°C annealed samples.

In figures 57 and 58, Cole-Cole plots generated by plotting ϵ'' vs. ϵ' for the unannealed sample and the sample annealed at 68°C for 48 hours, of the α and β transition peaks. From these plots is shown that there is a change of relaxation magnitude and a change in the position of the transition peak particularly for the α -transition. In Table II and III the relaxation magnitude of the α and β transition peak are shown. The Cole-Cole parameter obtained from the equation in section 5.2.3. are also shown. A comparison plot of the β -transition peak Cole-Cole arameters for the unannealed PET and the sample annealed at 68°C for 48 hours is shown in figure 59. The Cole-Cole parameter β increases with a decrease in the relaxation magnitude $(\epsilon_R - \epsilon_U) = \Delta\epsilon'$. The relaxation occurring in the annealed sample is due to excess energy and excess volume in the PET glasses which approach the equilibrium state.

A final analysis of the relaxation spectrum of the unannealed and annealed samples of PET is shown in Figures 60-63. The plots are of $\epsilon''/\epsilon''_{\text{max}}$ versus a normalized frequency scale $\text{Log}(f/f_{\text{max}})$. Each of these plots was created by time-temperature superposition (WLF). The WLF equation is a model which describes the shift in the relaxation spectrum from one equilibrium state to another. For each plot a different annealed sample is plotted with the unannealed PET sample. From these plots it is shown that as the annealing temperature approaches the glass

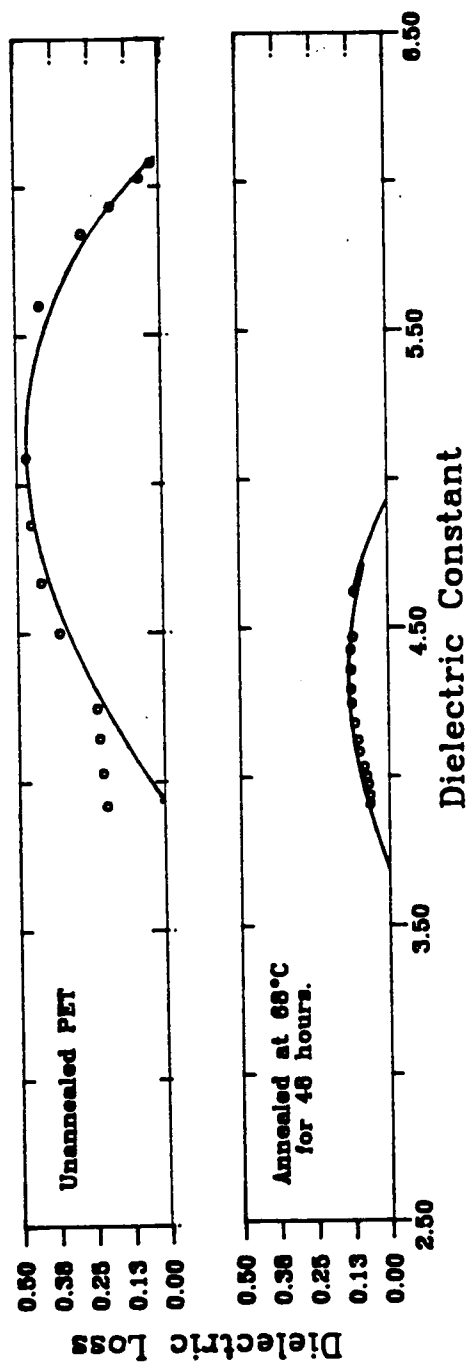


FIGURE 57: A comparison plot between unannealed and sample annealed at 68°C (48 hours) of the α -transition peak.

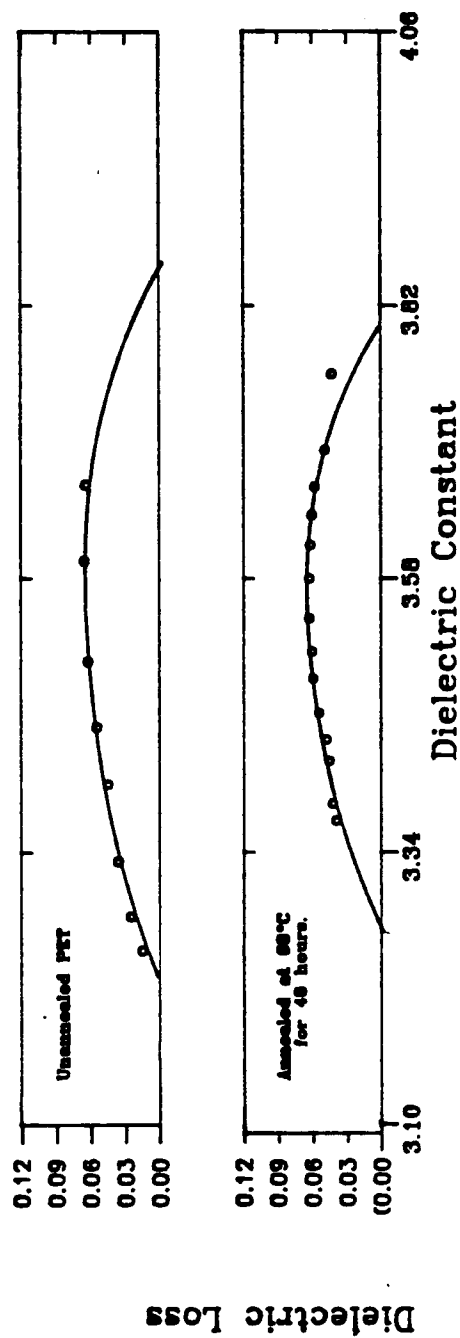


FIGURE 58: A comparison plot between unannealed and sample annealed at 68°C (48 hours) of the β -transition peak.

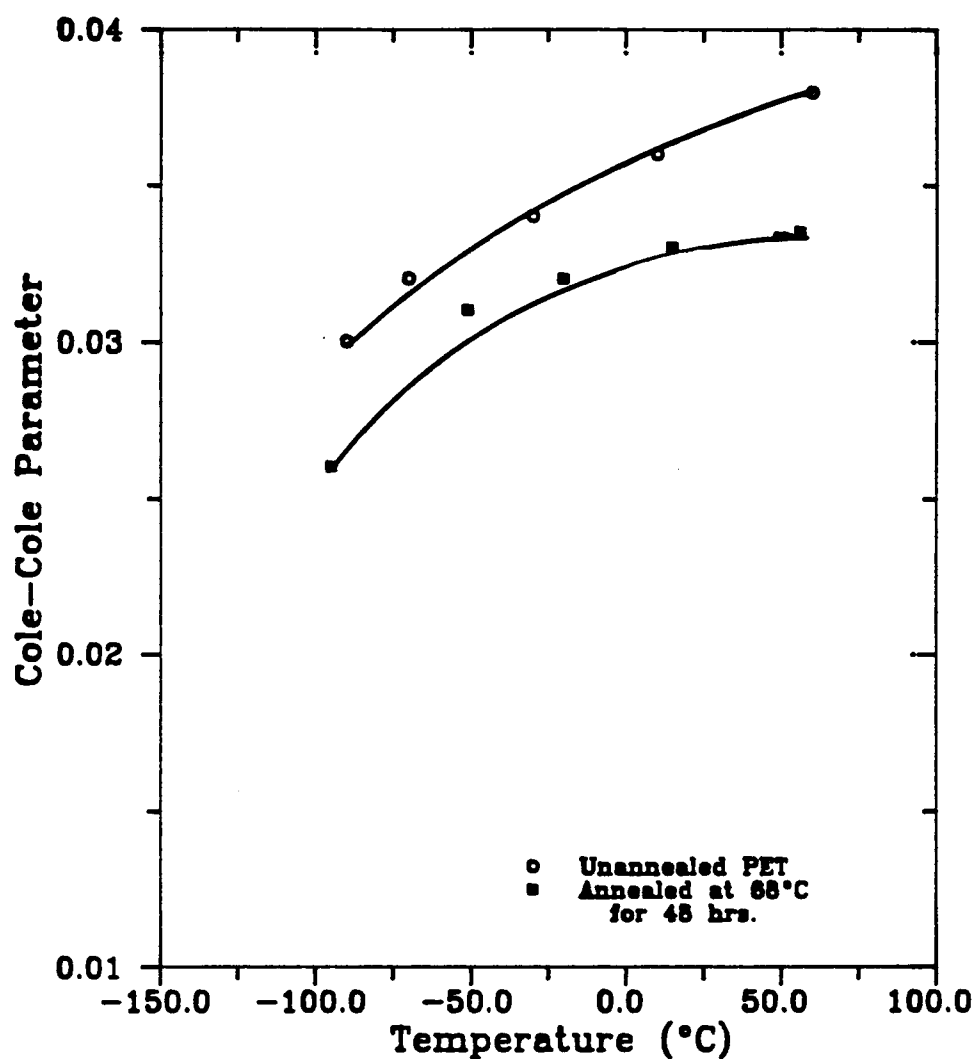


FIGURE 59: A comparison plot between the unannealed PET and sample annealed at 68°C for 48 hours of the Cole-Cole parameter of the β -transition peak.

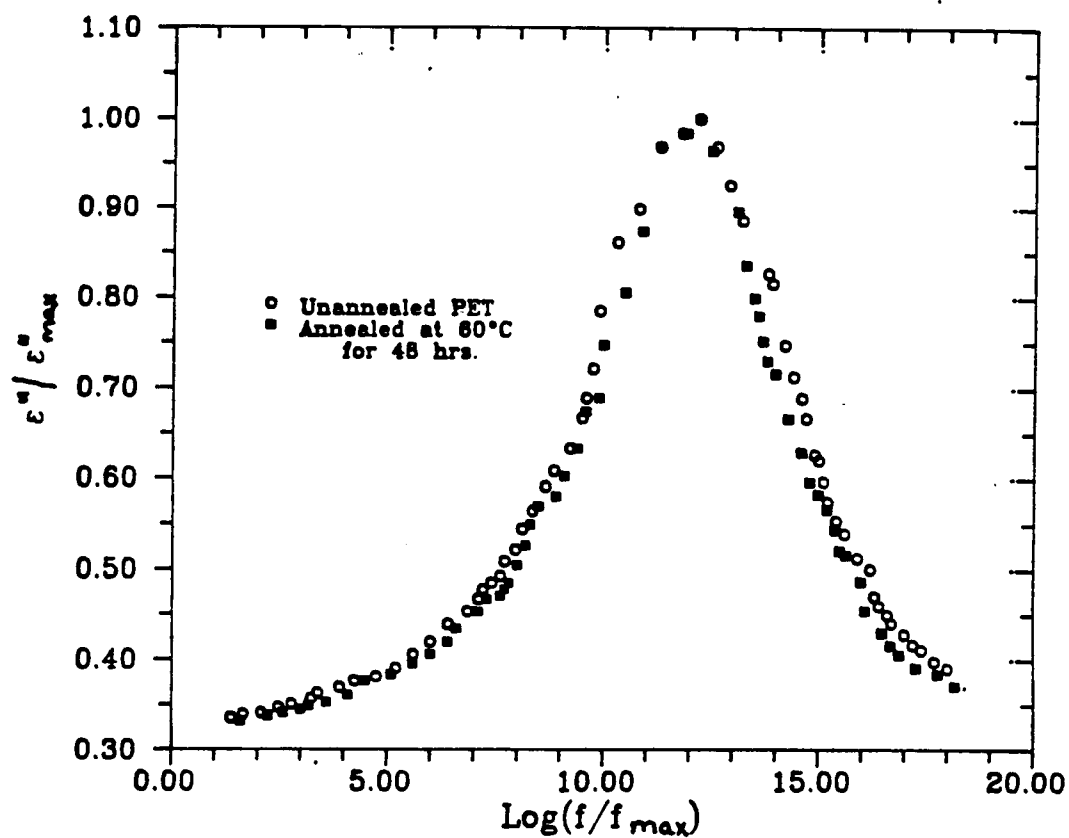


FIGURE 60: Plot of $\epsilon''/\epsilon''_{\max}$ vs. $\text{Log}(f/f_{\max})$ of unannealed and annealed sample at 60°C (for 48 hours).

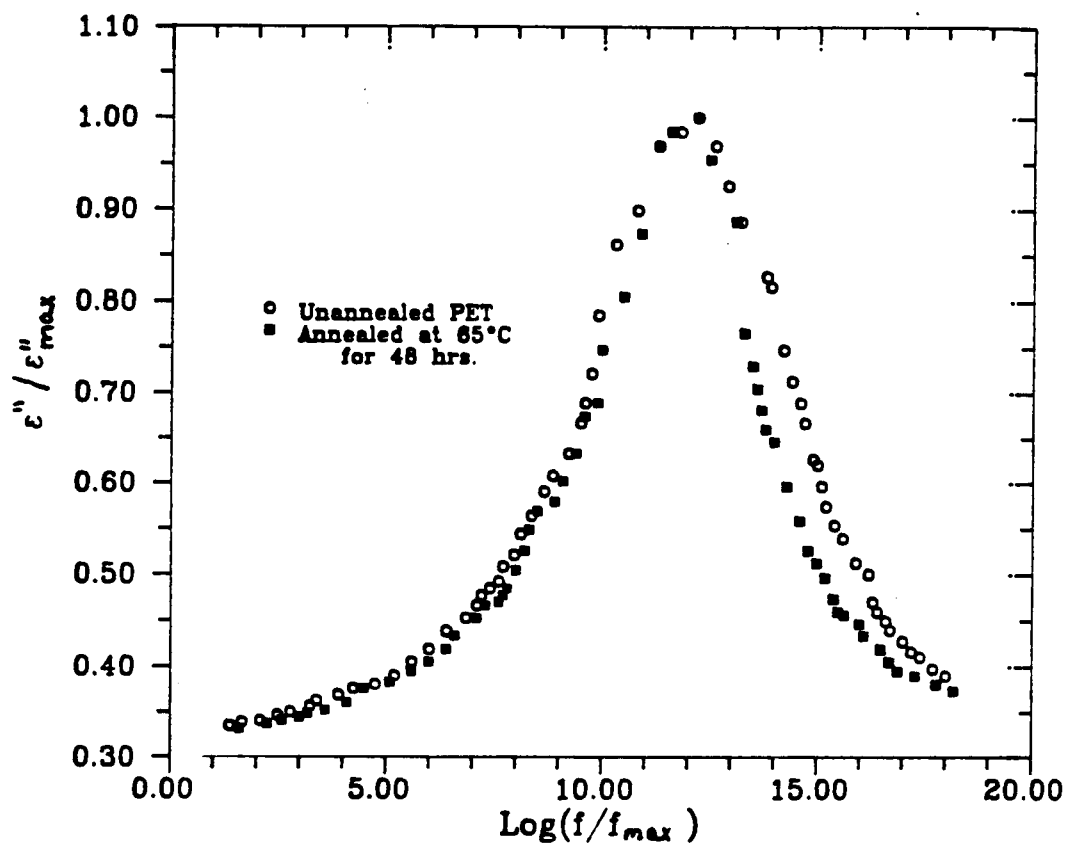


FIGURE 61: Plot of $\epsilon''/\epsilon''_{\max}$ vs. $\text{Log}(f/f_{\max})$ of unannealed and annealed sample at 65°C (for 48 hours).

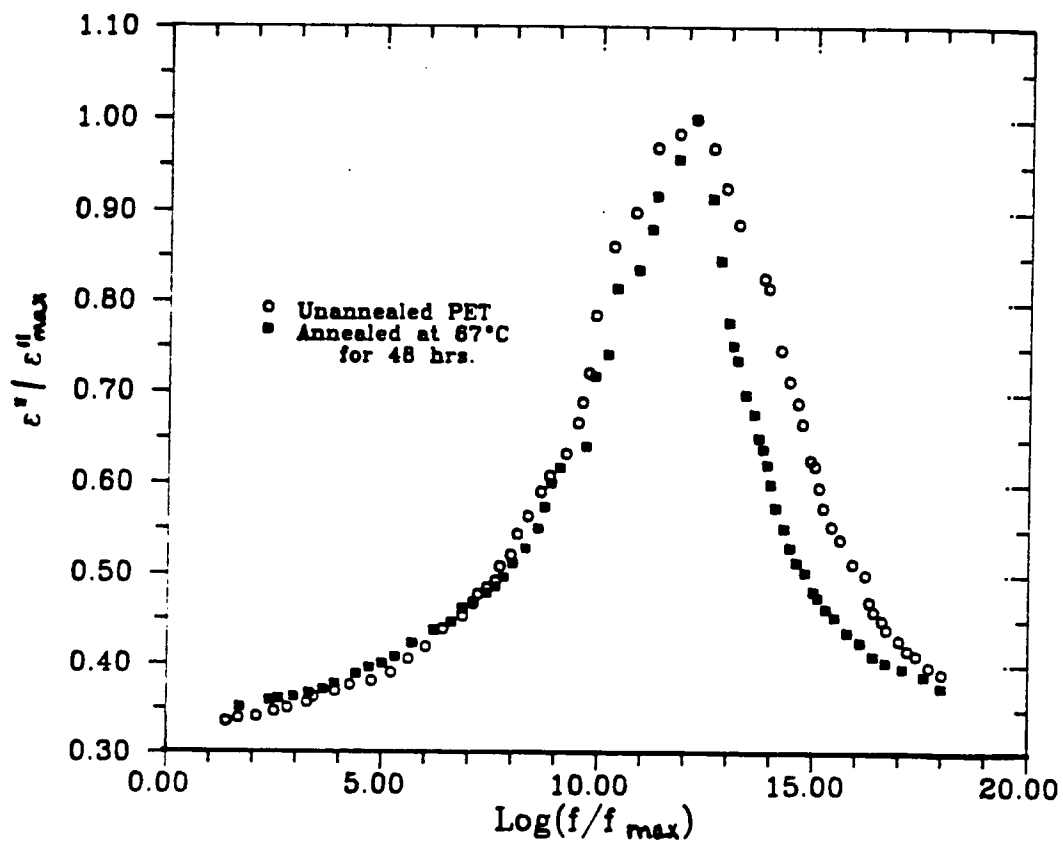


FIGURE 62: Plot of $\epsilon''/\epsilon''_{\max}$ vs. $\text{Log}(f/f_{\max})$ of unannealed and annealed sample at 67°C (for 48 hours).

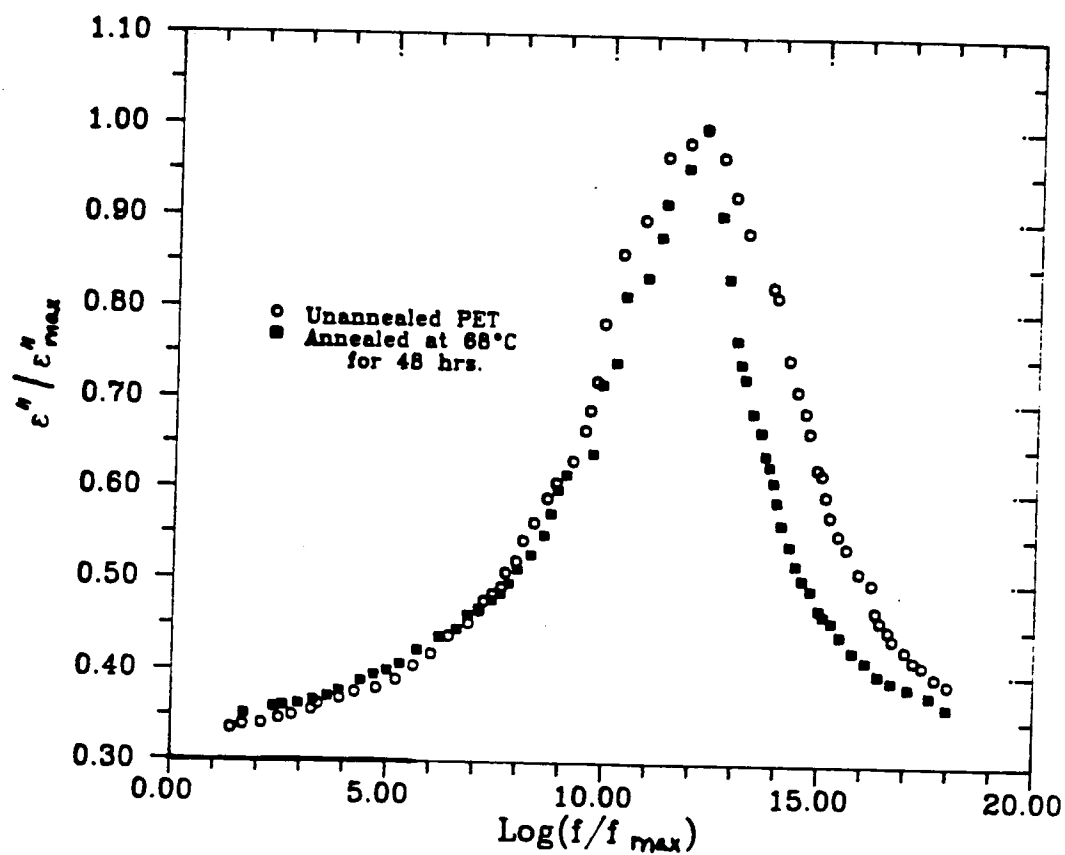


FIGURE 63: Plot of $\epsilon''/\epsilon''_{\max}$ vs. $\text{Log}(f/f_{\max})$ of unannealed and annealed sample at 68°C (for 48 hours).

transition temperature (70°C), the amount of relaxation taking place increases significantly. This is due to the fact that during the annealing cycle the excess energy and excess volume in the PET glasses approaches an equilibrium state.

The viscoelastic relaxation spectrum below T_g has been found by Matsuoka et al.¹⁰¹, (1) to shift during isothermal aging without changing the shape of the distribution, but (2) to change to progressively broader distributions at lower temperatures.

6.3. Specific Volume Studies

It is well known that phenomenon of physical aging in glassy polymers is associated with decreases in specific volume³⁷ and in excess enthalpy.⁴ However, the specific volume and the enthalpy are not always uniquely related, i.e. states with the same volume could exhibit different enthalpies depending on thermal¹⁰² or pressure histories.¹⁰³

Roe³⁰ found that the glass transition temperature may result from a metastable equilibrium present when a glassy polymer is brought to a temperature moderately below its T_g as the polymer undergoes a slow relaxation toward a limiting structure. In this study two observations seemed to suggest that (1) the limiting state might not be an equilibrium state or (2) the relaxation times for different properties may be quite different. This suggested that either the T_g

is not an equilibrium state or the different relaxation times for various properties reflect different moments of the relaxation time distribution. There were two types observations which seemed to suggest that the limiting state might not be an equilibrium state. The first relates to the thermal density fluctuation observable with small-angle x-ray scattering. The second limiting annealed state was reported in an early work by Kovacs³⁷ on volume relaxation of poly(vinyl acetate).

6.3.1 Specific Volume Measurements

In this study specific volume measurements were made from the three terminal dielectric system by measuring the air capacitance (specifics are in section 4). To determine specific volume from the measured air capacitance, the specific volume at 25°C $v(25^{\circ}\text{C})$ had to be determined. This was done by placing the prepared samples in a density gradient column. In Table IV the determined specific volumes from the densities are given. As the sample annealing temperature approaches the glass transition the samples increased in density. This results from the fact that excess volume and excess energy had dissipated from the glassy system and relaxation had taken place.

From the dielectric experiments the measured air capacitance allowed for determination of the specific volumes of each sample as a function of temperature. From

Table IV: Density and Specific Volume of Samples of PET obtained by the Density Gradient Column.

<u>Annealing*</u> <u>Temperature(°C)</u>	<u>Specific Volume</u> <u>(cc/g)</u>	<u>Density</u> <u>(g/cc)</u>
Unannealed	.7450	1.342
55.0	.7440	1.344
60.0	.7414	1.349
65.0	.7370	1.357
67.0	.7355	1.360
68.0	.7339	1.363

*All samples annealed for 48 hours.

Figure 16 in Section 5, the glass transition temperature was determined by extrapolation at the discontinuity in the plots for each sample, as shown in Table V. A plot of the glass transition versus the annealing temperature is shown in Figure 64. The glass transition temperature increased as the sample annealing temperature approached the glass transition temperature, 70°C. This is attributed to a decrease in free volume in the higher annealing temperature samples, therefore, the glassy system needs more energy to go from the glassy state into the rubbery state.

6.3.2. Fractional Free Volume and Relaxation Time

Phenomenological aspects of the temperature dependence of relaxation processes in the rubbery state have been studied extensively. An empirical formula, known as the WLF equation.⁶⁰

$$\ln a_T = \ln \frac{\tau}{\tau_0} = \frac{c_1(T - T_0)}{c_2 + T - T_0} \quad 6.1$$

has been demonstrated to be highly successful in predicting behavior. The values τ and τ_0 are the corresponding relaxation times at temperatures T and T_0 ; values common to many polymers when T_g is taken as T_0 .¹⁰⁴ These universal constants c_1 and c_2 can be related to the free volume fraction f , f_g fractional free volume at T_g ,

$$f = f_g + \alpha_f(T - T_g) \quad 6.2$$

Table V: Glass Transition Temperatures Determined from Dielectric Studies (specific volume measurements).

<u>Annealing*</u> <u>Temperature (°C)</u>	<u>Glass Transition Temperature</u> <u>T_g (°C)</u>
Unannealed	70.0
55.0	72.5
60.0	81.5
65.0	87.0
67.0	87.5
68.0	87.9

*All samples annealed for 48 hours.

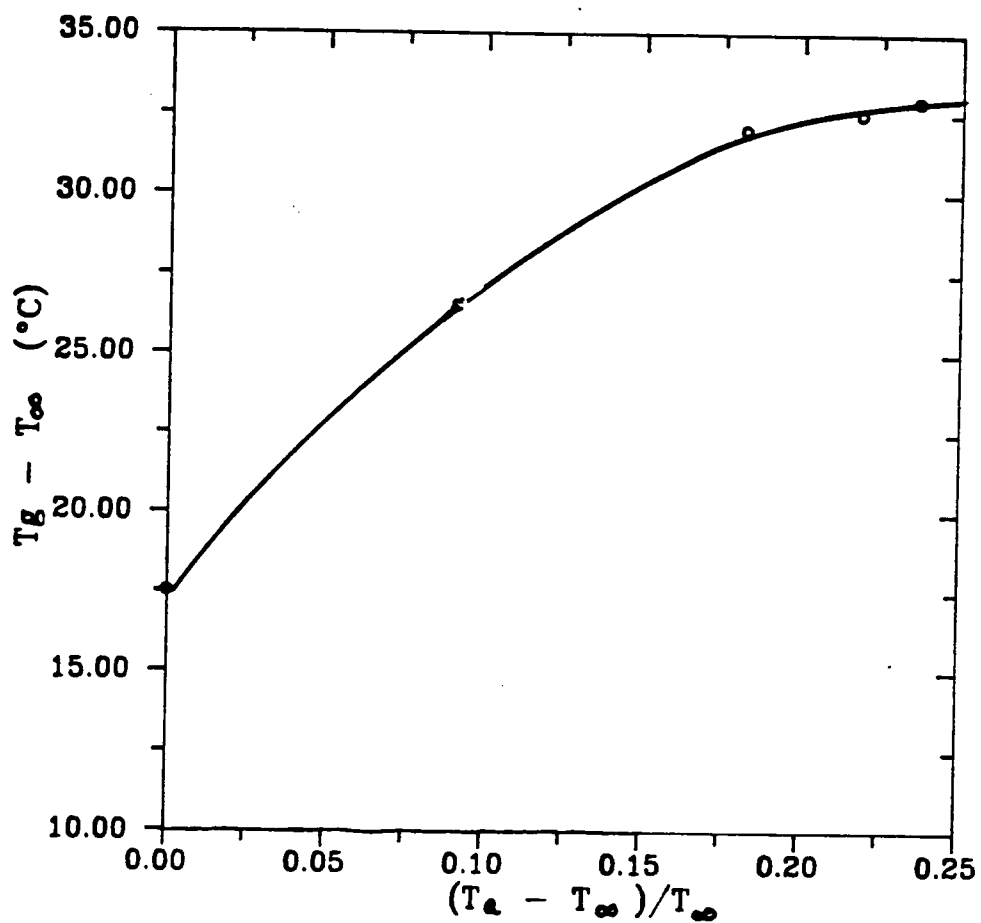


FIGURE 64: The glass transition temperature minus the equilibrium temperature vs. the relative annealing temperature.

and the thermal expansion coefficient of f , $\alpha_f = df/dT$ with the following relationship:

$$c_1 = \frac{1}{2.3fg} \quad \text{and} \quad c_2 = \frac{fg}{\alpha_f} \quad 6.3$$

The concept of free volume has been introduced to interpret the WLF equation terms of molecular structure, and the shift of relaxation time with temperature has been described through the use of a parameter called the fractional free volume, $f = v_f/v$ to obtain ¹⁰⁵

$$\ln \frac{\tau}{\tau_0} = \frac{1}{f} - \frac{1}{f_0} \quad 6.4$$

Equations of this form have been found to fit experimental relaxation data on many systems.^{60,106-110} The feature of the free volume concept as related to the WLF equation may be summarized as: (1). The WLF equation describes the shift in the relaxation spectrum from one equilibrium state to another e.g., from one temperature state to another, (2). The free volume fraction, f , is a characterization parameter for the shift in relaxation times and not directly a measurable volume quantity, (3). the occupied volume, another empirical parameter like the free volume, exhibits thermal expansion as well as compressibility, and (4). the fractional free volume consists of two parameters, free volume and occupied volume.

In Figure 65 the temperature dependence of volume for poly(ethylene terephthalate) annealed at 68°C for 48 hours

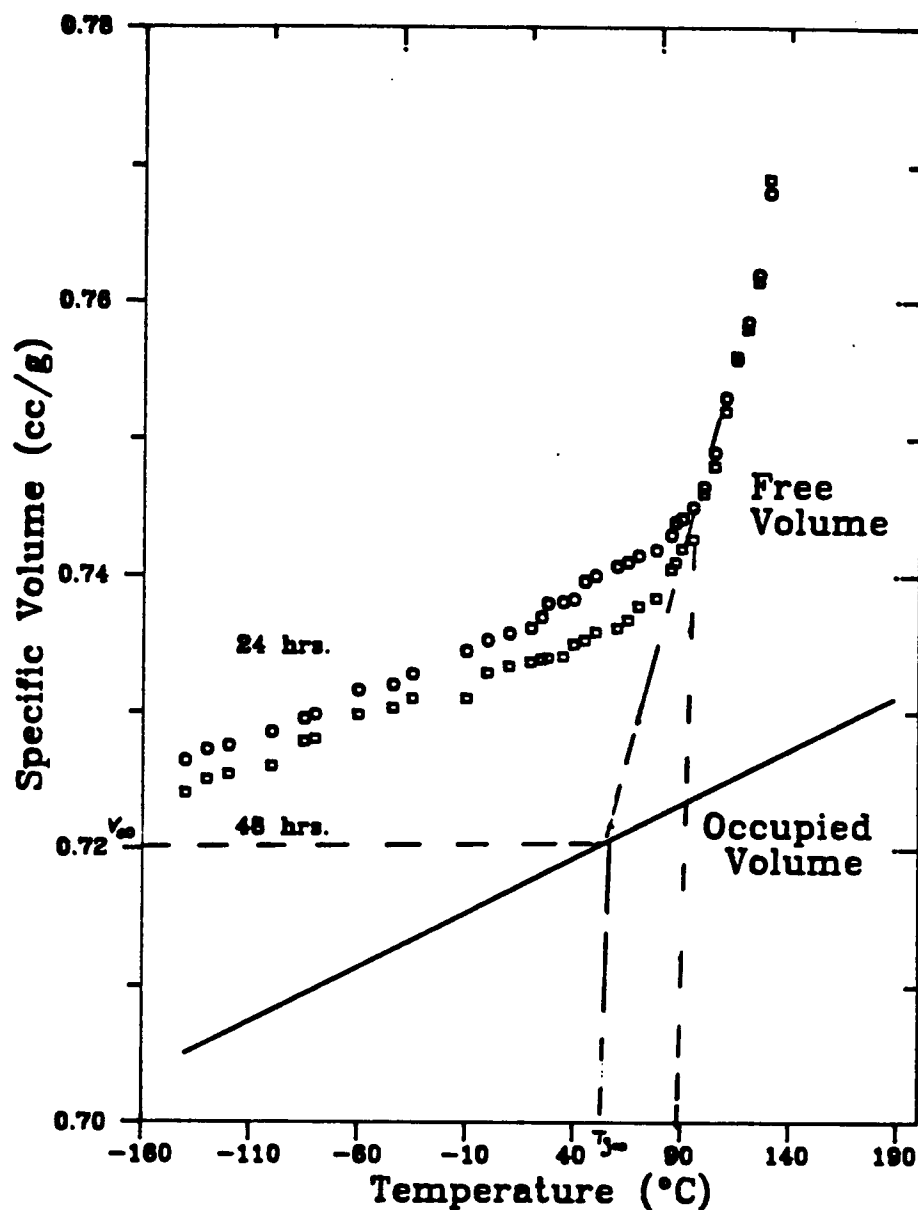


FIGURE 65: The specific volume of poly(ethylene terephthalate) vs. temperature. The glass transition temperature corresponds to the time range between 24 and 48 hours. The temperature at which the free volume of the liquid becomes zero is designated as $T_{g\infty}$.

and 24 hours is shown. The occupied volume and the free volume were calculated from the shift in the dielectric loss maximum along a logarithmic frequency axis with temperature change. The WLF equation for the shift is based on the T_g of 70°C, and is given by:

$$\log \omega = \frac{17.0 (T - T_g)}{31.2 + (T - T_g)} \quad 6.5$$

where ω is the frequency for the maximum dielectric loss factor in Hz.

Saito^{17,98} showed that the dielectric α -relaxation in amorphous PET obeyed the WLF equation. The parameters c_1 and c_2 found to be 17.1 and 31.7 degree for amorphous PET respectively. In Table VI, WLF parameters c_1 and c_2 were determined for the other annealed samples. Saito found that the WLF parameters increased with increasing crystallinity of PET. As seen in Table VI the values of the parameters increase with annealing temperature, but not very much as compared to what Saito found for crystalline PET ($c_1 = 30.4$ and $c_2 = 106.0$ degree for 31% crystalline PET).

From the above equations the values $fg = .0254$ and $\alpha_f = 8.021 \times 10^{-4} \text{°C}^{-1}$ were obtained. The occupied volume was computed at temperatures above T_g from these values and plotted in Figure 65.

The glass transition is affected by time.¹¹ The equilibrium volume curve above the liquidus line is extended to the lower temperature (Figure 65); it intersects the

Table VI: WLF Constants of samples annealed below the T_g.

<u>Sample</u>	<u>c₁</u>	<u>c₂</u> (degrees)
Unannealed	17.1	31.7
Annealed at 55°C for 48 hours.	17.1	31.7
Annealed at 60°C for 48 hours.	17.2	31.9
Annealed at 65°C for 48 hours.	18.4	33.0
Annealed at 67°C for 48 hours.	24.5	40.5
Annealed at 68°C for 48 hours.	26.8	45.6

occupied volume curve at a temperature, $T_{g\infty}$, which is approximately 50°C below the T_g . This corresponding volume is V_{∞} . This temperature is nearly the temperature where the conformational entropy is estimated to approach zero if the specific volume were allowed to decrease. This temperature is nearly the temperature at which the fractional free volume is estimated to become zero according to the theory of Gibbs and DiMarzio.⁶² From the number of hours it takes to densify, it is evident that the rate of contraction will become extremely long before such a volume is reached in an actual case.¹¹¹

Figures 66 and 67 show experimental data on the relative deviation of the volume from the equilibrium versus $\log(\text{annealing time})$ for samples annealed at 68°C. V_{∞} was determined from Figure 65. From these plots it can be seen that the time for the fractional free volume to be zero will be extremely long. At V_{∞} the system will be at equilibrium.

6.4. Crystallization Studies

Song and Roe¹¹² measured the x-ray intensities at small and intermediate angles to study the change in the structure of amorphous polystyrene as its volume was altered in several ways. The results showed that the large scale density fluctuation correlates fairly well with the change in specific volume, irrespective of the technique used to induce it. Conversely, the small scale density fluctuation,

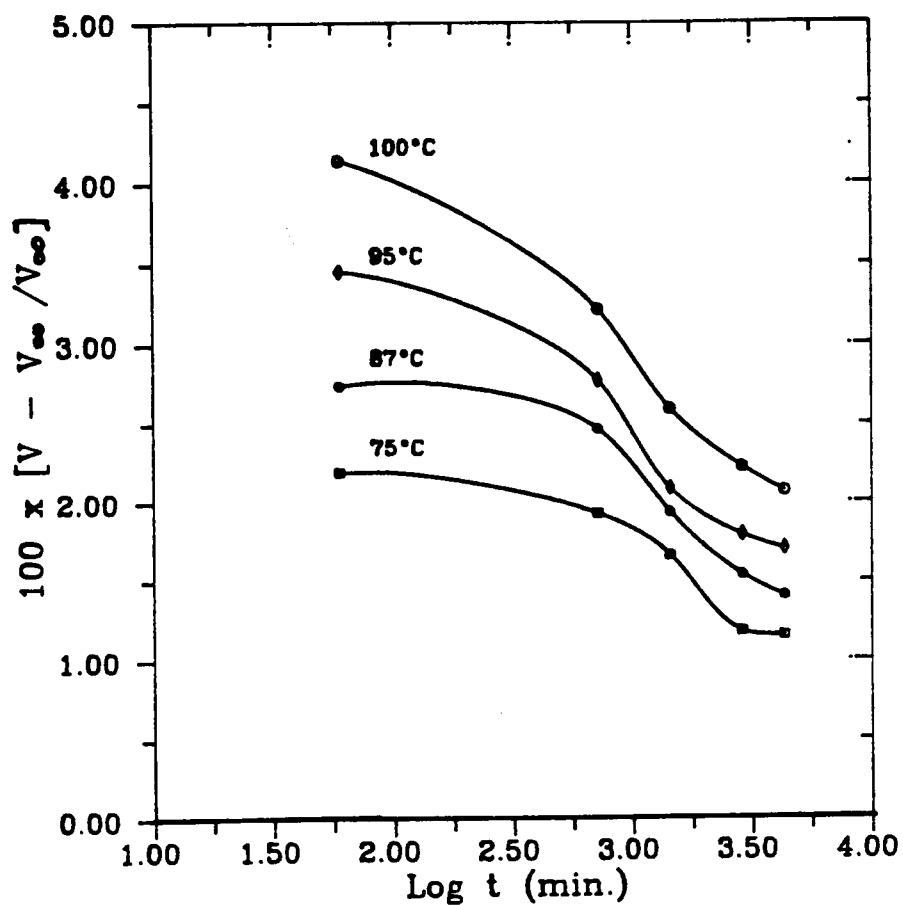


FIGURE 66: Experimental data on the relative deviation of the volume from equilibrium vs. Log (annealing time) annealing temperature was 68°C.

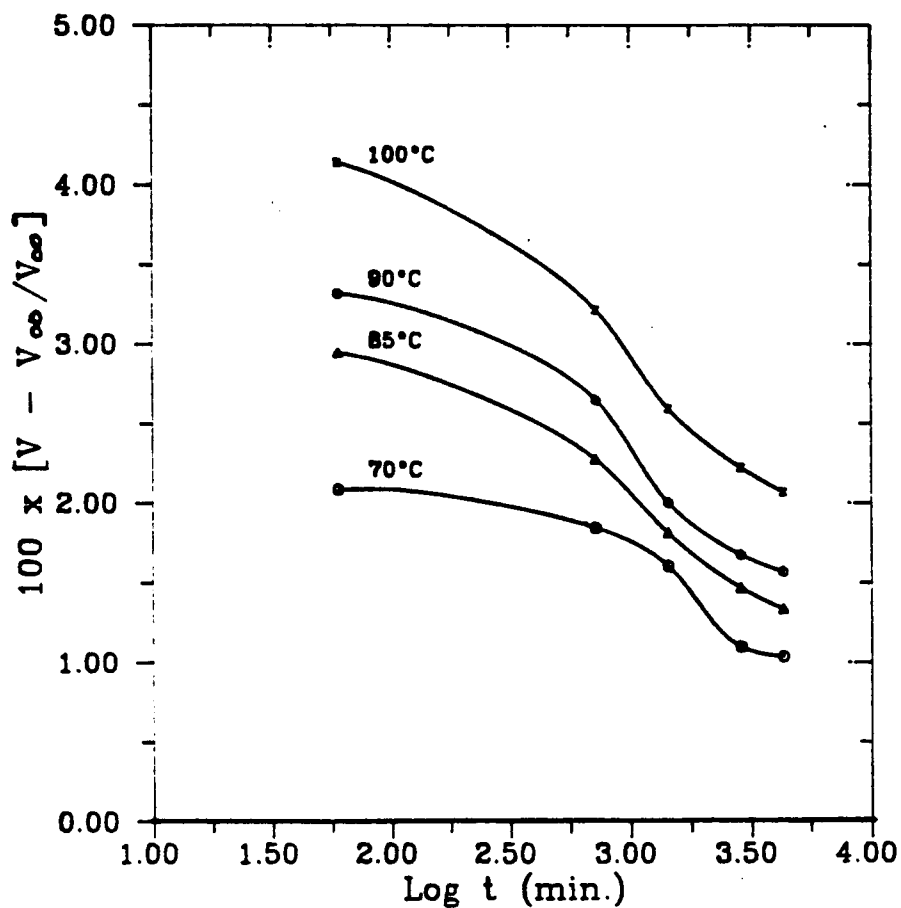


FIGURE 67: Experimental data on the relative deviation of the volume from equilibrium vs. Log (annealing time) annealing temperature was 68°C.

(indicating the degrees of local order), depends very sensitively on the method of volume change employed. In particular, physical aging gives rise to enhanced short-range ordering. The results suggested that the properties of glassy materials, such as the mechanical relaxation rate, are determined not only by the free volume content, but also by the state of local segment packing of segments. It was also shown that an approximate measure of the local structural order can be obtained in practice by measuring the height of the amorphous peak intensity.

6.4.1 Wide Angle X-ray Diffraction Studies

A wide angle X-ray diffraction (WAXD) 2θ scan was obtained for each sample to determine if crystallization had taken place during the annealing process. Figure is a comparison plot of an unannealed sample and a sample annealed at 68°C for 48 hours. The annealed sample's peak narrowed in width. This can be attributed to a free volume decrease during annealing and molecular relaxation. Because crystallization has not occurred, the system had undergone a densification process. The density of the system, therefore, increased because of the reduction of free volume in the system and not due to crystallization.

6.4.2 Small Angle Light Scattering Studies

The SALS experiments showed that the spherulite size decreased with annealing temperatures closer to the glass

transition temperature. This suggested that the nucleation density increased with higher annealing temperature, thus resulting in small spherulites as seen in Table VII. The nucleation density or number of nucleation sites increased due to annealing of the samples because the chains in the system will relax and tend to create more nucleation sites. In turn when the polymer crystallized the spherulites were smaller.

6.5 Molecular Theories of Relaxation

Unlike the phenomenological theories, the molecular theories attempt to explain the relaxation behavior in terms of proposed mechanisms for the motions of polymer molecules. Since most polymers exhibit more than one mechanical or dielectric relaxation region, no simple molecular mechanism is adequate to describe the behavior over a wide frequency and temperature range.

6.5.1 The Mechanism of Dielectric Relaxation

One of the early studies of the mechanism of dielectric relaxation in solids was performed by Debye.⁵⁷ He assumed that molecular dipoles placed in a constant electric field may align themselves, (to a first approximation) in two directions: parallel or antiparallel to the field. If no field is applied, both position are equivalent and have equal potential energies. If the potential energy of the

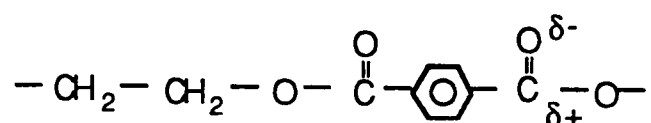
Table VII: Spherulite Size and Nucleation Density of samples annealed below the T_g.

<u>Annealing*</u> <u>Temperature</u> (°C)	<u>Spherulite Size</u> (microns)	<u>Nucleation Density</u> x 10 ⁻⁹ (cm ⁻³)
Unannealed	4.53	2.57
55.0	4.53	2.57
60.0	4.16	3.32
61.8	4.08	3.50
63.0	3.71	4.70
65.0	3.55	5.34
66.4	3.26	6.89
67.0	3.45	5.80
68.2	3.26	6.89
68.4	3.19	7.35

*All samples annealed for 48 hours.

dipole is represented as a function of the angle of rotation, it will be a curve with two equal minima separated by a maximum (the potential barrier). The height of the potential barrier relative to the minimum will determine the probability of the transtion of the dipole from one position to the other (rotation through 180°).

Dipoles can be experimentally distinguished from nonpolar molecules by their behavior in an electric field. Figure below illustrates the positive and negative ends of

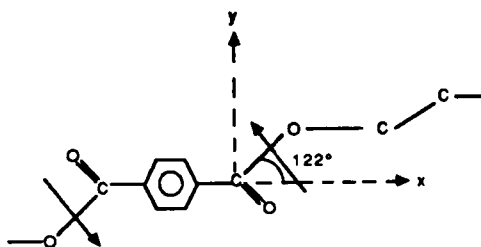


the dipole in a PET molecule. When polar molecules are placed between a pair of electrically charged plates, they tend to rotate and line up with the field. The negative end of each dipole tends to point toward the positively charged plate, and the positive end, toward the negatively charged plate.

When an electric field is applied, the energies of the dipoles situated on each side of the potential barrier are charged. The dipoles parallel to the field have a lower potential energy; the dipoles antiparallel to the field will have a potential energy minimum lying somewhat higher. The dipoles will oscillate at, frequencies about their equilibrium positions and their transition from one position to another will be associated with the probability of

rotation. A detailed examination of the process of jumping over the potential barrier leads one to the conclusion that the dielectric relaxation time depends on temperature in accordance with Arrhenius equation.

Conformational analysis, as well as analysis on the dipole direction in ester groups, have been reported for dimethyl terephthalate (DMT).^{113,114} The trans conformation of the PET repeat unit with information from DMT is illustrated below. The most stable conformations in PET are



the cis and trans conformation because coplanarity of the carbonyl groups with the benzene ring provide for maximum overlap of electrons. Both conformations are of equal energy.

Micro-Brownian motion is associated with the cooperative diffusional motion of main chain segments. The α process has been attributed to the larger scale micro-Brownian motions. In this study, the main chain consists of the benzene ring, carbonyl groups (which first moves in the β process), and the methyl groups. Motions of long chain segments in the PET structure had a profound effect on the dielectric loss. As the temperature was increased the rotational energy in the PET system increased, thus the

polymer system approached the glass transition. The dielectric loss is more sensitive to molecular motions than the dielectric constant. For example, in the glassy region the dielectric constant showed very little change, yet the dielectric loss exhibited damping peaks.

Sacher¹¹⁵ conjectured that local reorientation for the β process requires cooperative motion extending over several repeat units. This cooperative motion, according to Sacher,¹¹⁶ involves motions resembling wagging and rocking vibrations. This points out that the ability to reorient in the β region is substantially restricted where angular reorientation is much less than 180° and requires the effect of many repeat units.

In the β -process of poly(ethylene terephthalate) the $\text{O}=\text{CO}$ - ester group contributes to the motions and vibrations which take place in the β transition peak. As the PET samples were annealed at temperatures closer to the T_g , the β -transition peak decreased slightly. This was because the system had relaxed during the annealing process and in turn, the $\text{O}=\text{CO}$ - ester group does not have as much space to vibrate or rotate in the system.

Before small angle light scattering studies the samples were crystallized. The PET was crystallized from the glass state at a constant $T_C = 120^\circ\text{C}$. In the SALS study spherulitic morphology was observed. Spherulites consist of chain folded lamellae radiating out from a central nucleus

which grows linearly with time until impingement occurs with other spherulites. Precisely how a spherulite develops depends on how it is nucleated.

The nucleation density changed as the annealing temperature approached the glass transition temperature. So as the nucleation density increased the impingement of spherulites during crystallization was quite frequent. Thus bringing about smaller spherulites for the annealed system.

7. CONCLUSION

Annealing of polymer glasses at temperatures close to, but below, the glass transition results in an aging process which leads to embrittlement. The process is generally known as enthalpy relaxation because excess enthalpy is annealed out of the glass. It was monitored by differential scanning calorimetry (DSC). In this study it was attempted to correlate changes in thermal properties with changes in the relaxation time spectrum using dielectric spectroscopy. It has also been demonstrated that sub-T_g annealing exerts a major influence on the subsequent crystallization behavior. This was observed by small angle light scattering (SALS).

7.1 Thermal Properties

The poly(ethylene terephthalate) glasses studied exhibited excess free energy; annealing these samples produced an enthalpy peak and an increased glass transition temperature (T_g) when analyzed by DSC. The absorption of thermal energy can be viewed as a kinetic effect. The energy absorption near T_g paralleled the extent of molecular relaxation that took place during the annealing period. The enthalpy measured from the DSC peak during the transition was related to the enthalpy relaxation process. With longer annealing periods, more thermal recovery occurred with an increase in the transition endotherm.

7.2 Specific Volume Determination

In this study specific volume measurements were made from a three terminal dielectric system by measuring the air capacitance. As the sample annealing temperature approached the glass transition the sample density increased. This resulted from excess volume and excess energy which dissipated from the glassy system as the relaxation took place. The increase in density was not due to crystallization that could have occurred during the annealing process. Wide angle x-ray diffraction (WAXD) 2 θ scans obtained for each sample indicated that no crystallization took place. The annealed sample's peak narrowed in width; this attributed to a decrease in free volume during annealing and molecular relaxation. Because crystallization had not occurred, the system had gone through a densification process.

7.3 Dielectric Studies

The influence of annealing below the T_g on dielectric properties was evident in this study. Large changes in the intensity and the relaxation time distribution of the α and β relaxations have been measured. From Cole-Cole plots for the unannealed and the sample annealed at 68°C for 48 hours, changes appeared in the relaxation magnitude and in the position of the transition peak, particularly for the α

transition. The relaxation in the annealed sample is due to excess energy and excess volume in the PET which approached the equilibrium state. The viscoelastic relaxation spectrum below T_g has been found to shift during isothermal aging without changing the shape of the distribution but changed progressively to broader distributions at lower temperatures.

7.4 Crystallization Studies

The effects of annealing in the sub-glass region was observed by small angle light scattering (SALS). SALS showed that the crystallized sample spherulite size decreased on annealing. This is due to the increase in nucleation density. The nucleation density or number of nucleation sites per unit volume increased due to the annealing of the samples because the chains in the system relaxed and tended to create more nucleation sites. The excess enthalpy and free volume quenched into glassy systems decreased with sub- T_g annealing, thus bringing the system closer to equilibrium.

8. SUGGESTIONS FOR FURTHER WORK

I. Further dielectric studies of poly(ethylene terephthalate) under a pressurized system would be of much interest. This type of study could yield information regarding the rate of densification of the glassy material as a pressure is applied continuously. In addition, the relationship between the change in the glass transition temperature of a glass annealed at sub-T_g conditions with the pressure of the system (dT_g/dP) should be investigated.

II. Volume changes can be effected by several different techniques: (i) changing the temperature above T_g, (ii) changing the temperature below the T_g, (iii) densification by application of pressure above T_g and then subsequent release at room temperature, (iv) spontaneous volume expansion of the pressure densified material, and (v) spontaneous volume contraction on isothermal annealing below the glass transition (physical aging). The investigations of the effect of different volume change techniques on the PET system could be studied by X-ray scattering at small and intermediate angles. From these studies a measure of the change in the structure of the PET polymer as the volume is changed by different techniques can be determined.

III. The spherulite size of the annealed samples was determined after being isothermally crystallized by small

angle light scattering (SALS). Further studies of interest would be in the determination of spherulite size with different annealing time periods. In this way, the effect of different annealing time periods can be related to the nucleation density, which is related to the spherulite size. Such a study could allow for the analysis of the growth rates involved in a glassy system.

IV. The change in volume has been studied by FTIR studies, but the effect of different techniques of changing the volume needs to be studied. FTIR can be used to examine any changes in vibrational energies between the unannealed and samples aged by annealing below the glass transition temperature.

V. The prepared samples have a thermal history and sometimes memory effects play an important role in the study of them. Further investigations are necessary to determine if the effect of thermal history on the poly(ethylene terephthalate) films affect the system after annealing the samples below the glass transition. Further studies into the thermal history by dielectric spectroscopy are necessary to see if any changes occur in the relaxation spectrum.

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