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Light scattering studies of the crystallization of polyethylene terephthalate.

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LIGHT SCATTERING STUDIES OF THE
CRYSTALLIZATION OF POLYETHYLENE TEREPHTHALATE

A Thesis Presented
by
TAKEO YUASA

Submitted to the Graduate School of the
University of Massachusetts in partial
fulfillment of the requirements for the degree of

MASTER OF SCIENCE
August, 1975

Polymer Science & Engineering
LIGHT SCATTERING STUDIES OF THE
CRYSTALLIZATION OF POLYETHYLENE TEREPTHALATE

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August, 1975
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DEDICATION

To Sumiko
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CHAPTER I
INTRODUCTION

The structures present in a polymer are of considerable importance in the study of the physical properties such as strength, transparency, etc. A knowledge of the structures of the polymer is required for an understanding of the physical properties and their relationship to process conditions and methods of improvement. These structures may be considered at different levels of size ranging from the molecular to the macroscopic. One of the most important structures is that occurring in crystalline polymers.

A polymer molecule that possesses a high degree of chemical and structural regularity among its chain elements under appropriate conditions of temperature, pressure and stress, is capable of undergoing crystallization. Attempts to understand the crystalline nature of polymers have been made by many investigators. Results indicated that none of the polymers were completely crystalline but only partially crystallizable. Consequently, efforts to investigate crystalline polymers have been to consider them as complex composite systems which consist, in simplest terms, of a suspension of crystals in an amorphous matrix.

One of the first models for the morphology of crystalline polymers was called the fringed micelle model presented by Hermann, et al. (1). This is based on a two-phase concept in which randomly-oriented crystalline regions are considered as being dispersed in an amorphous matrix.
Individual molecules are assumed to extend from one crystallite to another passing through the amorphous region.

In 1957 Keller (2) and some other workers (3,4) discovered polymer single crystals grown from dilute solutions. The model for them involves folded-chain lamellae in which the polymer chains zigzag back and forth within a single crystal and do not pass from one crystal to the other. The chains are oriented normal to the lamella and are postulated to fold regularly and re-enter the crystal immediately adjacent to themselves.

Another compromise model was proposed by Hosemann (5). In this model, the crystalline regions occur in extended structures which are often thin and sheet-like, and the amorphous chains may fold back and re-enter the crystal with some degree of regularity.

The most prominent structural organization in unoriented crystalline polymers is the spherulite, which was first described in 1945 by Bunn and Alcock (6). Here the crystals are not uniformly and randomly distributed throughout the polymer but grow in spherically-symmetrical aggregates of a type well described by Keith and Padden (7). Spherulites are recognized by their characteristic appearance in the polarizing microscope, where they are often seen as circular birefringent areas possessing a dark Maltese cross and sometimes other patterns such as concentric rings. Those patterns are well explained as resulting from an interaction between polarized light and the optical indicatrix of the spherulites, and the extinction bands are due to zero amplitude and zero birefringence (8). The observations of spherulites show that they consist of fibrillar structures of lamellae radiating from the spherulite center
and neighboring lamellae over a considerable angular range often twist in phase with a fixed pitch (9-12). The spherulite is formed by crystallization initiating from a primary nucleus, with growth primarily proceeding in the immediate vicinity of the previous grown crystals. Keller and Waring (13) have postulated a regular branching mechanism which indicates that the spherulites begin growth by fibril branching and that this branching follows a regular pattern, repeating at constant distances with a constant angle, and leads to a sheaf-like structure which fans out and finally develops into spherulites. The primary nucleus is usually a foreign particle (heterogeneous nucleus) but may arise spontaneously in the melt (homogeneous nucleation).

Spherulites generally contain both crystalline and amorphous material. The crystalline material is believed to be contained within the lamellae, whereas the amorphous material may be in the form of loose loops of folded-chain crystals, tie chains between crystals, chain ends in interlamellar regions and defects within the crystal.

In order to characterize these structures of the crystalline polymers, various experimental methods have been developed and applied for studying the crystallization of polymers. For example, the crystallization of polymers has been followed by direct methods such as dilatometry (14), x-ray diffraction (15), calorimetry (16) and microscopy (17) and by indirect studies such as the depolarized light transmission technique (18) and birefringence (19). Each of these methods provides information about some aspect of the crystallization process. Any one method, however, may not suffice in general to make a complete characterization
which would provide information about the total change in crystallinity with time, nucleation and growth rates, changes in the amount and size or shape of the aggregation of crystallites and in the other regions, in other words, morphological changes, etc.

The light scattering technique provides a valuable complement to the other methods and can characterize the structures whose sizes are in the range from approximately 0.5μ to 10μ. Thus the light scattering overlaps small-angle x-ray scattering and conventional microscopy and can be further complemented by electron microscopy (20). It permits the characterization of shape and size of the highly-organized crystallites which may form superstructure of the nature of spherulites, rods or shish kebabs. It especially provides information about the spherulite growth with time, changes in their number and size, the volume fraction of the spherulites, the degrees of crystallinity of the spherulitic and non-spherulitic regions and the degree of perfectness of the spherulites. Furthermore, these quantities are given in a statistical evaluation which is most important for polymers. In addition, this technique has the experimental advantage that it is fast, non-destructive, economical and requires only small samples. These advantages are, in part, compensated by theoretical difficulties in its interpretation.

The purpose of this thesis is to characterize the crystallization and morphological behavior of polyethylene terephthalate by the quantitative light scattering analysis of both HV and VV modes.

Polyethylene terephthalate is one of the most useful commercial polymers. Besides it is a convenient sample to investigate the structural
changes with time since it can be quenched rapidly enough to freeze the crystalline morphology and may be, therefore, subsequently studied at the leisure of the investigator.

The application of light scattering to the crystallization of polymers has been studied qualitatively and much attention has been paid to the $H_v$ mode which gave spherulite growth rates (21-26). On the contrary, the quantitative $V_v$ measurement has rarely been studied (27). In the present investigation, the main emphasis is to study the relationship between the structure of polyethylene terephthalate and the optical properties given by the light scattering technique in the crystallization process and to clarify the changes with time in the number and size of spherulites, volume fraction of spherulites, degree of crystallinity inside and outside of spherulites, and degree of perfectness of spherulites. Portions of this thesis have been presented (28).
CHAPTER II
THEORY OF LIGHT SCATTERING

The discussion is limited to the small angle light scattering (SALS) for semi-crystalline systems having a spherulitic morphology under static conditions.

Polymers scatter light because they contain optical heterogeneities of dimensions comparable to the wavelength of light (29). In semi-crystalline polymers, three sources of heterogeneities could occur: (1) density fluctuations due to crystallinity, areas of differing density due to statistical fluctuations or voids; (2) orientation fluctuations due to anisotropy; and (3) anisotropy fluctuations due to areas of differing anisotropy. By selecting the proper mode of polarization, one can discriminate among the various types of fluctuations. In the \( H_V \) mode the polarizer and analyzer are crossed with respect to their polarization directions while in the \( V_V \) mode they are parallel. \( H_V \) scattering is insensitive to density fluctuations.

There are two different theoretical approaches to light scattering theory: (1) statistical approach and (2) model approach. Debye and Bueche (30) were the first to propose a general statistical theory of SALS. It is the well-known correlation function approach in which they considered local density fluctuations in an isotropic medium. This theory has been extended by Goldstein and Michalik (31) and Stein and Wilson (32) to include the fluctuations in orientation of anisotropic scattering entities in the medium as well as the density fluctuations. Although
several other attempts (33-36) have been made in developing the statistical approaches, they are not applicable to the practical analysis because of the theoretical complexity and the difficulties in characterizing the particular parameters.

On the other hand, Stein and coworkers (37-42) have made great efforts to develop the theory with a model approach. Stein and Rhodes (37) proposed the theory of SALS for a three-dimensional model of homogeneous anisotropic spheres with the optic axes fixed to the radius of the sphere in which all spheres are isolated. Their theory, which was corrected by Samuels (23), had a very good agreement with experimental observation qualitatively. This success made the technique of SALS very powerful in studying the superstructure of crystalline polymer. According to the theory, the scattered intensities in the \( H_V \) and \( V_V \) modes, respectively, are:

\[
I_{H_V} = A \cos^2 \rho_2 V^2 \left( \frac{3}{U^3} \right)^2 \left\{ (\alpha_t - \alpha_r) \left[ \cos^2 \left( \frac{\theta}{2} \right)/\cos \theta \right] \sin \psi \cos \psi \right. \\
\left. \times (4 \sin U - U \cos U - 3 \sin U) \right\}^2
\]  

(1)
\[ I_{VV} = A \cos^2 \rho_1 V^2 \left( \frac{3}{U^3} \right)^2 \left\{ (\alpha_t - \alpha_s) (2 \sin U - U \cos U - \sin U) \right. \\
+ (\alpha_r - \alpha_s) (\sin U - \sin U) \\
- (\alpha_t - \alpha_r) \left[ \cos^2 \left( \frac{\theta}{2} \right) / \cos \theta \right] \cos^2 \mu (4 \sin U - U \cos U \\
- 3 \sin U) \right\}^2 \] (2)

where the terms are defined below.

**A** = constant of proportionality

**V** = volume of the spherulite

\[ \cos \rho_2 = \cos \theta / (\cos^2 \theta + \sin^2 \theta \sin^2 \mu)^{1/2} \]

\[ \cos \rho_1 = \cos \theta / (\cos^2 \theta + \sin^2 \theta \cos^2 \mu)^{1/2} \]

\[ U = (4\pi R/\lambda) \sin(\theta/2) \] (3)

**R** = radius of spherulite

**\lambda** = wavelength of light in the scattering medium

**\theta** = scattering angle in the scattering medium (Figure 8)

**\mu** = azimuthal angle (Figure 8)
\[ \alpha_t = \text{tangential polarizability of the spherulite} \]
\[ \alpha_r = \text{radial polarizability of the spherulite} \]
\[ \alpha_S = \text{polarizability of the surroundings} \]
\[ \text{Si} \ U = \int_0^U (\sin x/x) \, dx \]

The equation of \( I_{HV} \) is proportional to \( (\alpha_t - \alpha_r)^2 \), i.e., the anisotropy of the spherulite. This means that \( I_{HV} \) is independent of density fluctuation as mentioned earlier. \( \cos \rho_2 \) and \( \theta \) terms are close to unity as far as small angles are concerned. \( \sin \mu \cos \mu \) term shows that \( I_{HV} \) has a maximum intensity at \( \mu = 45^0 \) and zero intensity at \( \mu = 0^0 \) and \( 90^0 \). All \( U \) terms can be rewritten as

\[ \phi_{HV}(U) = \frac{(4 \sin U - U \cos U - 3 \text{Si} \ U)}{U^3} \]  \( \text{(4)} \)

\( \{\phi_{HV}(U)\}^2 \) provides that \( I_{HV} \) is a maximum at \( U = 4.1 \). Combining with Equation (3), one can get

\[ U_{\text{max}} = \frac{4\pi R}{\lambda} \sin \left( \frac{\theta_{\text{max}}}{2} \right) = 4.1 \]  \( \text{(5)} \)

Equation (5) gives the statistical average size of spherulites when one obtains \( \theta_{\text{max}} \) which is the scattering angle where the intensity is maximum.
These $\mu$ and reduced angle $U$ or scattering angle $\theta$ terms provide the well-known four-leaf clover pattern (Figure 9). $I_{H_V}$ is also proportional to $V^2$, i.e., the intensity increases with $R$ because of $V = \frac{4}{3} \pi R^3$. Therefore, as spherulites grow during crystallization process, $I_{H_V}$ increases rapidly (Figure 10). Equation (5) is a very powerful and convenient means to follow the crystallization of polymers (21,22,24,25,44) (Figure 11).

Comparing to the equation of $I_{H_V}$, the equation of $I_{V_V}$ has two additional terms which contain $(\alpha_t - \alpha_s)$ and $(\alpha_r - \alpha_s)$. At early stages of crystallization of polymers, $\alpha_s$ is close to the polarizability of the amorphous phase and the size of the spherulitic region could be very small. Consequently $(\alpha_t - \alpha_s)$ and $(\alpha_r - \alpha_s)$ terms dominate Equation (2). They can be rewritten as:

$$\phi_{V_V}^A = (\alpha_t - \alpha_s) \left(2 \sin U - U \cos U - \text{Si} U/ U^3 \right)$$

$$(6)$$

$$\phi_{V_V}^B = (\alpha_r - \alpha_s) \left(\text{Si} U - \sin U)/ U^3 \right)$$

$$(7)$$
Since Equations (6) and (7) do not involve \( \mu \), they show circular patterns which are independent of \( \mu \). Moreover, \( I_{VV} \) is more intense than \( I_{HV} \) because the \((\alpha_t - \alpha_r)\) term in Equation (2) is very similar to \( I_{HV} \). As spherulites grow, \((\alpha_t - \alpha_s)\) and \((\alpha_r - \alpha_s)\) get greater. As a result, \( I_{VV} \) becomes more intense. However, as the volume fraction of spherulites becomes over 50\%, \( \alpha_s \) gets closer to the average polarizability of spherulites. In fact, when the whole system is occupied by spherulites, \( \alpha_s \) is

\[
\alpha_s = \frac{\alpha_r + 2\alpha_t}{2}
\]

This is nothing more than the average polarizability of spherulites. At this stage, the contribution of the \((\alpha_t - \alpha_r)\) term to \( I_{VV} \) is higher than that of \((\alpha_t - \alpha_s)\) and \((\alpha_r - \alpha_s)\). \( \cos^2 \mu \) in the \((\alpha_t - \alpha_r)\) term provides a two-fold symmetrical pattern. Thus \( I_{VV} \) shows the well-known dumbbell-shaped pattern (Figure 9). During the crystallization stage between the volume fraction of spherulite 50\% and 100\%, \((\alpha_t - \alpha_s)\) and \((\alpha_r - \alpha_s)\) terms decrease and the \((\alpha_t - \alpha_r)\) term increases. As a result, \( I_{VV} \) decreases. In other words, \( I_{VV} \) shows a maximum during the crystallization process. Once the system is volume-filled by spherulites, the \((\alpha_t - \alpha_r)\) term dominates Equation (2), then \( I_{VV} \) becomes comparable to \( I_{HV} \). This was proved experimentally (37,40,43) (Figure 12).
Both Equations (1) and (2) can predict another phenomenon. Suppose one observes the intensity of the light scattering for a volume-filling system at the same small scattering angle and $\mu = 45$ for $H_V$ and $\mu = 0$ and 90 for $V_V$. Since $\theta$ is small, $\cos \theta = 1$, $\cos \rho_2 = 1$, $\cos \rho_1 = 1$.

\[
I_{H_V} = A V^2 [(\alpha_t - \alpha_r) \phi_{H_V}(U)]^2 (\sin 45 \cos 45)^2
\]
\[= A V^2 [(\alpha_t - \alpha_r) \phi_{H_V}(U)]^2 (\frac{1}{4}) \quad (8)
\]

\[
I_{V_V} (\mu = 0) = A V^2 [(\alpha_t - \alpha_s) \phi_{V_V}^A + (\alpha_r - \alpha_s) \phi_{V_V}^B - (\alpha_t - \alpha_r) \phi_{H_V}(\cos 0)]^2 \quad (9)
\]

\[
I_{V_V} (\mu = 90) = A V^2 [(\alpha_t - \alpha_s) \phi_{V_V}^A + (\alpha_r - \alpha_s) \phi_{V_V}^B - (\alpha_t - \alpha_r) \phi_{H_V}(\cos 90)]^2 \quad (10)
\]

Since $\cos 0 = 1$ and $\cos 90 = 0$, 

\[ \left[ I_{VV}(\mu = 0) \right]^{1/2} - \left[ I_{VV}(\mu = 90) \right]^{1/2} = A^{1/2} V (\alpha_t - \alpha_r) \phi_{HV} \]

\[ = 2 \left[ I_{HV}(\mu = 45) \right]^{1/2} \quad (11) \]

Therefore, if one plots \( \left[ I_{VV}(\mu = 0) \right]^{1/2} - \left[ I_{VV}(\mu = 90) \right]^{1/2} \) against \( \left[ I_{HV}(\mu = 45) \right]^{1/2} \), one could obtain a straight line whose slope is 2. In the present investigation, this would be tried.

Recently, Yoon and Stein (45) proposed a compromise theory between a statistical approach and a model approach. They set up a model involving randomly-located assemblies of truncating anisotropic spherulites in the isotropic medium surrounding the spherulites. They started from Debye and Bueche's equation (30) and replaced the density by anisotropy as a scattering power. Using Sturgill's assumption (46) in which the correlation function for an assembly of spherulites is identical with that evaluated for a single spherulite, they calculated the correlation function and also the mean square fluctuation of the scattering power for an anisotropic sphere. Equating the results of the correlation function approach and the model approach, they got new but similar equations which are:
\[ I_{HV} = K_2 \phi_s \cos^2 \rho_2 R^3 \left\{ (\alpha_t - \alpha_r) \left[ \cos^2 (\theta/2)/\cos \theta \right] \sin \mu \cos \mu \phi_{HV} (U) \right\}^2 \]  

where \( K_2 \) is a constant of proportionality and \( \phi_s \) is a volume fraction of spherulites which can be expressed:

\[ \phi_s = N V \]  

where \( N \) is a number of spherulites in a unit volume.

Comparing with Equation (1), Equation (12) involves \( \phi_s \). Thus Equation (12) is a more suitable expression for following the crystallization of bulk polymers from the melt.

The equation of the intensity in the \( V_Y \) mode is:

\[ I_{V_Y} = K_1 \cos^2 \rho_1 V^2 B (\phi_s) \left\{ (\alpha_t - \alpha_d) \phi_{V_Y}^A (U) + (\alpha_r - \alpha_d) \phi_{V_Y}^B (U) \right\} \]

\[ - (\alpha_t - \alpha_r) \left[ \cos^2 (\theta/2)/\cos \theta \right] \cos^2 \mu \phi_{HV} (U) \left\}^2 \]  

(14)
where the terms are

$$K_1 = \text{constant of proportionality}$$

$$\alpha_d = \phi_s \left( \frac{\alpha_r + 2\alpha_t}{3} \right) + (1 - \phi_s) \alpha_m$$

(15)

$$B(\phi_s) = \cos \rho_1^2 \left[ \phi_s \left( 1 - \phi_s \right) (\alpha_t - \alpha_m) \left( \frac{2}{3} \alpha_r + \frac{1}{3} \alpha_t - \alpha_m \right) + \phi_s \left( \frac{1}{5} - \frac{\phi_s}{9} \right) (\alpha_r - \alpha_t) \right] + \sin^2 \rho_1 \left( \frac{\phi_s}{15} (\alpha_r - \alpha_t)^2 \right)$$

$$\cos \rho_1^2 \left[ \left( 1 - \phi_s \right)^2 (\alpha_t - \alpha_m) \left( \frac{2}{3} \alpha_r + \frac{1}{3} \alpha_t - \alpha_m \right) + (\alpha_r - \alpha_t) \left( \frac{1}{5} - \frac{2\phi_s}{9} + \frac{\phi_s^2}{9} \right) \right] + \sin^2 \rho_1 \left( \frac{\phi_s}{15} (\alpha_r - \alpha_t)^2 \right)$$

(16)

$$\sin^2 \rho_1 = \sin^2 \theta / (\cos^2 \theta + \sin^2 \theta \cos^2 \mu)$$

$$\alpha_m = \text{polarizability in the medium surrounding spherulites}$$

Equation (14) is also similar to Equation (2); however, Equation (14) involves the complicated term $B(\phi_s)$ and $\alpha_d$ instead of $\alpha_s$. $\alpha_d$ is average polarizability of the whole system. When the system becomes
volume filling, $\phi_s = 1$, $B(\phi_s) = 1$ and $\alpha_d = (\alpha_r + 2\alpha_t)/3$ so that

Equation (14) is exactly the same as Equation (2). When $\phi_s = 0$, that is, the system has low spherulite concentration, $B(\phi_s) = 0$, no scattering occurs. Equation (14) shows more clearly than Equation (2) that $I_{VV}$ passes through maximum at around $\phi_s = 50 - 60\%$ and minimum at $\phi_s = 1$. Once the system is volume filled by spherulites, the crystallization increases only within the spherulites, that is, the secondary crystallization takes place. At this stage, $I_{VV}$ increases monotonically with increasing crystallinity as well as $I_{HV}$. This can be explained by anisotropy differences during crystallization.

The anisotropy is given by:

\[
(\alpha_t - \alpha_r) = (\alpha_t - \alpha_r)_c \phi_{cs} f_{cs} + (\alpha_t - \alpha_r)_a (1 - \phi_{cs}) f_{as} + (\alpha_t - \alpha_r) F_s
\]

(17)

where the terms are defined as:

\[
(\alpha_t - \alpha_r)_c = \text{intrinsic anisotropy of pure crystal}
\]

\[
(\alpha_t - \alpha_r)_a = \text{intrinsic anisotropy of amorphous}
\]

\[
\phi_{cs} = \text{volume fraction crystallinity of inside spherulites}
\]
\( f_{cs}, f_{as} \) = orientation functions of the crystals and the amorphous segments with respect to the spherulite radius
\[
(\alpha_t - \alpha_r) F_s = \text{form polarizability difference of the crystals within the spherulite}
\]

\( (\alpha_t - \alpha_r)^0 \) can be calculated if the structure of the crystal and the idealized orientation of crystals within a spherulite are known. The crystalline structure of polyethylene terephthalate is triclinic (47) whose dimensions are, respectively, \( a = 4.56\AA \), \( b = 5.94\AA \), \( c = 10.75\AA \), \( \alpha = 98.5^0 \), \( \beta = 118^0 \), \( \gamma = 112^0 \). Using the bond polarizabilities given by Bunn and Danbeny (48), one can calculate the polarizabilities of three principal axes of the pure crystal of polyethylene terephthalate. The results of the polarizabilities per unit volume are:

\[
\begin{align*}
\alpha_x &= 0.0576 \\
\alpha_y &= 0.0958 \\
\alpha_z &= 0.1027
\end{align*}
\]

where the \( c \) axis is parallel to the \( z \) direction and the \( y \) direction is perpendicular to \( z \) and on the plane of the benzene ring. This was also done by some investigators (49,50) and agreement is fairly good.

The spherulite anisotropy is related to the spherulite birefringence, \( \Delta_s = n_t - n_r \), by the differential Lorenz-Lorentz equation:
\[ \Delta_s = n_t - n_r = \frac{2}{9} \pi \left( \frac{n^2 + 2}{\bar{n}} \right)^2 (\alpha_t - \alpha_r) \]  

(18)

where \( n_r \) and \( n_t \) are the radial and tangential refractive indices of the spherulite and \( \bar{n} \) is the average spherulite refractive index 
\[ \bar{n} = \frac{n_r + 2n_t}{3}. \]

If the orientation of crystals within the spherulite is like polyethylene (10) where the b crystal axis is radial and the a and c axes are tangential, one can calculate the intrinsic anisotropy of the pure crystal as:

\[ (\alpha_t - \alpha_r)_c^0 = \frac{\alpha_a + \alpha_c}{2} - \alpha_b \]

However, for polyethylene terephthalate, such a structure as crystal within the spherulite is ambiguous and only the c crystal axis is nearly perpendicular to the radius of the spherulite (10).

Therefore, one has to determine the anisotropy of the spherulite in another way. One possibility is a direct measurement of the birefringence but the spherulite of polyethylene terephthalate is usually too small for this. Another way is to assume the orientation of the crystals in the spherulite. By comparison with Figure 9 and the result
obtained by Samuels (27), it is concluded that the $b$ axis or $y$ direction in the PET spherulites cannot lie along the radius like polyethylene. If it did, the spherulites would be positive. Considering this fact, one may calculate the anisotropy. However, this method is quite arbitrary, so that it is best for the anisotropy to be obtained by the light scattering experiment itself.

The implicit assumption in Equation (17) has been that $f_{as}$ is zero, that is, there is no preferential orientation within the amorphous phase and this is so for undeformed spherulites; $(\alpha_t - \alpha_s) F_s$ is also negligible because of the small contribution. Thus the anisotropy of the spherulite is:

$$(\alpha_t - \alpha_r) = (\alpha_t - \alpha_r)^0 \phi_{cs} f_{cs}$$  

(19)

$\phi_{cs}$ differs from the overall volume fraction crystallinity, except when $\phi_s = 1$, and may vary with time. These quantities are interrelated by:

$$\phi_c = \phi_s \phi_{cs} + (1 - \phi_s) \phi_{cm}$$  

(20)
where $\phi_{cm}$ is the volume fraction crystallinity in the medium outside of the spherulite.

Since the spherulite structure is not perfect, that is, the orientation of the crystallite within the spherulite is not constant but fluctuates with respect to the radius, $f_{cs}$ is usually less than unity, leading to excess $H_V$ scattering intensity at large and small angles. This may be used to evaluate disorder parameters which are related to $f_{cs}$ (Figure 7). This will be discussed later.

Thus one may find three unknown variables which are $\phi_s$, $\phi_{cs}$ and $\phi_{cm}$ and there are three equations which are Equations (12), (14) and (20). As a result, we can solve them in principle. Consequently, combining three independent experimental results that are $I_{H_V}$, $I_{V_V}$ and $\phi_c$, one can obtain information about the number of spherulites, their size, the volume fraction of spherulites, crystallinity inside and outside of the spherulites and the degree of perfectness of the spherulites.

However, the reconciliation of experimental observations with scattering theory necessitates that the intensity of the scattering should be expressed in "absolute units" which is termed Rayleigh ratio. In the general sense, Rayleigh ratio could be defined:

$$R(\theta, \mu) = \frac{I(\theta, \mu)}{I_0} \times \frac{F_c}{V} \times k \quad (21)$$
where the terms are:

\[ I(\theta, \mu) = \text{experimentally-measured intensities} \]
\[ I_o = \text{intensity of incident beam} \]
\[ V = \text{volume irradiated by incident beam} \]
\[ F_c = \text{product of all necessary correction factors} \]
\[ k = \text{instrument calibration constant} \]

\( k \) is estimated using a system whose scattering power is known theoretically, such as benzene, and which can be measured experimentally (51).

Although the theory mentioned above has good qualitative agreement with experiments, the quantitative agreement is hardly obtained. For example, the excess \( I \) intensities at small and large angles on either side of the intensity maximum could not be accounted for theoretically. The discrepancy between theory and experiment was thought to be due to the relatively idealistic nature of the model. As mentioned before, the model assumes scattering from isolated perfect and homogeneous anisotropic spheres.

In real crystalline polymer films, spherulites are quite densely packed and they are no longer spheres but irregular polygons. This would take place even before the system is volume filled by spherulites. Since the location of nuclei could not be controlled, two or more spherulites may impinge upon each other as they increase their radii. This effect shifts \( \theta_{max} \) where the \( I \) intensity has maximum to small angle and reduces the maximum intensity. This is called the external disorder or truncation
effect. The theories for truncated spherulites have been developed by Stein and coworkers (52-57) and Kawai (58,59) but most of them were not applicable to experiments. Misra (57) proposed the computer simulation of the random generation of nuclei and subsequent truncated system. Prud'homme (56) calculated the $H_v$ intensity from this system and compared it with the original model theory. Although the system is two dimensional, it is simple to use and physically meaningful. However, it is applicable to only the volume-filling system. Therefore, the truncation effect in the non-volume filling system has developed in the present investigation (Appendix I).

Another kind of disorder is called internal disorder which comes from the fluctuation of the optic axis orientation with respect to the radii of spherulites. This effect could define the perfectness of the spherulites which has been already mentioned. Attempts to predict the excess scattering at small and large angles have been made by Stein and coworkers (60-65). Yoon and Stein (64) proposed a lattice model theory where a two-dimensional spherulite is divided into several shells and the shells into cells. Each cell has a constant surface area. It contains an optic axis which is allowed to deviate from the ideal value $\beta_0$ by an amount of $n\delta$, $n$ being positive or negative integers. A complex system of correlation makes the choice of $n$ at a given position dependent on the $n$ values of the surrounding cells. It is also assumed that the larger the deviation of the optic axis $\beta$ from $\beta_0$, the greater the tendency to return to $\beta_0$. Since
\[ \beta = \beta_0 + n\delta \] (22)

the higher the value of \( \delta \), the larger the deviation and the more disordered are the spherulites. This has been extended to three-dimensional systems (66).

In addition to the above factors, the deviation from the model theory is caused by multiple scattering. When the product of turbidity and the thickness of the sample become significant, the scattering ray plays a role as the incident beam to the next layer within the sample. This effect produces the excess \( H_\nu \) intensity at low and high angles as well as those of the other types of disorder. This theory has also been developed in this laboratory (67,68,69). In the theory (68), the sample is divided into a few layers and the amount of scattered energy and its distribution function, depending on the scattering and azimuthal angle on each layer, are calculated. The total scattering intensity is then expressed as the total sum of the product of the scattered energy and the distribution function. The depolarization and the internal disorder effect was also taken into consideration (69).

Stein and Keane (67) have shown how to obtain the absolute intensity of the light scattering from the experimental data taking into account the reflection and the refraction correction.
Thus the experimental data necessitate a series of corrections such as the reflection and the refraction correction, the truncation correction, the multiple scattering correction and the internal disorder correction in order to apply it to theoretical Equations (12) and (14). The internal disorder correction has the greatest effect of these.

A standard way of corrections has not been established yet. Each of the above corrections refers to the idealistic model theory individually and there is no theory interconnecting them. However, the real polymer system should have the above disorders and some deviations from the theory simultaneously. Then it is assumed here that each correction can be additive and independent of the others. Considering this assumption, the procedure of the corrections is summarized. The entire procedure is explained in detail elsewhere (70,71).

The experimental data $I_{\text{EXP}}$ is given by

$$I_{\text{EXP}} = I_{\text{OBS}} - I_{B}$$

where $I_{\text{OBS}}$ is the intensity measured experimentally and $I_{B}$ is the background intensity which is measured using the exact same procedure except without the sample present.
This data is corrected and expressed as Rayleigh ratios using the computer program (Appendix II). The program is based on the reflection and the refraction correction established by Stein and Keane (67) which requires other data such as sample thickness, refractive index, intensity of the incident beam and radius of the spherulite of the sample.

The radius of the spherulite could be obtained by Equation (5); however, when the system is truncated, \( \theta_{\text{max}} \) must be corrected. Since each spherulite is too small to measure the truncation parameter of the sample for polyethylene terephthalate, it is assumed that the system is randomly nucleated so that the truncation parameter is 0.132 (57) for the volume-filling system. The correction factor for \( \theta_{\text{max}} \) is 1.37 and 1.39 for the intensity (56) (Figures 1 and 2).

The other constant factors or some variables used in this program are valid only for the dynamic light scattering apparatus (72) whose apparatus constant has been measured (70). However, the secondary scattering (67) was ignored since the multiple scattering correction is applied in the next step.

The correction factor \( K(\theta, \mu) \) is given as a function of \( \tau d \) (68,69, 73) (Figures 3 and 4) where \( \tau \) is termed turbidity which can be expressed by:

\[
\tau = \frac{1}{d} \ln\left(\frac{100}{l}\right)
\]  

(23)
where \( d \) is the thickness of the sample and \( T \) is the transmittance which is:

\[
T = \left[ \frac{I_{\text{OBS}}(\theta = 0)}{I_{B}(\theta = 0)} \right] \times 100
\]

(24)

For example, the system is volume filling, so the maximum intensity in the \( H_V \) mode is given by

\[
(1.39) K (1.37 \theta_{\text{max}}, 45) R_{\text{EXP}} (1.37 \theta_{\text{max}}, 45)
\]

(25)

where 1.39 is the truncation correction factor, \( K \) is the multiple scattering correction factor with corresponding \( \tau d \) and \( R_{\text{EXP}} \) is the Rayleigh ratio obtained by computer.

After the above corrections have been made, the internal disorder correction is applied. The correction factor, \( F \), is given as a function of the disorder parameter, \( \delta \) (64) (Figure 5). The way to get \( \delta \) is to find the ratio of \([I_{H_V} (\mu = 45)/I_{H_V} (\mu = 0)]_{\mu=45}\). This relation is also graphically given (Figure 6). One can obtain \( f_{\text{CS}} \), the orientation function of the crystal within the spherulite, from \( \delta \) (Figure 7). Here \( I_{H_V} (\mu = 45) \) and \( I_{H_V} (\mu = 0) \) should have been already corrected like Equation (25).
Thus, the intensity equivalent to the left-hand term in Equation (12) or (14), $R_{\text{THER}}$, is given by

$$R_{\text{THER}}(\theta, \varphi) = f \cdot K \cdot F \cdot R_{\text{EXP}}$$  \hspace{1cm} (26)

where $f$ is the truncation correction factor.

It should be mentioned that the correction procedures for $V_Y$ scattering are not simple and have not been established yet. Because of $\alpha_d$ terms in $I_{VV}$ Equation (14), the correction factors cannot be given generally as $H_Y$. In order to solve this problem, one has to know the anisotropy of the spherulite and the average polarizability. However, this is not always possible. In the present investigation, therefore, the $V_Y$ intensity was sometimes not corrected or corrected assuming $\alpha_d$ or some other factors.
CHAPTER III
EXPERIMENTAL

A. Sample Preparation.

The samples used here are the same as those used by Misra (43). They were prepared from 13 mil thick amorphous film of polyethylene terephthalate obtained through the courtesy of the Film Division of E. I. duPont deNemours and Company. The film was characterized as:

$$M_w = 41,000, \quad M_n = 27,800$$

Pieces of the film were pressed between microscope cover glasses of thickness 1.5 - 2 mil and heated to $290^\circ C$ for 15 minutes in a silicone oil bath. They were then rapidly transferred to a crystallizing bath at $110^\circ C$ for a predetermined period of time such as from 5 minutes to 120 minutes. After that they were quenched into another silicone oil bath cooled to $0^\circ C$ by an ice-water mixture.

B. Measurement of Light Scattering.

The photographic light scattering experiment was done by Misra (43). The apparatus consists of a He-Ne laser light source, a polarizer, an analyzer and a camera (74). A schematic diagram of the apparatus is shown in Figure 8. Patterns were recorded on Polaroid Type 57 film.
The photometric experiment was carried out using the dynamic light scattering apparatus (72). The intensity of the incident beam was measured at θ = 0 in the $V_Y$ mode. The background intensity was measured using just the two cover glasses with the silicone oil in between whose refractive index was 1.567 which is equal to that of the amorphous sample.

The intensities of samples were measured by scanning θ manually at $\mu = 45^0$ for the $H_Y$ mode, and $\mu = 0$ and $\mu = 90^0$ for the $V_Y$ mode.

C. Density Measurement.

After finishing the light scattering measurements, samples were cut into small pieces and the density was measured at room temperature using a density gradient column made by mixing two solutions with different concentrations of potassium iodide. The column was calibrated by standard density floats (glass beads) in the range of 1.33 to 1.41 g/ml in steps of 0.01. The volume fraction crystallinity, $\phi_c$, from density measurements is calculated as:

$$\phi_c = \frac{\frac{1}{\rho_a} - \frac{1}{\rho}}{\frac{1}{\rho_a} - \frac{1}{\rho_c}} \times 100$$

(27)

where $\rho_a =$ density of complete amorphous polymer = 1.335  
$\rho_c =$ density of complete crystalline polymer = 1.455 (47)  
$\rho =$ density of sample
D. Refractive Index Measurement.

The average refractive index of the sample was measured by the Becke line method using a Zeiss standard GFL polarizing light microscope (75). Instead of obtaining the accurate value for each sample, first the refractive index of the amorphous sample was measured with silicone oil as an immersed liquid and Abbe refractometer, and the crystalline value was calculated in the previous chapter. Then, using the Lorenz-Lorentz equation:

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi \alpha_M \frac{\rho}{M} N_A
\]

where \( n \) = average refractive index

\( \alpha_M \) = average polarizability per mole

\( \rho \) = density

\( M \) = molecular weights

\( N_A \) = Avogadro number

The refractive index was obtained as a function of density for each sample. These values were confirmed by the experimental observation using the standard solvents whose refractive indices were known such as o-toluidine (1.57), silicone oil (1.58), aniline (1.586) and bromoform (1.59).
CHAPTER IV
RESULTS AND DISCUSSION

A. General Observations of $H_V$ Scattering.

The qualitative observations of $H_V$ scattering patterns were carried out by Misra (43) using the photographic technique. Since the complementary photometric observations have been made here, the general trends of changes in $H_V$ scattering with crystallization time are mentioned with some photographs duplicating his results.

A series of $H_V$ patterns is shown in Figure 10. It can be seen that the size of the patterns decreases with increasing crystallization time up to 60 minutes after which it stays constant. In view of the well-known inverse relationship between the size of the pattern and that of the scattering entity, this indicates that the spherulite size increases with crystallization time. This can be easily understood referring to Equation (3) where $\lambda$ and $\theta$ are values in the sample which cannot be directly observed.

However, using the relationship:

$$\lambda = \lambda_0 / n$$

$$\theta_{max} = \sin^{-1} \left( \sin \frac{\theta_{max}}{n} \right)$$
where \( \lambda_0 \) = wavelength of the incident light in air
\( n = \) refractive index of the sample
\( \theta_{\text{max}} = \) observed scattering angle

One can calculate the spherulite size from observation of \( \theta_{\text{max}} \). It should be mentioned here that small values of \( \sin (\theta_{\text{max}}/2) \) can be approximated by \( \theta_{\text{max}}/2n \) (in radians) so that Equation (5) turns out to be:

\[
R = \frac{4.1}{2} \frac{\lambda_0}{\pi \theta_{\text{max}}} \tag{29}
\]

This is a good approximation for \( \theta \) smaller than 20°.

Spherulite sizes obtained from the photographs are plotted as a function of crystallization time in Figure 11. There are three regions in such a plot: (1) an induction region, up to 5 minutes, in which the patterns are not spherulitic in nature (43); (2) a linear growth region from 5 - 50 minutes where the spherulite radius is proportional to time; and (3) an impingement region, beyond 50 minutes, where the spherulites impinge upon each other so that the radial growth rate tapers off and the limiting radius is about 6.75μ.

These photographs were taken with a constant sample-to-film distance but non-constant exposure time. Therefore, the sizes can be compared with each other but not the intensity. In order to complement this result, the photometric observations were carried out.
The $H_v$ scattering intensity along the 45° azimuthal direction is shown in Figure 14. It indicates that the intensity increases, the curve becomes sharper and the maximum scattering point ($\theta_{\text{max}}$) shifts to smaller angle with increasing crystallization time.

There is good agreement between the photometric and the photographic observations. The larger $\theta_{\text{max}}$, the bigger the pattern; and the sharper the peak, the more intense and the clearer the pattern. At times of 5 and 10 minutes, the photographs show diffused patterns and it is hard to indicate the point of the maximum intensity. This is reflected well in Figure 14 where, however, the $\theta_{\text{max}}$ is relatively clearly shown. Moreover, the spherulite size with crystallization time calculated from the photometric data is in quite good agreement with that from the photographic data.

As has been already mentioned in Chapter II, $H_v$ scattering intensity would increase monotonically as crystallization proceeds. This is due to the combined contribution from $\phi_s$, $(\alpha_t - \alpha_r)$ and $R(V)$ in Equation (12). This is shown experimentally in Figure 15 where the maximum $H_v$ intensities in Figure 14 are replotted as a function of crystallization time. Any increase after $\phi_s$ has attained a value of unity (beyond 60 minutes) would be further indicative of an increase in $(\alpha_t - \alpha_r)$ during the secondary crystallization.

At this moment the crystallinity would increase within the spherulite and may increase the degree of perfection. However, the increase of crystallinity would be small at this stage so that the increase of intensity would be small.
B. General Observation of $V_V$ Scattering.

A series of $V_V$ scattering patterns as a function of crystallization time is presented in Figure 12. The sample-to-film distance and the exposure times were the same for all pictures. It can be seen that the intensity increases up to 10 minutes of crystallization, decreases between 10 and 30 minutes and then begins to increase again. Those patterns are circularly symmetrical up to 20 minutes and then develop two-fold symmetry at 45 minutes. The circular patterns increase their size up to 10 minutes and then decrease.

It has been mentioned in Chapter II that $V_V$ intensity during crystallization passes through a maximum where the volume fraction of spherulite $\psi_s$ is nearly 50% and this is due to the contribution of terms involving the polarizability of the surroundings. The $V_V$ scattering patterns also change from circular symmetry to two-fold symmetry due to the same contribution.

The photographs indicate these phenomena which were more defined by the photometric measurement. The $V_V$ scattering intensities measured along $\mu = 0^0$ and $90^0$ are shown in Figures 17 and 18, respectively. The intensity decreases monotonically up to larger angles up to 45 minutes and they are almost equal in both $\mu = 0^0$ and $\mu = 90^0$. This indicates that the $V_V$ scattering patterns up to 45 minutes have circular symmetry. On the other hand, curves of 60 - 120 minutes show possible maxima in the small angle region in Figure 17 and the intensities at $\mu = 0^0$
are greater than those at $\mu = 90^\circ$. This is attributed to two-fold symmetrical patterns.

Changes in the $V_V$ intensity during the crystallization can be more easily seen in Figures 19 and 20. These clearly show that the intensities pass through maxima regardless of scattering and azimuthal angles. The maxima shift from 30 minutes to 10 minutes with increasing scattering angle $\theta$ and furthermore the relative intensity becomes higher in the early stage than beyond 30 minutes. This is due to the largest circular pattern at 10 minutes and the subsequent decrease of the size shown in Figure 12. On the other hand, the minima are constant and in 60 minutes of crystallization time.

In spite of the complicated equation of $V_V$ intensity [Equation (14)], the prediction is quite simple and clear. It is, therefore, worthwhile to interpret the results here in the same way as Stein and Rhodes did (37). They explained that the maximum $V_V$ intensity occurs at about $\phi_s = 0.5$ and the minimum at $\phi_s = 1$. If so, $\phi_s = 0.5$ happens at 10 - 30 minutes of crystallization time and $\phi_s = 1$ is accomplished at 60 minutes. The half crystallization time in $100^\circ$C from the melt is about 15 minutes. This will be shown later in the present investigation and also was shown by other investigators (76). If $\phi_{cm}$ is zero and $\phi_{cs}$ is constant in Equation (20), $\phi_s = 0.5$ occurs at half crystallization time. Consequently, one might believe that $\phi_s$ is 0.50 at about 15 minutes. This should be investigated in more detail later in the quantitative analysis section. $\phi_s$ would be unity at 60 minutes because the increase
in spherulitic radius is small after 60 minutes in Figure 16. After $\phi_s$ reaches unity, any increase of the $V_V$ scattering intensity could be due to the change in anisotropy within spherulites, which increases with secondary crystallization as mentioned in $H_V$ scattering. This phenomenon, that is, passing through the maximum and the minimum during crystallization, was also observed by using the light transmission technique (76-78). The random growth of crystallites which were formed prior to spherulitic growth was believed to be followed by the partial orientation of the crystallites into spherulites. Alternatively, the scattering maximum corresponded to the state where the aggregates had grown to a size comparable with the wavelength of the light and were suspended in about an equal volume of amorphous matrix. The scattering occurred because of the refractive index difference between crystalline and amorphous polymer (79). Indeed the refractive indices of the amorphous and crystalline phases are 1.57 and 1.64, respectively. The scattering ability was expected to be greater at the amorphous-crystalline boundary than at the area where spherulites were impinged. The latter explanation appears to be consistent with the observation of this investigation and also with the prediction from the light scattering theory.

C. Kinetics of Crystallization and Spherulitization.

A plot of crystallinity as a function of time is shown in Figure 21. The typical sigmoidal curve shows an induction period up to 5 minutes, a rapid growth region up to 45 minutes, and a slow increase
or level-off region, that is, the secondary crystallization region. While these data can be useful for Equation (20) in order to complement the light scattering analysis, the discussions in detail have already been carried out extensively (14, 76, 80-85) so that is would be enough to make a brief comment on it.

The Avrami equation (86) is a well-known means to describe the crystallization kinetics. The modified Avrami equation (14) which is necessary for polymer crystallization is:

\[ \phi_C = \phi_\infty [1 - \exp (-kt^n)] \]  

where \( \phi_C \) is the volume fraction of crystallinity at time \( t \), \( \phi_\infty \) is the attainable crystallinity at the end stage of the crystallization process, and \( k \) and \( n \) are Avrami constants. Especially \( n \) represents the dimensionality of the growth process. Equation (30) can be written in the form:

\[ \ln \left[ - \ln \left( \frac{V - V_\infty}{V_0 - V_\infty} \right) \right] = \ln k + n \ln t \]  

(31)
where \( V_0, V_t \) and \( V_\infty \) are the specific volume at the beginning, time \( t \) and the end, respectively. Since

\[
V_t = \frac{1}{\rho}
\]

the density measurement for the crystallization process can give the linear relationship between \( \ln [\ln \left( \frac{(V_t - V_\infty)/(V_0 - V_\infty)}{-1} \right)] \) and \( \ln t \) and the slope is \( n \).

Figure 22 shows the Avrami plot and the slope is 1.3. This result indicates that the crystallites grow linearly if the nucleation process is predetermined. Since the synthetic process of polyethylene terephthalate requires a catalyst such as \( \text{Sb}_2\text{O}_3, \text{GeO}_2, \text{Zn(AcO)}_2 \), etc., the polymer should contain foreign particles which could act as nucleating agents. Thus it is reasonable that the nucleation takes place heterogeneously; in other words, it is predetermined nucleation. In fact, Mayhan (76) showed \( n = 1.14 \) and also Ikeda's (85) result was 0.95. However, this value is not a material constant and it would depend upon the synthetic process, the sample preparation and the method of obtaining data.

The value of \( n \) depends upon the shape of crystallites in growth. If the heterogeneous nucleation process is assumed, \( n = 1 \) shows lineal
growth, n = 2 is for plate-like and n = 3 is for polyhedral growth. Apparently spherulites have a three-dimensional shape so that n should be 3. Is it necessary and the result obtained here is incorrect?

The spherulite is an aggregate of crystallites and it is not necessarily a similar structure to crystallites. Keller (13) proposed the regular periodic branching mechanism of the fibrillar units during spherulite formation. Their, first of all, nucleus is more-or-less rod-like structure and then the fibrillar unit grows with a constant finite period and a constant acute angle with respect to the former fibril. Successive branchings finally fill the space and form the spherulite. If it is true and one can assume that the fibrillar unit is equivalent to the crystallite, it could be possible that linearly-growing species can form a three-dimensional sphere. Thus the value obtained here has no discrepancy with the concept of the Avrami exponent.

The kinetics of spherulitization have already been shown in Figure 16. The linear growth rate proves the validity of the assumption for the derivation of the Avrami equation. This was supported by several investigators (22,24,25,87-89). It can be seen in Figure 16 that the growth rate is 0.105 μ/min and the limiting radius, R∞, is 6.98μ. These values also depend upon the nucleation process, the sample preparation and the experimental method. Therefore, the numerical results cannot be compared directly.

R∞ can be predicted, if the nucleation occurs heterogeneously and not sporadically, from the initial nuclei density. Similarly, from
the \( R_{\infty} \), one can obtain the number of nuclei at the initial stage using Equation (13). This will be done in the next section.

The application of the Avrami equation to spherulitization has been accomplished by Misra and Stein (44). They assume the three-dimensional growth process with heterogeneous nucleation, and then obtain the equation:

\[
\phi_{c} = \phi_{cs} \left[ 1 - \exp\left( -kt^{3}/3 \right) \right]
\]  

(31)

where \( \phi_{cs} \) is the volume fraction of crystals within the spherulite. As it has been seen, \( n \) is not 3 in this case. They also assume that \( \phi_{cs} \) is constant. However, this might not be true in polymer systems (90-92) and it will be discussed later.

The crystallization condition should also be mentioned. Overall kinetics of the polymer crystallization can be described by the nucleation process and succeeding growth process (104). Both were well studied and several theories were presented (94-103). Nevertheless many expressions started from the Turnbull-Fisher equation (96):
where \( G = \) spherulite growth rate (or the rate of nucleation)

\[
G_0 = \text{pre-exponential factor (It is considered to be constant.)}
\]

\[
\Delta f^* = \text{free energy of activation for transporting a chain segment from the supercooled liquid phase to the crystalline phase}
\]

\[
\Delta F^* = \text{free energy of formation of a nuclei of critical size}
\]

\[
k = \text{Boltzmann constant}
\]

\[
T = \text{crystallization temperature}
\]

This equation tells us the strong dependence of the rate on the crystallization temperature. When the change in the rate is plotted as a function of the crystallization temperature over the complete range, i.e., between the melting temperature, \( T_m \), and the glass transition temperature, \( T_g \), Equation (32) can predict that the curve has a value of zero at \( T_m \) and \( T_g \) and a maximum between them. In fact, when the time taken for half the crystallization to develop \((76,81)\) or the spherulite growth rate \((22,24)\) was plotted against the crystallization temperature, such a curve was obtained (Figure 23) \((24)\). Although, again, different experiments presented different temperatures in which the rate was maximum, they were around 180\(^0\)C. Let us call this temperature \( T_c \). It is well known that the \( \Delta f^* \) term dominates Equation (32) below \( T_c \) and the \( \Delta F^* \) term has greater influence above \( T_c \). The term containing \( \Delta f^* \) is usually called the diffusion term and is replaced by the empirical viscosity relation, that is, the WLF equation \((105)\) which was proposed
by Hoffman (106). On the other hand, the $\Delta F^*$ term is called the supercooling term and can be calculated by taking into account the geometrical factors of nucleation and growth (101,102). Assuming the two-dimensional growth (somehow related to the predetermined nucleation), Equation (32) is rewritten as:

$$\ln G = \ln G_0 - \frac{C_1}{R (C_2 + T - T_g)} - \frac{K T_m}{T \Delta T} \quad (33)$$

where $C_1, C_2 = \text{constant (6464 J/mole, 24°C)}$

$$R = \text{gas constant (8.31 J/mole - °K)}$$

$$\Delta T = T_m - T \quad \text{supercooling}$$

and

$$K = \frac{4 b_o \sigma \sigma_e}{k \Delta H_f} \quad ( = 942^\circ\text{K})$$

where $b_o = \text{thickness of polymer chain (length of C axis 10.75\AA)}$

$\sigma = \text{interfacial free energy between the crystalline and the amorphous state for the faces parallel to the chain direction}$

$\sigma_e = \text{interfacial free energy for the face perpendicular to the chain direction}$

$\Delta H_f = \text{heat of fusion per mole of monomer units}$
The crystallization condition in the present investigation is below $T_c$ so that it is in the range where the $\Delta f^*$ term may dominate. In fact, the calculation of Equation (33), using $T_g = 340^0K$ and $T_m = 573^0K$, indicates that the second term is $11.6$ and the third term becomes $7.4$. Consequently, when each sample is carried from the melting bath to the crystallizing bath, it must pass through $T_c$ no matter how short the time is. If the time when the sample stays at $T = T_C$ is comparable to the half-time for the crystallization, such an experiment can no longer represent the crystallization at $T = 110^0C$. However, the quenched sample in the $0^0C$ bath using the same procedure as crystallizing the sample shows no significant crystallinity. This indicates that we might not have to worry about the influence passing through $T_c$. Nevertheless, there is still the possibility that it might produce undetectable tiny crystallites in the sample. If so, those crystallites may play a role as nuclei. Thus, in this experimental condition, the heterogeneous nucleation would be more probable than the homogeneous one.

D. Quantitative Analysis of $H_V$ Scattering.

The Rayleigh ratio for three-dimensional perfect spherulites in the $H_V$ mode is expressed as:

$$
R_{H_V}(\theta, \mu) = \frac{144 \pi^4}{\lambda^4_0} \frac{V}{\phi_s} \cos^2 \rho_2 \left( \alpha_t - \alpha_r \right)^2 \phi_{H_V}(U) 
\times \cos^4 (\theta/2) \cos^2 \mu \sin^2 \mu
$$

(34)
where \( \lambda_0 \) is the wavelength of the incident beam in vacuum. The other terms have been previously defined.

Assuming that \( \phi_{cm} \) in Equation (20) is zero, Equation (19) leads to

\[
(a_t - a_r) = (a_t - a_r)c f_{cs} (\phi_c/\phi_s)
\]  

(35)

Taking the intensity observed at \( \theta = \theta_{\text{max}} \) and \( \mu = 45 \) (the maximum intensity for each sample in Figure 14), each term in Equation (12) can be estimated below.

\[
\cos^2 \phi_2 = 1 \text{ for small } \theta_{\text{max}}
\]

\[
\cos^4(\theta_{\text{max}}/2) = 1 \text{ for small } \theta_{\text{max}}
\]

\[
\cos^2 \mu = \sin^2 \mu = 0.5 \text{ for } \mu = 45^\circ
\]

\[
U = 4.1 \text{ for } \theta = \theta_{\text{max}}
\]

\[
\phi_{H_V}(U) = -0.0889 \text{ for } U = 4.1
\]

\[
\lambda_0 = 5461\text{A} \text{ for the green-filtered radiation of mercury lamp}
\]
\[ V = \frac{4}{3} \pi R^3 \]

Substituting all values and Equation (35) into Equation (34), it reduces to

\[ R_{HV} (\theta_{max}, 45^0) = 13.08 \times 10^{18} R^3 \left[ (\alpha_t - \alpha_r)^0 f_{cs} \right]^2 \]

\[ (\phi_c^2 / \phi_s) \]

(36)

where \( R \) is expressed in cm units. The left-hand side is a theoretical Rayleigh ratio so that it should be replaced by the experimental value corrected by Equation (26). \( R \) can be calculated by Equation (29) and \( \phi_c \) is illustrated in Figure 21.

As a result, \( \phi_s \) can be calculated as:

\[ \phi_s = \frac{13.08 \times 10^{18} R^3 \left[ (\alpha_t - \alpha_r)^0 f_{cs} \right]^2 \phi_c^2}{R_{HV} (\theta_{max}, 45^0)_{EXP} \cdot f \cdot K \cdot F} \]  

(37)
As has already been mentioned in Chapter II, \((\alpha_t - \alpha_r)^0_c\) has not been defined so far. However, \(\phi_s\) is unity after spherulites impinge each other and this has happened beyond 60 minutes of crystallization time. Therefore, using the experimental data, the intrinsic anisotropy of the crystal within the spherulite could be determined.

All experimental data are listed in Table I. Corrections were made in such a way as described in Chapter II and the results are listed in Table II. \(\phi_s\) was calculated by assuming that anisotropy

\[
(\alpha_t - \alpha_r)_c = (\alpha_t - \alpha_r)^0_c f_{cs}
\]  

is constant during the growth of spherulites. The anisotropy which was obtained at 60 minutes crystallization time was used. It is shown in Figure 24. The shape of the curve is similar to that for the degree of crystallinity changes with time (Figure 21). It can be seen that at 20 minutes crystallization time the system becomes half volume filling. Transmittance at this time is also low, as seen in Table II. This agrees with the general observation of \(V_y\) scattering as mentioned previously.

The value of the anisotropy used here is 0.00414. Using \(f_{cs}\) acquired from Figure 7, \((\alpha_t - \alpha_r)^0_c\) can be obtained and it is 0.01254. If we suppose that the \(c\) axis of the crystal of polyethylene terephthalate
within the spherulite is perpendicular to the radius (10), this value corresponds to the orientation of the benzene ring in such a way that the angle which the benzene ring makes with the plane composed of the radius of the spherulite and the c axis is about 86 degrees. When this angle becomes less than 20 degrees, spherulite turns to be positive (10).

\( \phi_{cs} \) was calculated using Equation (20) with an assumption of \( \phi_{cm} = 0 \). The data indicates that the degree of crystallinity within the spherulites decreases with increasing volume fraction of spherulite. In other words, the smaller the spherulites, the higher their crystallinities. As Keller proposed (13), if the spherulites grow with branching fibrils having constant length and angles, they should have the same density regardless of their size. Moreover, if they form "zwei blatt" at the early stage, they must have low density when they are small. However, Keith and Padden (43) mentioned that many of the primary nuclei were heterogeneous in nature and consisted presumably of disordered crystal layers absorbed on the surfaces of impurity specks, and spherulites might then grow from these nuclei without "zwei blatt" or sheaf-like precursors being formed. Furthermore, their theory indicates that spherulite growth consists of radiating fibrils and impurities may play a vital role in promoting a fibrous habit in spherulitic crystallization. Those impurities can influence the rate of crystallization with an interplay of the transport of heat and their diffusion. The growing crystal rejects impurity preferentially, and the concentration of impurity on the liquid side of the interface builds up to higher than its average value for the melt as a whole. The thickness of the impurity-rich layer depends upon the diffusion
coefficient for impurity in the melt and the growth rate of the spherulite. This impurity-rich layer may cause non-crystallographic branching and the thicker the layer, the coarser is the structure of the spherulite. These impurities may eventually be trapped between the fibrils and more likely between the spherulites when they impinge each other. They would be low molecular weight or stereo-irregular polymers. This was verified experimentally by the same authors (88).

As has been mentioned in the previous section, the system presented here might have heterogeneous nucleation and be considered to contain impurities such as condensation catalyst, low molecular weight material, small amount of diethylene glycol compounds, etc. If these impurities are segregated from the crystallite fibrils during crystallization and trapped between the fibrils or accumulated at the growing front of the spherulite, it could become reasonable that the early-stage spherulites have higher crystallinity than well-grown spherulites. It can also be easily imagined that the richest-impurity layer would be the impinging boundary of spherulites. Impingement obviously occurs more often as spherulites grow, that is, the volume fraction of spherulites increases. Thus the crystallinity within the spherulites would decrease with increasing $\phi_s$. After $\phi_s$ gets to unity, $\phi_{cs}$ would also increase due to secondary crystallization.

Alternatively, if $\phi_{cs}$ is constant during the growth of spherulites, any increase in the degree of crystallinity is due to the crystallization outside of the spherulites. This has been observed for polyamides (90) and polychlorotrifluoroethylene (91) using the microbeam technique of x-ray.
If it would happen, $\phi_{cm}$ can be calculated using Equation (20) letting $\phi_{cs} = 0.395$. Although all data in $\phi_s$ and $\phi_{cs}$ are calculated assuming $\phi_{cm} = 0$, one might estimate $\phi_{cm}$ using their values. Since $\phi_{cm} = 0$ is a first approximation, this appears to be a circuitous method. However, it would be very difficult to calculate all these three variables independently. The results are listed in the third column of Table III. Since the region outside of the spherulites cannot be defined after complete impingement, $\phi_{cm}$ cannot be estimated beyond 60 minutes and may also be in a big error when $\phi_s$ becomes close to unity. Thus, up to 30 minutes in crystallization time, $\phi_{cm}$ increases with time which is understandable. What is the physical meaning of $\phi_{cm}$? It could be due to the very tiny crystallites or just nuclei which are produced during the spherulitic growth process. They would be so tiny that they could not provide any scattering intensity or their intensity would be masked by the excess scattering intensity at smaller and larger angle regions due to the disordered structure. Because such tiny crystallites could give the rod-like or the sheaf-like pattern at the same regions.

An alternative method to get $\phi_{cm}$ has been adopted using Equation (15). $\alpha_m$ can be calculated knowing $\phi_s$ and the average polarizability of the whole system, $\alpha_d$, and the average polarizability within the spherulites, $(2\alpha_t + \alpha_r)/3$. $\alpha_d$ can be obtained using the Lorenz-Lorentz equation:
\[ \frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi \alpha_d \]  

(39)

where \( \alpha_d \) is the polarizability per unit volume. The results are listed in Table III. The procedure to obtain the average polarizability of the spherulites is as follows: Since the polarizability of the spherulites or the anisotropy was assumed to be constant up to 60 minutes and \( \phi_s \) is unity at 60 minutes of crystallization time \((2\alpha_t + \alpha_r)/3\) must be equal to \( \alpha_d \) at this stage. [See Equation (15) and let \( \phi_s = 1 \).] Then \( \phi_{cm} \) can be calculated by equation

\[ \alpha_m = \phi_{cm} \alpha_c + (1 - \phi_{cm}) \alpha_a \]  

(40)

where \( \alpha_c \) and \( \alpha_a \) are the average polarizability of perfect crystal and complete amorphous, respectively.

Another \( \phi_{cm} \) is listed as \( \phi_{cm} \) in Table III. Again the same trend can be seen as \( \phi_{cm} \). This method is also inevitable to be circuitous anyway.

Thus the increased crystallinity in the non-spherulitic region seems to be probable and if it would occur, the system could have two mixed nucleation processes that are predetermined and sporadic. However,
Keller reported (10) that x-ray diffraction of the interspherulitic regions gave a broad amorphous ring. Therefore it is not certain whether $\phi_{CM}$ obtained here is correct or a mere artifact at the present stage.

In addition, there is no reason why the secondary crystallization starts after complete impingement. If the rate of the secondary crystallization would be comparable to that of the spherulitic growth rate, the crystallization could take place in the intra- and interspherulitic regions. The former may increase $\phi_{CS}$ with time which differs from the present results and the latter may increase $\phi_{CM}$ with time. If the rate of secondary crystallization is defined as only that which occurred after $\phi_c$ reaches its asymptotic value (Figure 21), it would hardly occur. Even if it occurred, it is not known whether the rate of crystallization is higher in the intra- or the interspherulitic regions. The quantitative $V_V$ scattering analysis may give such information and it is discussed in the next section.

The number of spherulites was calculated using Equation (13) and listed in Table IV. It can be seen that the number of spherulites per unit volume decreases monotonically with crystallization time. This is not reasonable and is probably an artifact due to the limitations of the theory which we used. The volume of the spherulite is given as $V = (4/3) \pi R^3$, so that the system is assumed to be an assembly of isolated and equal size of complete spheres. This is not true for the present case. Especially after impingement, all spherulites turn to be irregular polygonal and their volume can no longer be defined as
(4/3) π R^3, but it should be multiplied by a certain shape factor, \( \xi \) (Appendix I). However, it is not easy to evaluate \( \xi \) because the average radius and the volume of the irregular polygons may depend upon the location of the primary nucleus.

If the nucleation is completely heterogeneous and predetermined, \( N \) should be constant with time. If it is so, \( \phi_s \) can be calculated as

\[
\phi_s = \frac{R^3}{R^3_{\infty}}
\]

where \( R_{\infty} \) is the maximum attainable radius of the spherulite in this system. This is shown in Table IV. It can be seen that there is quite a large discrepancy between this value and \( \phi_s \) in Table III. If sporadic nucleation takes place, \( N \) should increase with crystallization time. The data disagree with both cases. This could be explained only when it happens that the growing spherulites mask the other spherulites or nuclei subsequently. This has never been observed, yet it might happen in the light scattering investigation: Equation (1) tells us the intensity of \( H_V \) scattering is proportional to \( R^6 \). As impingement proceeds, some spherulites stop their growth with relatively small average radii. Then these small irregular polygons may give very small contributions to the total scattering intensity or sometimes they could be negligible. In other words, those small spherulites are seemingly absorbed by the neighboring big spherulites. Otherwise the \( H_V \) scattering intensity should have varied by
a factor of the order of $10^5$ under the present crystallization condition $[R^6_{(5 \text{ minutes})} \text{ to } R^6_\infty]$, but it changed only by a factor of the order of $10^2$ (Figure 15). Thus the data indicate that $(\alpha_t - \alpha_r)$ might vary during the crystallization. This corresponds to the change in $\phi_{CS}$. However, the maximum possibility of this change is still of the order of $10^2$, then $N$ might decrease seemingly during the process. In order to clarify this question, the following examination should be required. When the nucleation occurs randomly in space, the average radius and the truncation parameter for each irregular spherulite can be calculated. Since the total number of spherulites is fixed, the total average radius and the truncation parameter can also be obtained. Then the question is that the $H_V$ intensity calculated from such a truncated spherulitic system is equivalent to the $H_V$ intensity of the isolated perfect spherulites with the same total number in which (1) all spherulites have entirely the same radius as the total average radius or (2) each spherulite has equal radius to the average radius for each spherulite in the above truncated system. The present light scattering theory gives only case (1). If case (2) is correct and gives a different intensity from (1), the theory has to be modified to provide more proper radius of spherulite. In addition that, choosing one particular irregular polygon, it should be examined how the location of nucleus affects the average radius and the $H_V$ intensity. These will be studied in Appendix I.

The degree of perfectness of the spherulites should be mentioned here. The internal disorder parameter, $\delta$, reflects this quantity and is
listed in Table II. There seems to be no significant difference during the crystallization. The constant fluctuation of the orientation of the crystals within the spherulites indicates the fact that fibrillar branching is in the steady state during the growth of spherulites which was proposed by Keller (13). It also seems to support the assumption that \( \alpha_t - \alpha_r \) is constant during the growth of spherulites is valid and also the assumption that \( \phi_{CS} \) is constant is better than \( \phi_{CM} \) is zero.

So far the qualitative analysis for \( H_y \) scattering was done using a first approximation in which it was assumed that (1) all correction procedures are independent of each other and can be additive and (2) anisotropy of spherulites is constant during the growth of spherulites. Furthermore, quite a few assumptions were involved in the correction procedures. Those were applicability of two-dimensional theories for the truncation correction and the internal disorder correction, the random nucleation for the truncation correction, and the fixed surrounding polarizability, \( \alpha_d \), for the multiple scattering correction. It has not yet been proved that any of these assumptions are valid. Nevertheless, Prud'homme (70) and Khambatta (71) contend that "it is extremely encouraging to find a fair agreement between the experimental and theoretical \( H_y \) intensities" for polyethylene and polycaprolactone-polyvinylchloride blend system, respectively, using the same correction procedures. Besides, data presented here do not seem to be unreasonable so that such assumptions could be justified.
E. Quantitative Analysis of $V_Y$ Scattering.

Once it is assumed that the anisotropy within spherulites is constant during the growth of spherulites, all terms in Equation (14) can be calculated at $\mu = 45^0$ and $\theta = \theta_{\max}$. The results are listed in Table V.

It can be seen that there is a large discrepancy between the calculated and experimental intensities. While changes in the intensities in the former case are of the order of $10^6$, that in the latter is $10^2$. This is mainly due to $R^6$ term. Because the difference of the radius between 5 minutes and 60 minutes in crystallization time is a factor of 7. An alternative way to analyze the $V_Y$ scattering intensities is as follows. From Equation (14) one can derive the equation:

$$\sqrt{I_{V_Y}(\mu = 45^0)} - \sqrt{I_{V_Y}(\mu = 90^0)} = \sqrt{K_1} \sqrt{B(\phi_s)}$$

$$R^3 |(a_t - a_r) \phi_{H_Y}(U)|$$

(42)

Substituting each value obtained previously at 60 minutes, $\sqrt{K_1}$ can be estimated and it is $4.214 \times 10^{14}$. Using this value as a constant $\sqrt{B(\phi_s)}$ can be calculated. It is also listed in Table V. It shows again a large discrepancy with the former calculations.
The same analysis is carried out assuming that $\phi_{cm}$ is zero. Then $(\alpha_t - \alpha_r)$ cannot be constant any longer but varies as:

$$(\alpha_t - \alpha_r) = (\alpha_t - \alpha_r)_c \phi_{cs}$$

(43)

where $(\alpha_t - \alpha_r)_c = 0.00414$ as previously defined and $\phi_{cs}$ is in Table III.

Since the non-spherulitic region is amorphous ($\phi_{cm} = 0$), $\alpha_m$ is equal to $\alpha_a$ which is 0.07765. The average polarizability inside of spherulites, $\alpha_s$, is defined as:

$$\alpha_s = \frac{2 \alpha_t + \alpha_r}{3} = \phi_{cs} \alpha_c + (1 - \phi_{cs}) \alpha_a$$

(44)

Using Equations (43) and (44), $\alpha_t$ and $\alpha_r$ for each sample are obtained which are necessary to calculate $R_{VV}$ in Equation (14) and $B(\phi_s)$ in Equation (15).

There is again a large discrepancy between the calculated intensities ($R_{VV}/K_1$) and the experimental ones ($KR_{VV}$). Both, of course, cannot be compared directly because the units are not similar. However, a comparison is possible with normalized values.
There is also no significant difference between the two cases, so that it cannot be pointed out which assumption is more likely from the $V_V$ data.

Does this large discrepancy deny any validity of all assumptions which have been made so far? Before answering this question, it should be mentioned that the correction of the experimental $V_V$ intensity is necessary before applying the theory.

The correction factor for $H_V$ intensity was obtained from the ratio of the predicted intensity for the perfect spherulite case to that for the deviating case. Any $H_V$ intensity in the deviating case can be expressed as:

\[
I_{H_V} = A \cos^2 \rho_l \ \gamma^2 (\alpha_t - \alpha_r)^2 \left( \phi_{H_V}'(U) \cdot f(\theta, \mu) \right)^2
\]

(45)

where $f(\theta, \mu)$ is a function of only $\theta$ and $\mu$, and $\phi_{H_V}'$ is a proper expression for each case.

Therefore each correction factor for $H_V$ intensity is independent of the anisotropy. Consequently the master curve for each correction shown in Figures 1 to 6 which was obtained in the case of polyethylene is applicable to any other polymer or experimental condition. In contrast with $H_V$, $I_{V_V}$ contains three different polarizability terms. As can be easily seen, in obtaining the ratio between the perfect and the deviating case, the polarizability terms do not cancel. Therefore it is impossible to obtain a
master correction curve but the correction factor must be calculated for each individual case with a particular set of $\alpha_t$, $\alpha_r$ and $\alpha_d$. This is also true for the $H_V$ correction factor of the multiple scattering because the equation of the intensity contains $V_V$ components (68,73).

Thus, $\alpha_t$, $\alpha_r$ and $\alpha_d$, or $(\alpha_t - \alpha_r)$ and $\alpha_m$, should be predetermined before the $V_V$ intensity observation.

In other words, whereas the three unknowns, $\phi_s$, $\phi_{cs}$ and $\phi_{cm}$, are in three equations [(12), (14) and (20)] as mentioned in Chapter II, there are six unknowns, $\alpha_t$, $\alpha_r$, $\alpha_m$, $\phi_s$, $\phi_{cs}$ and $\phi_{cm}$, with five equations such as Equations (12), (14), (15), (20) and (40). [Strictly speaking, there are five unknowns with four equations because $\alpha_m$ depends upon $\phi_{cm}$ in Equation (40).] Therefore, one cannot solve the equation unless at least one unknown is predetermined by either assumption or observation. If the orientation of crystals within the spherulite has been determined, the anisotropy can be calculated. On the contrary, if it has not been defined yet, as is the case for polyethylene terephthalate, the anisotropy should be observed by an independent method. Although the interference microscope can provide such information, it is not always possible especially when the size of spherulites is too small and unfortunately this is the case for the present investigation.

As a consequence, it seems to be impossible to analyze the $V_V$ scattering intensity quantitatively at the present moment. However, Samuels tried to interpret the $V_V$ observation quantitatively. He made a polypropylene sample which contained spherulites which were big enough to measure
the birefringence and assumed that the samples under observation had the
same birefringence which represented anisotropy when the samples were
volume filling. Assuming the average refractive index of spherulites \( (a_d) \)
he got \( a_t \) and \( a_r \). He then calculated the theoretical \( V_V \) patterns using
Equation (2) and substituting these polarizabilities. When those theore-
tical patterns matched the experimental \( V_V \) patterns, the assigned \( a_d \) repre-
sented the true \( a_d \). Comparing this \( a_d \) to the experimental value which
was obtained by the Beche line method, he concluded that crystallization
occurred faster at the boundary of the spherulite than it did within the
spherulite. Although he misunderstood that the volume-filling system was
still \( \phi_S < 1 \) even though he took into account truncated spherulites, his
attempt encourages us to investigate the quantitative \( V_V \) scattering inten-
sity.

Consequently a plot of \( \sqrt{I_V(\mu = 0^\circ)} - \sqrt{I_V(\mu = 90^\circ)} \) against
\( \sqrt{I_{H_V}(\mu = 45^\circ)} \), as mentioned in Chapter II, seems not to be meaningful.
In fact, there is a lot of scattering of points in Figure 25 but there
might exist a straight line at least beyond 45 minutes where \( \phi_S \) is close
to unity.
CHAPTER V
CONCLUSIONS

The main theme of this work was to study the relationship between the morphological behavior under the isothermal crystallization of polyethylene terephthalate and the properties represented by the light scattering.

A very good qualitative agreement between the theory of the light scattering and the experimental observation was obtained by not only the photographic technique but also the photometric technique.

In a quantitative analysis, the observation of $H_{V}$ scattering intensity indicated fairly good agreement with the theory with a certain approximation so that it could provide the size of spherulites, the rate of growth of spherulites, volume fraction of spherulites, the degree of crystallinity inside and outside of spherulites, and the degree of perfectness of spherulites. More refinement could be obtained by combining the $V_{V}$ scattering observations. However, the method of application of the theory for $V_{V}$ scattering has not been yet established. Therefore, further study is necessary to interpret the $V_{V}$ scattering intensity.
CHAPTER VI
SUGGESTIONS FOR FURTHER RESEARCH

The discussion is restricted to a consideration of obtaining a better interpretation of the light scattering data from the undeformed samples under the isothermal crystallization of polymers.

There were many uncertainties through the analysis of data. In order to reduce them, the following suggestions could be helpful:

The proper sample should be chosen whose crystalline structure and its orientation within the spherulite is known or the spherulites are big enough for direct measurement of the birefringence and the refractive index independent of the light scattering technique.

Since two-dimensional theories for the truncation correction and the internal disorder correction are easy to understand and were well established, it might be a good idea to choose a sample which has two-dimensional spherulites, that is, their radii are greater than the thickness of the sample.

If it is possible, the microbeam analysis of x-ray should be a very powerful complement with the light scattering technique.

Each sample was prepared separately and it was assumed that there was no difference, except crystallization time, among samples. This may cause a significant error which is greater than any other experimental errors. For example, the sample at 90 minutes had the highest intensity and the biggest spherulite radius. Therefore it is better to use one sample
and to observe any change of the sample with real time. For this, it will be possible to use a Mettler hot stage and the Optical Multichannel Analyzer which will probably be set up in our laboratory (107).

The dependence of any correction factor on the polarizabilities, $\alpha_t$, $\alpha_r$ and $\alpha_d$, should be clarified.

Finally the equipment used to measure the intensity of the light scattering should be mentioned. The dynamic light scattering apparatus (72) was made and the apparatus constant was calibrated in 1972. Although it can be used for static measurement, it is good to set up new equipment for the static measurement and to calibrate the apparatus constant in every experiment using a standard sample whose absolute scattering intensity is known. This is in progress presently.
BIBLIOGRAPHY

   (Symposium on Resinographic Methods), 59 (1963).
   (1967).
41. S. Clough, J. J. van Aartsen and R. S. Stein, J. Appl. Phys. 36,
   3072 (1965).
   (1974).
46. D. T. Sturgill, presented at the American Ceramic Society Symposium on
   Nucleation, 1971; Advances in Nucleation and Crystallization in Glasses,
   American Ceramic Society, Special Pub. No. 5, L. L. Hench and S. W.
50. I. Kuriyama, K. Tomiita and K. Shirakashi, Sen-I Gakkaishi (Japan)
61. R. S. Stein and T. Hashimoto, ibid, 9, 1747 (1971).
64. D. Yoon and R. S. Stein, ibid, 12, 763 (1974).
69. R. T. Natarajan, R. E. Prud'homme and R. S. Stein, ibid, in press.
73. L. Bourland, private communication.
84. I. Uematsu and Y. Uematsu, Kobunshi Kagaku, Japan 17, 222 (1960).
86. M. Avrami, J. Chem. Phys. 7, 1103 (1939); ibid, 8, 212 (1940); ibid, 9, 177 (1941).
CAPTIONS FOR TABLES

I. Experimental data of the Rayleigh ratios, \( R_{HV}(\theta_{\text{max}}, \mu = 45^0) \), \( R_{V}(\theta_{\text{max}}, \mu = 0^0) \) and \( R_{V}(\theta_{\text{max}}, \mu = 90^0) \) and of the degree of crystallinity, \( \phi_c \), and the refractive index, \( n \).

II. Correction factors for the Hy scattering intensities.

\[ T = \text{transmittance} \]
\[ \tau_d = \text{turbidity times thickness of sample} \]
\[ K = \text{multiple light scattering correction factor} \]
\[ R_{HV}(\mu = 45^0)/R_{HV}(\mu = 0^0) = \text{ratio of the } H_y \text{ intensity at } \mu = 45^0 \text{ and } \mu = 0^0 \text{ at } U = 4 \]
\[ \delta = \text{internal disorder parameter} \]
\[ F = \text{internal disorder correction factor} \]

III. Quantitative analysis of the Hy scattering intensities.

\[ \phi_s = \text{volume fraction of spherulites} \]
\[ \phi_{cs} = \text{crystallinity inside of the spherulites} \]
\[ \phi_{cm} = \text{crystallinity outside of the spherulites} \]
\[ \alpha_d = \text{average polarizability of the sample per unit volume} \]
\[ \alpha_m = \text{average polarizability outside of the spherulite per unit volume} \]
\[ \phi_{cm} = \text{crystallinity outside of the spherulites} \]
IV. Number of spherulites, N, and the volume ratio of the sample between a non-volume-filling system and a volume-filling system. This could be compared to $\phi_S$ in Table II.

V. Quantitative analysis of the $V_V$ scattering intensities.

\[ KR_{V_V} = \text{multiple light scattering correction factor times} \]
\[ \text{experimentally-observed intensity at } \mu = 0, \theta_{\text{max}}. \]

On substituting the following values into Equation (14), $U = 4.1$, $\cos^2 (\theta/2)/\cos \theta = 1$, $\cos^2 \mu = 1$, $\cos^2 \rho_1 = 1$, one can get the theoretical intensity:

\[ R_{V_V}/K_1 = B(\phi_S) R^6 \left\{ (a_t - a_d) \phi_{V_V}^A + (a_r - a_d) \phi_{V_V}^B - (a_t - a_r) \phi_{H_Y} \right\}^2 \]

If one assumes $\phi_{cs}$ is constant and 0.3954, $(a_t - a_r)$ is constant and 0.00164. Using $a_d$ and $a_m$ in Table III, one can calculate $B(\phi_S)$ with Equation (15).

If one assumes $\phi_{cm}$ is zero, $(a_t - a_r)$ can be obtained from the equation $(a_t - a_r)_c \phi_{cs}$ where $(a_t - a_r)_c = 0.00414$. The average polarizability inside of spherulites, $\alpha_s$, can be calculated as:
\[ \frac{2\alpha_t + \alpha_r}{3} = \alpha_s = \phi_{cs} \alpha_c + (1 - \phi_{cs}) \alpha_a \]

Taking \( \alpha_m = \alpha_a \) in Equation (15), \( B(\phi_s) \) is obtained as is the theoretical intensity \( R_V / K \).

\[
\sqrt{B(\phi_s)} = \frac{\sqrt{K R_V(V)}(\mu = 0^0) - \sqrt{K R_V(V)}(\mu = 90^0)}{\sqrt{K_1 R^3 |(\alpha_t - \alpha_r)| \phi_{H_v} (4.1)|}}
\]

where \( \sqrt{K_1} = 4.214 \times 10^{14} \)

When \( \phi_{cs} \) is constant, \( (\alpha_t - \alpha_r) \) is constant. On the other hand when \( \phi_{cm} \) is zero, \( (\alpha_t - \alpha_r) \) varies.
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<th>10</th>
<th>20</th>
<th>30</th>
<th>45</th>
<th>60</th>
<th>90</th>
<th>120</th>
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<td>39.6</td>
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<td>0.395</td>
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<td>1.581</td>
<td>1.585</td>
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<td>1.588</td>
<td>1.588</td>
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</table>

**TABLE 1**

EXPERIMENTAL DATA OF THE RAYLEIGH RATIOS

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<th>Cryst. Time</th>
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<th>10</th>
<th>20</th>
<th>30</th>
<th>45</th>
<th>60</th>
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<tbody>
<tr>
<td>$R_{H_V} (\theta_{max})$</td>
<td>5.0</td>
<td>11.6</td>
<td>39.6</td>
<td>131.9</td>
<td>139.3</td>
<td>787.1</td>
<td>1416.7</td>
<td>846.2</td>
</tr>
<tr>
<td>$R_{V_V} (\theta_{max})$</td>
<td>68</td>
<td>120</td>
<td>400</td>
<td>720</td>
<td>728</td>
<td>1376</td>
<td>3233</td>
<td>2160</td>
</tr>
<tr>
<td>$\phi_c$</td>
<td>0.108</td>
<td>0.117</td>
<td>0.292</td>
<td>0.353</td>
<td>0.370</td>
<td>0.395</td>
<td>0.404</td>
<td>0.404</td>
</tr>
<tr>
<td>$n$</td>
<td>1.570</td>
<td>1.571</td>
<td>1.581</td>
<td>1.585</td>
<td>1.586</td>
<td>1.588</td>
<td>1.588</td>
<td>1.588</td>
</tr>
<tr>
<td>Cryst. Time (%)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>45</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>----------------</td>
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<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>50.5</td>
<td>42.9</td>
<td>30.5</td>
<td>38.1</td>
<td>41.9</td>
<td>36.2</td>
<td>24.8</td>
<td>36.2</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.82</td>
<td>1.25</td>
<td>0.99</td>
<td>0.92</td>
<td>0.99</td>
<td>1.32</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>1.46</td>
<td>1.80</td>
<td>1.59</td>
<td>1.42</td>
<td>1.59</td>
<td>1.88</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>1.46</td>
<td>1.80</td>
<td>1.59</td>
<td>1.42</td>
<td>1.59</td>
<td>1.88</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.82</td>
<td>4.50</td>
<td>4.27</td>
<td>4.56</td>
<td>4.23</td>
<td>4.83</td>
<td>3.41</td>
<td>3.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.225</td>
<td>0.212</td>
<td>0.213</td>
<td>0.212</td>
<td>0.23</td>
<td>0.219</td>
<td>0.219</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>16</td>
<td>17</td>
<td>16</td>
<td>17</td>
<td>15</td>
<td>22</td>
<td>19</td>
</tr>
</tbody>
</table>

**TABLE II**
CORRECTION FACTOR FOR \( H_v \) SCATTERING INTENSITIES

\[
R_{H_v}^{(0)}(\mu = 0) = \frac{R_{H_v}^{(\mu = 45)}}{R_{H_v}^{(\mu = 45)}}
\]
### TABLE III

**QUANTITATIVE ANALYSIS OF THE $H_v$ SCATTERING INTENSITIES**

<table>
<thead>
<tr>
<th>Cryst. Time</th>
<th>$\phi_s$</th>
<th>$\phi_{cs}$</th>
<th>$\phi_{cm}$</th>
<th>$\alpha_d \times 10^2$</th>
<th>$\alpha_m \times 10^2$</th>
<th>$\phi_{cm}'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.101</td>
<td>1</td>
<td>0.076</td>
<td>7.83</td>
<td>7.81</td>
<td>0.067</td>
</tr>
<tr>
<td>10</td>
<td>0.125</td>
<td>0.934</td>
<td>0.077</td>
<td>7.85</td>
<td>7.82</td>
<td>0.086</td>
</tr>
<tr>
<td>20</td>
<td>0.501</td>
<td>0.584</td>
<td>0.189</td>
<td>7.97</td>
<td>7.90</td>
<td>0.191</td>
</tr>
<tr>
<td>30</td>
<td>0.634</td>
<td>0.556</td>
<td>0.279</td>
<td>8.01</td>
<td>7.96</td>
<td>0.281</td>
</tr>
<tr>
<td>45</td>
<td>0.889</td>
<td>0.416</td>
<td>0.165</td>
<td>8.02</td>
<td>7.89</td>
<td>0.175</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>0.395</td>
<td>-</td>
<td>8.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>1.0</td>
<td>0.404</td>
<td>-</td>
<td>8.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>1.0</td>
<td>0.404</td>
<td>-</td>
<td>8.05</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE IV

Number of Spherulites, N, and the Volume Ratio of the Sample between a Non-Volume-Filling and a Volume-Filling System

<table>
<thead>
<tr>
<th>Cryst. Time</th>
<th>N x 10^-8 (cm^3)</th>
<th>R^3/R_\infty^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>81</td>
<td>0.009</td>
</tr>
<tr>
<td>10</td>
<td>61</td>
<td>0.014</td>
</tr>
<tr>
<td>20</td>
<td>38</td>
<td>0.093</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>0.224</td>
</tr>
<tr>
<td>45</td>
<td>16</td>
<td>0.392</td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>6.2</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>9.5</td>
<td>1</td>
</tr>
</tbody>
</table>
### TABLE V

**Quantitative Analysis of the \( V \) Scattering Intensities**

<table>
<thead>
<tr>
<th>Cryst. Time</th>
<th>( K_{R_{VV}} )</th>
<th>( \phi_{CS} = \text{Constant} )</th>
<th>( \phi_{cm} = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( B(\phi_s) ) &amp; ( \frac{R_{VV}}{R_{LV}} \times 10^{31} ) &amp; ( \sqrt{B(\phi_s)} )</td>
<td>( B(\phi_s) ) &amp; ( \frac{R_{VV}}{R_{LV}} \times 10^{31} ) &amp; ( \sqrt{B(\phi_s)} )</td>
</tr>
<tr>
<td>5</td>
<td>93.2</td>
<td>0.11 &amp; 0.204 &amp; 7.37</td>
<td>0.11 &amp; 1.484 &amp; 2.92</td>
</tr>
<tr>
<td>10</td>
<td>171.6</td>
<td>0.14 &amp; 0.665 &amp; 15.72</td>
<td>0.14 &amp; 4.332 &amp; 6.67</td>
</tr>
<tr>
<td>20</td>
<td>660.0</td>
<td>0.84 &amp; 107.5 &amp; 5.92</td>
<td>0.95 &amp; 366.2 &amp; 4.02</td>
</tr>
<tr>
<td>30</td>
<td>1073</td>
<td>0.92 &amp; 577.8 &amp; 2.66</td>
<td>1.53 &amp; 2495 &amp; 1.89</td>
</tr>
<tr>
<td>45</td>
<td>1108</td>
<td>1.66 &amp; 3025 &amp; 1.28</td>
<td>2.89 &amp; 6162 &amp; 1.22</td>
</tr>
<tr>
<td>60</td>
<td>2119</td>
<td>1.0 &amp; 7905 &amp; 1.0</td>
<td>1.0 &amp; 7905 &amp; 1.0</td>
</tr>
<tr>
<td>90</td>
<td>5917</td>
<td>1.0 &amp; 32850 &amp; 1.0</td>
<td>1.0 &amp; 32850 &amp; 1.0</td>
</tr>
<tr>
<td>120</td>
<td>3370</td>
<td>1.0 &amp; 9382 &amp; 1.0</td>
<td>1.0 &amp; 9382 &amp; 1.0</td>
</tr>
</tbody>
</table>
CAPTIONS FOR FIGURES

1. Truncation correction factors for $\theta_{\text{max}}$ with truncation parameters $(\sigma^2/a^2)$ using the ratio $\theta_{\text{max}}(0)/\theta_{\text{max}}(\sigma^2/a^2)$.

2. Truncation correction factor for the maximum $H_V$ intensities with truncation parameters using the curve $V = 1$.

3. Multiple scattering correction factors for the maximum $H_V$ intensities with product of turbidity and thickness, $\tau_d$. ($U_4$, $\nu_{45}$).

4. Multiple scattering correction factors for $V_Y$ intensities at $U = 4$ and $\mu = 0^\circ$ and $90^\circ$ with $\tau_d$.

5. The internal disorder correction factors for the maximum $H_V$ intensities with disorder parameter, $\delta$. ($\omega = \text{random}$)

6. The variation of ratio of $H_V$ intensities at $\omega = 4.0$, $\mu = 45^\circ$ to that at $\mu = 0^\circ$ and $15^\circ$ with $\delta$. ($\omega = \text{random}$)

7. The variation of the crystalline orientation functions with respect to the radius of spherulite with $\delta$. $\omega = 0$: no lamella twist. $\omega = \text{random}$: lamella twist randomly.

8. Schematic diagram of the photographic light scattering set-up.

9. Typical $H_V$ and $V_Y$ light scattering patterns of polyethylene terephthalate crystallized at $110^\circ$C for 90 minutes from the melt.

10. $H_V$ scattering patterns during the spherulitic growth of PET when crystallized from the melt at $110^\circ$C.

11. A plot of spherulite radius as a function of crystallization times of PET samples crystallized from the melt at $110^\circ$C.
12. $V_V$ scattering patterns with the same conditions as Figure 10.
13. Photomicrograph of PET samples crystallized from the melt at $110^\circ$C.
14. $H_V$ intensities with scattering angle $\theta$ at an azimuthal angle $\mu = 45$ for various crystallization times.
15. Maximum $H_V$ intensities with crystallization times at $\theta = \theta_{\text{max}}$ and $\mu = 45$
16. Spherulite radius with crystallization time obtained from photometric observations.
17. $V_V$ intensities with reduced angle at $\mu = 0^\circ$.
18. $V_V$ intensities with reduced angle at $\mu = 90^\circ$.
19. $V_V$ intensities with crystallization times at $\mu = 0$ and various $\theta$.
20. $V_V$ intensities with crystallization times at $\mu = 90$ and various $\theta$.
21. Volume fraction of crystallinity with crystallization times.
22. Avrami plot for crystallization of PET at $110^\circ$C from the melt.
23. A plot of spherulite growth rate as a function of temperature for PET from the melt and from the glassy state. $M_n = 27,400$. [J. Polym. Sci. 10, 2425 (1972).]
25. A plot of $\sqrt{I_{VV}(\mu = 0^\circ)} - \sqrt{I_{VV}(\mu = 90^\circ)}$ vs. $\sqrt{I_{HV}(\mu = 45^\circ)}$ for all samples.
\( \bar{a} = 5 \mu m \)
\( \lambda = 0.4280 \mu m \)

\[ \theta_{\text{max}} \text{ in air (}\mu = 45^\circ\text{)} \]

\[ \text{Truncation parameter (}\sigma^2/\bar{a}^2\text{)} \]
FIG. 6

$X = 0^\circ$

$X = 15^\circ$
FIG. 10

a. 5 mins
b. 10 mins
c. 20 mins
d. 30 mins
e. 45 mins
f. 60 mins
g. 90 mins
FIG. 14  PET Crystallization at 110°C from the melt

Time (min)
- D: 120
- ○: 90
- △: 60
- △: 45
- □: 30
- ○: 20
- ■: 10
- ○: 5

$R_{HV} (\mu = 45^\circ)$

$\theta$
FIG. 15  Crystallization of PET at 110°C from the melt
FIG. 17

Crystallization Time (min)

- 120
- 90
- 60
- 45
- 30
- 20
- 10
- 5

$R_V \left( \mu = 0 \right)$ vs $U$
FIG. 18
PET Crystallization at 110°C from the melt

Crystallization Time (min)
- 120
- 90
- 60
- 45
- 30
- 20
- 10
- 5

$R_{vv} (\mu = 90^\circ)$ vs $U$
Crystallization of PET at 110°C from the melt

\[ \phi_c = 1 - \frac{1}{\rho_a} - \frac{1}{\rho_c} \]

Time (min)

Crystallinity (\(\phi\)%)
FIG. 22

\[
\ln \left\{ -\ln \left( \frac{V(t) - V_\infty}{V_0 - V_\infty} \right) \right\}
\]

vs. \( \ln t \)
FIG. 25 Crystallization of PET at 110°C from the melt

\[ \sqrt{R_{VV}(\mu=90^\circ)} - \sqrt{R_{VV}(\mu=0^\circ)} \]

\[ \sqrt{R_{HH}(\mu=45^\circ)} \]
APPENDIX I

Computer Program for Evaluation of the $H_V$ Scattering Intensity from Truncated Spherulites under Non-Volume Filling System

This program was extended from that obtained by A. Misra (43) and R. Prud'homme (70). It is composed of a main program, TRUNK, and sub-programs, NOMBRE, SELECT, COMPUTE and QSF.

First of all, NOMBRE can generate a fixed number of points in a definite area. Those points represent nuclei or the center of each spherulite. Some of them are then chosen with a limitation of smaller area in order to eliminate the complication caused by the outer boundary.

SELECT can then pick up one point and search the nearest points within a fixed sub-area.

TRUNK can draw any bisectional line between the point in question and any selected nearest point. This procedure provides the boundary of the spherulite when the impingement is completed. A circle with a fixed radius, $R$, is made at this point and radiating lines are drawn which make an angle between two neighboring lines of $2^\circ$ from the point. The distance between the center and the boundary along each radiating line is compared to the fixed radius. The shorter distance is called $a_i$. The $H_V$ light scattering intensity; the average radius, $\bar{a}$; the truncation parameter, $\sigma^2/\bar{a}^2$; and the area, $A$, are calculated for this spherulite. It may be a perfect circle, a truncated circle, or an irregular polygon which depends upon the given radius. COMPUTE can calculate $\bar{a}$ and $\sigma^2/\bar{a}^2$ and QSF provides
This part was done mainly by the invaluable help of Dr. A. Wasiak.

The author again wishes to express his appreciation.
PROGRAM TRUNK

00100  PROGRAM TRUNK(INPUT, OUTPUT, NOMBRE, SELECT, COMPUTE, QSF)
00110  TAPE1=NOMBRE, TAPE2=SELECT, TAPE3=COMPUTE, TAPE4=QSF
00120  COMMON XX(850), YY(850), NUC
00130  COMMON SPHX(600), SPHY(600), NSPH
00140  COMMON X(100), Y(100), IS, N
00150  COMMON LNUM(100), AI(200), Z(200)
00160  COMMON D(100), SLOPE(100), GAM(100), XMID(100), YMID(100)
00170  COMMON DH(100), TH(100)
00180  COMMON HM(100), HC(100), XINT(100), YINT(100)
00190  DIMENSION XXINT(20), YYINT(20), GAMMAR(200), MU(20)
00200  DIMENSION SA(20), A(20), STH(20), THETA(20), GAM(20)
00210  DIMENSION SUM(25), SUM6(25), SUM7(25), SUMV(25), SUMV6(25)
00220  DIMENSION SUMINT(10, 2, 25), AIRED(20), SUMA(L0)
00230  DO 20 IEM=1, 10
00240  SUM(IEM)=0 $ AIRED(IEM)=0
00250  SUM6(IEM)=0 $ SUM(IEM)=0
00260  SUM7(IEM)=0 $ SUMV(IEM)=0
00270  SUMV6(IEM)=0
00280  USE(NOMBRE)
00290  USE(SELECT)
00300  USE(COMPUTE)
00310  USE(QSF)
00320  DO 20 ICS=1, 2
00330  DO 20 IST=1, 25
00340  SUMINT(IEM, ICS, IST)=0
00350  20 CONTINUE
00360  PI=4.*ATAN(1.)
00370  NINC=180
00380  LAMBDA= 0.00005461
00390  C= 126320.
00400  ARMAT= -0.003
00410  DELALP=(2.*PI)/FLOAT(NINC-1)
00420  XK=2.*PI/LAMBDA
00430  DELGAMR = (2.*PI)/FLOAT(NINC-1)
00440  CALL NOMERE
00450  TOT=PI*RClR**2
00460  DO 27 LL=1, 50
00470  27 LNUM(LL)=0
00480  DO 450 IS=1, NSPH
00490  CALL SELECT
00500  PRINT 35, IS, SPHX(IS), SPHY(IS)
00510  35 FORMAT(1/5*SPHERULITE NO*, I3, 5X, *SPHX=*, F6.1, 5X, *SPHY=*, F6.1)
00520  DO 63 IJ=1,N
00530  K=I
00540  DO 60 IJ=1,N
00550  X(IJ)=X(IJ)-SPHX(IS)
00560  IF(X(IJ) .EQ. 0.) 42, 44
00570  42 X(IJ)=X(IJ)+.01
00580  44 Y(IJ)=Y(IJ)-SPHY(IS)
D(IJ) = X(IJ)**2 + Y(IJ)**2
IF(IJ = EQ. 1) GO TO 60
DIFF = D(IJ) - D(K)
IF(DIFF .GE. 0.) GO TO 60
K = IJ
60 CONTINUE
DO 91 J = 1, N
SLOPE(J) = Y(J) / X(J)
GAM(J) = ATAN(SLOPE(J))
GAM(J) = ABSF(GAM(J) * 180. / PI)
IF(Y(J) .GT. 0.) 77, 78
GAM(J) = 90. - GAM(J)
GO TO 90
77
IF(X(J) .GT. 0.) 78, 80
GAM(J) = 90. + GAM(J)
GO TO 90
78
GAM(J) = 270. - GAM(J)
GO TO 90
79
IF(XCJ) .GT. 0.) 83, 85
GAMCJ) = 90. + GAM(J)
GO TO 90
83
GAMCJ) = 270. - GAM(J)
XY = 0.
91
DO 100 IA = N - 1
IA = N - 1
ID = 136 I = IA
IB = I + 1
DO 135 J = IB, N
IF(GAM(I) .LE. GAM(J)) GO TO 135
V1 = GAM(I)
V2 = X(I)
V3 = Y(I)
V4 = D(I)
GAM(I) = GAM(J)
D(I) = D(J)
X(I) = X(J)
Y(I) = Y(J)
135 CONTINUE
GO TO 135
142, 144
142 HX(JJ) = 1000.
GO TO 146
HMCJJ)»-XC  
JJ) /2.  
YMID(JJ) = Y(JJ) /2.  
HC(JJ) = YMID(JJ) - HM(JJ) * XMID(JJ)  
CONTINUE  
HCCJJ = YMIDCJJ) - HMCJJ) * XMIDCJJ)  
GAMCN+1 = 360.  
KJ = 1  
IM = 165  
FOPMATC/*N0*, 6X#*XINT*, 7X,*YINT*, 7X,*AJ*, 5X,*GAMMAJ*  
> *THETA*  
XIMT(1) = G.  
YINT(1) = 0.  
JJ = KJ + 1  
I = 165  
M=N  
GO TO 177  
GO TO 170  
IC = KJ + 1  
DO 320 JJ = IC, M  
ANGLE = GAM(JJ) - GAM(KJ)  
IF(ANGLE .EQ. 0.) GO TO 300  
IF(ANGLE .GE. 179.) GO TO 302  
XINT(JJ) = (HC(KJ) - HC(JJ)) / (HM(JJ) - HM(KJ))  
YINT(JJ) = XINT(JJ) * HM(KJ) + HC(KJ)  
TH(JJ) = (XINT(KJ) - XINT(JJ)) ** 2 + (YINT(KJ) - YINT(JJ)) ** 2  
GAMMAJ  
IF(JJ .EQ. KJ + 1) GO TO 300  
THETACIN) = ATAN(STH(IN))  
THETACIN) = 180. * THETACIN) / PI  
IF(YINT(JJJ) .GE. 0.) GO TO 322  
THETACIN) = THETACIN) + 180.  
GO TO 326  
322 IF(XINT(JJJ) .GE. 0.) GO TO 326  
THETACIN) = THETACIN) + 360.  
326  
IF(THETA(IN) .LT. GAMMA) GO TO 336  
THETACIN) = THETACIN) - GAMMA  
GO TO 340  
336  
THETACIN) = THETACIN) + 360. - GAMMA  
340  
XXINT(IN) = XINT(JJJ) + SFHXC(IS)  
YYINT(IN) = YINT(JJJ) + SFHY(IS)  
SA(IN) = XMID(KJ) ** 2 + YMID(KJ) ** 2  
A(IN) = SORT(SA(IN))
01650  GAMM(IN)=GAMM(KJ)
01660  IF(GAMM(IN) .LE. 360.)GO TO 370
01670  GAMM(IN)=GAMM(IN)-360.
01680  370  PRINT 372,IN,XXINT(IN),YYINT(IN),A(IN),GAMM(IN),
01690  THETA(IN)
01700  372  FORMAT(5X,12,5X,F6.2,5X,F6.2,5X,F5.2,5X,F5.1,5X,F5.1)
01710  KJ=JJJ
01720  IF(JJJ .GE. M)400,
01730  DO 450 IEM=1,10
01740  READ397, DELRMAX
01750  397  FORMAT(F5.2)
01760  XILM=IBM
01770  PMAX=XIEM*DELRMAX
01780  PRINT 399,RMAX
01790  399  FCPUATC/,*MAX.RADIUS=*,F10.6)
01800  412  DO 426 JJJ=1,NINC
01810  ALPHAR=0.
01820  DO 420 I=1,NINC
01830  AA = MUR-ALPHAR
01840  BB = 2.*ALPHAR
01850  AD = AA*ALPHAR
01860  TRC(I)=((COS(AD)/(AA**2))+(AI(I)*SIN(AD)/AA)-(1./AA**2))*/2.
01870  TI(I) = ((SIN(AD)/(AA**2))-(AI(I)*COS(AD)/AA))*BB
01880  CALL QSF(DELALP,TR,Z,NINC)
01890  EHVR = COEF*Z(NINC)
01900  CALL QSF(DELALP, TI,Z,NINC)
01910  EHVI = COEF*Z(NINC)
01920  DO 422 I=2,NINC
01930  AIRE2=AIRECIR(I)*AIRECIEM(I)
01940  DO 426 JJJ=1,NINC
01950  ALPHAR=0.
01960  DO 420 I=1,NINC
01970  AA = MUR-ALPHAR
01980  BB = 2.*ALPHAR
01990  AD = AA*ALPHAR
02000  TRC(I)=((COS(AD)/(AA**2))+(AI(I)*SIN(AD)/AA)-(1./AA**2))*/2.
02010  TI(I) = ((SIN(AD)/(AA**2))-(AI(I)*COS(AD)/AA))*BB
02020  CALL QSF(DELALP,TR,Z,NINC)
02030  EHVR = COEF*Z(NINC)
02040  CALL QSF(DELALP, TI,Z,NINC)
02050  DO 422 I=2,NINC
02060  AIRE2=AIRECIR(I)*AIRECIEM(I)
02070  AIR = AI(I)*AI(I-1)*SIN(DELALP)/2.
02080  422  AIREC1EM)=AIREC1EM)+AIR
02090  PRINT 424,AIREC1EM)
02100  DO 424 IEM=1,NINC
02110  AIRE2= AIREC1EM*AIREC1EM
02120  424  FORMAT(/,*SPHERULITE AREA=*,F6.3)
02130  AIRE2= AIREC1EM*AIREC1EM
$2160 \; \text{XIHV} = \{(EHV \star R^2) + (EHV \star I^2)\} / \text{AIRES2}

$2170 \; Y3(JJJ) = \text{XIHV}

$2180 \; \text{DO} \; 426 \; I = 1, \text{NSPH}

$2190 \; 426 \; \text{GAMMAR}(I) = \text{GAMMAR}(I) + \text{DELGAMR}

$2200 \; \text{CALL QSF(DELGAMR, Y3, Z, NINC)}

$2210 \; \text{XIHV} = Z(\text{NINC})

$2220 \; \text{XLOGIHV} = \text{ALG10}(\text{XIHV})

$2230 \; \text{PRINT 428,} \; \text{STHETAMU, XIHV, XLOGIHV}

$2240 \; \text{PRINT 428} \; \text{FORMAT(} / 10X, F6.2, 5X, F5.2, 5X, E12.3, 5X, E12.3)\n
$2250 \; \text{SUMINT(IEM, ICS, IST)} = \text{SUMINT(IEM, ICS, IST)} + \text{XIHV}

$2260 \; \text{SUMAC(IEM)} = \text{SUMAC(IEM)} + \text{AIRES(IEM)}

$2270 \; \text{SUM(IEM)} = \text{SUM(IEM)} + \text{AMean}

$2280 \; \text{SUM6(IEM)} = \text{SUM6(IEM)} + \text{AMean**6}

$2290 \; \text{SUM7(IEM)} = \text{SUM7(IEM)} + \text{AMean**7}

$2300 \; \text{SUMV(IEM)} = \text{SUMV(IEM)} + \text{VARAA}

$2310 \; \text{SUMV6(IEM)} = \text{SUMV6(IEM)} + \text{VARAA*(AMean**6)}

$2320 \; 450 \; \text{CONTINUE}

$2330 \; \text{XNSPH} = \text{NSPH}

$2340 \; \text{DO} \; 600 \; \text{IEM} = 1, 10

$2350 \; \text{XJEM} = \text{IEM}

$2360 \; \text{RMAX} = \text{XJEM} * \text{DELRMAX}

$2370 \; \text{PRINT 399, RMAX}

$2380 \; \text{AAVG} = \text{SUM(IEM)} / \text{XNSPH}

$2390 \; \text{AAVG6} = \text{SUM7(IEM)} / \text{SUM6(IEM)}

$2400 \; \text{VARAVG} = \text{SUMV(IEM)} / \text{XNSPH}

$2410 \; \text{VARAVG6} = \text{SUMV6(IEM)} / \text{SUM6(IEM)}

$2420 \; \text{PRINT 471, AAVG, AAVG6}

$2430 \; \text{471 FORMAT(} / 5X, \text{*AAVG} = *, F8.3, 10X, \text{*AAVG6} = *, F8.3)\n
$2440 \; \text{PRINT 476, VARAVG, VARAVG6}

$2450 \; \text{476 FORMAT(} / 5X, \text{*VARAVG} = *, F9.4, 7X, \text{*VARAVG6} = *, F9.4)\n
$2460 \; \text{PRINT 480, SUMA(IEM)}

$2470 \; \text{480 FORMAT(} / 5X, \text{*TOTAL AREA} = *, F8.3)\n
$2480 \; \text{AAA} = \text{SUMAC(IEM)} / \text{TOT}

$2490 \; \text{PRINT 490, AAA}

$2500 \; \text{490 FORMAT(} / 5X, \text{*DEGREE OF SPHERE} = *, F5.3)\n
$2510 \; \text{AAA} = \text{SUMA(IEM)} / \text{XNSPH}

$2520 \; \text{PRINT 495, AAA}

$2530 \; \text{495 FORMAT(} / 5X, \text{*AVERAGE AREA} = *, F8.6)\n
$2540 \; \text{DO} \; 600 \; \text{ICS} = 1, 2

$2550 \; \text{PRINT 500, MU(ICS)}

$2560 \; \text{500 FORMAT(} / 5X, \text{*AZIMUTHAL ANGLE} = *, F3.1)\n
$2570 \; \text{PRINT 510}

$2580 \; \text{510 FORMAT(} / \text{*THETA}, 5X, \text{*AVER. INT.}, 5X, \text{TOT. INT.}, 5X, \text{LOG. INT.}, /)\n
$2590 \; \text{DO} \; 600 \; \text{IST} = 1, 25

$2600 \; \text{STHETAD = IST}

$2610 \; \text{BBB} = \text{SUMINT(IEM, ICS, IST)} / \text{XNSPH}

$2620 \; \text{AAA = ALOG10(SUMINT(IEM, ICS, IST))}

$2630 \; \text{PRINT 520, STHETA, BBB, SUMINT(IEM, ICS, IST), AAA}

$2640 \; \text{520 FORMAT(} / 5X, F3.1, 3*(5X, E12.3))\n
$2650 \; \text{600 CONTINUE}

$2660 \; \text{END}
SUBROUTINE NOMBRE

This subroutine is used in the main program Trunk.

It specifies the total number of spherulites (NUC) and the radius of the circle (RCIR) in which they are located. It also selects the number of spherulites (NSPH) for which the size and truncation parameter are calculated.

In the present case nuclei are generated randomly. If nuclei centers are known, statements from 70 to 90 should be replaced by read statements.

COMMON XX(850), YY(850), NUC
COMMON SPHX(620), SPHY(600), NSPH
COMMON X(100), Y(100), IS, N

NUC = 20
RCIR = 225.
DO 90 I = 1, NUC
70 XX(I) = RANF(2) * 450.
YY(I) = RANF(0) * 450.
RADIUS = (225 - XX(I)) ** 2 + (225 - YY(I)) ** 2
RCNST = 225. ** 2
IF (RADIUS .GE. RCONST) GO TO 70
IF (I .EQ. 1) GO TO 90
IX = I - 1
DO 90 J = 1, IX
DIFF = (XX(I) - XX(J)) ** 2 + (YY(I) - YY(J)) ** 2
XDIF = 0.01 ** 2
IF (DIFF .LT. XDIF) GO TO 70
CONTINUE
90 CONTINUE

CHECK = (XX(I) - 225.) ** 2 + (YY(I) - 225.) ** 2
XLIM = 190. ** 2
IF (CHECK .GE. XLIM) GO TO 150
IJ = IJ + 1
SPHX(IJ) = XX(I)
SPHY(IJ) = YY(I)
CONTINUE
NSPH = IJ
PRINT 171, NUC
171 FORMAT (/5X, *TOTAL NO. OF SPHERULITE CENTERS =*, 14)
PRINT 176, NSPH
176 FORMAT (/5X, *NUMBER OF SPHERULITES CONSIDERED =*, 14)
RETURN
END
PROGRAM SELECT

00100 SUBROUTINE SELECT
00110* THIS SUBROUTINE IS USED WITH THE MAIN PROGRAM TRUNK..
00120* FOR ANY GIVEN SPHERULITE "I" IT SELECTS ITS NEAREST
00130* Neighbours. IN THIS CASE ALL NEIGHBOURING SPHERULITES (N)
00140* IN A CIRCLE OF RADIUS 60 MICRONS WERE CONSIDERED
00150 COMMON XX(850), YY(850), NUC
00160 COMMON SPHX(600), SPHY(600), NSPH
00170 COMMON X(100), Y(100), IS, N
00180  JI=0
00190  DO 100  I=1, NUC
00200  DCHECK=(XX(I)-SPHX(IS))**2+(YY(I)-SPHY(IS))**2
00210  IF(DCHECK .EQ. 0.) GO TO 100
00220  DCONS=60.*2
00230  IF(DCHECK .GT. DCONS) GO TO 100
00240  JI=JI+1
00250  X(JI)=XX(I)
00260  Y(JI)=YY(I)
00270  100 CONTINUE
00280  N=JI
00290  IF(N .LT. 90) GO TO 120
00300  PRINT, N
00310  120 CONTINUE
00315  RETURN
00320  END
SUBROUTINE COMPUTE(AMEAN, VAR, VARAA, A, GAMM, THETA, IN, LL, LNUM)

* THIS SUBROUTINE IS USED WITH THE MAIN PROGRAM TRUNK *

IT CALCULATES THE AVERAGE SIZE AND THE TRUNCATION PARAMETER FOR EACH SPHERULITE.

DIMENSION A(20), GAMM(20), THETA(20)
DIMENSION AI(200), DA(200)
DIMENSION LNUM(100)

PI=4.*ATAN(1.)
NINC=180
XINC=NINC
DELA=360./XINC
AMEAN=0.
J=1
THETA(IN+1)=360.
A(IN+1)=A(1)
GAMM(IN+1)=360.+GAMM(1)
DO 100 I=WNINC

XI=I-1
ALPHA=XI*DELA
ERRCR=THETA(J)-ALPHA
ERR=DELA
IF(ABS(THETA(J)-ALPHA)*PI/180. .LT. ERR)80,82
80 J=J+1
82 GAMAL=(GAMM(J)-ALPHA)*PI/180.
AI(I)=ABS(A(J)/COS(GAMAL))
IF(AI(I).GT.RMAX)85,90
85 AI(I)=RMAX
CALL AI(I)
AMEAN=AMEAN+AI(I)
100 CONTINUE

AMEAN=AMEAN/XINC
SQAN=AMEAN**2
VAR=0.
DO 150 I=1,NINC
DA(I)=AI(I)-AMEAN
VAR=VAR+DA(I)**2
150 CONTINUE
VAR=VAR/XINC
VARAA=VAR/SQAN
DO 220 L=1,IN
AL(L)=A(L)**2
LL=A(L)
LNUM(LL)=LNUM(LL)+1
220 CONTINUE
RETURN
END
SUBROUTINE QSF(H, Y, Z, NDIM)

DIMENSION Z(NDIM), Y(NDIM)

HT = 0.333333*H

IF(NDIM - 5) 330, 335, 145

145 SUM1 = Y(2) + Y(2)

SUM1 = SUM1 + SUM1

SUM1 = HT*(Y(1) + SUM1 + Y(3))

AUX1 = Y(4) + Y(4)

AUX1 = AUX1 + AUX1

AUX1 = SUM1 + HT*(Y(3) + AUX1 + Y(5))

AUX2 = HT*(Y(1) + 3.875*(Y(2) + Y(5)) + 2.625*(Y(3) + Y(4)) + Y(6))

SUM2 = Y(5) + Y(5)

SUM2 = SUM2 + SUM2

SUM2 = AUX2 - HT*(Y(4) + SUM2 + Y(6))

Z(1) = 0.

AUX = Y(3) + Y(3)

AUX = AUX + AUX

Z(2) = SUM2 - HT*(Y(2) + AUX + Y(4))

Z(3) = SUM1

Z(4) = SUM2

IF(NDIM - 6) 295, 295, 335

295 DO 290 I = 7, NDIM, 2

SUM1 = AUX1

SUM2 = AUX2

AUX1 = Y(I-1) + Y(I-1)

AUX1 = AUX1 + AUX1

AUX1 = SUM1 + HT*(Y(I-2) + AUX1 + Y(I))

Z(I-2) = SUM1

IF(I-NDIM) 275, 310, 310

275 AUX2 = Y(I) + Y(I)

AUX2 = AUX2 + AUX2

AUX2 = SUM2 + HT*(Y(I-1) + AUX2 + Y(I+1))

290 Z(I-1) = SUM2

295 Z(NDIM-1) = AUX1

Z(NDIM) = AUX2

RETURN

310 Z(NDIM-1) = SUM2

Z(NDIM) = AUX1

RETURN

330 IF(NDIM - 3) 440, 410, 335

435 SUM2 = 1.125*HT*(Y(1) + Y(2) + Y(2) + Y(2) + Y(3) + Y(3) + Y(3) + Y(4))

SUM1 = Y(2) + Y(2)

SUM1 = SUM1 + SUM1

SUM1 = HT*(Y(1) + SUM1 + Y(3))

Z(1) = 0.

AUX1 = Y(3) + Y(3)

AUX1 = AUX1 + AUX1

Z(2) = SUM2 - HT*(Y(2) + AUX1 + Y(4))
IF(NDIM = 5) 395, 380, 380
AUX1 = Y(4) + Y(4)
AUX1 = AUX1 + AUX1
Z(5) = SUM1 + HT*(Y(3) + AUX1 + Y(5))
Z(3) = SUM1
Z(4) = SUM2
RETURN
410 SUM1 = HT*(Y(1) + Y(2) + Y(2) - .25*Y(3))
SUM2 = Y(2) + Y(2)
SUM2 = SUM2 + SUM2
Z(3) = HT*(Y(1) + SUM2 + Y(3))
Z(1) = 0.0
Z(2) = SUM1
RETURN
END
**PROGRAM SPHER**

```
00100 PROGRAM SPHER (INPUT, OUTPUT)
00120* THIS PROGRAM CALCULATES LIGHT SCATTERING INTENSITIES
00130* FROM TWO DIMENSIONAL SPHERULITES AND IS USED IN CHAPTER III
00140 DIMENSION T(100)
00150 DIMENSION RR(50)
00170 PI = 4*ATAN(1.)
00180 LAMBDANU = 0.00005461
00190 C = 126300.0
00200 ARMAT = -2.003
00220 PRINT 52, ARMAT, C
00230 52 FORMAT(//10X,*WAVE LENGTH = 5461 A*,//10X,*POLARIZABILITY
00240+ DIFFERENCE =*, FS. 4, //10X,*CONSTANT C=*, E9.1)
00270 READ (RR(J), J = 1, 21)
00280 D0 350 J = 1, 21
00290 R = RR(J)
00300 PRINT 75, J
00310 75 FORMAT(//, 10X,*SPHERULITE NUMBER*, 14)
00320 PRINT 82, R
00330 82 FORMAT(10X,*AVERAGE SPHERULITIC RADIUS=*, F9.6, **CM*, //)
00340 PRINT 96
00350 96 FORMAT(10X,*THETA*, 7X,*MU*, 13X,*IHV*, 10X,*LOGIHV*, //)
00360 THETA = .4
00370 MU = 45.
00380 120 MUR = MU * PI / 180.
00390 THETAR = THETA * PI / 180.
00400 W = (2. * PI * R * SIN(THETAR)) / LAMBDANU
00410 COSRHO2 = COS(THETAR) / SQRT(COS(THETAR)**2 + SIN(THETAR)**2*
00420+ SIN(NUR)**2)
00430 CALL BES(0, W, 0, J0W, T)
00440 CALL BES(1, W, 0, J1W, T)
00450 XX = 2. * MUR
00460 EHV = C * ARMAT * COSRHO2 * ((PI * R * R) / (W**2)) * (2*(1-JOW)-W*J1W)
00470+ *SIN(XX)
00480 XHV = EHV * EHV
00490 XLOGIHV = ALOG10(XHV)
00500 PRINT 225, THETA, MU, XHV, XLOGIHV
00520 225 FORMAT(10X, FS. 2, 5X, FS. 2, 5X, E12.3, 5X, E12.3)
00540 IF(THETA .GE. 3.) GO TO 306
00550 THETA = THETA + .2
00560 GO TO 120
00570 306 IF(THETA .GE. 5.) GO TO 314
00580 THETA = THETA + .5
00590 GO TO 120
00600 314 IF(THETA .GE. 10.) GO TO 320
00610 THETA = THETA + 1.
00620 GO TO 120
00630 320 IF(THETA .GE. 16.) GO TO 350
00640 THETA = THETA + 2.
00650 GO TO 120
00660 350 CONTINUE
00670 END
```
APPENDIX II

Computer Program for the Calculation of the Rayleigh Ratio involving the Refraction and Reflection Correction (67) from the Experimental Data Obtained Using the Dynamic Light Scattering Apparatus (70,71)
PROGRAM NRAJ

10 PROGRAM RAJ(INPUT, OUTPUT, DANE, BCGR, TAPE1=DANE, TAPE2=BCGR)
20* XN = REFRACTIVE INDEX OF SAMPLE
21* DPF=DPF1*DPF2=DEPOLARIZATION RATIO
22* TRANS = TRANSMITTANCE ()
23* THICK = SAMPLE THICKNESS IN (MILS)
24* XK = APPARATUS CONSTANT (CM**2)
25* RINC = RADIUS OF INCIDENT BEAM (CM)
26* TETA = ANGLE THETA (IN AIR)
27* PMU = ANGLE MU (AZIMUTHAL)
28* READING = READING OF THE RECORDER (THIS IS TRUE READING
29* MINUS BLANK READING, GIVEN FOR STANDARD 10)
30* CN = REFRACTION CORRECTION
31* REFL = REFLECTION CORRECTION
32* TETAS = ANGLE THETA(IN SAMPLE)
33* ANGR = ANGLE IN (RADIANS)
34* RAY = RAYLEIGH RATIO
35* RADII = RADIUS OF SPHERULITE
36* FACT0R=MULTIPLIATION FACTOR FOR TRUNCATION
90 READ(1,95)C, S
92 PI =3.1415927
95 95 FORMAT(F2.1, F5.1)
96 CALL GET(SHTAPE1, 4HDANE, 0, 0)
97 CALL GET(SHTAPE2, 4HBGR, 0, 0)
100 IF(C.EQ.1.) 101, 107
101 101 PRINT 102
102 102 FORMAT (\\\\\\\"///, 25X,*THI THIS IS A THETA SCAN\", 24X,*--------
103+-------------------*
104 GO TO 111
107 107 PRINT 108
108 108 FORMAT (\\\\\\\"///, 21X,*THI THIS IS AN AZIMUTHAL SCAN *, /, 22X,
109+-------------------*
110 GO TO 113
111 111 READ(1, 115)PMU
112 DPF2=1.
113 113 PRINT 114, S
114 114 FORMAT (\\\\\\\"///,*SAMPLE = *F6.2)
115 115 FORMAT (F4.1)
116 PRINT 117
117 117 FORMAT (\\\\\\\"/*DATE = */\")
118 READ (1, 121) XN, TRANS, THICK, XK, RINC, RADII, VVI, DPF1, FM, SF
119 A=(THICK/1000.)*2.54
120 TD=ALOG(100./TRANS)
121 121 FORMAT(F5.3, F4.1, F5.1, F8.7, 2(F4.2), F8.2, 3(F5.4))
125 VOL=A*(RING**2)*PI
130 PRINT 135,"N, TRANS, THICK, XK, RINC, RADII
135 135 FORMAT(5X,*REFRACTIVE INDEX **, F7.3, /,
136+5X,*TRANSMITTANCE () **, F7.3, /5X,*SAMPLE
137+THICKNESS (MILS) = **, F7.3, /5X,*APPARATUS CONSTANT
138+ (SQ. CM.) = **, F9.5, /5X,*INCIDENT BEAM RADIUS
139+ (CM) = **, F7.3, /5X,*RADIUS OF SPHERULITE (MICR
140+ONS) = **, F7.3//")
145 PRINT 146, TD, VOL
147+ (CC) = *, F7.5, /**/)
148 PRINT 149
150+ 3X, *RAYLEIGH*, 5X, *RED. ANGLE*/**)
151 PRINT 152
152 152 FORMAT (3X, *(AIR)*, 3X, *(SAMPLE)*, 3X, *(AZIMUTH)*, 3X,
153** *(INSTR)*, 4X, *(RATIO)*, 3X, *(U)*, /**)
155 155 READ(1, 156) TETA, READING
156 156 FORMAT(F6.2, F8.2)
157 CTR=0
165 IF (TETA = EQ. 0.) GO TO 390
167 167 TETA=TETA*SF
170 TETAR=TETA*PI/180.
175 SINTET=SINF(TETAR)
180 COSTET=CCSF(TETAR)
190 TETASR=ASINF(TETAR/XN)
195 COSTES=CCSF(TETASR)
200 TETAS=TETASR*180.*PI
205 CN=XN*XN*SQRF(1.-SINTET/XN)**2.)/COSTET
215 PA=((XN-1.)/(XN+1.))**2.
220 ANGR=ASINF(SINTET/XN)
225 ANGA=TETAR-ANGR
230 ANGB=TETAR+ANGR
235 TANA=TANF(ANGA)
240 TANB=TANF(ANGB)
245 SINA=SINF(ANGA)
250 SINB=SINF(ANGB)
254 XPMU=PMU*PI/180.
255 FC=(SINF(XPMU))**2
260 RC=(FC*(SINA/SINE)**2.+(1.-FC)*(TANA/TANB)**2.)
265 REFLEC=0.96/((1.-RA)*(1.-RC))
270 U=4.*PI*RAI*I*XN*SINF(TETASR/2.)/5461
275 Z=READING*(3300./VVI)*DPF1*DPF2
285 RAY=XK*CN**(REFLEC/VCL)**Z*FM
295 PRINT 296, TETA, TETAS, PMU, READING, RAY, U
296 296 FORMAT (F8.3, F10.3, F10.1, F12.1, F12.3, F12.3)
300 IF (CTR .EQ. 0.0) 395, 460
390 390 CTRF=10.0
400 PRINT 410
410 410 FORMAT (* BACKGROUND*, /**)
422 420 CONTINUE
425 READ(2, 156) TETA, READING
440 GO TO 167
460 460 CONTINUE
465 IF (TETA = EQ. 0.0) 470, 420
470 470 CONTINUE
480 END