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Light scattering studies of the crystallization of polyethylene terephthalate.

Takeo Yuasa

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LIGHT SCATTERING STUDIES OF THE
CRYSTALLIZATION OF POLYETHYLENE TEREPTHALATE

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 TEREPHTHALATE

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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 \( H_V \) and \( V_V \) 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:

\[
I_{H_V} = A \cos^2 \rho_2 \cos^2 \left( \frac{3}{U^3} \right) \left\{ (\alpha_t - \alpha_r) \left[ \cos^2 \left( \frac{\theta}{2} \right)/\cos \theta \right] \sin \nu \cos \nu \right. \\
\left. \times (4 \sin U - U \cos U - 3 \sin U) \right\}^2 \tag{1}
\]
\[ I_V = A \cos^2 \rho_1 V^2 \left( \frac{3}{u^3} \right)^2 \left\{ (\alpha_t - \alpha_s) (2 \sin U - U \cos U - Si U) \\
+ (\alpha_r - \alpha_s) (Si U - \sin U) \\
- (\alpha_t - \alpha_r) \left[ \cos^2 \left( \frac{\theta}{2} \right) \cos \theta \right] \cos^2 \mu (4 \sin U - U \cos U \\
- 3 Si U) \right\}^2 \]

where the terms are defined below.

- \( A \) = constant of proportionality
- \( V \) = volume of the spherulite
- \( \cos \rho_2 = \cos \theta / (\cos^2 \theta + \sin^2 \theta \sin^2 \mu)^{1/2} \)
- \( \cos \rho_1 = \cos \theta / (\cos^2 \theta + \sin^2 \theta \cos^2 \mu)^{1/2} \)

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

- \( R \) = 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)
\[ \alpha_t = \text{tangential polarizability of the spherulite} \]
\[ \alpha_r = \text{radial polarizability of the spherulite} \]
\[ \alpha_S = \text{polarizability of the surroundings} \]
\[ \text{Si} U = \int_0^U \left( \frac{\sin x}{x} \right) \, dx \]

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. \( \cos \varphi_2 \) 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

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

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

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

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). \( I_{H_W} \) 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, \( I_{H_W} \) 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 \( I_{H_W} \), the equation of \( I_{V_W} \) 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:

\[
(\alpha_t - \alpha_s) \phi_{V_W}^A = (\alpha_t - \alpha_s) \left( 2 \sin U - U \cos U - Si U \right)/U^3 \quad (6)
\]

\[
(\alpha_r - \alpha_s) \phi_{V_W}^B = (\alpha_r - \alpha_s) \left( Si U - \sin U \right)/U^3 \quad (7)
\]
Since Equations (6) and (7) do not involve $\mu$, they show circular patterns which are independent of $\mu$. Moreover, $I_{V_V}$ is more intense than $I_{H_V}$ because the $(\alpha_t - \alpha_r)$ term in Equation (2) is very similar to $I_{H_V}$. As spherulites grow, $(\alpha_t - \alpha_s)$ and $(\alpha_r - \alpha_s)$ get greater. As a result, $I_{V_V}$ 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 $I_{V_V}$ 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 $I_{V_V}$ 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, $I_{V_V}$ decreases. In other words, $I_{V_V}$ 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 $I_{V_V}$ becomes comparable to $I_{H_V}$. 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, \( \cos \theta = 1 \), \( \cos \rho_2 = 1 \), \( \cos \rho_1 = 1 \).

\[
I_{H_V} = A V^2 \left[ (\alpha_t - \alpha_r) \phi_{H_V} (U) \right]^2 (\sin 45 \cos 45)^2
\]

\[
= A V^2 \left[ (\alpha_t - \alpha_r) \phi_{H_V} (U) \right]^2 (\frac{1}{4}) \quad (8)
\]

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

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

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

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

(11)

Therefore, if one plots \([I_{VV} (\mu = 0)]^{1/2} - [I_{VV} (\mu = 90)]^{1/2}\) against \([I_{HV} (\mu = 45)]^{1/2}\), 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:
\[ I_{H_V} = K_2 \phi_s \cos^2 \rho_2 R^3 \{ (\alpha_t - \alpha_r) \left[ \cos^2 \left( \theta/2 \right)/\cos \theta \right] \sin \mu \cos \mu \phi_{H_V}^2(U) \} \]

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 \( V_V \) mode is:

\[ I_{V_V} = K_1 \cos^2 \theta_1 V^2 B (\phi_s) \left\{ (\alpha_t - \alpha_d) \phi_{V_V}^A(U) + (\alpha_r - \alpha_d) \phi_{V_V}^B(U) \right\} - (\alpha_t - \alpha_r) \left[ \cos^2 \left( \theta/2 \right)/\cos \theta \right] \cos^2 \mu \phi_{H_V}^2(U) \]

(14)
where the terms are

\[ K_1 = \text{constant of proportionality} \]

\[ \alpha_d = \phi_s \left( \frac{\alpha_r + 2\alpha_t}{3} \right) + (1 - \phi_s) \alpha_m \quad (15) \]

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

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

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

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

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:

$$(\alpha_t - \alpha_r)_c^0 = \text{intrinsic anisotropy of pure crystal}$$

$$(\alpha_t - \alpha_r)_a^0 = \text{intrinsic anisotropy of amorphous}$$

$\phi_{cs} = \text{volume fraction crystallinity of inside spherulites}$
\( f_{cs}, f_{as} \) = orientation functions of the crystals and the amorphous segments with respect to the spherulite radius

\[(\alpha_t - \alpha_r) F_s = \) 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, \( a = 4.56 \text{Å}, b = 5.94 \text{Å}, c = 10.75 \text{Å}, \alpha = 98.5^0, \beta = 118^0, \gamma = 112^0 \). 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:
\[ \Delta_s = n_t - n_r = 2 \pi \left( \frac{n^2 + 2}{\bar{n}} \right)^2 (\alpha_t - \alpha_r) \]  

(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 \( \bar{n} = (n_r + 2n_t)/3 \).

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:

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

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:

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

(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 $I_{Hv}$, $I_{Vv}$ 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:

$$R(\theta, \mu) = \frac{I(\theta, \mu)}{I_0} \times \frac{F_c}{V} \times k$$ (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 \( H_V \) 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 \( \theta_{\text{max}} \) where the \( H_V \) 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 \( H_y \) 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 $I_{EXP}$ is given by

$$I_{EXP} = I_{OBS} - I_B$$

where $I_{OBS}$ 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:

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

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

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

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

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

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 \( [I_{H_V}(\mu = 45)/I_{H_V}(\mu = 0)]_{\text{U}=4} \). This relation is also graphically given (Figure 6). One can obtain \( f_{cs} \), 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), $R_{\text{THEO}}$, is given by

$$R_{\text{THEO}} (\theta, \mu) = f \cdot K \cdot F \cdot R_{\text{EXP}}$$

(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 $I_{yV}$, 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°C for 15 minutes in a silicone oil bath. They were then rapidly transferred to a crystallizing bath at 110°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°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 $\theta = 0$ 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 $\theta$ 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 $\rho_a = \text{density of complete amorphous polymer} = 1.335$

$\rho_c = \text{density of complete crystalline polymer} = 1.455$ (47)

$\rho = \text{density of sample}$
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:

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

(28)

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:

$$\lambda = \frac{\lambda_0}{n}$$

$$\theta_{\max} = \sin^{-1} \left( \sin \frac{\theta'_{\max}}{n} \right)$$
where $\lambda_0$ = wavelength of the incident light in air

$n$ = refractive index of the sample

$\theta_{max}$ = observed scattering angle

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

$$R = \frac{4.1}{2} \frac{\lambda_0}{\pi \theta_{max}}$$ (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 $45^\circ$ 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 $\phi_s$ 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 $\mu = 0^\circ$ and $90^\circ$ 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 $\mu = 0^\circ$ and $\mu = 90^\circ$. 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 $\mu = 0^\circ$
are greater than those at \( \mu = 90^0 \). 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\(^0\)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:

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

(30)

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 \( \ln \left[ -\ln \left( \frac{(V_t - V_\infty)}{(V_0 - V_\infty)} \right) \right] \) 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 \( \mu \)/min and the limiting radius, \( R_\infty \), is 6.98\( \mu \). These values also depend upon the nucleation process, the sample preparation and the experimental method. Therefore, the numerical results cannot be compared directly.

\( R_\infty \) 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:

$$\dot{\phi}_c = \phi_{cs} [1 - \exp (-kt^3/3)]$$  \hspace{1cm} (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):

$$G = G_0 \exp (-\Delta f^*/kT) \exp (-\Delta F^*/kT)$$  \hspace{1cm} (32)
where $G = \text{spherulite growth rate (or the rate of nucleation)}$

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

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

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

$k = \text{Boltzmann constant}$

$T = \text{crystallization temperature}$

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 $180^\circ\text{C}$. 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:

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

(33)

where $C_1, C_2 = \text{constant (6464 J/mole, } 24^\circ\text{K)}$  
$R = \text{gas constant (8.31 J/mole } - ^\circ\text{K)}$  
$\Delta T = T_m - T \text{ supercooling}$

and

$$K = \frac{4 b_0 \sigma \sigma_e}{k \Delta H_f} \quad ( = 942^\circ\text{K})$$

where $b_0 = \text{thickness of polymer chain (length of C axis 10.75Å)}$  
$\sigma = \text{interfacial free energy between the crystalline and the amorphous state for the faces parallel to the chain direction}$  
$\sigma_e = \text{interfacial free energy for the face perpendicular to the chain direction}$  
$\Delta H_f = \text{heat of fusion per mole of monomer units}$
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 $T_g = 340^\circ K$ and $T_m = 573^\circ K$, 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 $T = 110^\circ C$. However, the quenched sample in the $0^\circ C$ 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:

$$ R_{H_V} (\theta, \mu) = \frac{144 \pi^4}{\lambda_0^4} \phi_s V \cos^2 \rho_2 (\alpha_t - \alpha_r)^2 \phi_{H_V} (U) $$

$$ \times \cos^4 \left( \frac{\theta}{2} \right) \cos^2 \mu \sin^2 \mu $$

(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

$$ (\alpha_t - \alpha_r) = (\alpha_t - \alpha_r)^0 f_{cs} (\phi_c/\phi_s) $$

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

$\cos^2 \rho_2 = 1$ for small $\theta_{max}$

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

$\cos^2 \mu = \sin^2 \mu = 0.5$ for $\mu = 45^0$

$U = 4.1$ for $\theta = \theta_{max}$

$\phi_{Hv}(U) = -0.0889$ for $U = 4.1$

$\lambda_0 = 5461$A for the green-filtered radiation of mercury lamp
Substituting all values and Equation (35) into Equation (34), it reduces to

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

\[
\left( \frac{\phi_c^2}{\phi_S} \right)
\]

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:

\[
\phi_S = \frac{13.08 \times 10^{18} R^3 \left[ (\alpha_t - \alpha_r)_c f_{cs} \right]^2 \phi_c^2}{R_{HV} (\theta_{max}, 45^0) \exp \cdot f \cdot K \cdot F}
\]
As has already been mentioned in Chapter II, \((\alpha_t - \alpha_r)_c^0\) 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

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

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, \((\alpha_t - \alpha_r)_c^0\) can be obtained and it is 0.01254. If we suppose that the \(c\) axis of the crystal of polyethylene terephthalte
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) \pi 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

$$\phi_S = \frac{R^3}{R_\infty^3}$$

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 $[R_6^6 \text{ (5 minutes)} \rightarrow R_\infty^6]$, 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 \((\alpha_t - \alpha_r)_c\) 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 \(H_v\) 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 \(H_v\) 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 \( V_{V} \) 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 \( \theta = \theta_{\text{max}} \). 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 \( V_{V} \) scattering intensities is as follows. From Equation (14) one can derive the equation:

\[
\sqrt{I_{V_{V}}} (\mu = 90) - \sqrt{I_{V_{V}}} (\mu = 0) = \sqrt{K_1} \sqrt{B(\phi_s)} \\
R^3 |(\alpha_t - \alpha_r) \phi_H (U)|
\]

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:

\[
I_{H_{v}} = A \cos^{2} \rho_{1} \frac{V^{2}}{V_{p}} \{ \phi_{H_{v}}^{'} (U) \cdot f (\theta, \mu) \}^{2}
\]  

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 \( H_{v} \), \( V_{v} \) 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 $V_V$ scat-
tering intensity quantitatively at the present moment. However, Samuels
tried to interpret the $V_V$ observation quantitatively. He made a polypro-
pylene 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 ($\alpha_d$) he got $\alpha_t$ and $\alpha_r$. He then calculated the theoretical $V_V$ patterns using Equation (2) and substituting these polarizabilities. When those theoretical patterns matched the experimental $V_V$ patterns, the assigned $\alpha_d$ represented the true $\alpha_d$. Comparing this $\alpha_d$ 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 intensity.

Consequently a plot of $\sqrt{I_{V_V}(\mu = 0^\circ)} - \sqrt{I_{V_V}(\mu = 90^\circ)}$ 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 $V_Y$ scattering observations. However, the method of application of the theory for $V_Y$ scattering has not been yet established. Therefore, further study is necessary to interpret the $V_Y$ 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.
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CAPTIONS FOR TABLES

I. Experimental data of the Rayleigh ratios, $R_{hv}^{(\theta \max, \mu = 45^0)}$, $R_{vv}^{(\theta \max, \mu = 0^0)}$ and $R_{vv}^{(\theta \max, \mu = 90^0)}$ and of the degree of crystallinity, $\phi_c$, and the refractive index, $n$.

II. Correction factors for the $H_v$ scattering intensities.

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

III. Quantitative analysis of the $H_v$ scattering intensities.

- $\phi_s =$ volume fraction of spherulites
- $\phi_{cs} =$ crystallinity inside of the spherulites
- $\phi_{cm} =$ crystallinity outside of the spherulites
- $\alpha_d =$ average polarizability of the sample per unit volume
- $\alpha_m =$ average polarizability outside of the spherulite per unit volume
- $\phi_{cm} =$ 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:

\[ R_V / K_1 = B(\phi_s) R^6 \left( (\alpha_t - \alpha_d) \phi_{V_V}^A + (\alpha_r - \alpha_d) \phi_{V_V}^B - (\alpha_t - \alpha_r) \phi_{V_V}^C \right)^2 \]

If one assumes $\phi_{cs}$ is constant and 0.3954, $(\alpha_t - \alpha_r)$ is constant and 0.00164. Using $\alpha_d$ and $\alpha_m$ in Table III, one can calculate $B(\phi_s)$ with Equation (15).

If one assumes $\phi_{cm}$ is zero, $(\alpha_t - \alpha_r)$ can be obtained from the equation $(\alpha_t - \alpha_r) c \phi_{cs}$ where $(\alpha_t - \alpha_r) c = 0.00414$. 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 \( R_{\nu \nu} / K \).

\[
\sqrt{B(\phi_s)} = \frac{\sqrt{KR_{\nu \nu} (\mu = 0^0)} - \sqrt{KR_{\nu \nu} (\mu = 90^0)}}{\sqrt{K_1} R^3 |(\alpha_t - \alpha_r)| \phi_{H_{\nu \nu}} (4.1)|}
\]

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.
**TABLE I**

**EXPERIMENTAL DATA OF THE RAYLEIGH RATIOS**

<table>
<thead>
<tr>
<th>Cryst. Time</th>
<th>$R_{HV} (\theta_{max}, \mu = 45^0)$</th>
<th>$R_{V_H} (\theta_{max}, \mu = 0^0)$</th>
<th>$R_{V_V} (\theta_{max}, \mu = 90^0)$</th>
<th>$\phi_c$</th>
<th>$n$</th>
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<td>2160</td>
<td>708</td>
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TABLE II
CORRECTION FACTOR FOR $H_V$ SCATTERING INTENSITIES

<table>
<thead>
<tr>
<th>Cryst. Time</th>
<th>$T$ (%)</th>
<th>$\tau_d$</th>
<th>$K$</th>
<th>$\frac{R_{HV} (\mu = 45)}{R_{HV} (\mu = 0)}$</th>
<th>$\delta$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>50.5</td>
<td>0.72</td>
<td>1.38</td>
<td>2.82</td>
<td>0.225</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>42.9</td>
<td>0.82</td>
<td>1.46</td>
<td>4.50</td>
<td>0.212</td>
<td>16</td>
</tr>
<tr>
<td>20</td>
<td>30.5</td>
<td>1.25</td>
<td>1.80</td>
<td>4.27</td>
<td>0.213</td>
<td>17</td>
</tr>
<tr>
<td>30</td>
<td>38.1</td>
<td>0.99</td>
<td>1.59</td>
<td>4.56</td>
<td>0.212</td>
<td>16</td>
</tr>
<tr>
<td>45</td>
<td>41.9</td>
<td>0.92</td>
<td>1.42</td>
<td>4.23</td>
<td>0.213</td>
<td>17</td>
</tr>
<tr>
<td>60</td>
<td>36.2</td>
<td>0.99</td>
<td>1.59</td>
<td>4.83</td>
<td>0.211</td>
<td>15</td>
</tr>
<tr>
<td>90</td>
<td>24.8</td>
<td>1.32</td>
<td>1.88</td>
<td>3.41</td>
<td>0.219</td>
<td>22</td>
</tr>
<tr>
<td>120</td>
<td>36.2</td>
<td>1.02</td>
<td>1.59</td>
<td>3.84</td>
<td>0.216</td>
<td>19</td>
</tr>
<tr>
<td>Cryst. Time</td>
<td>$\phi_s$</td>
<td>$\phi_{cs}$</td>
<td>$\phi_{cm}$</td>
<td>$a_m \times 10^2$</td>
<td>$a_d \times 10^2$</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.101</td>
<td>1</td>
<td>0.076</td>
<td>0.076</td>
<td>7.83</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.125</td>
<td>0.934</td>
<td>0.077</td>
<td>0.077</td>
<td>7.85</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.501</td>
<td>0.584</td>
<td>0.189</td>
<td>0.189</td>
<td>7.90</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.634</td>
<td>0.556</td>
<td>0.279</td>
<td>0.279</td>
<td>7.96</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>0.889</td>
<td>0.416</td>
<td>0.165</td>
<td>0.165</td>
<td>7.89</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>0.395</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>1.0</td>
<td>0.404</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>1.0</td>
<td>0.404</td>
<td>0.02</td>
<td>-</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 \times 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>8.3</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 $V_V$ Scattering Intensities

<table>
<thead>
<tr>
<th>Cryst. Time</th>
<th>$K_{R_{V_V}}$</th>
<th>$\phi_{CS} = \text{Constant}$</th>
<th>$\phi_{cm} = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B(\phi_s)$</td>
<td>$\frac{R_{V_V}}{K_1} \times 10^{31}$</td>
<td>$\sqrt{B(\phi_s)}$</td>
</tr>
<tr>
<td>5</td>
<td>93.2</td>
<td>0.11</td>
<td>0.204</td>
</tr>
<tr>
<td>10</td>
<td>171.6</td>
<td>0.14</td>
<td>0.665</td>
</tr>
<tr>
<td>20</td>
<td>660.0</td>
<td>0.84</td>
<td>107.5</td>
</tr>
<tr>
<td>30</td>
<td>1073</td>
<td>0.92</td>
<td>577.8</td>
</tr>
<tr>
<td>45</td>
<td>1108</td>
<td>1.66</td>
<td>3025</td>
</tr>
<tr>
<td>60</td>
<td>2119</td>
<td>1.0</td>
<td>7905</td>
</tr>
<tr>
<td>90</td>
<td>5917</td>
<td>1.0</td>
<td>32850</td>
</tr>
<tr>
<td>120</td>
<td>3370</td>
<td>1.0</td>
<td>9382</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 $H_Y$ intensities with truncation parameters using the curve $V = 1$.

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

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

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

6. The variation of ratio of $H_Y$ intensities at $\omega = 4.0, \mu = 45^0$ to that at $\mu = 0^0$ and $15^0$ 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 $H_Y$ and $V_Y$ light scattering patterns of polyethylene terephthalate crystallized at $110^0C$ for 90 minutes from the melt.

10. $H_Y$ scattering patterns during the spherulitic growth of PET when crystallized from the melt at $110^0C$.

11. A plot of spherulite radius as a function of crystallization times of PET samples crystallized from the melt at $110^0C$. 
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 $\mu = 45^\circ$ for various crystallization times.

15. Maximum $H_V$ intensities with crystallization times at $\theta = \theta_{\text{max}}$ and $\mu = 45^\circ$.

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 $\sqrt{I_{V_V}(\mu = 0^\circ)} - \sqrt{I_{V_V}(\mu = 90^\circ)}$ vs. $\sqrt{I_{H_V}(\mu = 45^\circ)}$ for all samples.
\[ \bar{a} = 5 \, \mu m \]

\[ \lambda = 0.4280 \, \mu m \]

**FIG. 1**

Truncation parameter \( (\sigma^2/\bar{a}^2) \)

\[ (\theta = \pi) \] in air

\[ \text{in air}, \quad \text{in air} \]
FIG. 3

\( (p^2 \eta^2 \eta) \Pi \)
FIG. 5

\[
\frac{I_{HV}(S=0)}{I_{HV}(S=x)} \quad \text{at } U_1 = 4
\]

\(\omega = \text{Random}\)

\(\omega = 0\)
FIG. 8

INCIDENT BEAM

SCATTERED BEAM

VERTICAL DIRECTION

LIGHT SOURCE (LASER)

PHOTOGRAPHIC FILM

ANALYZER

SAMPLE

HORIZONTAL DIRECTION

X

Y

Z

\( \mu \)
FIG. 14 PET Crystallization at 110°C from the melt

Time (min)

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

\[ \theta \]
Crystallization of PET at 110°C from the melt

FIG. 15
FIG. 17  Crystallization Time (min)

- 120
- 90
- 60
- 45
- 30
- 20
- 10
- 5
FIG. 18
PET Crystallization at 110°C from the melt

Crystallization Time (min)
D 120
D 90
A 60
A 45
D 30
O 20
D 10
O 5

$R_{vv} (\mu = 90^\circ)$ vs. $U$
FIG. 21 Crystallization of PET at 110°C from the melt

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

Crystallinity vs. Time (min)
FIG. 22

\[ \ln \left\{ \ln \left( \frac{V_t - V_0}{V_0} \right) \right\} \] vs \[ \ln t \]
FIG. 24

CRystallization Time (min.)

0 30 60 90 120

$\frac{s}{\phi}$

0.2 0.4 0.6 0.8 1.0
FIG. 25 Crystallization of PET at 110°C from the melt

\[ \sqrt{R_{V_V}(\mu = 90^\circ)} - \sqrt{R_{V_V}(\mu = 0^\circ)} = \sqrt{R_{H_V}(\mu = 45^\circ)} \]
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, GSF,
00110+ TAPE1=NOMBRE, TAPE2=SELECT, TAPE3=COMPUTE, TAPE4=GSF)
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), MUC(20)
00200 DIMENSION SA(20), AC(20), STH(20), THETA(20), GAMM(20)
00210 DIMENSION SUM(25), SUM6(25), SUM7(25), SUMV(25), SUMV6(25)
00220 DIMENSION SUMINT(10, 2, 25), AIRE(20), SUMA(20)
00230 DO 20 IEM=1,10
00240 SUM(IEM)=0 $ AIRE(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(GSF)
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 LAMBD= 0.00005461
00390 C= 126300.
00400 ARMAT= -0.003
00410 DELALP=(2.*PI)/FLOAT(NINC-1)
00420 XK=2.*PI/LAMBD
00430 DELGAMR=(2.*PI)/FLOAT(NINC-1)
00440 DO 450 63
00450 CALL NOMERE
00460 CALL USECN
00470 CALL USEC
00480 CALL USECCC
00490 CALL USECC
00500 CALL USECCC
00510 CALL USECCC
00520 CALL USECCC
00530 CALL USECCC
00540 CALL USECCC
00550 CALL USECCC
00560 CALL USECCC
00570 CALL USECCC
00580 CALL USECCC
00590 CALL USECCC
00600 CALL USECCC
00610 CALL USECCC
00620 CALL USECCC

00630 DO 20 IJ=1,N
00640 X(IJ)=X(IJ)-SPHX(IJ)
00650 IF(X(IJ)<=.0.)42,44
00660 42 X(IJ)=X(IJ)+.01
00670 44 Y(IJ)=Y(IJ)-SPHY(IJ)
D(I,J) = X(I,J)**2 + Y(I,J)**2
IF(I,J .EQ. 1) GO TO 60
DIFF = D(I,J) - D(K)
IF(DIFF .GE. 0.) GO TO 60
K = I,J
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, 82
77 IF(X(J) .GT. 0.) 78, 80
78 GAM(J) = 90. - GAM(J)
G0 TO 90
G0 TO 90
82 IF(X(J) .GT. 0.) 83, 85
83 GAM(J) = 90. + GAM(J)
G0 TO 90
G0 TO 90
85 GAM(J) = 270. - GAM(J)
GAMMA = GAM(J)
DO 10 KK = 1, N
IF(KK .EQ. K) GO TO 98
IF(GAM(KK) .LE. GAMMA) 102, 98
GAM(J) = GAM(KK) - GAMMA
GO TO 110
GAM(KK) = GAM(KK) + 360. - GAMMA
100 IA = N - 1
DO 136 I = 1, 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)
GAM(J) = V1
D(J) = V4
X(J) = V2
Y(J) = V3
135 CONTINUE
136 CONTINUE
DO 155 J = 1, N
IF(Y(J) .EQ. 0.) 142, 144
142 HM(JJ) = 1000.
GO TO 146
01140 144 HM(JJ) = X(JJ)/Y(JJ)
01150 146 XMID(JJ) = X(JJ)/2.
01160 YMID(JJ) = Y(JJ)/2.
01170 HC(JJ) = YMID(JJ) - HM(JJ) * XMID(JJ)
01180 155 CONTINUE
01190 HC(N+1) = HC(1)
01200 HM(N+1) = HM(1)
01210 GAM(N+1) = 360.
01220 KJ = 1
01230 IN = 0
01240 PRINT 165
01250 165 FORMAT(/6X,*NO*, 6X,*XINT*, 7X,*YINT*, 7X,*AJ*, 5X,*GAMMA*
01260+ , 5X,*THETA*)
01270 XINT(1) = 0. $ YINT(1) = 0.
01280 172 JJJ = KJ + 1
01290 IF(IN .GE. 1) GO TO 177
01300 M = N
01310 GO TO 180
01320 180 M = N + 1
01330 180 IC = KJ + 1
01340 DO 300 JJ = IC, M
01350 ANGLE = GAM(JJ) - GAM(KJ)
01360 IF(ANGLE .EQ. 0.) GO TO 300
01370 IF(ANGLE .GE. 179.) GO TO 302
01380 XINT(JJ) = (HC(KJ) - HC(JJ))/(HM(JJ) - HM(KJ))
01390 YINT(JJ) = XMID(JJ) * HM(KJ) + HC(KJ)
01400 TH(JJ) = (XINT(KJ) - XINT(JJ))**2 + (YINT(KJ) - YINT(JJ))**2
01410 IF(JJ .EQ. KJ + 1) GO TO 300
01420 IF(TH(JJ) .LE. TH(JJJ)) GO TO 300
01430 300 JJJ = JJ
01440 300 CONTINUE
01450 302 IN = IN + 1
01460 IF(YINT(JJJ) .EQ. 0.) GO TO 305, 310
01470 305 YINT(JJJ) = YINT(JJJ) + .01
01480 310 SIXTH(IN) = XINT(JJJ) / YINT(JJJ)
01490 THETA(IN) = ATAN(SIXTH(IN))
01500 THETA(IN) = 180. * THETA(IN) / PI
01510 IF(YINT(JJJ) .GE. 0.) GO TO 322
01520 THETA(IN) = THETA(IN) + 180.
01530 GO TO 326
01540 322 IF(XINT(JJJ) .GE. 0.) GO TO 326
01550 THETA(IN) = THETA(IN) + 360.
01560 326 XYXY = 0.
01570 IF(THETA(IN) .LT. GAMMA) GO TO 336
01580 THETA(IN) = THETA(IN) - GAMMA
01590 GO TO 340
01600 336 THETA(IN) = THETA(IN) + 360. - GAMMA
01610 340 XXINT(IN) = XINT(JJJ) + SFH(15)
01620 YYINT(IN) = YINT(JJJ) + SFH(15)
01630 SA(IN) = XMID(KJ)**2 + YMID(KJ)**2
01640 A(IN) = SQRT(SA(IN))
GAMM(IN) = GAM(MIN)

IF(GAMM(IN) .LE. 360.) GO TO 370

GAMM(IN) = GAMM(IN) - 360.

PRINT 372, IN, XXINT(IN), YYINT(IN), A(IN), GAMM(IN), THETA(IN)

372 FORMAT(5X, I2, 5X, F6.2, 5X, F6.2, 5X, F5.2, 5X, F5.1, 5X, F5.1)

KJ = JJJ

IF(JJJ .GE. M) 400, 172

DO 450 IEM = 1, 10

READ 397, DELRMAX

WRITE 397, FORMAT(F5.2)

XILM = IBM

PMAX = XEM*DELRMAX

PRINT 399, RMAX

WRITE 399, FORMAT(/, 'AMEAN, VAR, VARAA, A, GAMM, THETA, IN, LL, LNUM')

WRITE 412, AMEAN, VAR, VARAA

WRITE 410, 1800, 4100, CALL COMPUTEAMEAN, VAR, VARAA, A, GAMM, THETA, IN, LL, LNUM

WRITE 414, AMEAN, VAR, VARAA

MUC1 = 0.0

MUC2 = 45.0

DO 450 IST = 1, 25

STHETA = IST

STHETAR = STHETA*PI/180.

MUR = MUC*PI/180.

COSRH02 = COS(STHETAR)/SQRT(COS(STHETAR)**2 + SIN(STHETAR)**2)

SIN(MUR)**2)

COEF = C*COSRH02*ARMAT

KXX = XK*SIN(STHETAR)

DO 426 JJJ = 1, NINC

ALPHAR = 0.

DO 420 I = 1, NINC

AA = MUR - ALPHAR

AA = XKK*COS(AA)

BB = 2.*ALPHAR

BB = SIN(BB)

AD = AA*AI(I)

TR(I) = (COS(AD)/(AA**2)) + (AI(I)*SIN(AD)/AA) - (1./AA**2)*

BB

TI(I) = ((SIN(AD)/(AA**2)) - (AI(I)*COS(AD)/AA))*BB

CALL QSFCDELALP, TR, Z, NINC

EHVR = COEF*Z(NINC)

CALL QSFCDELALP, TI, Z, NINC

EHVI = COEF*Z(NINC)

DO 422 I = 2, NINC

AIR = AI(I)*AI(I-1)*SIN(DELALP)/2.

AIRE(1EM) = AI(1EM) + AIR

PRINT 424, AIRE(1EM)

DO 424 FORMAT(/, 'Spherulite area =', F6.3)

AIRE(1EM) = AIRE(1EM)
$02160 \ XIHV = (\times EH\%**2 + (EH\%**2)) / \text{AIRE2}$
$02170 \ Y3(JJJ) = XIHV$
$02180 \ D0 426 \ I = 1, NSPH$
$02190 \ G426 \ GAMMAR(I) = GAMMAR(I) + DELGAMR$
$02200 \ \text{CALL GSF}(\text{DELGAMR}, Y3, Z, \text{NINC})$
$02210 \ XIHV = Z(\text{NINC})$
$02220 \ XLOGIHV = XLOGIHV \times (XIHV)$
$02230 \ \text{PRINT} 428, STHETA, M\%U, XIHV, XLOGIHV$
$02240 \ \text{FORMAT}(10X, F6.2, 5X, F5.2, 5X, E12.3, 5X, E12.3)$
$02250 \ \text{SUMINT}(\text{IEM}, ICS, IST) = \text{SUMINT}(\text{IEM}, ICS, IST) + XIHV$
$02260 \ \text{SUM}(\text{IEM}) = \text{SUM}(\text{IEM}) + \text{AMean}$
$02270 \ \text{SUM}(\text{IEM}) = \text{SUM}(\text{IEM}) + \text{AMean}$
$02280 \ \text{SUM}(\text{IEM}) = \text{SUM}(\text{IEM}) + \text{AMean}$
$02290 \ \text{SUM}(\text{IEM}) = \text{SUM}(\text{IEM}) + \text{AMean}$
$02300 \ \text{SUM}(\text{IEM}) = \text{SUM}(\text{IEM}) + \text{VARAA}$
$02310 \ \text{SUM}(\text{IEM}) = \text{SUM}(\text{IEM}) + \text{VARAA} \times (\text{AMean})$
$02320 \ \text{CONTINUE}$
$02330 \ \text{XNSPH} = \text{NSPH}$
$02340 \ \text{D0 600} \ \text{IEM} = 1, 10$
$02350 \ \text{XIEM} = IEM$
$02360 \ \text{RMAX} = IEM \times DElRMAX$
$02370 \ \text{PRINT} 399, \text{RMAX}$
$02380 \ \text{AAVG} = \text{SUM}(\text{IEM}) / \text{XNSPH}$
$02390 \ \text{AAVG} = \text{SUM}(\text{IEM}) / \text{SUM}(\text{IEM})$
$02400 \ \text{VARAVG} = \text{SUM}(\text{IEM}) / \text{XNSPH}$
$02400 \ \text{VARAVG} = \text{SUM}(\text{IEM}) / \text{SUM}(\text{IEM})$
$02420 \ \text{PRINT} 471, \text{AAVG}, \text{AAVG}$
$02430 \ \text{FORMAT}(10X, \%A AVG = *, F8.3, 10X, \%AAVG6 = *, F8.3)$
$02440 \ \text{PRINT} 476, \text{VARAVG}, \text{VARAVG6}$
$02440 \ \text{FORMAT}(10X, \%VARAVG = *, F9.4, 7X, \%VARAVG6 = *, F9.4)$
$02460 \ \text{PRINT} 480, \text{SUM}(\text{IEM})$
$02470 \ \text{FORMAT}(10X, \%\text{TOTAL AREA} = *, F8.3)$
$02480 \ \text{AAA} = \text{SUM}(\text{IEM}) / \text{TOT}$
$02490 \ \text{PRINT} 490, \text{AAA}$
$02500 \ \text{FORMAT}(10X, \%\text{DEGREE OF SPHER.} = *, F5.3)$
$02510 \ \text{AAA} = \text{SUM}(\text{IEM}) / \text{XNSPH}$
$02520 \ \text{PRINT} 495, \text{AAA}$
$02530 \ \text{FORMAT}(10X, \%\text{AVERAGE AREA} = *, F8.6)$
$02540 \ \text{D0 600} \ \text{ICS} = 1, 2$
$02550 \ \text{PRINT} 500, \text{MU}(\text{ICS})$
$02560 \ \text{FORMAT}(10X, \%\text{AZIMUTHAL ANGLE} = *, F3.1)$
$02570 \ \text{PRINT} 510$
$02580 \ \text{FORMAT}(/\%\text{THETA}, 5X, \%\text{AVER. INT.}, 5X, \%\text{TOT. INT.}, 5X, \%\text{LOG. INT.}, /
\text{THETA}, 5X, \%\\text{INT.}, /)$
$02590 \ \text{D0 600} \ \text{IST} = 1, 25$
$02610 \ \text{STHETA} = \text{IST}$
$02620 \ \text{BBB} = \text{SUMINT}(\text{IEM}, ICS, IST) / \text{XNSPH}$
$02630 \ \text{AAA} = \text{ALOG10}((\text{SUMINT}(\text{IEM}, ICS, IST)))$
$02640 \ \text{PRINT} 520, \text{STHETA}, \text{BBB}, \text{SUMINT}(\text{IEM}, ICS, IST), \text{AAA}$
$02650 \ \text{PRINT} 520, \text{FORMAT}(10X, F3.1, 3*(5X, E12.3))$
$02660 \ \text{D0 600} \ \text{CONTINUE}$
$02660 \ \text{CONTINUE}$
$02660 \ \text{CONTINUE}$
$02660 \ \text{CONTINUE}$
$02670 \ \text{END}$
PROGRAM NOMBRE

00100 SUBROUTINE NOMBRE
00110* THIS SUBROUTINE IS USED IN THE MAIN PROGRAM TRUNK.
00120* IT SPECIFIES THE TOTAL NUMBER OF SPHERULITES (NUC) AND
00130* THE RADIUS OF THE CIRCLE (RCIR) IN WHICH THEY ARE LOCA
00140* IT ALSO SELECTS THE NUMBER OF SPHERULITES (NSPH) FOR WHICH
00150* THE SIZE AND TRUNCATION PARAMETER ARE CALCULATED
00160* IN THE PRESENT CASE NUCLEI AREGENERATED RANDOMLY.
00170* IF NUCLEI CENTERS ARE KNOWN, STATEMENTS FROM 70 TO 90
00180* SHOULD BE REPLACED BY READ STATEMENTS
00190 COMMON XX(850),YY(850),NUC
00200 COMMON SPHX(620),SPHY(600),NSPH
00210 COMMON X(100),Y(100),IS,N
00220 NUC=20
00230 RCIR=225.
00240 DO 90 I=1,NUC
00250 70 XX(I)=RANF(2)*450.
00260 YY(I)=RANF(0)*450.
00270 RADIUS=(225.-XX(I))**2+(225.-YY(I))**2
00280 RC0NST=225.*2
00290 IF(RADIUS .GE. RC0NST)GO TO 70
00292 IF(I .EQ. 1) GO TO 90
00295 IX=I-1
00300 DO 90 J=1,IX
00310 DIFF=(XX(I)-XX(J))**2+(YY(I)-YY(J))**2
00320 XDIF=0.01**2
00330 IF(DIFF .LT. XDIF)GO TO 70
00340 90 CONTINUE
00350 IJ=0
00360 DO 150 I=1,NUC
00370 CHECK=(XX(I)-225.)**2+(YY(I)-225.)**2
00380 XLIM=190.*2
00390 IF(CHECK .GE. XLIM)GO TO 150
00400 IJ=IJ+1
00410 SPHX(IJ)=XX(I)
00420 SPHY(IJ)=YY(I)
00430 150 CONTINUE
00440 NSPH=IJ
00450 PRINT 171,NUC
00460 171 FORMAT(/5X,*TOTAL NO. OF SPHERULITE CENTERS =*,14)
00470 PRINT 176,NSPH
00480 176 FORMAT(/5X,*NUMEBER OF SPHERULITES CONSIDERED=*,14)
00485 RETURN
00490 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(100),YY(100),NUC
00160 COMMON SPHX(600),SPHY(600),NSPH
00170 COMMON X(100),Y(100),I,N
00180 JI=0
00190 DO 100 I=1,NUC
00200 DCHECK=(XX(I)-SPHX(I))*2+(YY(I)-SPHY(I))*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
PROGRAM COMPUTE

00100 SUBROUTINE COMPUTE(AMEAN, VAR, VARAA, A, GAMM, THETA, IN, LL, LNUM)
00110* THIS SUBROUTINE IS USED WITH THE MAIN PROGRAM TRUNK
00120* IT CALCULATES THE AVERAGE SIZE AND THE TRUNCATION
00130* PARAMETER FOR EACH SPHERULITE.
00140 DIMENSION A(20), GAMM(20), THETA(20)
00150 DIMENSION AI(200), DA(200)
00160 DIMENSION LNUM(100)
00170 PI=4.*ATAN(1.)
00180 NINC=180
00190 XINC=NINC
00200 DELAL=360.*XINC
00210 AMEAN=0.
00220 J=1
00230 THETA(IN+1)=360.
00240 A(IN+1)=A(1)
00250 GAMM(IN+1)=360.+GAMM(1)
00260 DO 100 I=WNINC
00270 XI=I-1
00280 ALPHA=XI*DELAL
00290 ERRCR=THETAC(J)-ALPHA
00300 ERR=DELAL
00310 IFERROR.LT.ERR80,82
00320 80 J=J+1
00330 82 GAMAL=(GAMM(J)-ALPHA)*PI/180.
00340 AI(I)=ABS(A(J)/COS(GAMAL))
00350 IF(AI(I).GT.RMAX)85,90
00360 85 AI(I)=RMAX
00370 90 AMEAN=AMEAN+AI(I)
00380 100 CONTINUE
00390 AMEAN=AMEAN/XINC
00400 SQAM=AMEAN**2
00410 VAR=0.
00420 DO 150 I=1,NINC
00430 DA(I)=AI(I)-AMEAN
00440 VAR=VAR+DA(I)**2
00450 150 CONTINUE
00460 VAR=VAR/XINC
00470 VARAA=VAR/SQAM
00480 DO 220 L=1,IN
00490 A(L)=A(L)**2
00500 LL=A(L)
00510 LNUM(LL)=LNUM(LL)+1
00520 220 CONTINUE
00525 RETURN
00530 END
PROGRAM QSF

00100 SUBROUTINE GSF(H, Y, Z, NDIM)
00110 DIMENSION Z(NDIM), Y(NDIM)
00120 HT = 0.33333333333333333333
00130 IF(NDIM - 5) 330, 335, 145
00140 145 SUM1 = Y(2) + Y(2)
00150 SUM1 = SUM1 + SUM1
00160 SUM1 = HT*(Y(1) + SUM1 + Y(3))
00170 AUX1 = Y(4) + Y(4)
00180 AUX1 = AUX1 + AUX1
00190 AUX1 = SUM1 + HT*(Y(3) + AUX1 + Y(5))
00200 AUX2 = HT*(Y(1) + 3.875*(Y(2) + Y(5)) + 2.625*(Y(3) + Y(4)) + Y(6))
00210 SUM2 = Y(5) + Y(5)
00220 SUM2 = SUM2 + SUM2
00230 SUM2 = AUX2 - HT*(Y(4) + SUM2 + Y(6))
00240 Z(1) = 0.
00250 AUX = Y(3) + Y(3)
00260 AUX = AUX + AUX
00270 Z(2) = SUM2 - HT*(Y(2) + AUX + Y(4))
00280 Z(3) = SUM1
00290 Z(4) = SUM2
00300 IF(NDIM - 6) 295, 295, 235
00310 235 DO 290 I = 7, NDIM, 2
00320 SUM1 = AUX1
00330 SUM2 = AUX2
00340 AUX1 = Y(I-1) + Y(I-1)
00350 AUX1 = AUX1 + AUX1
00360 AUX1 = SUM1 + HT*(Y(I-2) + AUX1 + Y(I))
00370 Z(I-2) = SUM1
00380 IF(I - NDIM) 275, 310, 310
00390 275 AUX2 = Y(1) + Y(1)
00400 AUX2 = AUX2 + AUX2
00410 AUX2 = SUM2 + HT*(Y(I-1) + AUX2 + Y(I+1))
00420 290 Z(I-1) = SUM2
00430 295 Z(NDIM-1) = AUX1
00440 Z(NDIM) = AUX2
00450 RETURN
00460 310 Z(NDIM-1) = SUM2
00470 Z(NDIM) = AUX1
00480 RETURN
00490 330 IF(NDIM - 3) 440, 410, 335
00500 335 SUM2 = 1.125*HT*(Y(1) + Y(2) + Y(2) + Y(2) + Y(3) + Y(3) + Y(3) + Y(4))
00510 SUM1 = Y(2) + Y(2)
00520 SUM1 = SUM1 + SUM1
00530 SUM1 = HT*(Y(1) + SUM1 + Y(3))
00540 Z(1) = 0.
00550 AUX1 = Y(3) + Y(3)
00560 AUX1 = AUX1 + AUX1
00570 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))

395 Z(3) = SUM1

Z(4) = SUM2

RETURN

410 SUM1 = HT*(1.25*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

440 RETURN

END
PROGRAM SPHER

00100 PROGRAM SPHER(INPUT, OUTPUT)
00120* THIS PROGRAM CALCULATES HV 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 LAMBDA=0.00005461
00190 C=126300.
00200 ARMAT=-2.003
00220 PRINT 52, ARMAT, C
00230 52 FORMAT(//,10X,*WAVE LENGTH = 5461 A*,//10X,*POLARIZABILITY
00240+ DIFFERENCE =*,F5.4,//10X,*CONSTANT C=*,E9.1)
00270 READ(RR(J),J=1,21)
00280 DO 350 J=1,21
00290 R=RR(J)
00300 PRINT75,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*SINC(THETAR))/LAMBDA 
00410 COSRH02=COS(THETAR)/SORT(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*COSRH02*((PI*R*R)/(W**2))*(2*(1-J0W)-W*J1W)
00470+ *SIN(XX)
00480 XIHV=EHV*EHV
00500 XLOGIHV=ALOG10(XIHV)
00510 PRINT 225,THETA,MU,XIHV,XLOGIHV
00520 225 FORMAT(10X,F5.2,5X,F5.2,5X,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  NRAJ(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
37  PI = 3.1415927
38  CALL GET(SHTAPE1,4HDANE,0,0)
39  CALL GET(SHTAPE2,4HBCGR,0,0)
40  IF(C.EQ.1.) 101, 107
41  101 101 PRINT 102
42  102 102 FORMAT (\\\\\T\T THIS IS A THETA SCAN\\\\\T, 24X,********
43  103+---------------------)
44  104  GO TO 111
45  107 107 PRINT !08
46  108 108 FORMAT (\\\\\T\T THIS IS AN AZIMUTHAL SCAN \\
47  109+---------------------*)
48  110  GO TO 113
49  111 111 READ(1, 115)PMU
50  112  DPF2=1.
51  113 113 PRINT 114, S
52  114 114 FORMAT (\\\\\T\T SAMPLE = *F6.2)
53  115 115 FORMAT (F4.1)
54  116 PRINT 117
55  117 117 FORMAT (\\DATE = */*)
56  118 READ (1, 121) XN, TRANS, THICK, XK, RINC, RADII, VVI, DPF1, FM, SF
57  119 A=(THICK/1000.)*2.54
58  120 TD=AL CG(100., TRANS)
59  121 121 FORMAT(F5.3,F4.1,F5.1,F8.7,F4.2,F8.2,3(F5.4))
60  125 VOL=A*(RINC**2)*PI
61  130 PRINT 135, "N, TRANS, THICK, XK, RINC, RADII
62  135 135 FORMAT(5X,*REFRACTIVE INDEX
63  136+5X,*TRANSMITTANCE () = *,F7.3, /
64  137 THICKNESS (MILS) = *,F7.3, /, 5X,*APPARATUS CONSTANT
65  138+ (SQ. CM.) = *,F9.5, /, 5X,*INCIDENT BEAM RADIUS
66  139+ (CM) = *,F7.3, /, 5X,*RADIUS OF SPHERULITE (MICR
67  140+ONS) = *,F7.3//)
145 PRINT 146, TD, VOL
146 146 FORMAT (5X, *TURBIDITY = *, F5.3, /, 5X, *VOL. I PPA D.
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 CONTR=0
165 IF (TETA * EQ. 0.) GO TO 390
167 167 TETA=TETA*SF
170 TETAR=TETA*PI/180.
175 SINET=SINF(TETAR)
180 COSTET=CO SF(TETAR)
190 TETASR=ASINF(TETAR/XN)
195 COSTES=CO SF(TETASR)
200 TETAS=TETASR*180. /PI
205 CN=XN*XN*SQRTF(1.-(SINET/XN)**2.)/COSTET
215 PA=((XN-1.)/(XN+1.))**2.
220 ANGR=ASINF(SINET/XN)
225 ANGA=TETAR-ANGR
230 ANGB=TETAR+ANGR
235 TANA= TANF(ANGA)
240 TANB= TANF(ANGD)
245 SINA=SINF(ANGA)
250 SIND= SINF(ANGE)
254 XPMU=PMU*PI/180.
255 FC= (SINF(XPMU))**2
260 RC=(FC*(SINA/ SINB)**2.)*((1.-FC)* (TANA/TANB)**2.)
265 REFLEC=0.96/((1.-RA)*(1.-FC))
270 U=4.*PI*RADI I*XN*SINF(TETASR/2.)/5461
275 Z=READING*(3300. /VVI)*DP F1*DPF2
285 RAY=XX*CN*(REFLEC/VCL)*Z*FM
295 PRINT 296, TETA, TETAS, FMU, READING, RAY, U
296 296 FORMAT (F8.3, F10.3, F10.1, F12.1, F12.3, F12.3)
300 IF (CONTR * EQ. 0.0) 155, 460
390 390 CONTF=10.0
400 PRINT 410
410 410 FORMAT (* BACKGROUND*, /)
420 420 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