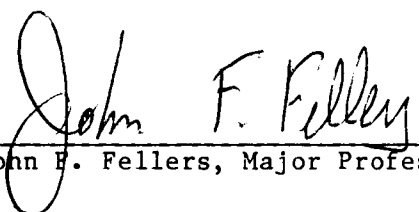
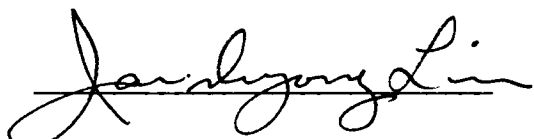


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QUANTITATIVE SMALL ANGLE LIGHT SCATTERING
OF LIQUID CRYSTALLINE COPOLYESTER FILMS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Lawrence J. Effler, Jr.

August 1987

DEDICATION

To Jesus Christ, with whom all things are possible.

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No piece of work is ever the sole result of one individual's efforts. Keeping this in mind, I would like to acknowledge the help and assistance of Dr. John F. Fellers, my major professor. Also, I would like to thank the Center for Material Processing for partially funding my research, and the National Center for Small Angle Scattering, for making available the 10 m small angle X-ray scattering camera at Oak Ridge National Laboratories. In addition, I would like to thank Steven Stiner, and Dr. David N. Lewis for their help with hardware and software problems. Additional help with user generated software was given by T. Levitte Cox. I would also like to acknowledge Dr. Donald G. Baird and Thomas Wilson of Virginia Polytechnic Institute for making available extrusion drawn films to be analyzed. Finally, I would like to thank the various staff and graduate student members of the University of Tennessee for their support, and help in preparing this work.

ABSTRACT

A new detection apparatus for small angle light scattering (SALS) was developed and used to characterize liquid crystalline copolyesters of poly(ethylene terephthalate) (PET), and para-oxybenzoic acid (POB). The detection device combines video and microcomputer technology to allow for a two-dimensional position sensitive detector SALS. Using this detector, the compression molded films of PET/POB were found to be composed of randomly ordered fibrillar domains, that do not orient upon cold stretching. Also, the size of these domains were found to be slightly dependent on their molding temperature, but independent of their cooling condition. Also, extrusion drawn films were found to contain a high degree of order suggesting that the copolyesters must have their orientation imposed while still in the melt. In performing this work, a unique analytical technique employing a polynomial regression analysis to data slices in the form of intensity versus the square of the scattering vector. It was found that the moments of the particle size distribution calculated from this analysis yielded values which were all very similar in magnitude. Indicating that higher moments of the size distribution calculated from the polynomial analysis are strongly influenced by the smaller particle sizes in the distribution.

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CHAPTER I

INTRODUCTION

The morphological nature of liquid crystalline copolyester films, their basic structural components, and extent or lack of orientation imposed by various processing techniques have been determined primarily through the use of a revolutionary characterization method. For years small angle light scattering (SALS) has been used mainly as a qualitative structural investigative tool. Mainly because photographic film or photo-multipliers the most readily available detecting device. Quantitative results could only be obtain through the use of a microdensitometer to determine the photographic density of the negative, or through changing the position of the photo-multiplier. Unless using an automated densitometer, this process can prove tedious and requires some skill on the part of the user. Thus, SALS has often lagged behind analogous scattering experiments such as small angle X-ray, and neutron scattering (SAXS, SANS) as a morphological tool for which electronic detectors are available. However, recent advances in micro-computers, coupled with breakthroughs in video imaging technology, have allowed for the creation of a two-dimensional position sensitive detector for SALS. One of the first video-SALS units was reported by Tabar, Stein, and Long in 1982 [1]. Their system allowed for a 3000 data point collection net or approximately 55x55 matrix, tied into a mini-computer. In the work presented here, a similar system has been developed and enhanced so that the data software digitizes the video image into a 249x236 grid on a micro-computer (IBM

PC). This system allows for iso-intensity contour plots to be taken, as well as data slicing and averaging. So, data collection and manipulation are reduced to a few keystrokes on the computer. Thus, it is now possible to easily perform Guinier, Debye, Porod analyses [2,3] and other common and novel data analyses using SALS.

Polymeric liquid crystals (PLC) made from the copolymerization of poly(ethylene terephthalate) (PET) and p-oxybenzoic acid (POB) were studied using the video-SALS system. These materials were selected, since the scattering pattern obtained from liquid crystalline systems depends highly on the process history of the sample being studied. Also, due to their rigid rod-like chemical structure, highly oriented samples can be made from the melt resulting in a specimen with enhanced mechanical properties in the direction of orientation. Much of the previous morphological work in PLC's has been done with systems oriented in the melt. In this work an examination of compression molded films was undertaken using films having been molded at different temperatures and cooled under three various conditions. Also, attempts were made to develop orientation by cold working the films, by stretching the films uniaxially at temperatures below their melting points. Finally, films that were extrusion drawn, courtesy of D. G. Baird and T. Wilson at Virginia Polytechnic Institute, were also studied. To supplement and confirm the SALS results, the films were also studied using SAXS, optical microscopy, and scanning electron microscopy.

To analyze the SALS patterns a new technique employing a polynomial regression analysis of the data in the form of intensity versus the square of the scattering vector was employed. This technique is truer to the original scattering function proposed by Debye, and allows for a wider range of data to be included in the analysis. Thus data is not arbitrarily included or excluded from the analysis. Also, the information regarding size distribution moments indicated that the higher moments calculated from the regression analysis tend to be strongly influenced by the smaller particle sizes due to the nature of reciprocal space.

CHAPTER II

ELECTROMAGNETIC SCATTERING, THEORY AND APPLICATION

General Scattering Theory

Introduction

When an electromagnetic wave strikes a molecule of a material, it disturbs the molecule's electron cloud. The electromagnetic field of the wave causes the cloud to oscillate sympathetically to the frequency of the impinging wave. Thus, the molecule becomes a source of electromagnetic radiation. If the molecule is dispersed in a matrix of identical molecules, with no long range order, the radiation that is emitted is canceled by the destructive interference of radiation emitted by the other molecules. However, if there are variations within the material, not all of the radiation will be suppressed, and scattering will occur [2,3]. So then, scattering arises from inhomogeneities within the material [2-9]. In the case of light scattering, these inhomogeneities are localized fluctuations in the dielectric constant, which in turn result in variations in the refractive index [2,3]. X-ray scattering arises from localized changes in the electron density, the number of electrons per unit volume, in the material [2,3]. Neutron scattering results from a change in nuclear density [2,3]. By measuring the scattered radiation the extent of these fluctuations can be determined. If the scattering is due to

particulates (spheres, rods, ellipsoids, etc.) the shape of the particles, their average size, and specific surface may be obtained.

A typical small angle scattering setup is shown schematically in Figure 2.1. A source device emits monochromatic radiation, that impinges on the specimen to be studied. The scattered radiation is then collected on a detection device such as photographic film, or some sort of electronic two-dimensional position sensitive detector. The desired theoretical variables are the scattering angle (θ), the azimuthal angle (μ), and the scattered intensity, at θ and μ or $I(\theta, \mu)$. However, measured laboratory variables are the sample-to-detector distance (SD), the distance from the center of the collected pattern to the point of interest (d), and either the photographic density of the film (D), the shade of gray (SG), or the number of counts (C). The value of θ is found by recognizing it as the $\tan^{-1}(d/SD)$. A number of methods can be employed to determine μ . It can be directly measured on a film pattern, or if a two-dimensional detector is used it can be given by the trigonometric expression: $\mu = \tan^{-1}[(y-cy)/(x-cx)]$, where x and y represent the location of the datum point, and cx and cy are the X,Y coordinates of the center of the pattern. In this scheme, the Y-axis is the meridional or vertical axis, and the X-axis is the equatorial, or horizontal axis. If a relative intensity scale is adequate for obtaining the desired information from the scattering pattern, not much manipulation is done to the measured value for intensity (film density, counts, etc.), except correcting for any background noise, and perhaps normalizing the intensity by the highest value. However, if intensity is desired on an absolute scale (cm^{-1}),

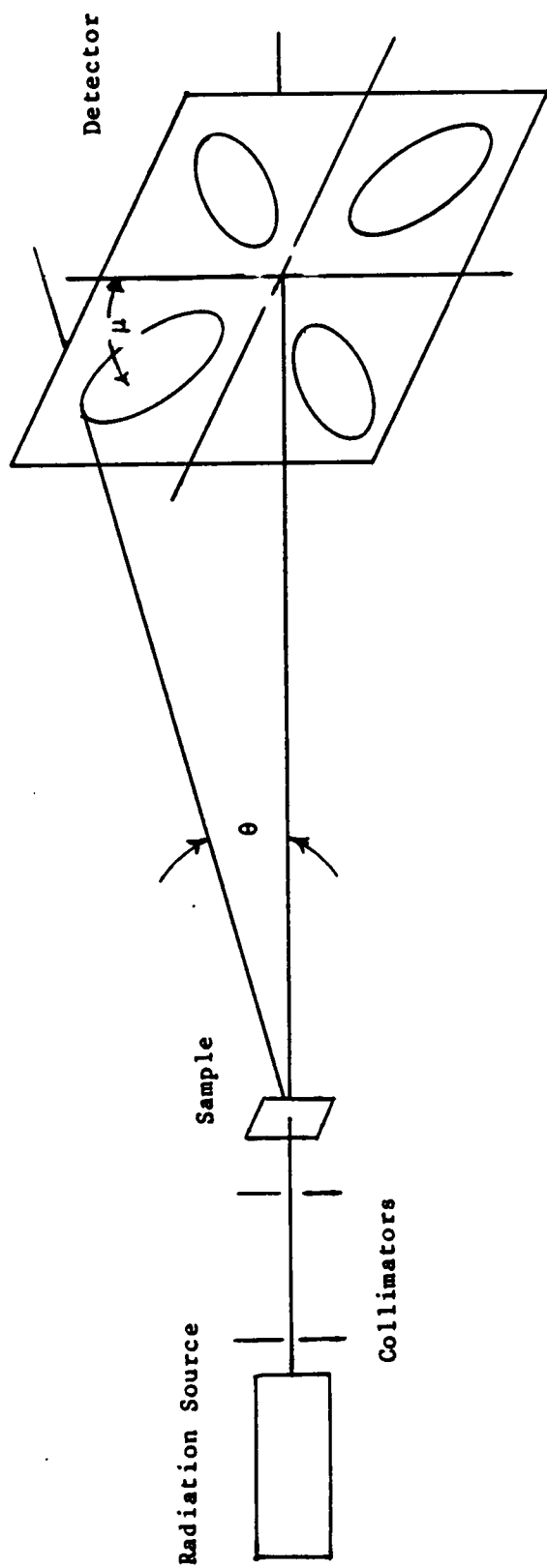


Figure 2.1: Typical small angle scattering setup.

a number of considerations must be made. These factors include sample thickness, beam diameter, absorption properties of the sample, the intensity of the primary beam, and the time frame of the experiment.

General Analyses

First, let's consider scattering in which the resulting pattern is statistically isotropic. In other words, the pattern is independent of orientation effects, and is only a function of size distribution. In 1915, P. Debye examined the problem of electro-magnetic scattering, and in particular X-ray scattering [4]. Using the Maxwell-Lorentz equations of electrodynamics, Debye was able to show that for an amorphous body containing N scattering centers, the ratio $(I(s)/I_0)$ of the intensity scattered at an angle, θ , to the primary beam is given by:

$$\frac{I(s)}{I_0} = N\gamma_T \frac{1+\cos^2(\theta)}{2} \frac{1}{L^2} \sum_i \sum_j \frac{\sin(sr)}{sr} \quad (2.1)$$

where: I_0 = the zero angle scattering intensity
 N = the number of scattering elements
 γ_T = Thompson scattering factor for a
 free electron = $7.94 \times 10^{-26} \text{ cm}^2$
 L = the sample to detector distance
 r = the separation between the i^{th} and
 j^{th} scattering element, and $i+j=N$
 $s = (4\pi/\lambda)\sin(\theta/2)$, commonly called the
 scattering vector
 λ = the wavelength of the primary beam

If only small scattering angles ($\theta < 10^\circ$) are considered the term $(1+\cos^2(\theta)/2) \rightarrow 1$. So Equation 2.1 becomes:

$$\frac{I(s)}{I_o} = \frac{N\gamma_T}{L^2} \sum_i \sum_j \frac{\sin(sr)}{sr} \quad (2.2)$$

The term $\sin(sr)/sr$ in the above equations is an oscillating decay function. The value of this function is dependent on the product of sr . As $sr \rightarrow 0$, $\sin(sr)/sr \rightarrow 1$, and as $sr \rightarrow \infty$, $\sin(sr)/sr \rightarrow 0$. Since the value of s is bounded by 0 and $2\pi/\lambda$, the value of r relative to λ will generally determine the rate of decay. This relationship is shown in Figure 2.2 a and b, which are plots of $\sin(sr)/sr$ versus θ . In Figures 2.2a, $\lambda = .6328 \mu\text{m}$, and four values of r , 1, 5, 10, and 50 μm , were used. One notes that as the value of r increases, the function $\sin(sr)/sr$ decays more rapidly. Thus, in the double summation, smaller center-to-center distances will have higher values over the entire scattering range than larger distances. Therefore, nearer neighbors will have a greater affect on the scattering behavior than more distant neighbors. The effect of wavelength is demonstrated in Figure 2.2b. In this plot, the value of r is kept constant at 5 μm , while curves using three values of λ , 0.1, 0.6328, and 1.0 μm , are plotted. As expected, the rate of decay is inversely related to the wavelength. So, the distances that are measured in a scattering experiment are dependent on the wavelength of light used. The separations will be more easily measured when using wavelengths of the same order of magnitude as the separation distances.

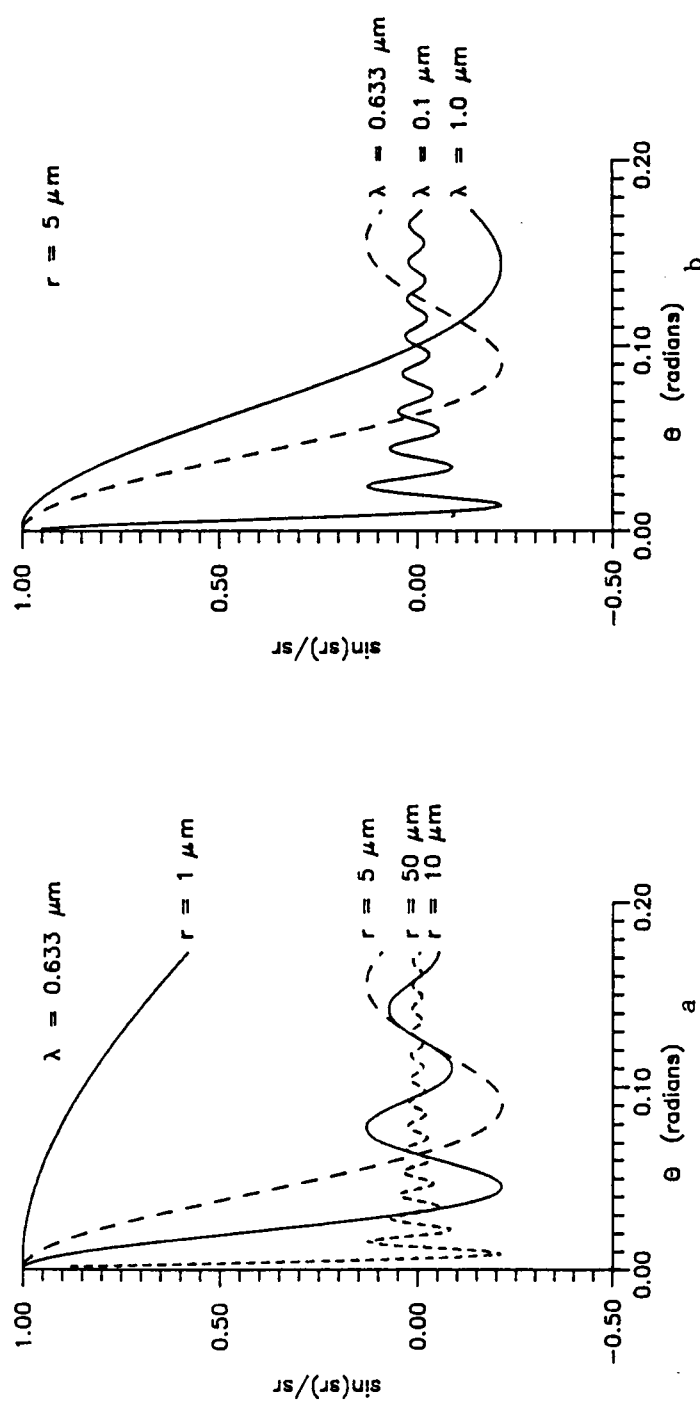


Figure 2.2: Plots of $\sin(sr)/sr$ vs. θ . a) $\lambda = 0.633 \mu\text{m}$, $r = 1, 5, 10, 50 \mu\text{m}$, b) $\lambda = 0.1, 0.633, 1.0 \mu\text{m}$, $r = 5 \mu\text{m}$.

Prior to the advent of computers, it was often difficult and tedious work to fit equation 2.2 to any experimental data. To circumvent this problem models were employed to approximate the scattering function. Perhaps the most famous of these models is the Guinier approximation [2,3,5]. If the term $\sin(sr)/sr$ is expanded by a Taylor's series, equation 2.2 becomes:

$$\frac{I(s)}{I_0} = \frac{N\gamma_T}{L^2} \sum_i \sum_j 1 - \frac{s^2 r^2}{3!} + \frac{s^4 r^4}{5!} - \dots \quad (2.3)$$

Now if the n^{th} moment of r is defined as:

$$\langle r^n \rangle = (1/N) \sum_i \sum_j r^n \quad (2.4)$$

then equation 2.3 may be expressed as:

$$\frac{I(s)}{I_0} = \frac{N\gamma_T}{L^2} \left(1 - \frac{s^2 \langle r^2 \rangle}{3!} + \frac{s^4 \langle r^4 \rangle}{5!} - \dots \right) \quad (2.5)$$

Guinier noted that if equation 2.5 is truncated after the quadratic term ($-s^2 \langle r^2 \rangle / 3!$), the series resembles the Taylor's series for $\exp(x)$, with $x = -s^2 \langle r^2 \rangle / 3!$ [5]. Furthermore, he defined an average radius-of-gyration ($\langle R_g \rangle$) such that $\langle R_g^2 \rangle = \langle r^2 \rangle / 2$. Also, N can be defined as $N = V\Delta\rho$, where V is the irradiated volume, and $\Delta\rho$ is the scattering contrast between the scattering elements and their surrounding matrix, per unit volume. For X-rays, $\Delta\rho$ is the electron density difference, while for light it's the change in refractive index.

Equation 2.5 can now be approximated as:

$$\frac{I(s)}{I_0} = Y_T \frac{V^2 \Delta \rho^2}{L^2} \exp\left(-\frac{s^2 \langle R_g^2 \rangle}{3}\right) \quad (2.6)$$

Note, that the scattered intensity is proportional to the square of the volume and the square of the scattering contrast. Thus, assuming no increase in absorption (typically not the case), doubling the thickness of a specimen will increase the scattered intensity four-fold, and the same is true if the contrast is doubled. Finally, the intensity decreases exponentially with the square of the average particle size. Once again, with large particles, the intensity will decay more rapidly than with small particles.

If the experimental data are plotted as $\ln[I(s)]$ versus s^2 , the initial portion of the curve will be linear, according to equation 2.6. By performing a linear regression, so that $\ln[I(s)] = B_0 + B_1(s^2)$, the slope, B_1 , will yield $\langle R_g^2 \rangle$ as per: $\langle R_g^2 \rangle = -3(B_1)$ [2,3,5]. Occasionally, the data will not be linear, but will be curved. Recently, Gethner [10] suggested that a way to handle this curvature is to empirically fit the intensity data to a fourth order polynomial. So that:

$$\ln[I(s)] = B_0 + B_1(s) + B_2(s^2) + B_3(s^3) + B_4(s^4) \quad (2.7)$$

Thus, $\langle R_g^2 \rangle = -3B_2$. The problem with this analysis is that it ignores the behavior of the scattering function as indicated by the Taylor's series expansion in the preceding equations, where odd powers of s

were not present. An alternative approach based on equations 2.5 and 2.6 has been given by Stoll, Fellers, and Lin. In their method, they allow x , in the Taylor's Series expansion of $\exp(x)$, to be equal to $(-s^2\langle r^2 \rangle/3! + s^4\langle r^4 \rangle/5!)$. The 4th order term now allows for curvature in the semi-log plot. The data will not be fitted linearly, but rather to a 2nd order polynomial, $B_0 + B_1(y) + B_2(y^2)$, where $y = s^2$. The value $\langle R_g^2 \rangle$ is now equal to $-3(B_1)$ [6]. It is expected that B_2 should yield information concerning $\langle r^4 \rangle$, however, Stoll et al. indicate that this does not occur due to the affects of polydispersity in particle sizes. Care must be taken in evaluating R_g for any system. Guinier's definition of R_g is the electronic radius-of-gyration, and it may or may not correspond to the spatial radius-of-gyration. However, the value of R_g obtained from scattering will be of the same order of magnitude as the spatial radius-of-gyration.

Another method for determining the average size of the fluctuations would be to plot the data in the form of I versus s^2 and fit the data to an m^{th} order polynomial. This approach is essentially fitting the data to equation 2.5, with the accuracy of the results dependent, in part, on the order of the polynomial chosen. In such a fit, the value of $\langle r^n \rangle$, where n is even, is given by:

$$\langle r^n \rangle = (-1)^{n/2} [B(n/2)] [(n+1)!] / B_0 \quad (2.8)$$

For example $\langle r^2 \rangle = -B_1(3!)/B_0$ and R_g^2 would be $3(B_1/B_0)$, while $\langle r^8 \rangle = B_4(9!)/B_0$. This method should permit the determination of higher moments of the scatterers' distance distribution from the higher regression coefficients. In order to test equation 2.7, normal

distributions were created about a given mean value of r ($\langle r \rangle$) and various values for the standard deviation (σ), see Table 2.1. Each of the normal distributions consisted of 1000 data points. Next, a normalized scattering function, $P(s)/P(0)$, was calculated using the distributed data, where $P(s) = \sum \sum \sin(sr)/sr$. The data from the calculated scattering functions were then fitted to a sixth order polynomial. Figures 2.3a and 2.3b are plots of the normalized scattering functions, and their corresponding regression analyses. In these plots the data symbols indicate the calculated values of $P(s)/P(0)$, while the lines are the polynomial fits. As can be seen, as σ increases, $P(s)/P(0)$ decreases less rapidly and damps out sooner. In fact, the function behaves as if $\langle r \rangle$ was a smaller value than it is in actuality. Table 2.1 gives the polynomial regression coefficients and the average root mean moments (RMM) as determined from the distributions and the regression coefficients. Note that while the fits are quite good, the RMM calculated from the regression coefficients is always less than the RMM calculated directly from the distribution. The amount of underestimation increases with σ , and with the moment's order. Also, for a given $\langle r \rangle$ and σ , the RMM's yielded from the regression analysis are within 10% of each other. This behavior indicates that equation 2.7 will not only underestimate the actual moments, but appears as if the polynomial sees the scattering function as a unique value of r or at least very narrow spread of r 's.

Table 2.1: Comparison of RMM's Calculated Directly from a Normal Distribution and from a Polynomial Analysis of a Simulated Scattering Curve Calculated from the Distribution.

$\langle r \rangle$ (μm)	σ (μm)	RMM	Normal Distribution	Polynomial Analysis	Per. Diff.
5.0	0.00	2nd	5.00	4.99	0.20
		4th	5.00	4.99	0.20
		6th	5.00	4.96	0.80
		8th	5.00	4.91	1.80
		10th	5.00	4.78	4.40
		12th	5.00	4.51	9.80
5.0	0.25	2nd	5.00	4.80	4.00
		4th	5.01	4.80	4.19
		6th	5.03	4.79	4.77
		8th	5.04	4.74	5.95
		10th	5.05	4.64	8.12
		12th	5.07	4.39	13.41
5.0	2.50	2nd	5.62	3.53	37.19
		4th	6.34	3.82	39.75
		6th	6.94	3.99	42.51
		8th	7.40	4.09	44.73
		10th	7.78	4.09	47.43
		12th	8.10	3.94	51.36
10.0	0.00	2nd	10.00	9.65	3.50
		4th	10.00	9.55	4.50
		6th	10.00	9.42	5.80
		8th	10.00	9.25	7.50
		10th	10.00	9.02	9.80
		12th	10.00	8.72	12.80
10.0	0.50	2nd	10.01	9.39	6.19
		4th	10.04	9.31	7.27
		6th	10.06	9.21	8.45
		8th	10.09	9.06	10.21
		10th	10.11	8.86	12.36
		12th	10.13	8.58	15.30
10.0	5.00	2nd	11.18	6.94	37.92
		4th	12.62	7.46	40.89
		6th	13.71	7.72	43.69
		8th	14.57	7.83	46.26
		10th	15.26	7.82	48.75
		12th	15.84	7.70	51.39

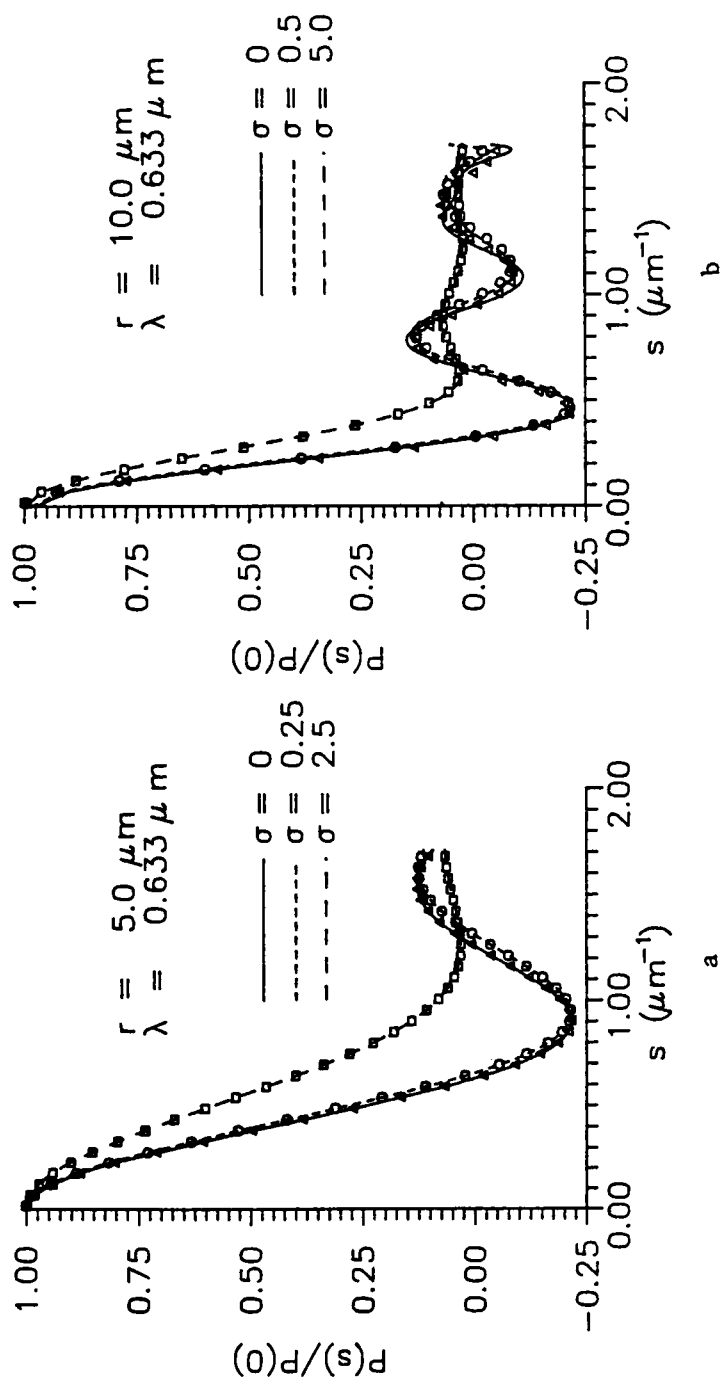


Figure 2.3: Plots of $P(s)/P(0)$ vs. s . a) $\langle r \rangle = 5 \mu\text{m}$, $\sigma = 0, 0.25, 2.5 \mu\text{m}$, b) $r = 10 \mu\text{m}$, $\sigma = 0, 0.5, 5.0 \mu\text{m}$. In both a and b, the data symbols represent the values of $P(s)/P(0)$ calculated from the normal distribution, and the curves are the fit of these points to the polynomial regression.

Correlation Function

The preceding analyses assumed an amorphous material with a uniform density distribution of scattering elements. Unfortunately, this is not always the case. Debye and Bueche [7] defined a spatial, or density, correlation function $\gamma(r)$ such that:

$$\gamma(r) = \langle \rho_i \rho_j \rangle / \langle \rho^2 \rangle \quad (2.9)$$

where: ρ_i = the fluctuation of the i^{th} volume element
 $\langle \rho^2 \rangle$ = the mean square average of ρ
 $\langle \rho_i \rho_j \rangle$ = the average product of $\rho_i \rho_j$

This function is such that as $\gamma(r)$ ranges from 1 to 0 as r increases from 0 to ∞ . Using this definition equation 2.2 becomes:

$$\frac{I(s)}{I_0} = \frac{4\pi \langle \rho^2 \rangle V}{L^2} \int \frac{r^2 \gamma(r) \sin(sr)}{sr} dr \quad (2.10)$$

In order to use equation 2.10, an assumption has to be made about the nature of the distribution of scattering centers. If a two phase random scattering system is assumed, the correlation function can be defined as [8]:

$$\gamma(r) = \exp(-r/a) \quad (2.11)$$

Thus, that a is some sort of average correlation distance. Using this definition of $\gamma(r)$, a solution for equation 2.10 is:

$$I(s) = \frac{A}{(1+s^2 a^2)^2} \quad (2.12)$$

where: A = proportionality constant

By plotting $I(s)^{-0.5}$ versus s^2 and fitting the data to the linear expression: $I(s)^{-0.5} = B_0 + B_1(s^2)$ the value of a is given as:

$$a = (B_1/B_0)^{0.5} \quad (2.13)$$

Note that the average distance given by a will not be the same as R_g given by the Guinier or similar approximations. This is due to the fact that the two averages arise out of different assumptions about $\gamma(r)$.

Small Angle Light Scattering

Introduction

Small angle light scattering (SALS) differs from other scattering experiments, such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS), not only in the wavelength of radiation used, but primarily in that polarized light is employed. So in SALS, patterns are also characterized as to the position of the analyzer relative to the polarizer. Typically, the direction of polarization

is vertical, and when the analyzer is parallel to the polarizer the resulting pattern is called a Vv pattern for vertical-vertical. Likewise, if the analyzer is perpendicular to the polarizer, an Hv pattern is obtained [9]. A schematic of a typical SALS experimental setup is shown in Figure 2.4. In order to obtain a monochromatic, well collimated light source, a laser is normally used. If additional collimation is required, either pinhole collimators or collimating lenses are used.

Spherulitic Scattering

In 1960, Stein and Rhodes [9] were able to show that the SALS behavior exhibited by low density polyethylene (LDPE) films is consistent with a model of anisotropic spheres imbedded in an amorphous matrix. This model was chosen since LDPE crystallites tend to form into spherulites, and that due to the orthorhombic structure of the unit cell, the crystallites are optically anisotropic. Also, if the film is not very crystalline, the material surrounding the spherulites can be thought of as being stochastic. Starting with the relation for the amplitude of a scattered ray (E):

$$E = K \int (\mathbf{M} \cdot \mathbf{O}) \cos(sr) r^2 \sin\alpha \, dV \quad (2.14)$$

where: K = proportionality constant

M = the induced dipole moment of the scattering element

O = a unit vector in the direction of the analyzer

r = the distance from the scattering element to the center of the spherulite

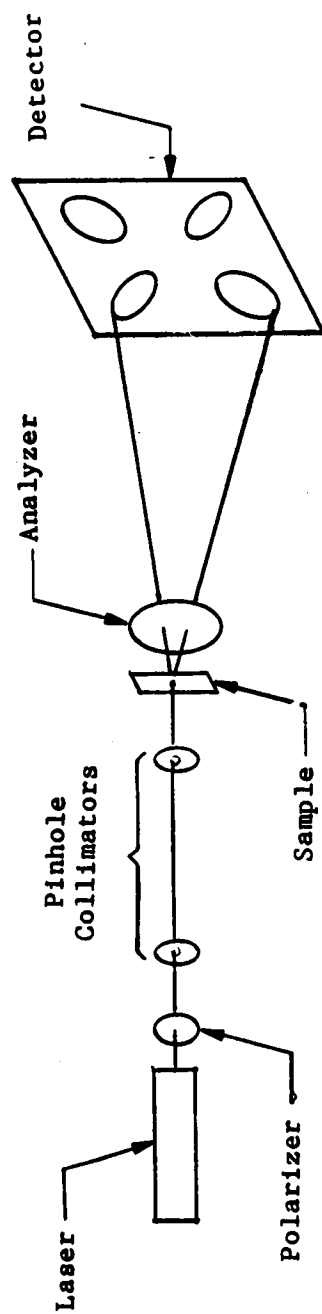


Figure 2.4: Schematic of a typical SALS setup.

$$s = 2\pi/\lambda \sin(\theta)$$

α = the polarizability of the material

they were able to develop the following expressions for I_{Vv} and I_{Hv} , with a minor correction made by Samuels [9,11]:

$$\begin{aligned} I_{Vv} = AV_o^2 (3/U^3)^2 [& (\alpha_t - \alpha_s)(2\sin U - U\cos U - SiU) \\ & + (\alpha_r - \alpha_s)(SiU - \sin U) + (\alpha_r - \alpha_t)\cos^2(\theta/2)\cos^2\mu \\ & \times (4\sin U - U\cos U - 3SiU)]^2 \end{aligned} \quad (2.15)$$

and

$$\begin{aligned} I_{Hv} = AV_o^2 (3/U^3)^2 [& (\alpha_r - \alpha_t)\cos^2(\theta/2)\sin\mu\cos\mu(4\sin U \\ & - U\cos U - 3SiU)]^2 \end{aligned} \quad (2.16)$$

where: A = proportionality constant

V_o = the irradiated volume

α_s = the average polarizability of the matrix

α_r = the average radial polarizability of the spherulite

α_t = the average tangential polarizability of the spherulite

U = sR, shape factor

R = average spherulite radius

SiU = $\int \sin(sr)/sr$

μ = the azimuthal angle

From these equations it is obvious that the scattering behavior is not only a function of position (s, μ , r), but a function of the material's optical properties. Note that the Vv pattern is due to the optical anisotropy within the spherulite ($\alpha_t - \alpha_r$), and between the spherulite and the matrix ($\alpha_t - \alpha_s$), ($\alpha_r - \alpha_s$), while the Hv pattern is due solely to intra-spherulitic effects. This type of behavior is typical of all SALS theory. Thus the Vv pattern yields information

pertaining to the particle and its surroundings, while the Hv pattern gives data on only the particle itself. For example, qualitative information on the birefringence of the spherulites may be obtained from the Vv pattern. If the material is isotropic ($\alpha_r = \alpha_t$), the pattern will show circular symmetry since only the intra-particle term of the I_{Vv} equation is dependent on μ . However, if the spherulites are positively birefringent ($\alpha_r > \alpha_t$), the intra-particle term will add to the scattering due to the particle and the matrix ($\alpha_r - \alpha_s$, $\alpha_t - \alpha_s$), while if the spherulites are negatively birefringent ($\alpha_r < \alpha_t$) the term will subtract. The additive or subtractive effects will be maximized at $\mu=0$ and minimized at $\mu=\pi/2$. Thus, vertical extension of the Vv pattern indicates positive birefringence, while horizontal extension means negative birefringence.

The average radius of the spherulites may be found through the analysis of the Hv pattern. Due to the term $\sin\mu\cos\mu$ in the I_{Hv} expression, the Hv pattern will show four-fold symmetry in the now classical "cloverleaf" form (see Figure 2.5 for typical LDPE Hv and Vv patterns). The lobes of the cloverleaf will contain a maximum along $\mu=\pi/4$, and will be located at $U=4.08$ [9,11], since this value of U maximizes the bracketed trigonometric terms involving U in equation 2.16. So, by determining the value of h that this maximum occurs at, the radius can be found using the definition of U as follows:

$$R = 4.08/s_{\max} \quad (2.17)$$

Recently, Meeten et al. [12,13] have suggested that the approach taken by Stein and other workers in the field may not always be applicable,

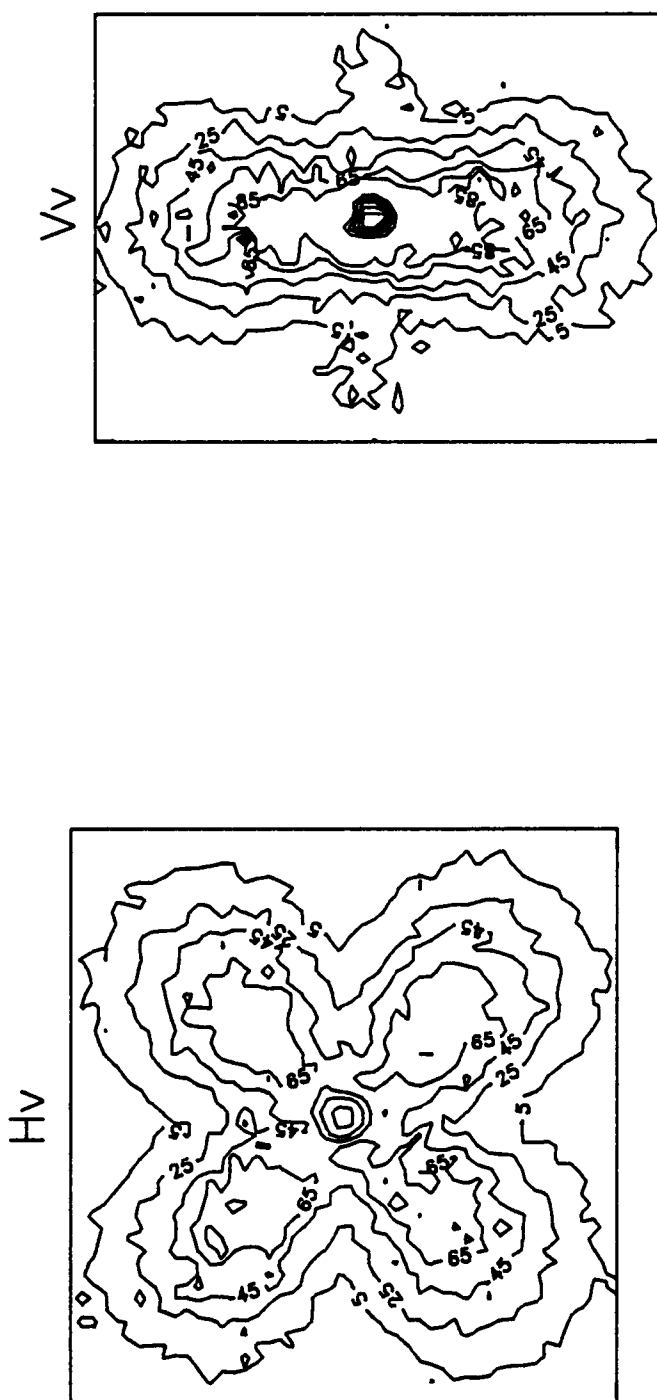


Figure 2.5: Typical Hv and Vv SALS patterns from a spherulitic polymer.

and in some cases the scattering might be better be approximated using Mie scattering theory, or anomalous diffraction. Meeten suggests that Stein's work applies only when the refractive index of the spherulites do not differ much from their surroundings, and for small spherulite sizes.

Scattering by Rod-like Particles

Not all polymers form spherulitic aggregates. Polymeric liquid crystals tend to form rod-like aggregates due to their rigid components. A number of authors have dealt with SALS patterns obtained from systems modeled as rigid, or semi-rigid rods [14-19]. The basic scheme is to approach the problem using Debye type correlation functions [14]. These functions are attempts to describe how a volume element can vary in polarizability, anisotropy, and orientation. In the initial work [14], the optic axis and the rod axis were assumed to be the same. However, subsequent work dealt with the optic axis being oriented at some angle, β , to the rod axis [15-19]. As was the case for spherulitic scattering, the Vv pattern is a result of the variations within the particle and between the particle and its surrounding matrix, while the Hv arises solely from intra-particle fluctuations. In the case of the Hv pattern, the pattern will exhibit circular symmetry if the rods are oriented at random, or will show four-fold symmetry if there is some ordering among the rods [18,19]. In either case, the intensity will decay monotonically from the center of the pattern and will not show a secondary maximum as was the case in spherulitic scattering [11-19]. Also, if the rods are highly ordered

the pattern will break down from a cross type pattern to a streak, where the direction of the streak will be normal to the direction of orientation [18].

Prud'homme and Stein [19] dealt with the Hv pattern for rod-like aggregates under the following conditions: small rods ($<5 \mu\text{m}$) with random orientations, small rods with non-random orientations, large rods with random orientations, and large rods with non-random orientations. In the case of small rods with random orientations they arrive at the following expression for I_{Hv} :

$$I_{\text{Hv}} = KL^2\delta^2 \int T_0(r) [\sin(sr)/sr] r dr \quad (2.18)$$

where: K = proportionality constant

L = the rod length

δ = the average anisotropy of the material

r = the center-to-center distance between rods

$T_0(r)$ = the correlation function of r

If a Gaussian function is assumed for $T_0(r)$, so that

$T_0(r) = \exp(-r^2/a_0^2)$, where a_0 is the correlation distance then equation 2.18 becomes:

$$I_{\text{Hv}} = \frac{KL^2\delta^2}{2} a_0^2 \exp\left(-\frac{s^2 a_0^2}{4}\right) \quad (2.19)$$

Notice that this equation is in a Guinier format. Thus, a plot of $\ln(I_{\text{Hv}})$ versus s^2 will yield the value of a_0 . However, if equation 2.18 is recognized as another form of equation 2.2, and $T_0(r)=1$, then an alternative solution will be:

$$I_{Hv} = KL^2 \delta^2 \left(1 - \frac{s^2 \langle r^2 \rangle}{3!} + \frac{s^4 \langle r^4 \rangle}{5!} \dots \right) \quad (2.20)$$

Now, if the data are plotted as I_{Hv} versus s^2 and fitted to a polynomial expression, the regression coefficients will give the values of $\langle r^n \rangle$.

In the case of nonrandom orientations, they defined two correlation functions $T(r, \beta)$ and $S(r, \beta)$. Upon expanding these functions using a Fourier series, the equivalent to equation 2.18 is:

$$I_{Hv} = KL^2 \delta^2 \int \{ T_0 J_0(sr) - 1/2(T_4 - S_4) \sin[4(\mu - \beta)] J_4(sr) \} r dr \quad (2.21)$$

where: T_n = the nth coefficient of a Fourier expansion of $T(r, \beta)$
 S_n = the nth coefficient of a Fourier expansion of $S(r, \beta)$
 J_n = nth order Bessel function

If a Gaussian assumption is made for the two correlation functions (so: $T_n = \eta_n \exp(-r^2/a_n^2)$, and $S_n = \sigma_n \exp(-r^2/b_n^2)$) then the expression for I_{Hv} becomes:

$$I_{Hv} = KL^2 \delta^2 / 2 \left[\eta_0 a_0^2 \exp(-s^2 a_0^2 / 4) - 1/2 \sin[4(\mu - \beta)] \right. \\ \times \{ \eta_4^2 a_4^2 [(48/s^2 a_4^2) [\exp(-s^2 a_4^2 / 4) - 1 + (s^2 a_4^2) / 4] \\ - [8/(s^2 a_4^2)] [1 - \exp(-s^2 a_4^2 / 4)] + 1/2 \exp(-s^2 a_4^2 / 4)] \\ - \sigma_4^2 b_4^2 [(48/s^2 b_4^2) [\exp(-s^2 b_4^2 / 4) - 1 + (s^2 b_4^2) / 4] \\ - [8/(s^2 b_4^2)] [1 - \exp(-s^2 b_4^2 / 4)] + 1/2 \exp(-s^2 b_4^2 / 4)] \} \left. \right] \quad (2.22)$$

Four-fold symmetry is produced due to the $\sin[4(\mu-\beta)]$ term. The position of the lobes is dependent both on β and on the orientation of the rods as described by the correlation functions $(\eta_4-\sigma_4)$. Hence in order to determine one of the two, an assumption must be made about the nature of the other. Also, note that if $a_4=b_4$ then $\eta_4=\sigma_4$, and random orientation occurs, so equation 2.22 reverts to equation 2.19. Finally a_0 may be evaluated by taking a data slice along $\mu-\beta=0$, and placing the data in the form of $\ln(I_{Hv})$ versus s^2 . Figure 2.6 indicates schematically the resulting Hv SALS pattern for various microstructures of rod-like particulates.

Detecting Devices

For years, SALS and SAXS patterns were collected by exposing photographic film plates to the scattered light. This method captured the resulting pattern and allowed for considerable qualitative analysis. Quantitative work could be done by examining the negative with a microdensitometer, but this procedure can often be quite tedious. An alternative technique would be to use a position adjustable photo-multiplier (SALS), or Geiger, proportional or scintillation counter (SAXS), but this was often a time consuming task. In the mid- to late-1970's two-dimensional position sensitive detectors were developed for SAXS experiments [20]. The basic setup involved an array of anode wires sandwiched between two cathode wire planes. As the charge builds up on the anode, it in turn causes a charge on the cathode planes. By measuring the charge on each cathode strip, and by knowing the sampling rate and the distance separating the cathodes from the

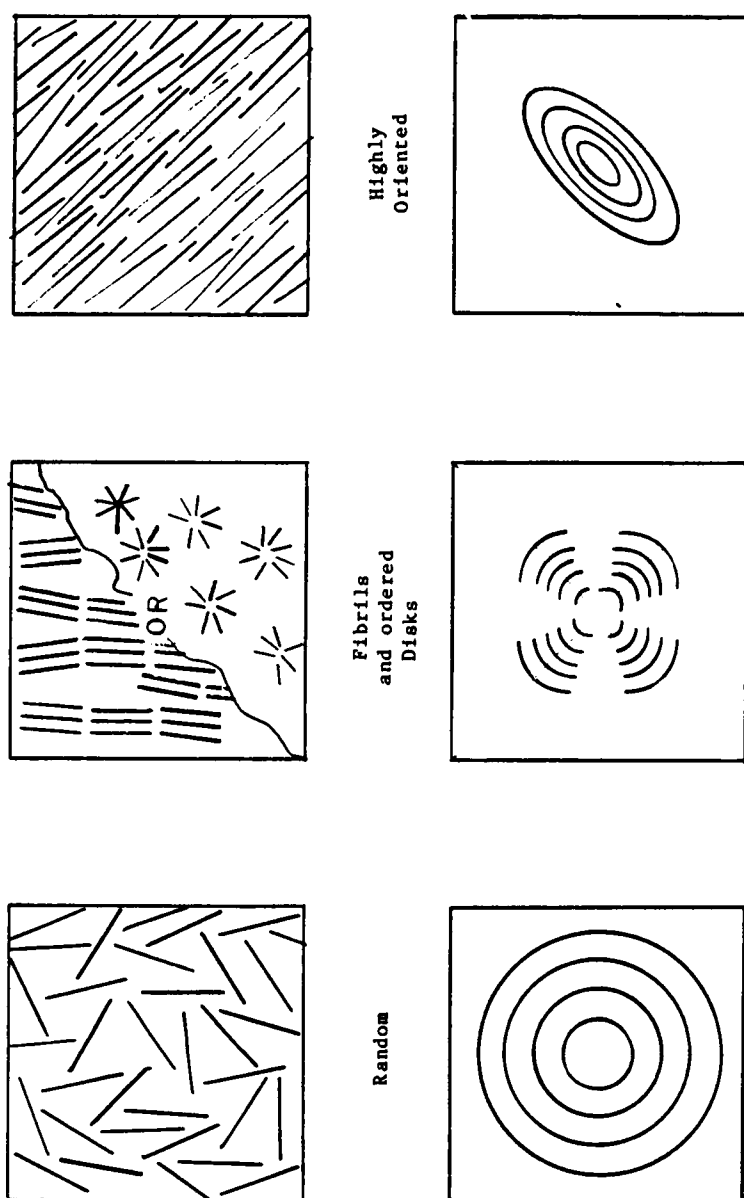


Figure 2.6: Theoretical Hv SALS patterns for various microstructural arrangements of rod-like particles.

anode, the location of the charge can be determined [20]. Such a method is employed at the 10m SAXS camera at the Oak Ridge National Laboratory (ORNL). The development of an electronic two-dimensional detector permitted quantitative analysis to be performed quite easily, speeded up data collection, and permitted a wide variety of analyses to be performed from the same basic data set [20].

Two-dimensional detectors for SALS are based on vidicon imaging devices [1,21-24]. The detection is accomplished through the use of an array of photodiodes imbedded on a silicon chip [25,26]. The chip is scanned by an electron beam in much the same manner as a television camera. The electron beam sets the diodes to a default electron-voltage (eV). When light photons strike the silicon chip, they create electron-hole pairs that deplete the charge on the surrounding photodiodes. Thus, when the electron beam rescans the area, it must recharge the diodes to their original default value. By measuring the amount of voltage required to recharge the diodes, the number of light photons striking the chip in that area can be determined. The position of the charge can be determined from the scanning rate, the sampling rate, and the starting point of the scan [25,26]

It was also in the mid- to late-1970's that the first vidicon type detectors were being reported in SALS work. In 1976, Wasiak, Peiffer, and Stein developed a one-dimensional detector using an optical multichannel analyzer (OMA) tied into a microprocessor [21]. This device allowed for quantitative analysis of data slices of SALS patterns [21,22]. This device was enhanced, and in 1982, Tabar, Stein,

and Long [1] reported a two-dimensional detector using a vidicon OMA . This device allows for collection of the entire or selected portions of the scattering pattern, and has been mainly used for the study of the crystallization kinetics of spherulitic films [1,23,24]. The scattered image was focused onto the vidicon camera by a series of lenses. The resulting signal was collected by a DEC LSI 11/2 micro-processor and stored on floppy disks. Data analysis was performed on a Cyber 175 computer [1].

A similar device to Stein's has been developed as a part of this thesis. This detection device employs a vidicon camera as does Stein's, but focuses the camera on to a mylar imaging screen, upon which the pattern is projected. In addition, all data collection and analysis are performed on an IBM PC with 640 KB RAM, a 20 MB hard disk, 5 MB removable cartridge disk, and two floppy disk drives. Finally, Stein's device stores 2500 data points per scan, at a rate of one scan every 10 s, while this system stores 63,750 points per scan, at a rate of one scan every 6 s.

CHAPTER III

LIQUID CRYSTALLINE THEORY

General Theory

Introduction

A material is considered liquid crystalline if it exhibits a phase(s) which is intermediate between a solid three-dimensional crystal, and a stochastic fluid [27-30]. A liquid crystal will show some of the properties of an ordered solid such as diffracting light and X-rays, but will exhibit the fluidity of a liquid. This mesomorphic behavior is due to ordered clusters or domains of rod-like molecules, and forms when the material is in the melt or solution [27,30]. Usually, liquid crystallinity is manifested over a limited temperature range, and/or concentration. Upon heating, or increasing dilution, the mesophase will transform into an isotropic melt or solution [27-30]. Liquid crystals are typically categorized as to their system type, lyotropic or thermotropic, and as to their structural type, smectic, nematic, or cholesteric.

Lyotropic systems are comprised of materials which demonstrate mesomorphic behavior when dissolved in an appropriate solvent, within a certain concentration, temperature, and pressure range. Some examples of lyotropic polymers are: poly(p-phenylene terephthalamide) (Kevlar®) in sulfuric acid, hydroxypropylcellulose (HPC) in water and poly(γ-benzyl-L-glutamate) (PBLG) in m-cresol. In contrast, ther-

motropes form a mesophase directly upon heating. Some polymers that have shown thermotropic behavior are: HPC, and copolyesters of poly(ethylene terephthalate)/para-oxybenzoic acid (PET/POB).

Figure 3.1 demonstrates the different structural classes of liquid crystals. Smectic liquid crystals form two-dimensional arrays, in which the long axes of the molecules are aligned parallel to each other, and tend to arrange themselves in some sort of "row" or planar structure [27-30]. Nematic mesophases are one-dimensional and are characterized by molecules solely with their long axes parallel to each other [27-30], with no planar registration. Finally, cholesteric structures can be thought of as a twisted nematic, where the long axes of the molecules rotate to form a helical arrangement. A liquid crystalline material may form only one or several of these structures as a function of temperature, or concentration [27,30]. As an example, a material may transform from solid to smectic to nematic to isotropic fluid.

Thermodynamics

Liquid crystals tend to form ordered phases or domains in the melt or solution due to their highly anisometric shape. In packing rigid rods of some length to width (aspect) ratio, x , into a fixed volume, only a given number of rods can be placed into the volume randomly. Beyond this number, the rods must be packed into some ordered array, before any more rods may be entered [31,32]. P. J. Flory considered this problem in 1956 [31,32]. He derived a partition function

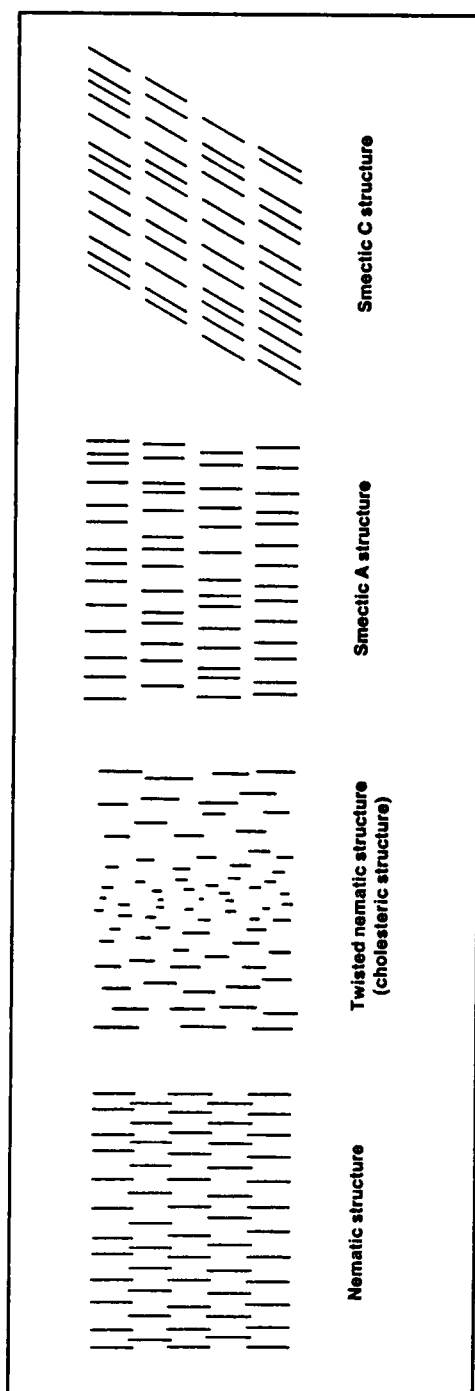


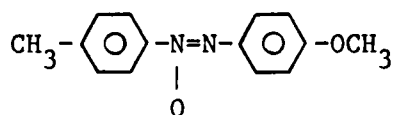
Figure 3.1: Structural classes of liquid crystals. Reprinted from J. A. Castellano, G. H. Brown, *Chemtech*, Jan., 47 (1973) [30].

by considering the number of ways the $j+1$ rod could be placed into a cubic lattice after j rods had been entered. This partition function was then used to determine the free energy of mixing ($\Delta G_M/kT$), and showed that an ordered phase would spontaneously form beyond a minimum value of x (x_{cr}). In a lyotropic system x_{cr} is inversely proportional to solute concentration. Thus, the minimum value of x_{cr} exists in the bulk or thermotropic state, and is given by Flory as 5.44. Other authors [33-37] have also examined the problem of packing rod-like particles and have developed expressions that qualitatively agree with Flory's 1956 results. Their expressions also predict that an ordered phase will occur beyond a critical aspect ratio. However, the value obtained for x_{cr} in the bulk state differs among the authors: x_{cr} is equal to 3.65 for Alben [34], 6.417 for Flory and Ronca [35,36], and 5.3 for Straley [37]. These differences arise from various assumptions made about the degree of rod flexibility, and the distribution of rod alignment, as well as analytical approaches: lattice theories [31-36] and virial expansion theories [37]. Still, it must be kept in mind that all of these treatments are at best approximations of observed behavior, and as such, do provide some insight as to the thermodynamic mechanisms involved in mesomorphic behavior, though not quantitatively exact.

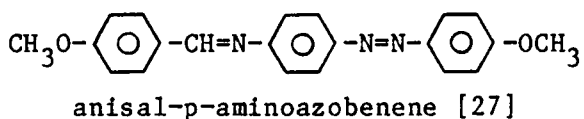
Chemical Structure

Liquid crystalline molecules are composed of long relatively inflexible sequences of aromatic rings or some other ring-like structure (e.g. cellulose). As such, they can be thought of as rigid rods, in

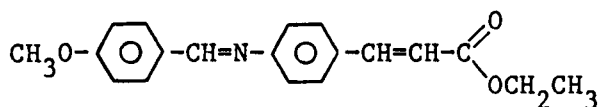
which translational (along the axis) forces between the molecules will be weaker than lateral (cross axis) forces [27]. Some low molecular weight examples are :



p-azoxyanisole [27]

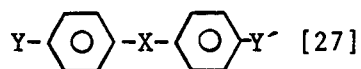


and

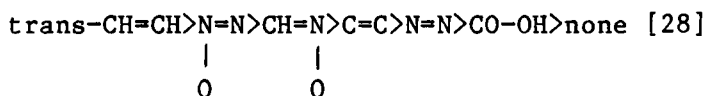


ethyl anisal p-amino-cinnamate [27]

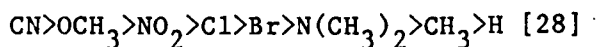
It should be obvious that a general liquid crystalline model would be:



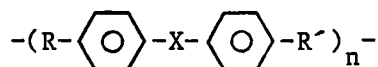
As might be expected, a rigid central X group promotes liquid crystallinity. A typical central group order for nematic efficiency is:



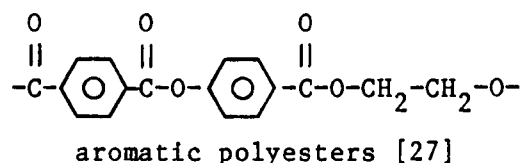
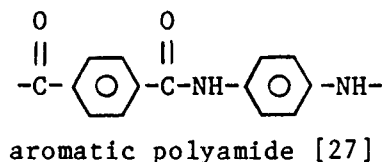
Generally, any terminal group (Y,Y'), other than H, promotes mesomorphic behavior, provided it does not broaden or lengthen the molecule too much. A typical terminal group order for nematic efficiency is:



Using low molecular weight liquid crystals as an example, many polymeric liquid crystals have the following general structure:



Some examples of polymeric liquid crystals are:



The mesomorphic behavior of these polymers depend not only on the rigidity of the aromatic segments, but on the length and flexibility of the spacing R and R' segments.

Microstructure

A common microstructural model for liquid crystalline polymers, due to their rigid chemical structures, are fibers and tapes [38-40]. Upon review of several lyotropic and thermotropic polymers, Sawyer and Jaffe [38] have found a common microstructural hierarchy (Figure 3.2). While hierarchy is dependent upon the mode of manufacture, the basic microstructural unit is fibrillar. The general microstructure consists of macrofibrils that are approximately 5 μm in diameter, which in turn are composed of fibrils of 0.5 μm in diameter. These

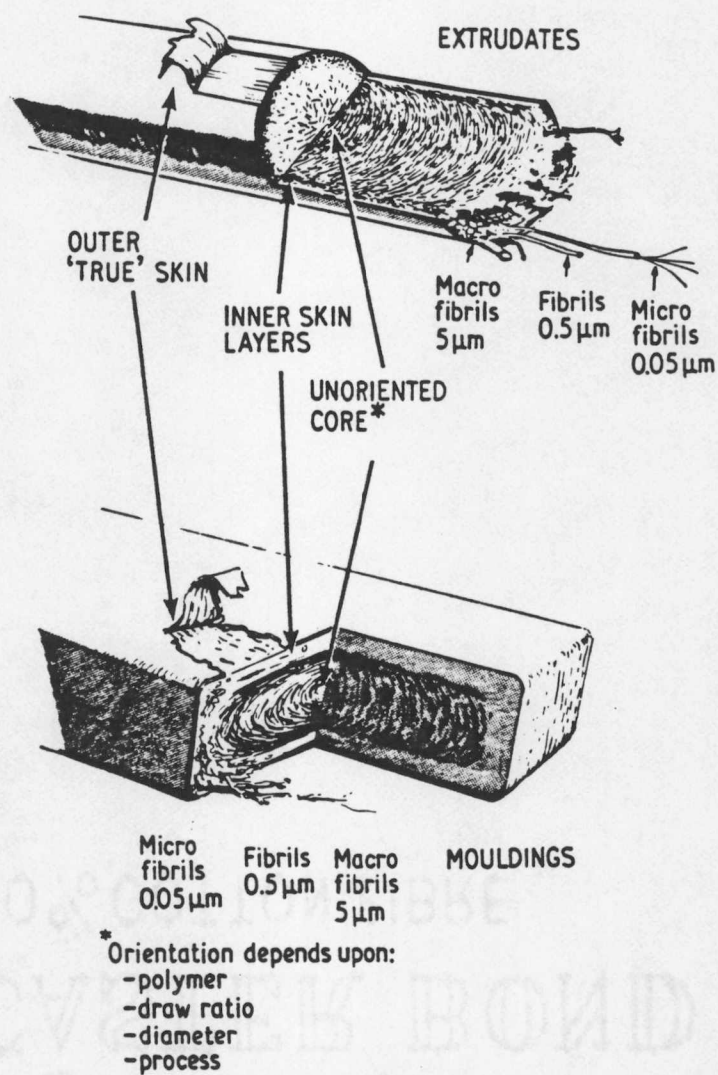


Figure 3.2: Liquid crystalline microstructural hierarchy. Reprinted from L. Sawyer, and M. Jaffe, J. Mat. Sci., 21(6), 1897 (1986) [38].

fibrils are merely aggregates of microfibrils of $0.05\text{ }\mu\text{m}$ in diameter. If the sample was processed into a fiber, these structures tend to be round, while in a film these constituents are tape-like, and in moldings they are sheet-like [38].

Also, virtually all the polymers reviewed by Sawyer and Jaffe had an oriented skin, relaxed core type of structure. The degree of orientation and the skin-to-core ratio was found to be dependent on the polymer, draw ratio or stress orienting mechanism (e.g. gating effects), sample diameter or thickness, and other processing variables such as temperature, pressure, cooling rate, etc. Other authors have also noticed these effects. For example, Flood [39] reported skin-core structures in Kevlar[®] films, and Joseph, Wilkes, and Baird [40] noted not only skin-core structures, but fibrillar and sheet-like structures in fibers and plaques of Tennessee Eastman's 40/60 PET/POB copolyesters.

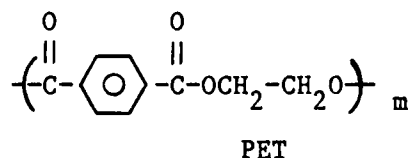
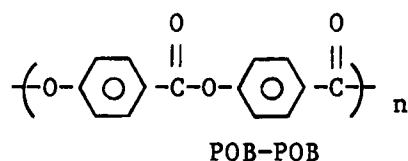
PET/POB Copolyesters

Jackson and Kuhfuss, of the Tennessee Eastman Corporation, reported the formation of a thermotropic polymeric liquid crystal through the copolymerization of PET and POB in 1973 [41]. The copolyester exhibited liquid crystalline behavior when the POB content exceeded 30 mole% POB [41,42]. Liquid crystalline behavior mani-

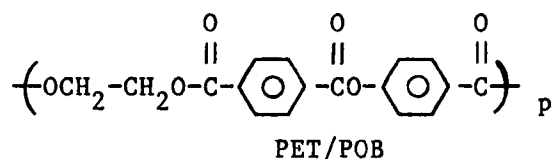
tested itself in the copolymer through:

1. A dramatic decrease in melt viscosity vs. mole% POB after 30 mole% POB.
2. A discontinuous change in the slope of the Density vs. Composition curve at 30 mol% POB.
3. Highly anisotropic mechanical properties of injection molded bars.
4. Turbid, birefringent melts for compositions above 30 mole% POB.

The copolyester is comprised of segments of:



and



As might be expected, the POB segments of the polymer tend to be the most rigid, and the PET segments are the most flexible. The POB homopolymer has also been reported to be liquid crystalline, while pure PET is known to be a relatively flexible polymer. So, it is no

surprise that after reaching a certain mole percentage of POB, the copolyester would exhibit mesomorphic behavior.

On basis of wide line NMR studies by McFarlane, Nicely, and Davis, and on the observation that the copolymer crystallinity increased with POB content, the copolyesters were originally thought to be random copolymers [41,42]. However, other authors have recently disputed this claim [40,43-47], and maintain that there is some tendency for homopolymerization. These authors find evidence for PET-rich and POB-rich domains from optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), differential thermal analysis (DTA), wide angle X-ray diffraction (WAXD), and wide angle electron diffraction (WAED). Thermal analyzes gave multiple endotherms and two glass transitions [43,44]. Optical microscopy showed two separate optically anisotropic structures, at temperatures above 235 °C, with the darker of the two phases solidifying below the temperature of the uppermost endothermic transition [43,44]. Also, WAXD patterns of compression molded films yielded POB type reflections which did not disappear until molded above the upper endotherm [44,45]. TEM indicated lamellar domains embedded in an amorphous matrix, where the lamellar structures yielded a WAED pattern that is consistent with pure POB, while the matrix yielded an diffuse halo [45]. Finally, more recent NMR work by Nicely, Dougherty, and Renfro [48] using a high-field spectrometer indicates slightly longer POB to POB sequences for the copolyesters than should be present for a random copolymer. This result is especially true as the POB content increases. Also, they

suggest that at least three to four POB repeat groups are required to form a structure which is liquid crystalline.

The microstructures reported for the PET/POB copolyesters are consistent with Sawyer and Jaffe's general model [38]. Fibrillar structures were observed using OM, SEM, and TEM for fibers of the copolyester, while compression molded and solution cast films gave sheet-like microstructures [40,46,49,50]. Also, skin-core structures were reported for both fibers [40,49], as well as for injection molded and compression molded plaques [40]. The skin tends to be oriented with a fibrillar microstructure. There is even some evidence that suggests that the skin is primarily composed of the POB-rich phase and core with the PET-rich phase [40]. This evidence comes in the form of more pronounced etching in the core than in the skin. In addition, WAXD patterns of microtomed sections of the skin gave reflections that are consistent with POB, while the spectra of the core resembled PET [40].

CHAPTER IV

EXPERIMENTAL METHODS AND ANALYTICAL TECHNIQUES

Materials

The main materials studied in this thesis are PET/POB copolyesters which were graciously supplied by the Tennessee Eastman Corporation. Copolyesters with the following compositions and intrinsic viscosities were used: 28 mole% POB, $[\eta] = 0.58$; 40 mole% POB, $[\eta] = 0.61$; 50 mole% POB, $[\eta] = 0.58$; 60 mole% POB, $[\eta] = 0.76$; 70 mole% POB, $[\eta] = 0.65$. In addition to the copolyesters, melt extruded films of the 60 mole% POB copolyester and Celanese's Vectra® A900 copolyester were supplied by D. G. Baird and T. Wilson of Virginia Polytechnic Institute, while high and low density polyethylene were used as typical flexible chain polymers.

Compression Molding

In order to determine the quiescent structure of the materials, films of the copolyesters were formed by compression molding. The films were molded in a hot press between ferroplates with Kapton® film as a mold release agent. To obtain thin films needed for SALS, aluminum foil was used as a spacer plate. The materials were given a one minute preheat at the molding temperature, followed by a one minute mold close time, with the molding pressure being about 11 GPa. Films made in this manner ranged in thickness from 0.025 mm to 0.15 mm. The copolyesters were molded at temperatures of 210 °C, 230 °C, 255 °C,

and 285 °C. These temperatures were selected to be approximately 10 °C from the endotherms indicated on DSC traces of the copolyesters (Figure 4.1). Finally an attempt was made to vary cooling conditions of films molded at the same temperature. At each molding temperature and composition, films were made that were quenched into an ice water bath, removed from the press and cooled in the ambient air, and cooled in the press with the power to the press off. Using these conditions it was hoped that any cooling rate dependence of the resulting structure might be crudely detected.

Uniaxial Stretching

An attempt was also made to orient quenched films made of the 60 mole% POB copolyester molded at 285 °C using a 0.075 mm spacer plate. Specimens of 60 mm x 60 mm were cut and taken to the T. M. Long biaxial stretching apparatus. Following a five minute preheat, the films were stretched 2x1 at 740%/min. with the transverse direction unconstrained. The stretching temperatures were chosen so that some of the films were stretched above the DSC endotherm at 145 °C, and some below. However, all the temperatures were selected below 190 °C, which has been reported as the temperature for the onset of flow [45,46] The stretching temperatures used were 90 °C, 110 °C, 160 °C, and 170 °C.

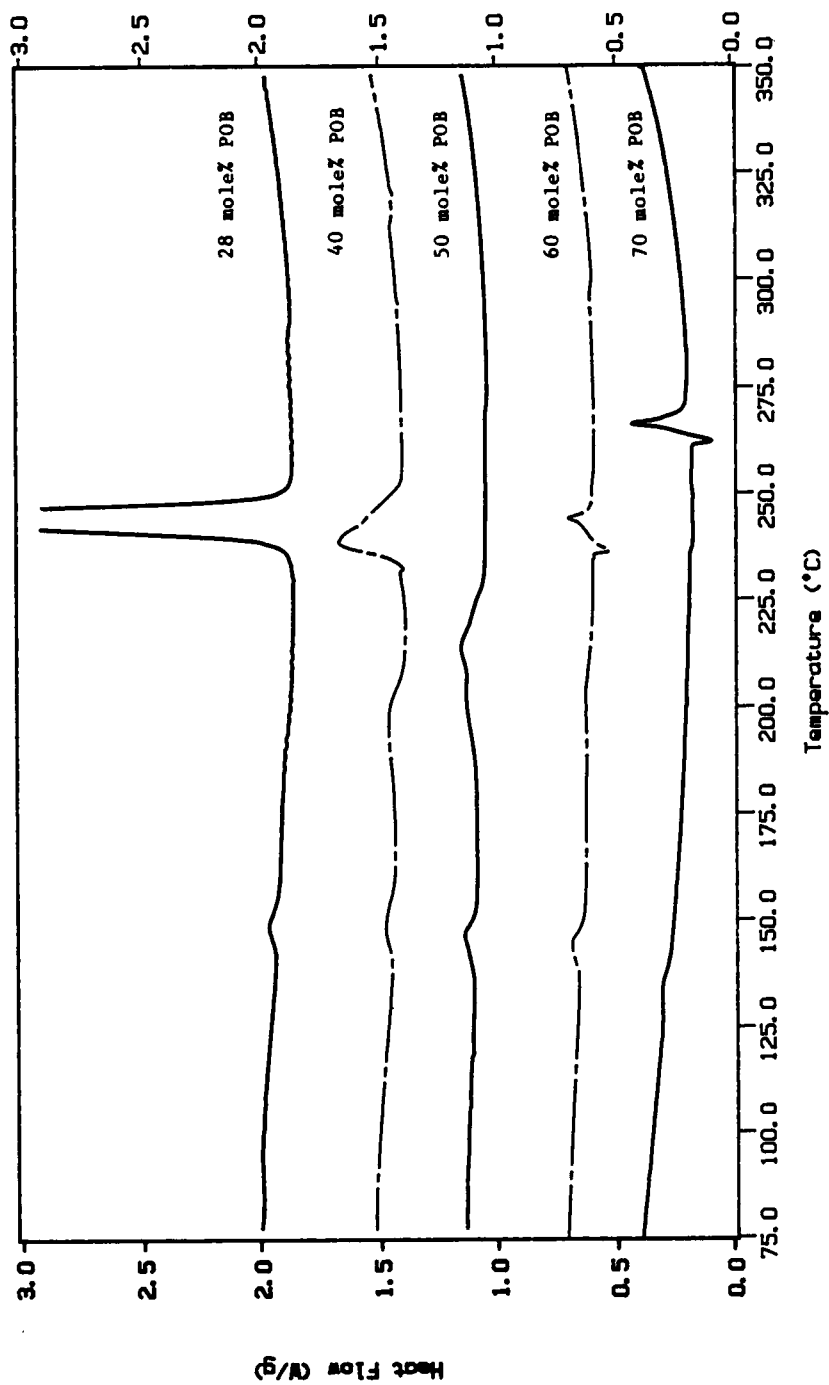


Figure 4.1: DSC traces of PET/POB copolyesters.
Scan rate = 20 °C/min.

Extrusion Drawn Films

Films that had been drawn while being extruded were graciously provided by D. G. Baird and T. Wilson of Virginia Polytechnic Institute (VPI). Two different copolyesters were drawn a 40/60 PET/POB copolyester of Tennessee Eastman's, and Celanese's Vectra® copolyester. According to T. Wilson these films were extruded through a die that was at a lower temperature than the extruder barrel walls and were subjected to a manual draw upon exiting the die.

Small Angle Light Scattering

Hardware

The video SALS setup developed and employed in this thesis is shown schematically in Figure 4.2. Much of the hardware, Aerotech laser, Dage-MTI silicon-vidicon camera, pinhole collimators, IBM PC and accessories, was either purchased or assembled by my colleague David N. Lewis. The writer integrated such items as the rotatable-translatable sample stage, mylar imaging screen, optical table, 20 MB hard disk, and videotape backup unit into the system.

As the system is currently designed, all the optical components are mounted on an optical rail set on a stainless steel skin/aluminum honeycomb core optical table, to provide vibrational damping, and a rigid, flat working surface. The optical rail has a metric scale graduated in 1 mm increments. Thus, the position of each optical component can be readily determined. An Aerotech 2 mW, He-Ne laser is

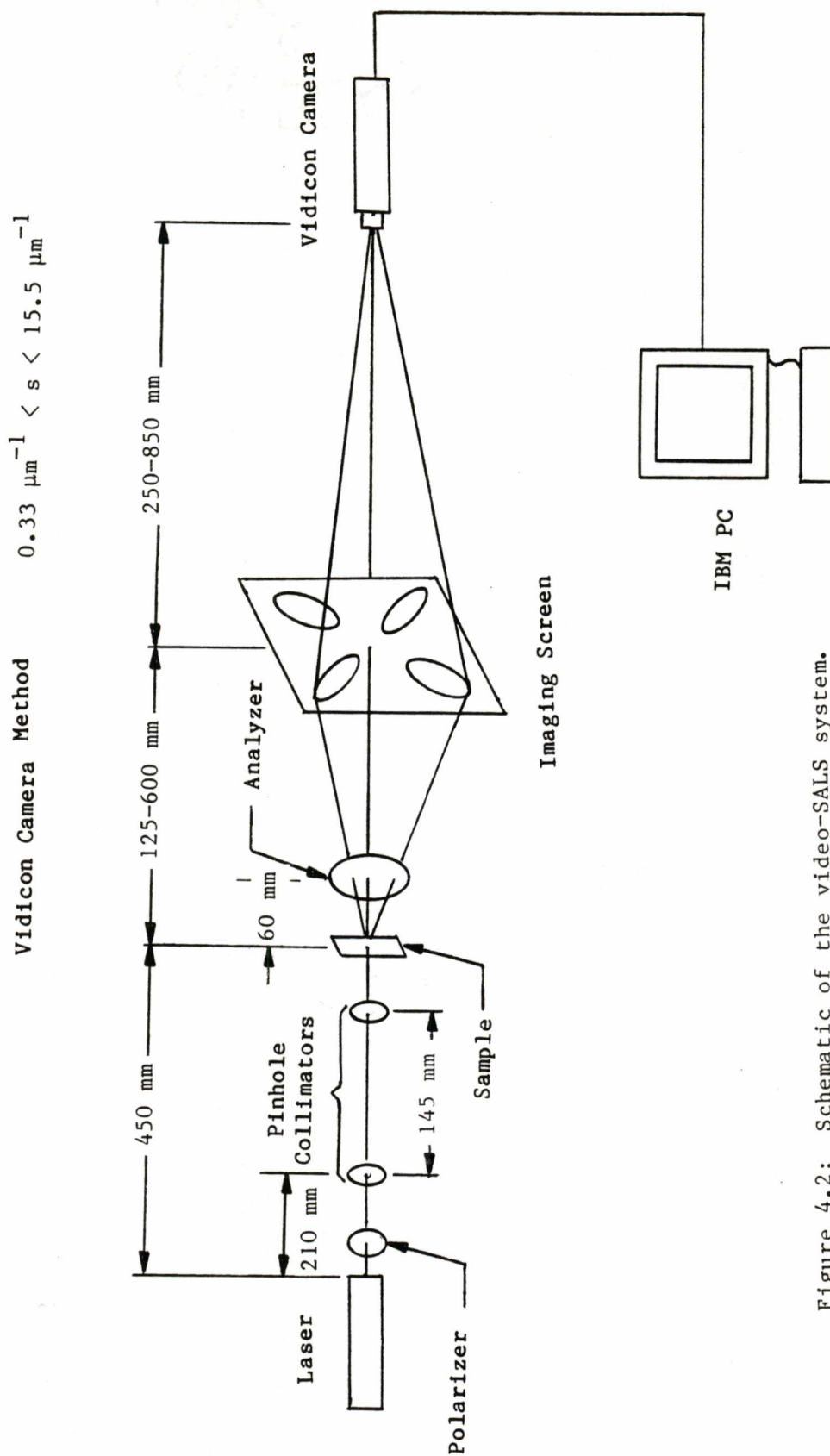


Figure 4.2: Schematic of the video-SALS system.

used as the light source for the SALS experiment. The laser beam is passed through a vertical polarizer, and then through two pinhole collimators separated by 145 mm to reduce the beam's cross-sectional diameter to 0.67 mm when it strikes the sample. The sample holder permits 360° rotation about the beam direction, as well as translation in the vertical and transverse directions. These adjustments allow not only for accurate positioning of the specimen, but also for orientation effects to be investigated. The scattered light is then passed through an analyzer whose direction of polarization is rotatable by 360° about the beam direction. Typically, the analyzer is set either parallel to (Vv) or normal to (Hv) the polarizer's position. Next, the scattered radiation is projected onto the mylar imaging screen. The screen is 125 mm x 90 mm in size, with a 5.0 mm diameter beam stop in the center and is of uniform texture. The mylar screen is optically translucent, and thus allows the scattered image to be viewed from the rear of the screen by the camera. An MTI silicon-vidicon camera is used to detect the projected image. The gain control is set at the maximum and the contrast at 3/4 maximum. The primary control of light intensity is through the selection of the f-stop. The resultant video image is displayed at all times on a video monitor, while digitizing and data analysis are done on the microcomputer. The IBM PC has 640 KB of RAM, with two floppy disk drives, an external 20 MB fixed hard disk, an external 5 MB removable cartridge hard disk drive, a dot matrix printer, a six pen plotter, and a videotape backup system for the hard disks. The digitized SALS patterns are stored on the 20 MB hard disk and later backed-up on videotape for protection and

archival purposes. The addresses of all hardware and software equipment suppliers is given in APPENDIX A.

Software

The software employed was purchased whenever possible or was generated by the writer, with assistance from his colleagues when needed. Tecmar's Video Van Gogh® package was used for digitizing, storing, and retrieving, SALS patterns. The program digitizes a video image into a grid of 249x236 pixel locations, with pixel location 2,16 representing the upper left corner of the screen and 250,251 the lower right corner. Each pixel location is assigned a computer buffer address and a shade-of-gray (SG) value that is in proportion to the intensity of light striking the detector at that location. The SG scale ranges from 0 for pure black to 255 for pure white. As such, the SG provides a relative intensity for a monochromatic light source that is dependent upon the gain and contrast setting of the camera, the f-stop of the lens, and the camera-to-imaging screen distance. The digitized image is loaded into a 64 KB buffer in the RAM of the PC. This image can then be stored onto the hard disk in a 64 KB binary array. The stored image file can only be accessed through the Video Van Gogh® software library. Thus, it was necessary to incorporate this library in most user written data analysis packages.

Other purchased software packages included Golden Software's QGRID, TOPO and GRAPHER plotting packages, and Omicron's PLOTTRAX plotting and statistics package. QGRID and TOPO were used to generate

two-dimensional iso-intensity contour plots of the SALS patterns. In using this plotting package some compromises had to be made. TOPO requires smooth binary data that is in a regularly arrayed grid of no more than 100x100. However, to achieve good resolution for intensity data slices the SALS patterns were often much larger than 100x100. Also, the intensity data was seldom smooth due to the speckled nature of the patterns that arise, in part, from interparticle interference [52]. QGRID will take an X,Y,Z ASCII data file, smooth the data and place it in a regular grid. However, QGRID is limited to 3000 data points maximum or a 50x60 grid. So, a user written program was used (VVGCVN) to generate a reduced ASCII data file from the binary image file. Thus, the contour plots shown in this thesis should only be used qualitatively to indicate the shape and size of the SALS pattern. It should be noted that Golden Software's contouring package was one of two packages that the writer was able to find that would generate contour plots of data files larger than 1000 data points, and was also the most user friendly of the packages investigated. The Golden Software package GRAPHER was used to create all the conventional X,Y plots shown in this thesis. Finally, Omicron's PLOTTRAX package was used to perform regression analyses of data slices taken from the image files.

A number of analysis programs that were needed could not be purchased. In these cases the software was written by the author with the help of colleagues David N. Lewis, T. Levitte Cox, and Senior Engineering Technician, Steven Stiner. Each program is fully listed in APPENDIX B. The program DES generates a description or identification file (.DES file) for the image file saved by the Tecmar software. The

.DES file contains the image's operation window (minimum and maximum X,Y pixel coordinates), the beam stop's pixel coordinates, the sample-to-screen distance, and the screen-to-camera distance. This file is used in conjunction with all user written image analysis programs.

As was mentioned earlier in the description of the QGRID and TOPO software, a user written program called VVGCNV was used to convert the binary image file to an ASCII file in an X,Y,Z format and to reduce the number of data points to less than 3000. VVGCNV utilizes the Video Van Gogh® command library to load the binary file back into the 64 KB buffer. The user is told the number of rows and columns of his current operating window, and is then prompted for row and column divisors. The divisors are really step sizes so that every n^{th} row and m^{th} column are outputted. For example, if the operating window consists of 18,000 data points in 120 rows and 150 columns, a row divisor of 2 and a column divisor of 3 will yield a reduced file of 60 rows and 50 columns or 3000 data points. The program assumes that the beam stop coordinates represent the center of the pattern, and converts from pixels to cm's using equations of the form:

$$X_{\text{cm}} = (CX - X)/CF_x \quad (4.1)$$

$$Y_{\text{cm}} = (Y - CY)/CF_y \quad (4.2)$$

where: CX = the beam stop's X pixel coordinate
 CY = the beam stop's Y pixel coordinate
 $CF_x = \frac{X_{1x}}{(SC)^n}$ = the x-axis pixel-to-cm conversion factor
 X_{1x} = the number of pixels per cm at the limiting focal length of the camera

SC = the screen-to-camera distance
 n = a constant between 1 and 2
 CF_y = the y-axis pixel-to-cm conversion factor

The values governing the conversion factors were determined experimentally and will be discussed later. Finally, VVGCV also allows for the intensity at a given point to be normalized by the maximum intensity present in the image file.

The programs SLICE and 2FOLD are two similar programs, in that both programs are used to take data slices of intensity versus scattering angle along a given azimuthal angle of the image file. The programs differ in that SLICE assumes that there is at least four-fold symmetry in the pattern, while 2FOLD assumes only two-fold symmetry. Both programs take data slices along a user inputted azimuthal angle, in degrees, and error width, in cm (see Figure 4.3). The upper and lower limits of the data slice are given as:

$$UL = Y_{cm}[\tan(\mu_{in})] + \text{err} \quad (4.3)$$

$$LL = Y_{cm}[\tan(\mu_{in})] - \text{err} \quad (4.4)$$

where: Y_{cm} = the Y location, in cm, of an X,Y,Z data point to be checked
 μ_{in} = the inputted azimuthal angle
 err = the inputted error width

The value X_{cm} of the data point is now checked to see if it lies within UL and LL. If it does, the X,Y,Z datum point is taken as part of the slice and the scattering angle and other manipulations are performed. If not, the point is rejected and the next point is checked. This method has advantages in that it minimizes the fraction of larger

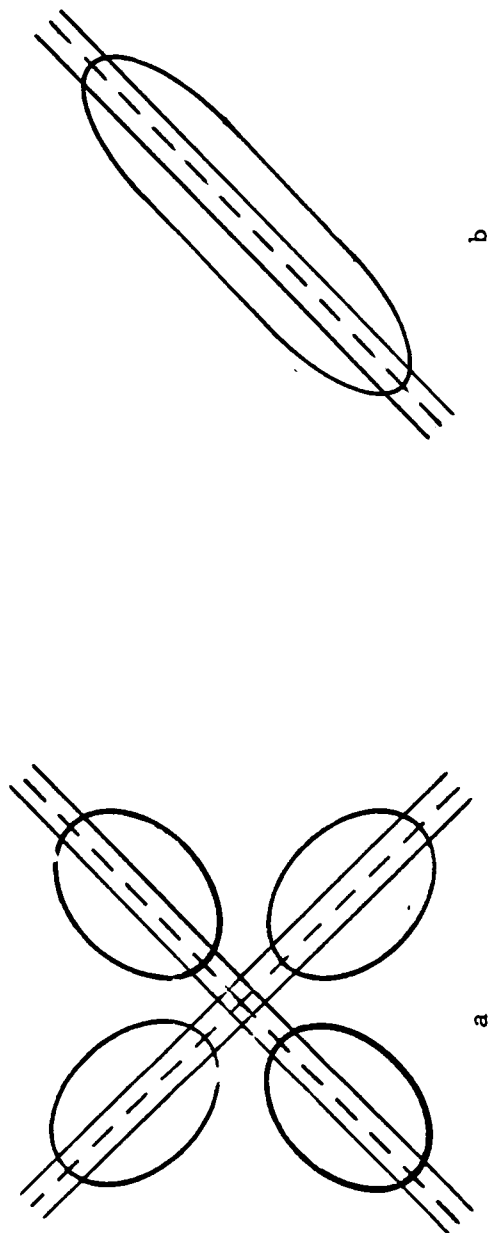


Figure 4.3: Schematic of the data slicing performed by a) SLICE, and
b) 2FOLD.

angular terms with respect to smaller terms and as such improves the accuracy of the slice. Its main disadvantage is that at smaller angles, there is more error involved in the range of azimuthal angles selected. However, this error is minimized by the tendency for the intensity to approach I_0 at smaller angles. As was the case with VVGCNV, the image file is loaded into the 64 KB buffer using the Video Van Gogh® command library. The conversion from pixels to cm's is likewise identical. The azimuthal angle of the datum point (μ) and the scattering angle (θ) are determined using the following expressions:

$$\mu = \tan(X_{cm}/Y_{cm}) \quad (4.5)$$

and

$$\theta = [(X_{cm}^2 + Y_{cm}^2)^{0.5}]/SS \quad (4.6)$$

where: SS = the sample-to-screen distance

The data slice may be outputted in one of thirteen different output options (I vs. θ , I vs. s, I vs. s^2 , $\ln(I)$ vs. s^2 , etc.). Averaging the intensity at a constant scattering angle, may be done if the user so desires. Also, the user may opt for the program to eliminate any data that are in the beam stop area (a radius of 3.6 mm), and normalize the data by the maximum intensity value in the the image file.

Finally, the program POLYGEN was written to produce a data file from the regression coefficients of a data slice given by PLOTTRAX. This data file was used with GRAPHER to generate the regression curve. In POLYGEN the user specifies the starting and ending points, and the step size to be used in the calculations. Next, the order of the

polynomial is entered followed by the regression coefficients.
POLYGEN is capable of generating curves from first to eighth order.

Equipment Calibration

A number of calibrations and checks were performed to assure the accuracy of the SALS patterns obtained using the vidicon camera system. "Hot spots" on the detector was checked by illuminating the imaging screen with a uniform light source (sodium vapor lamp), at various camera f-stops. This process yielded no irregularities in the detector. Next, the magnifying affects of the camera was checked by replacing the imaging screen with a grid spaced in 1 mm increments, and illuminating the grid with the sodium vapor light source. The number of pixels required to make up a cm on the grid, in both the x- and the y-directions were determined as a function of the screen-to-camera distance (SC). This process gave the limiting focal length of the camera as 25 cm, and the conversion factors as:

$$CF_x = 712.6(SC)^{-1.05} \quad (4.7)$$

$$CF_y = 905.9(SC)^{-1.04} \quad (4.8)$$

It is obvious from equations 4.7 and 4.8 that the y-direction is slightly elongated as compared to the x-direction. This is common among video packages, and is done so that when the image is displayed on the rectangular video screen, it will appear in proper perspective.

Experimental

SALS specimens were obtained by cutting small sections (5 mm diameter typical) from the compression molded films, using a standard hole punch. In the case of stretched or extruded films, a rectangular sample was cut using a scalpel. In this case the long side of the rectangle corresponds to the stretching or machine direction. The specimen was then coated with immersion oil ($\eta = 1.52$) and placed between two glass cover slips. The sides of the cover slips were sealed with cellophane tape, and the entire sandwich was labeled for identification. Next, the specimen was mounted on the rotatable sample holder, and illuminated by the He-Ne laser. After adjusting the screen and the camera for the optimum image, the SALS pattern was digitized using the Video Van Gogh[®] package and saved on the hard disk. The operating window of the pattern was noted, as were the beam stop location, the screen position, and the camera position. These data were then used to create a .DES file for the saved image file. If desired, contour plots were created using the software described above. SLICE or 2FOLD was used to take data slices when appropriate. The size of the error width ranged from 0.5 mm to 1.5 mm, with the width of the slice being adjusted so as to obtain between 75 to 125 data points for regression analysis. The slices were outputted in the form of I versus s^2 , and were fitted to a sixth order polynomial using PLOT-TRAX. The correlation distance and other moments of the particle size distribution were determined as per equation 2.7.

To check the reliability of the video-SALS system results, a simple experiment was performed using flexible coil polymers. In this experiment, samples of LDPE and HDPE were melted, and then quenched into an ice water bath. Hv SALS patterns were then obtained using both the video method and with Polaroid film at the same sample-to-detector distance. For the video system data slices at $\mu = \pm 45^\circ$ were taken using SLICE, and the value of intensity maximum ($s_{\max}$) was found from a plot of intensity versus s , Figure 4.4. Using the Polaroid film negatives, the distance separating the maximums in opposing quadrants was found using a light box, dividers and a rule graduated in 0.5 mm increments. The value for the distance from the center to the maximum ($d_{\max}$) was taken as half this value. For the film technique at least two different exposures were analyzed for each sample, while for the video method only one pattern per sample was used. The scattering angle was determined using equation 4.6, where $d_{\max}$ was used as the numerator. The spherulite radius for both techniques was determined as per equation 2.17.

Small Angle X-ray Scattering

Equipment

All the SAXS work in this thesis was performed at Oak Ridge National Laboratories (ORNL) on their 10 m SAXS camera, with the camera in the 5 m sample-to-detector position and Cu K α radiation. Power settings on the Rikagu rotating anode X-ray source were 40 kV and 50 mA. The camera uses a two-dimensional position sensitive detector to

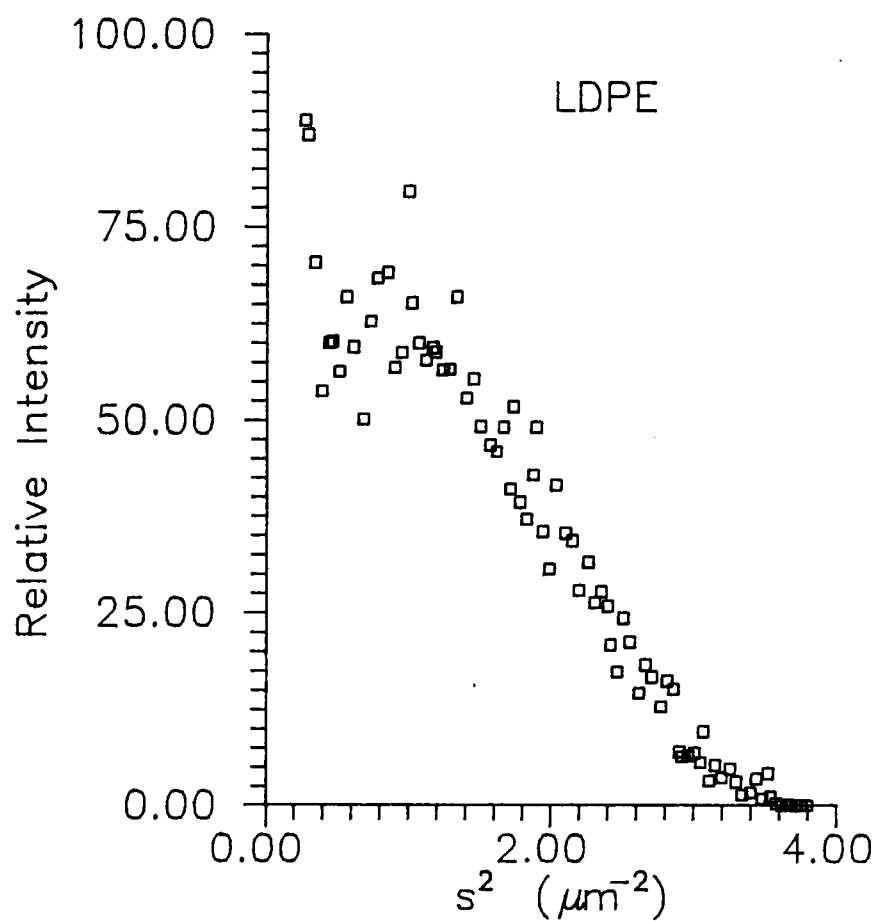


Figure 4.4: Typical plot of intensity vs. scattering angle for a LDPE quenched film.

collected the scattered radiation, which is tied into an Mod-Comp minicomputer [20].

Experimental

Specimens for SAXS work were sandwiches of several small rectangular pieces cut from molded films. Again, if the sample was stretched, the long side of the rectangle was cut in the machine direction. These sandwiches were made because the thickness of the molded films (0.05-0.15 mm) did not provide enough mass to scatter X-rays effectively. The sandwiches were between 0.3 and 0.75 mm thick, and were carefully constructed to avoid masking any machine direction biases. The transmission coefficients (T_m) of the each specimen was determined with the aid of a standard glassy carbon scatterer. The run time for the SAXS experiment was 1.5 hours for each specimen. The collected patterns were corrected for dark current and detector sensitivity effects using ORNL BKC program. If the pattern was isotropic, circularly averaged data was calculated using program RAD, while if it was anisotropic, data slices at a given azimuthal angle were taken using a subroutine in program CON. The corrected patterns and data slices were then transferred onto floppy disks, so that they could be analyzed using some of the software that had been developed for SALS (such as TOPO, PLOTTRAX, GRAPHER, etc.). User written programs such as SAXVERT creates a file to be used with QGRID, and SAXS2-D allows the data slices to be manipulated into various output forms (I vs. s , $\ln(I)$ vs. s^2 , etc.) for analysis with PLOTTRAX.

Wide Angle X-ray Diffraction

A Philips Cu K α radiation source was used with a flat plate film camera. Power settings of 20 kV and 30 mA were used, with exposure times of 12 hours. As will be discussed in Chapter V, only selected films from the stretching experiment were used.

The same film sandwiches used for the ORNL SAXS were used for the WAXD experiments. Each film was mounted onto the pinhole sample holder and exposed to the X-ray radiation for 12 hours. Following the exposure, the photographic film was developed and photocopies made from the resulting negative.

Optical Microscopy

An Olympus BH-2 transmitted, polarized light microscope was used in conjunction with a Polaroid 4"x5" flat plate film camera. The magnifying powers of the four objective lens were 4x, 10x, 20x, 40x. When these are coupled with the 10x eye- and photoeye- pieces yielded magnifications of 40x, 100x, 200x, and 400x. All the photomicrographs of the PET/POB copolyesters shown in this work were taken at 100x magnification, while the polyethylene samples were taken at 400x. All samples were viewed between crossed polars.

Samples for optical microscopy were cut from the films using a standard hole punch in the case of the compression molded films, while for stretched and oriented films, rectangular samples were cut in the manner described earlier. The specimens were then placed on a glass

microscope slide, and a glass cover slip was placed over the specimen and secured with tape. The samples were placed in an X-Y adjustable mechanical stage, and sample moved into the path of the polarized light. The mechanical stage was situated on larger 360° rotatable stage, that permitted any optical orientation in the film plan to be examined by rotating the stage.

Scanning Electron Microscopy

All scanning electron microscopy was performed at 30 kV. Samples were glued onto aluminum sample holders with epoxy cement. The samples then had a thin gold coating sputtered onto them, to improve their conductivity. Photo-micrographs were taken off the video screen using a Polaroid 4"x5" flat plate film camera. Typical magnifications were 2000x, 5000x, and 10,000x. Magnifications above 10,000x were not possible due to damage to the specimen from the beam.

CHAPTER V

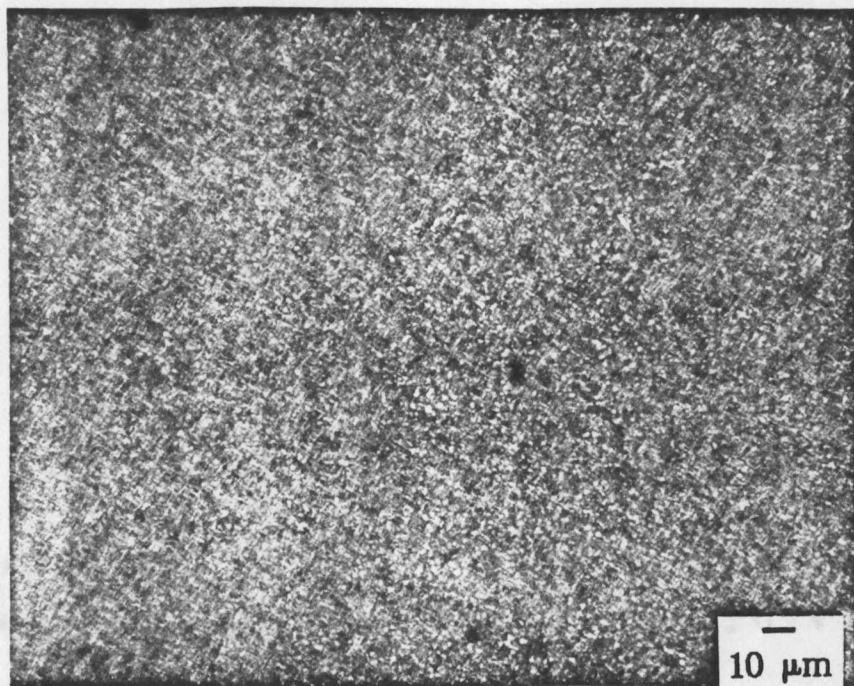
RESULTS AND DISCUSSION

SALS System Verification

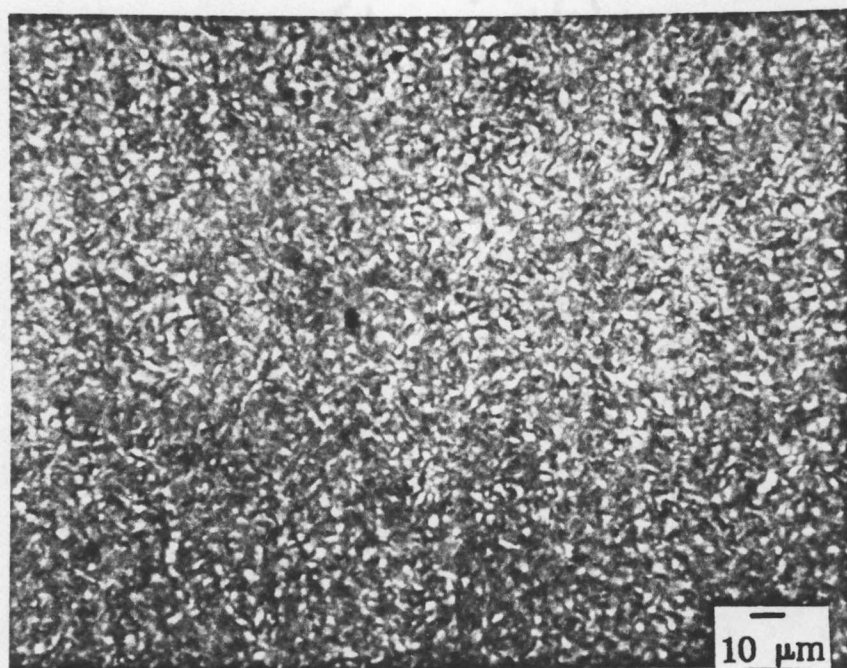
The spherulite radii determined from the video technique are comparable to that from the film method. Table 5.1 indicates the sample-to-detector distance, and the average spherulite radii determined from both techniques. The values from the video method are within 4% of those from the film technique. For example the average spherulite radius determined for the LDPE film from the Polaroid film is 4.71 μm , and from the video technique, 4.53 μm , for a percent difference (video to film) of -3.8%. Optical photomicrographs (Figure 5.1) show spherulites that are of the order of magnitude indicated by Table 5.1.

Table 5.1: Comparison of Spherulite Radii Determined from Polaroid Film SALS and Video SALS.

Material	Sample-Detector (mm)	Film Radius (μm)	Video Radius (μm)	Per. Diff.
LDPE	143	4.71	4.53	-3.82
HDPE	268	9.84	9.60	-2.44



a



b

Figure 5.1: Optical micrographs of a) LDPE, and b) HDPE quenched films.

Polynomial Analysis

The root-mean-square (RMS) correlation moments obtained from the sixth order polynomial regression analysis agree well with those obtained from a standard Guinier analysis. In Table 5.2, the RMS correlation moment, the coefficient of determination (R^2), and the number of data points used in each analysis is given for a variety of compositions, molding temperatures, and cooling conditions. As can be seen, the RMS values for a given material are in close agreement. However, the polynomial analysis has higher coefficients of determinations (where a value of 1.0 equals a perfect fit) and utilizes all the data from the data slice. For example, in the case of the 50 mole% POB material molded at 210 °C and quenched, the Guinier analysis yielded an RMS moment of 1.37 μm , with an R^2 of 0.973 from 29 data points. In contrast the polynomial analysis yield an RMS moment of 1.52 μm , with an R^2 of 0.996 using 119 data points. In fact the main advantage of this method is that little if any data must be discarded in order to yield meaningful results. Thus, data are not arbitrarily included or excluded. Further support for the polynomial analysis is given in Table 5.3 which is an example of two typical polynomial regression analyses, and in Figure 5.2 which shows the plots of the data analyzed (triangles) and the regression curve (solid line). A look at the regression coefficients given in Table 5.3 reveals that the coefficients oscillate in sign in accordance to equation 2.5, indicating consistency with the Taylor's Series expansion of the scattering function. The regression curve fits the data quite well as indicated in Figure 5.2. The values of R^2 for the polynomial regression analysis

Table 5.2: Comparison of Results between the Guinier Analysis
and the Polynomial Analysis

Composition Mole% POB	Mold Temp. (°C)	Cooling Cond.	Guinier Analysis			Polynomial Analysis		
			RMS	No.	R^2	RMS	No.	R^2
			Mom. (μm)	Data Pts.		Mom. (μm)	Data Pts.	
28	210	air	2.59	66	0.840	2.96	112	0.951
28	230	press	1.64	76	0.983	1.90	143	0.997
28	255	air	2.13	67	0.964	2.55	123	0.987
40	210	quench	1.61	50	0.993	1.80	91	0.998
40	230	quench	1.63	71	0.985	1.96	127	0.995
40	285	quench	2.29	59	0.938	2.39	133	0.965
50	210	quench	1.37	29	0.979	1.52	119	0.996
50	255	quench	1.82	38	0.932	2.07	120	0.987
50	285	quench	2.99	33	0.871	3.06	142	0.947
60	210	quench	1.70	56	0.989	1.88	96	0.997
60	255	quench	1.92	39	0.962	2.16	82	0.989
60	285	air	1.97	36	0.662	2.36	129	0.961
70	255	air	2.30	58	0.964	2.61	129	0.988
70	255	quench	1.98	82	0.976	2.17	109	0.991
70	285	press	2.97	61	0.871	3.05	100	0.970

Table 5.3: Typical Polynomial Regression Analyses Results

Comp. Mole% POB	Molding Temp. (°C)	Cool. Cond.	No. Data Pts.	B0	B1	B2	B3	B4	B5	B6	R ²
28	255	air	152	89.5	-97.2	62.0	-23.6	4.93	-0.519	2.15E-02	0.987
40	210	press	129	87.5	-47.7	14.5	-2.38	0.208	-9.12E-03	1.56E-04	0.994
50	285	quench	119	81.4	-127	102	-44.5	10.2	-1.15	5.03E-02	0.947
60	230	air	102	90.5	-38.4	9.45	-1.41	0.119	-5.10E-03	8.70E-05	0.996
70	285	press	100	107	-166	149	-115	62.9	-18.2	2.06	0.966

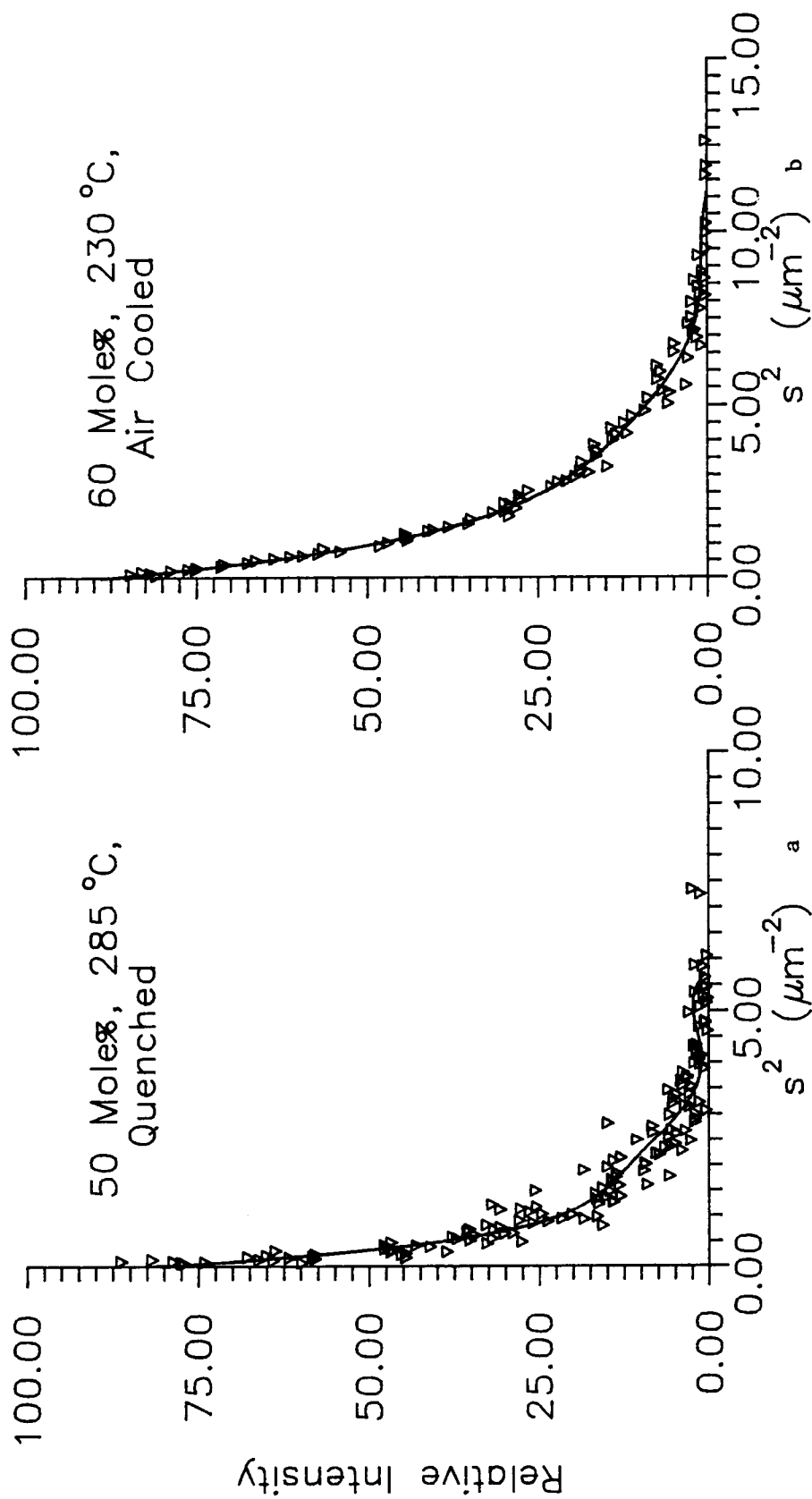


Figure 5.2: Plots of intensity vs. the scattering vector squared. In both a and b, triangles represent SALS data, curves are the polynomial fit.

of the SALS data presented in this work ranged from 0.900 to 0.998, with an average value of 0.981. The value of R^2 is an indicator of the goodness-of-fit of the regression analysis, with a value of 1.0 representing total correlation between the regression curve and the data points, and a value of 0.0 represent no relationship between the two. Therefore, the values of R^2 obtained indicates the polynomial analysis does a very good job in describing the data.

The behavior of the roots of higher moments determined from higher order terms of the polynomial is as predicted from theory. For the most part, as the order of the moment increases, the root-mean-moment (RMM) increases, though not substantially from the RMS, or second, moment. This behavior can be seen in Figure 5.3 which displays plots of the second through eighth RMM's versus the molding temperature for a variety of compositions that were quenched after molding, and in Table 5.4 which contains all RMM's for the samples plotted. The only exception to the general rule of higher moments being larger than lower moments are the twelfth and occasionally the tenth moments. While both of these moments are larger than the second (RMS) moment, the twelfth is always less than the tenth, and the tenth is occasionally less than the eighth. As an example, for the 70 mole% POB sample molded at 285 °C, the RMS moment is 2.06 μm , the eighth RMM is 3.67 μm , the tenth RMM is 3.53 μm , and the twelfth is 2.84 μm . This researcher can only offer two postulates to account for this behavior. The first explanation is that the higher regression coefficients may carry additional statistical uncertainty since they are more influenced by the larger s^2 values. These larger s^2 values tend to contain

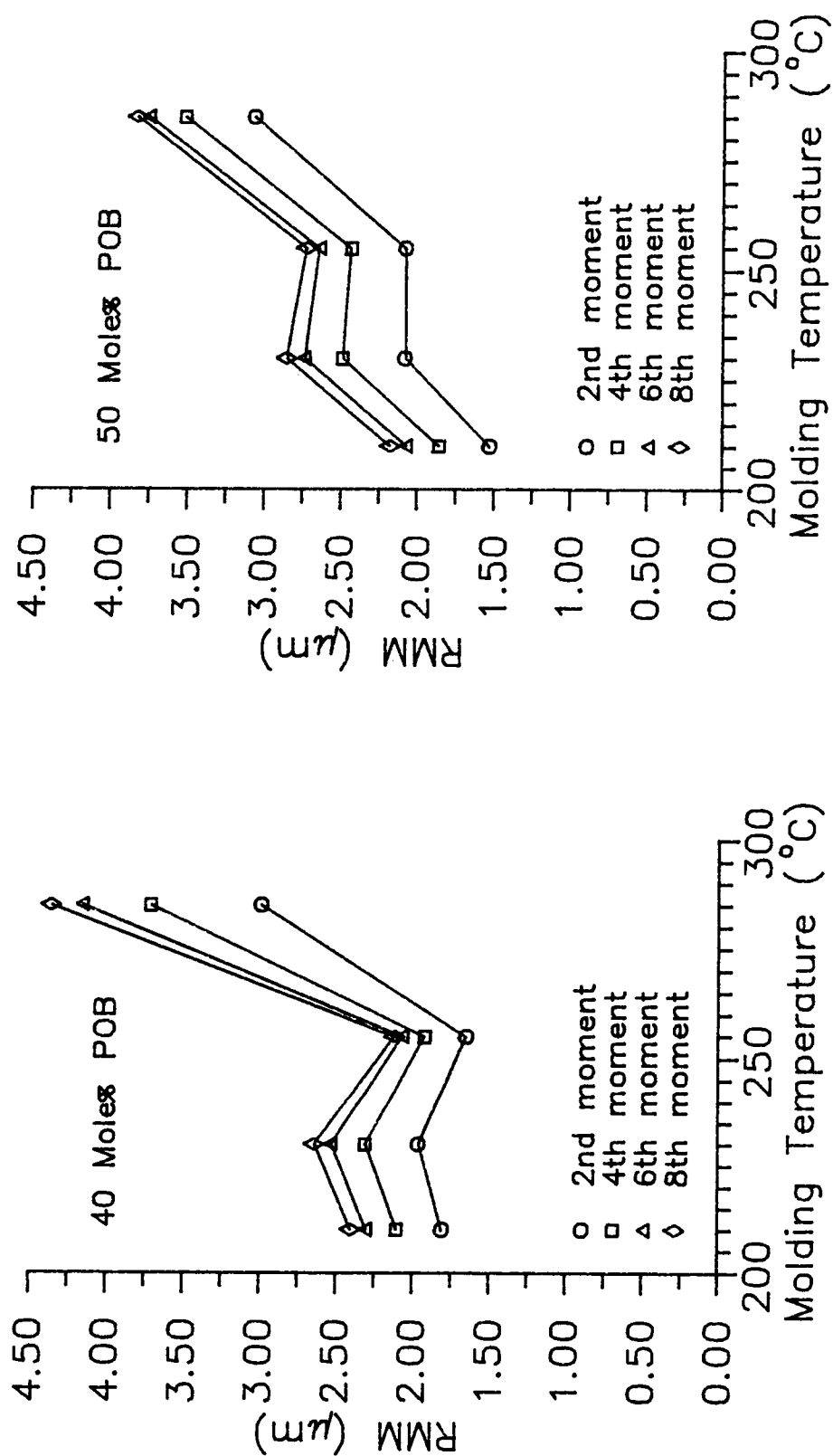


Figure 5.3: Plots of the RMM vs. molding temperature for quenched PET/POB films.

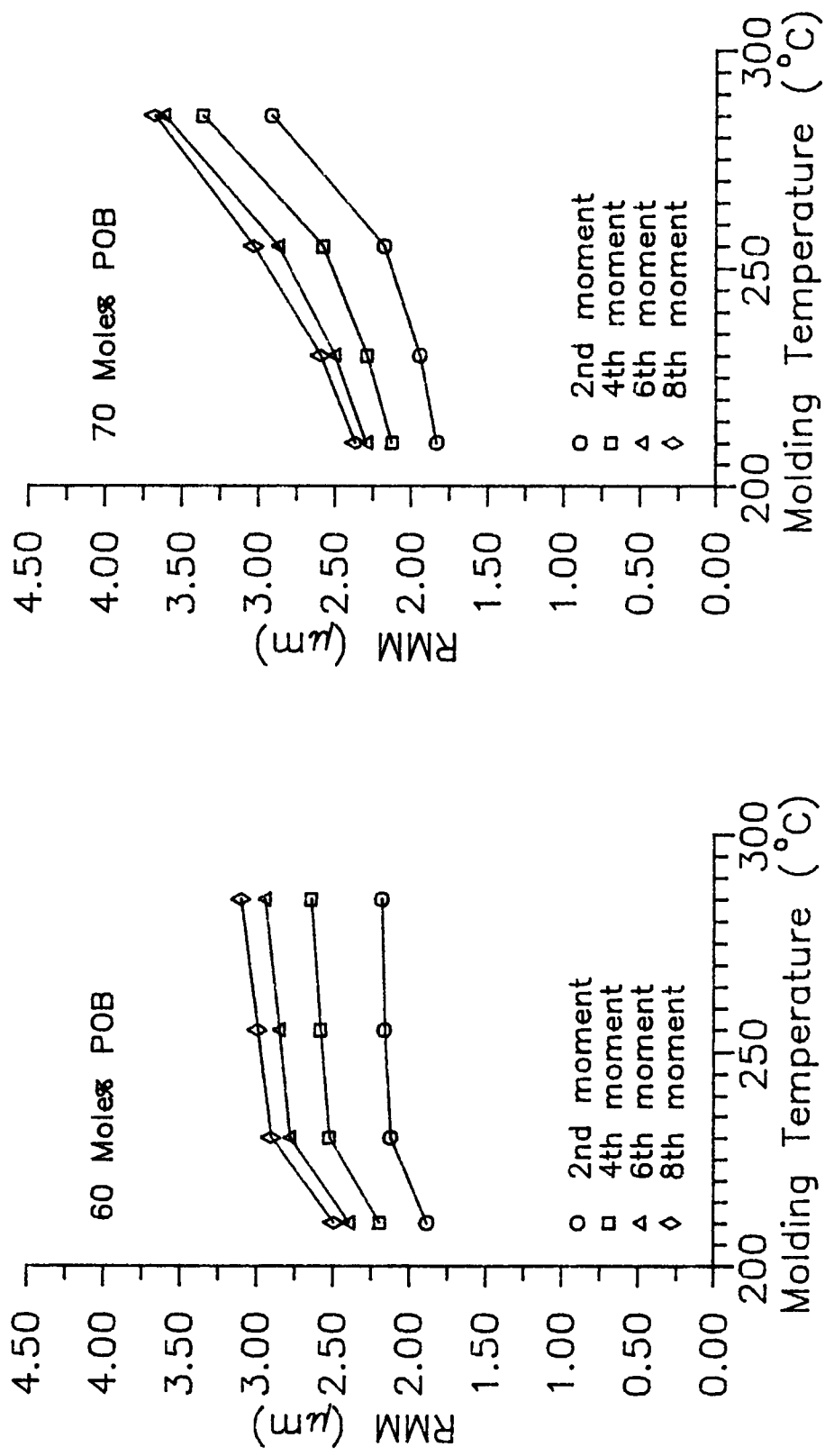


Figure 5.3 continued.

Table 5.4: RMM's for Quenched PET/POB Copolyesters

Comp. Mole% POB	Molding Temp. (°C)	R ²	2nd (μm)	4th (μm)	6th (μm)	8th (μm)	10th (μm)	12th (μm)
40	210	0.998	1.80	2.09	2.30	2.40	2.40	2.30
40	230	0.995	1.96	2.30	2.53	2.64	2.65	2.53
40	255	0.996	1.65	1.92	2.06	2.11	2.09	1.97
40	285	0.942	2.99	3.71	4.15	4.35	4.36	4.16
50	210	0.996	1.52	1.85	2.06	2.17	2.19	2.10
50	230	0.994	2.08	2.48	2.73	2.85	2.85	2.72
50	255	0.987	2.07	2.43	2.63	2.72	2.70	2.55
50	285	0.947	3.06	3.51	3.74	3.82	3.76	3.54
60	210	0.997	1.88	2.19	2.39	2.49	2.49	2.38
60	230	0.993	2.12	2.52	2.79	2.90	2.90	2.76
60	255	0.989	2.16	2.58	2.85	2.99	2.99	2.86
60	285	0.946	2.18	2.64	2.95	3.10	3.12	2.99
70	210	0.998	1.83	2.12	2.29	2.35	2.33	2.21
70	230	0.997	1.94	2.29	2.50	2.59	2.58	2.45
70	255	0.991	2.17	2.58	2.87	3.03	3.06	2.93
70	285	0.970	2.91	3.36	3.62	3.67	3.53	2.84

more scatter in their intensity values. Hence, the moments determined from the higher coefficients may also tend to contain additional error. Next, accepting that higher order regression coefficients tend to be more strongly influenced by larger s^2 values, then a trade off of two competing affects may be occurring. Typically, higher order terms yield information regarding higher moments of the size distribution. Yet, higher values of s^2 represent smaller particle sizes, since scattering occurs in reciprocal space. So, two competing phenomena are occurring, one which is trying to increase the size of the RMM and another which is attempting to decrease the size. So, a balance is reached that tends to direct the higher order RMM's towards lower values. This explanation would be consistent with the relatively narrow range of values indicated by the RMM's. Note that in Table 5.4, that the spread of values is between 1.5 μm and 4.5 μm , and that for a given composition and molding temperature the RMM values fall within 1 μm . This result indicates that either the size distribution of the copolyesters are either very narrow, or more likely, that the higher order moments are being influenced by some other affect as has been suggested. Further support comes from the comparison in Table 2.1 (page 14) between the RMM's determined directly from computer simulated particle size distribution and those determined from polynomial fits to the calculated scattering functions from the distribution. In this study the RMM determined from the polynomial fit was always less than the RMM determined directly from the distribution. The speculation on the competing affects of s^2 values requires further work. Perhaps the best mode of study is to employ computer

generated data sets from various statistical distributions (normal, log-normal, etc.) and compare the moments determined directly from the data sets to those determined from a simulated scattering experiment.

Morphology of Liquid Crystalline Films

Compression Molded Films

The compression molded PET/POB copolyester films are comprised of fibrils, which are organized into rather loosely defined domains. While the fibrils are oriented within the domains, the domains themselves are randomly oriented. Figure 5.4 shows a schematic of the proposed structure for the compression molded films. Support for this type of structure comes from SALS and SAXS patterns, as well as optical and SEM photomicrographs. Figure 5.5 shows iso-intensity contour plots of Hv patterns for several different copolyester films. As is readily seen, all the patterns exhibit circular symmetry, which is consistent with the prediction by Prud'homme and Stein for a random array of rods or disks [19]. Optical micrographs of the copolyesters display a fine "salt and pepper" texture indicating no global orientation in the films (Figure 5.6). Also, fibrils can be seen extending from the edges of the films in some of the micrographs. SEM micrographs (Figure 5.7) reveals a coarse fibrillar texture which is oriented within a domain but not between domains. The localized nature of the orientation is of no real surprise for compression molded films, and is consistent with the WAXD, and SEM work of Joseph et al. [40,44]. Also, the observed coarse fibril texture in the SEM micro-

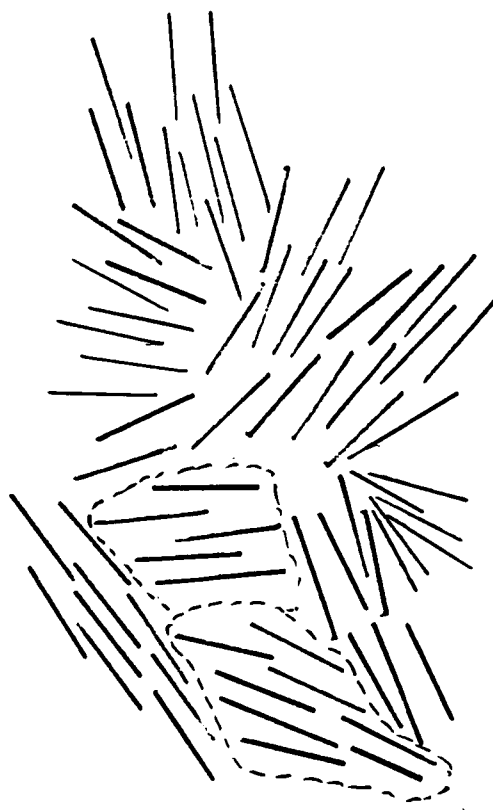
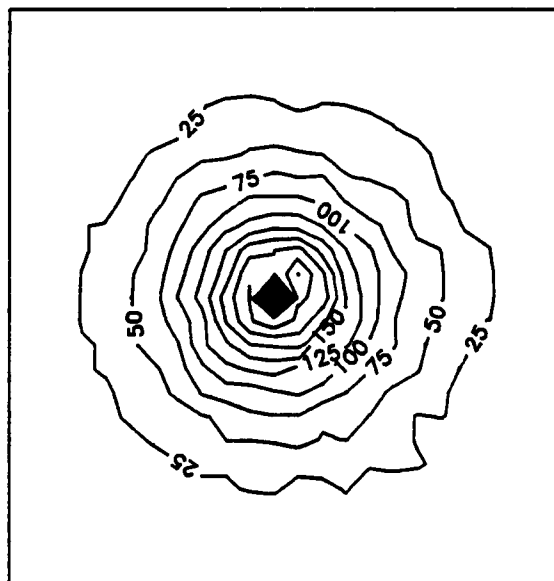


Figure 5.4: Proposed microstructure for the PET/POB copolyesters.
Dotted lines indicate domain boundaries

40 moles POB, 255 C, Quenched



60 moles POB, 285 C, Quenched

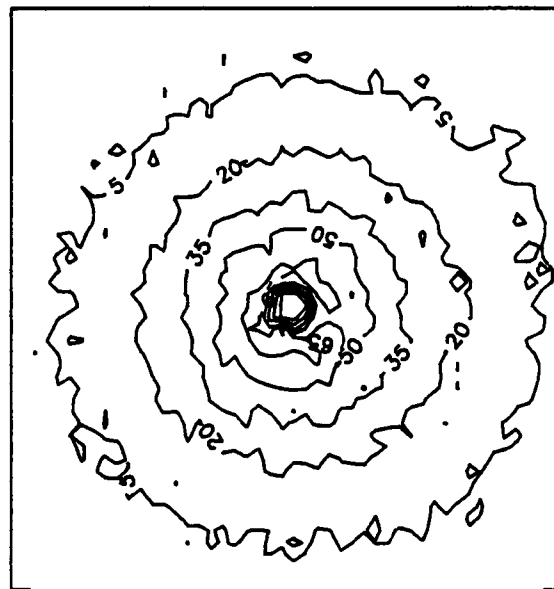
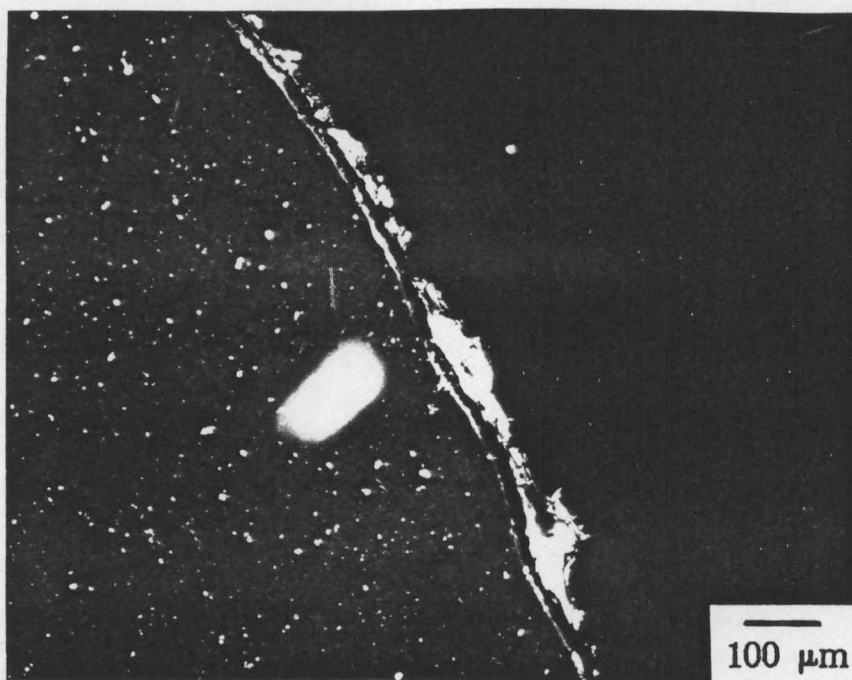
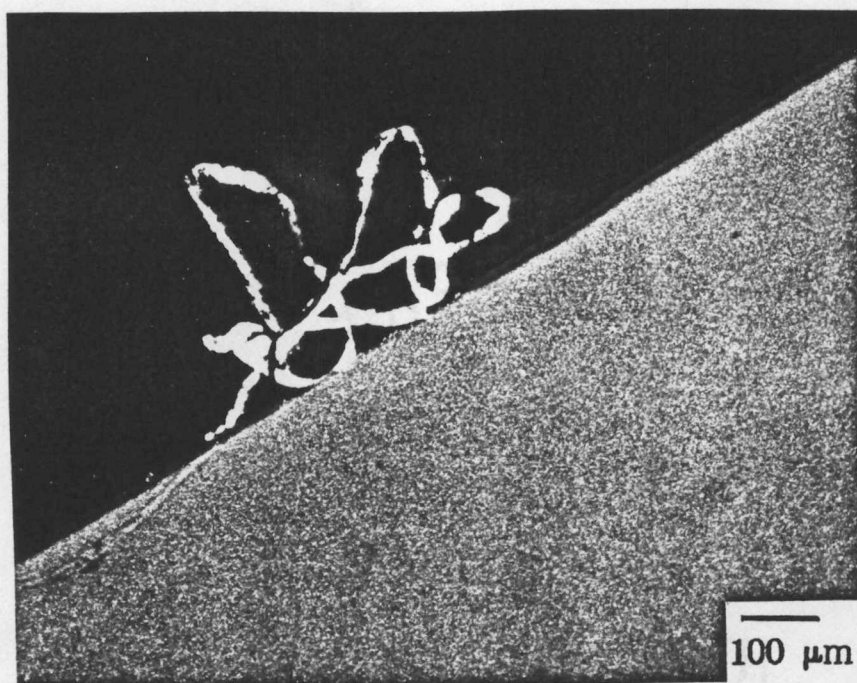


Figure 5.5: Typical Hv SALS contour plot for compression molded PET/POB films.

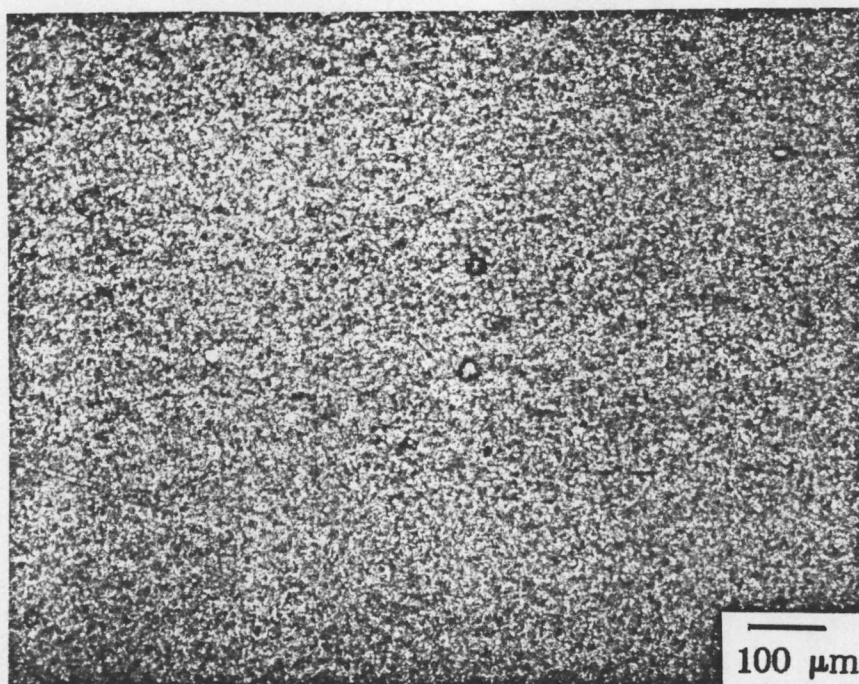


a

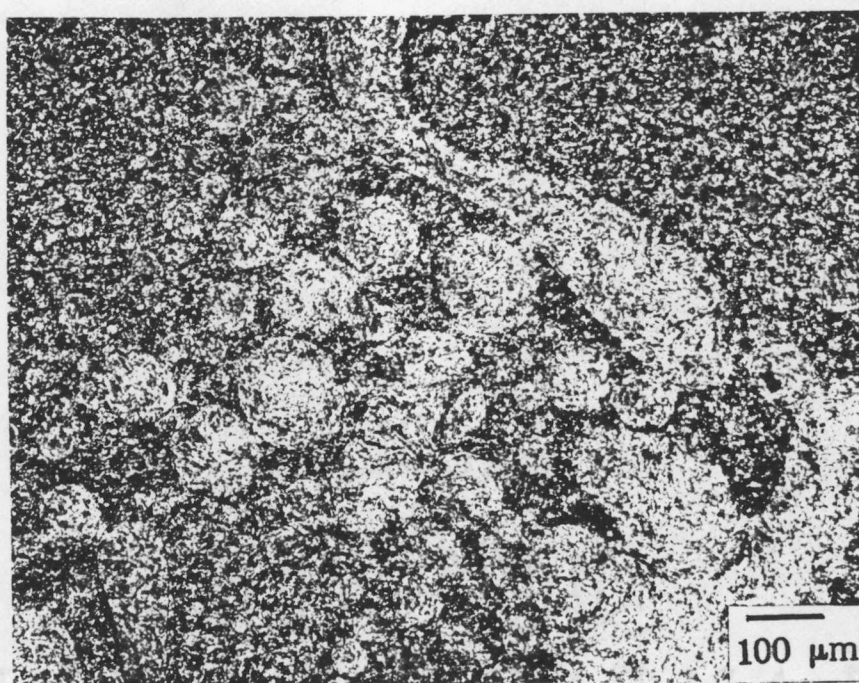


b

Figure 5.6: Optical micrographs of various compression molded PET/POB films. a) 28 mole% POB, 285 °C, quenched, b) 28 mole% POB, 210 °C.

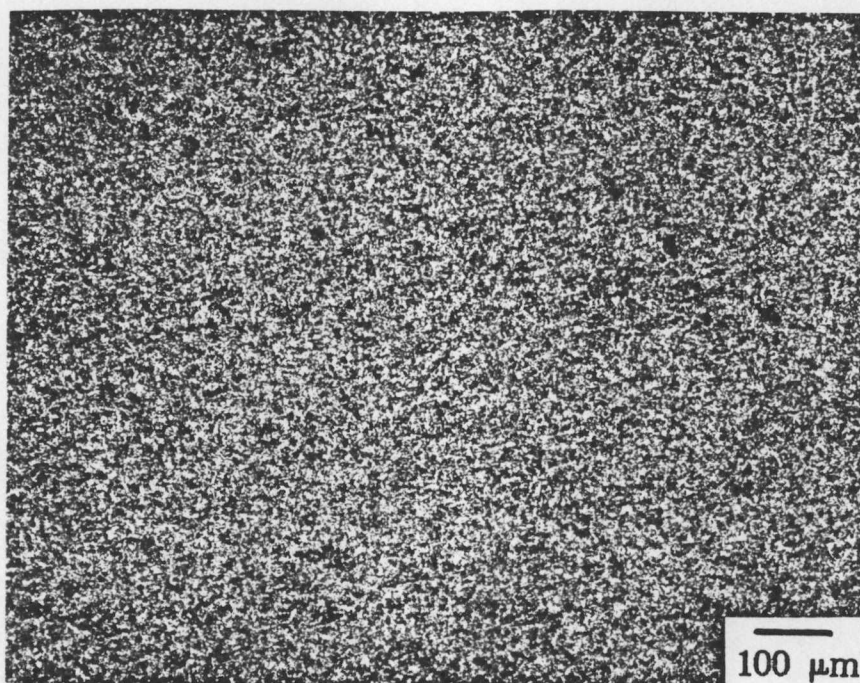


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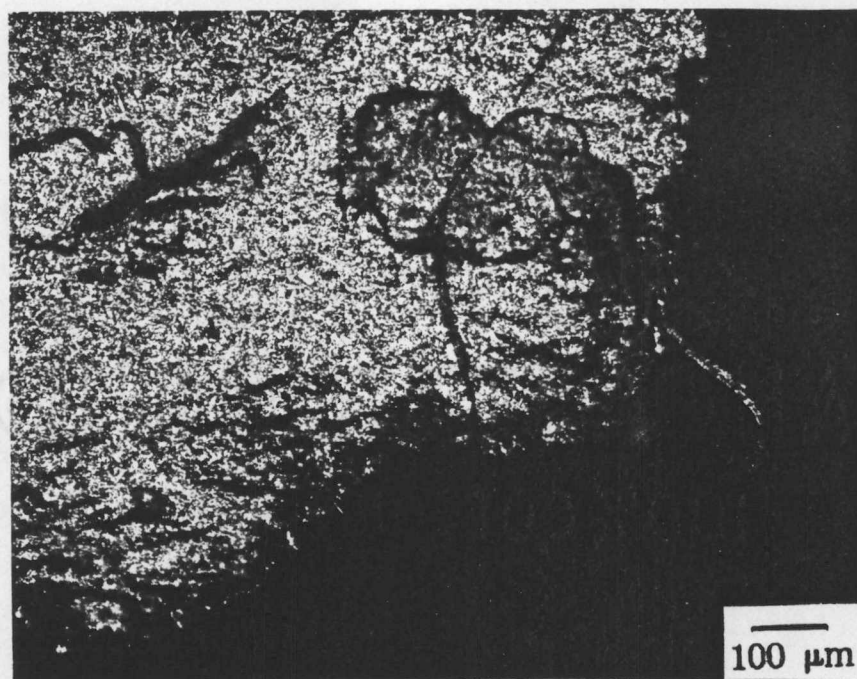


d

Figure 5.6 continued: c) 40 mole% POB, 285 °C, quenched, d) 50 mole% POB, 285 °C, quenched.

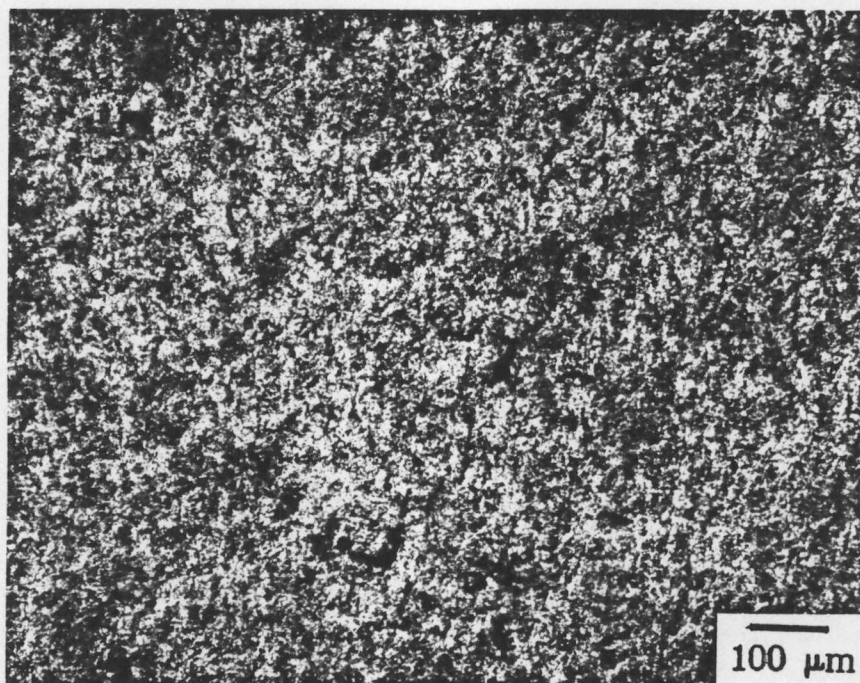


e

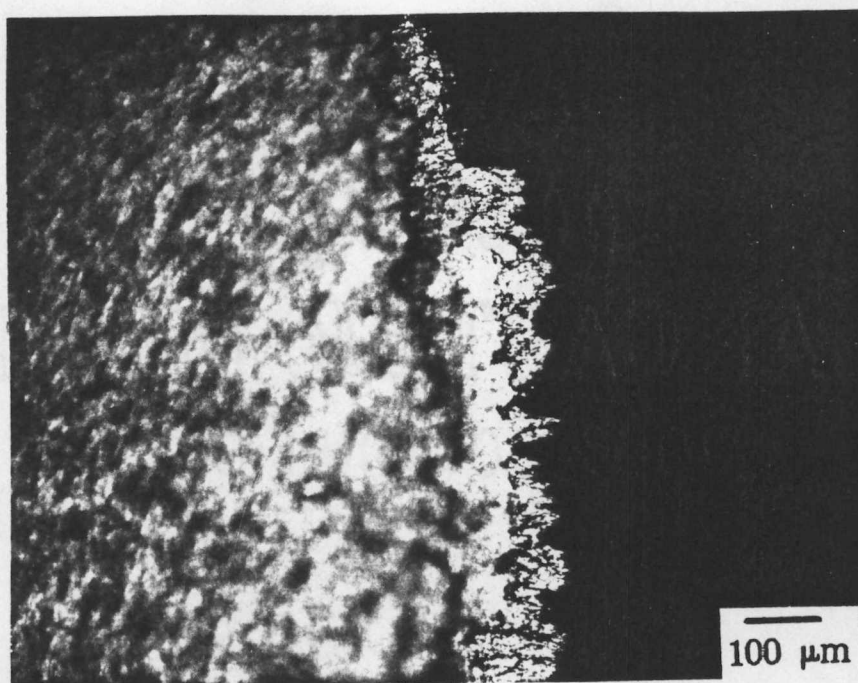


f

Figure 5.6 continued: e) 60 mole% POB, 285 $^{\circ}\text{C}$, air cooled, f) 60 mole% POB, 285 $^{\circ}\text{C}$, air cooled, top view of edge.

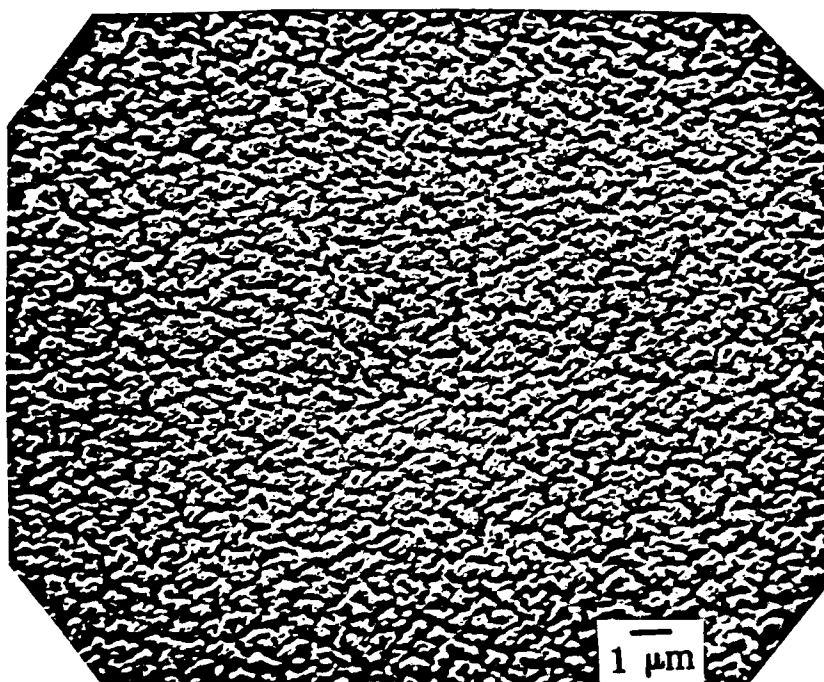


g

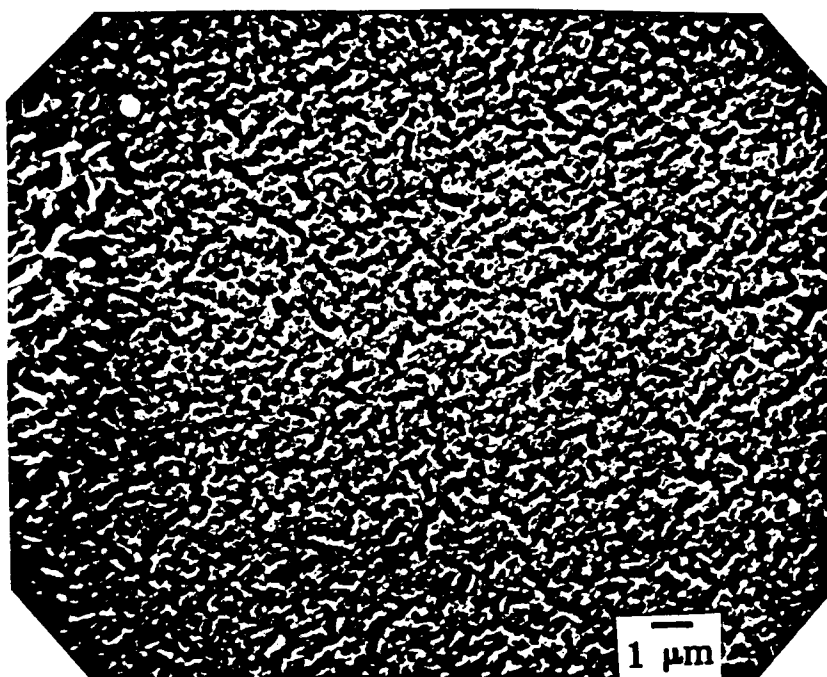


h

Figure 5.6 continued: g) 70 mole% POB, 285 °C, quenched, h) 70 mole% POB, 285 °C, quenched, top view of edge

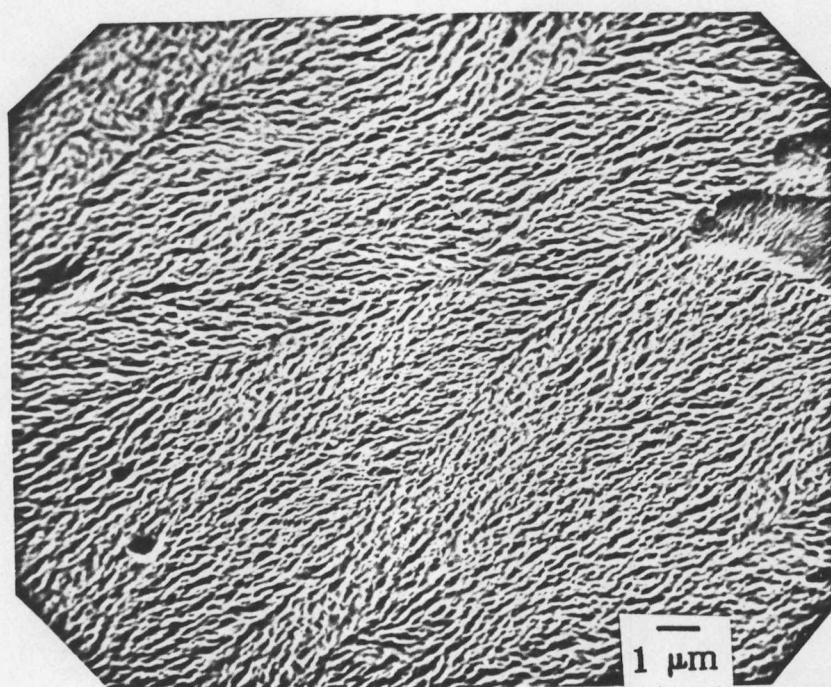


a

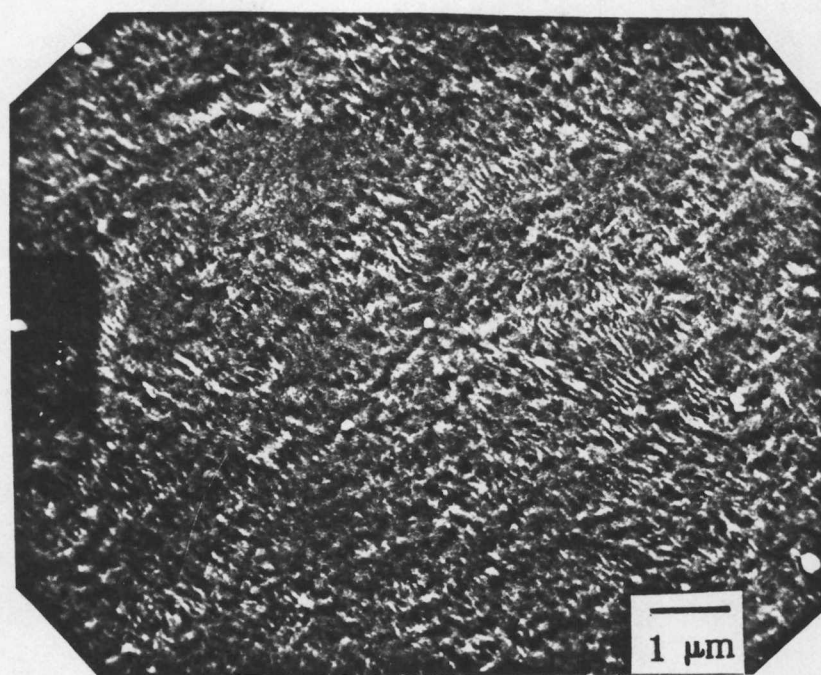


b

Figure 5.7: SEM micrographs of various compression molded PET/POB films. a) 40 mole% POB, 285 °C, quenched, b) 50 mole% POB, 285 °C, quenched.

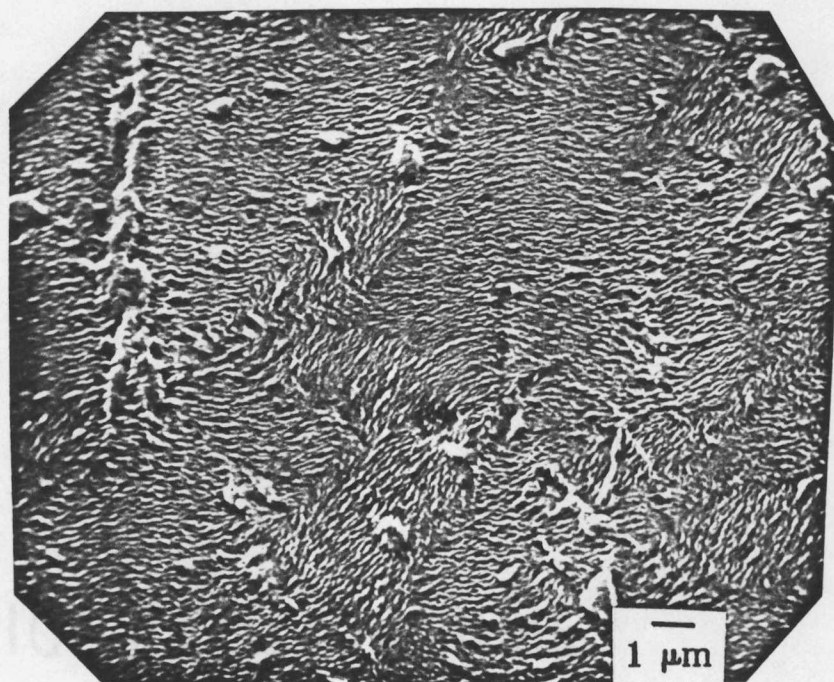


c

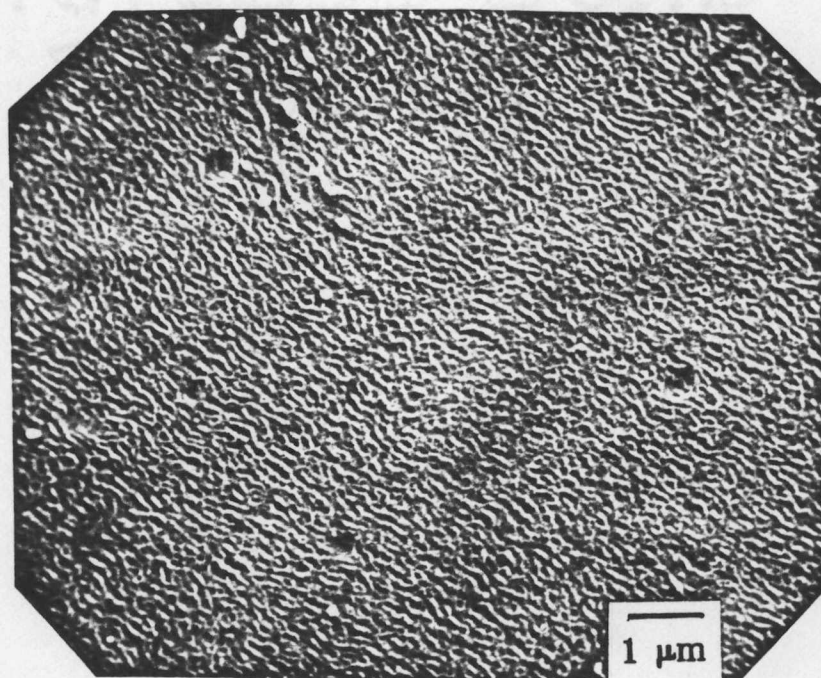


d

Figure 5.7 continued: c) 60 mole% POB, 255 °C, quenched, d) 70 mole% POB, 230 °C, quenched.

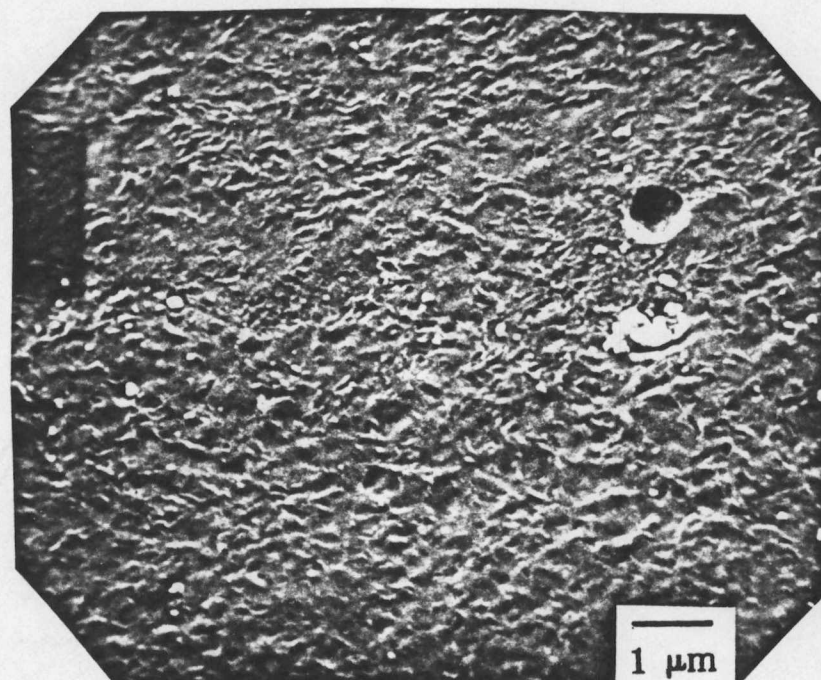


e

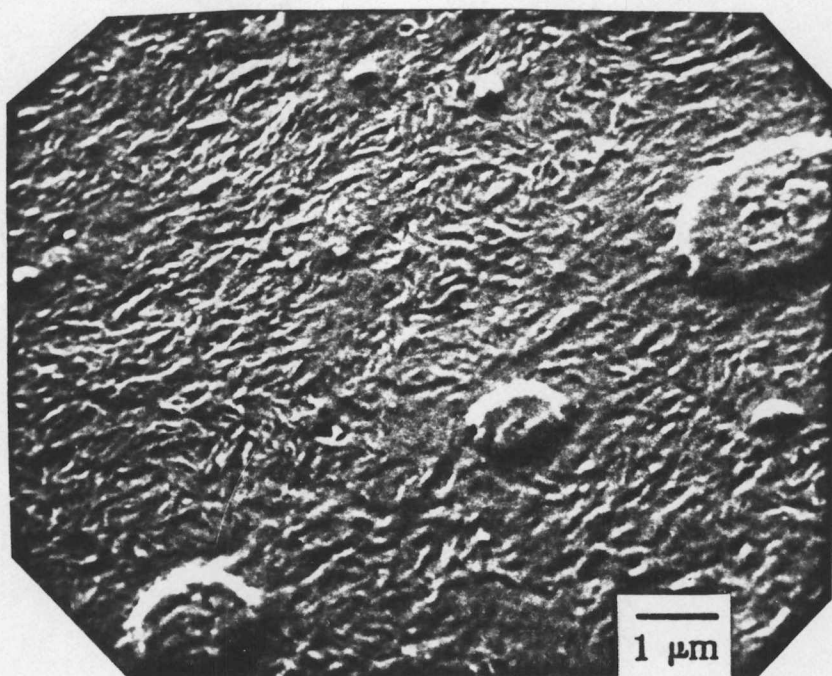


f

Figure 5.7 continued: e) 60 mole% POB, 285 °C, quenched, f) 60 mole% POB, 285 °C, air cooled.



g



h

Figure 5.7 continued: g) 60 mole% POB, 210 °C, quenched, h) 60 mole% POB, 210 °C, air cooled.

graphs was seen by Joseph et al. [40] for films molded between two lubricated plates. It is interesting to note that two different etching techniques, plasma etching in this work, and chemical etching in Joseph's et al.'s, yielded similar microstructures. This agreement among two different methods lends further support to Sawyer's and Jaffe's [38] common microstructural model for liquid crystalline system. Finally, more support for the random arrangement of domains comes from the iso-intensity contour plots from SAXS. Figure 5.8 shows two typical SAXS patterns. The cylindrical symmetry present in the pattern is consistent with scattering from a random array of rods.

The average size of the domains ranges from 1.5 μm to 3.5 μm . Data slices in the form of I versus s^2 were taken at $\pm 45^\circ$ from the Hv SALS patterns. The slices were then fitted to a sixth order polynomial as per equation 2.5. Figure 5.9 indicates the RMS correlation moment determined from the polynomial analysis versus molding temperature, a complete listing of the RMS correlation moments can be found in APPENDIX C. As can be seen the RMS moments run from 1.5 μm to 3.5 μm . This result is further supported by the optical micrographs which indicate that the domains extend from as small as 2 μm to as large as 100 μm . However, it would appear that the preponderance are between 2 μm to 4 μm . This result is especially clear from the micrograph for the thin section of the 50 mole% POB film, molded at 285 $^\circ\text{C}$ and quenched (Figure 5.6, page 75).

The size of the fibrils that compose the domains range from 0.009 μm to 0.030 μm . These sizes were determined from data slices of the

60 Mole% POB, 255 C, Air Cooled

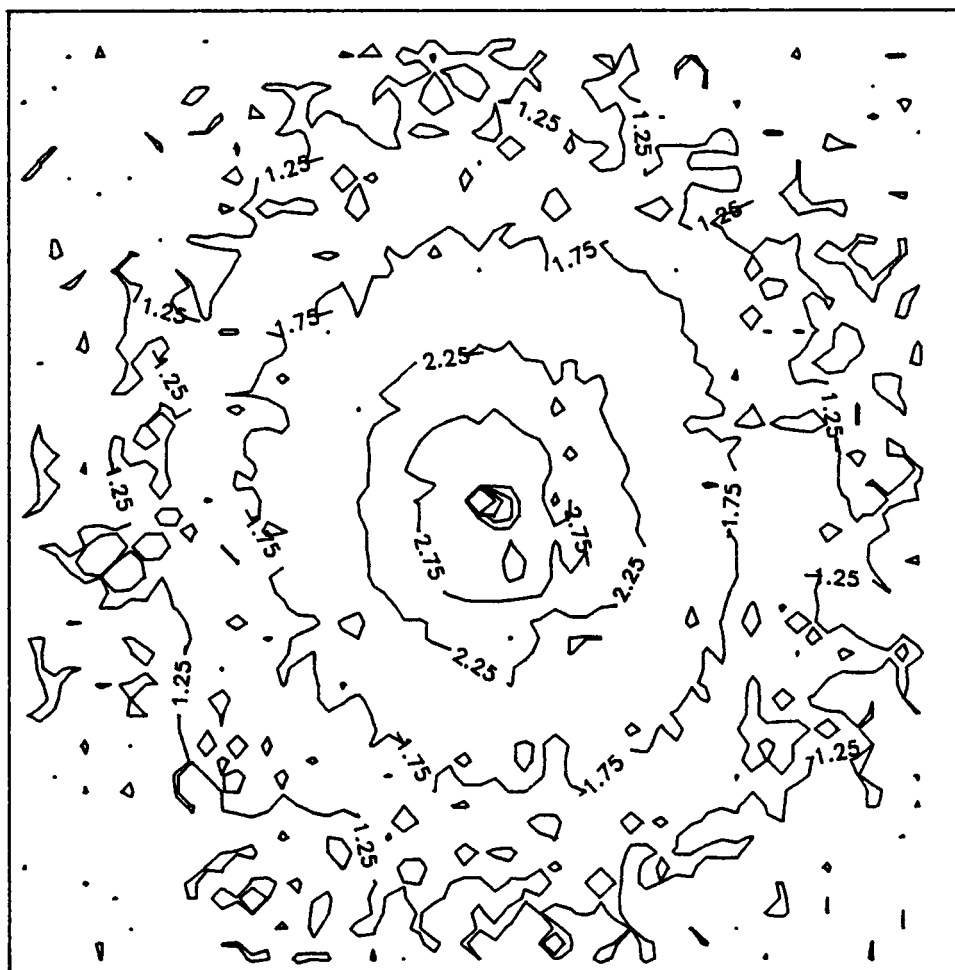


Figure 5.8: Typical SAXS contour plots for compression molded PET/POB films.

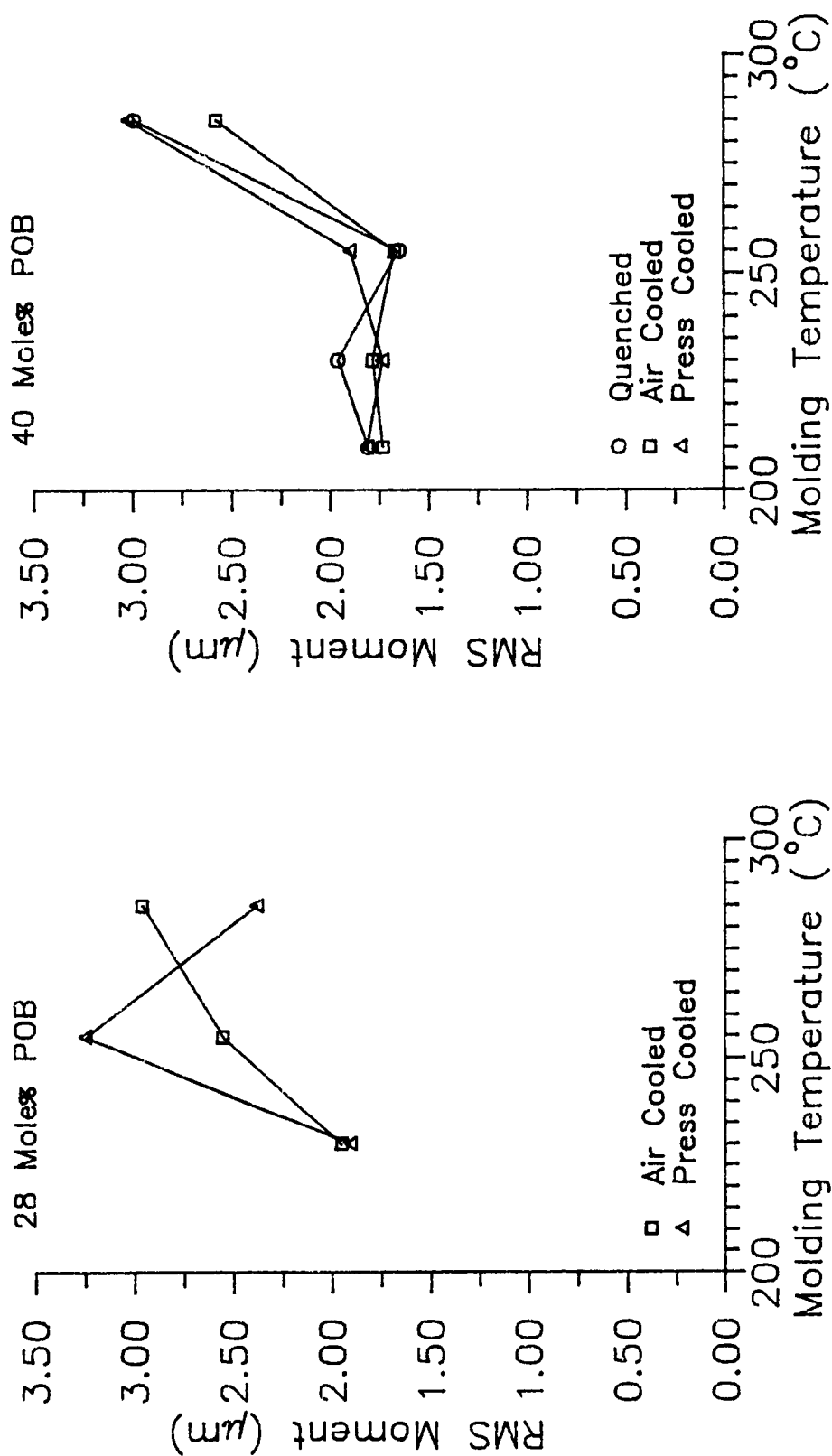


Figure 5.9: Plots of the RMS moment vs. molding temperature.

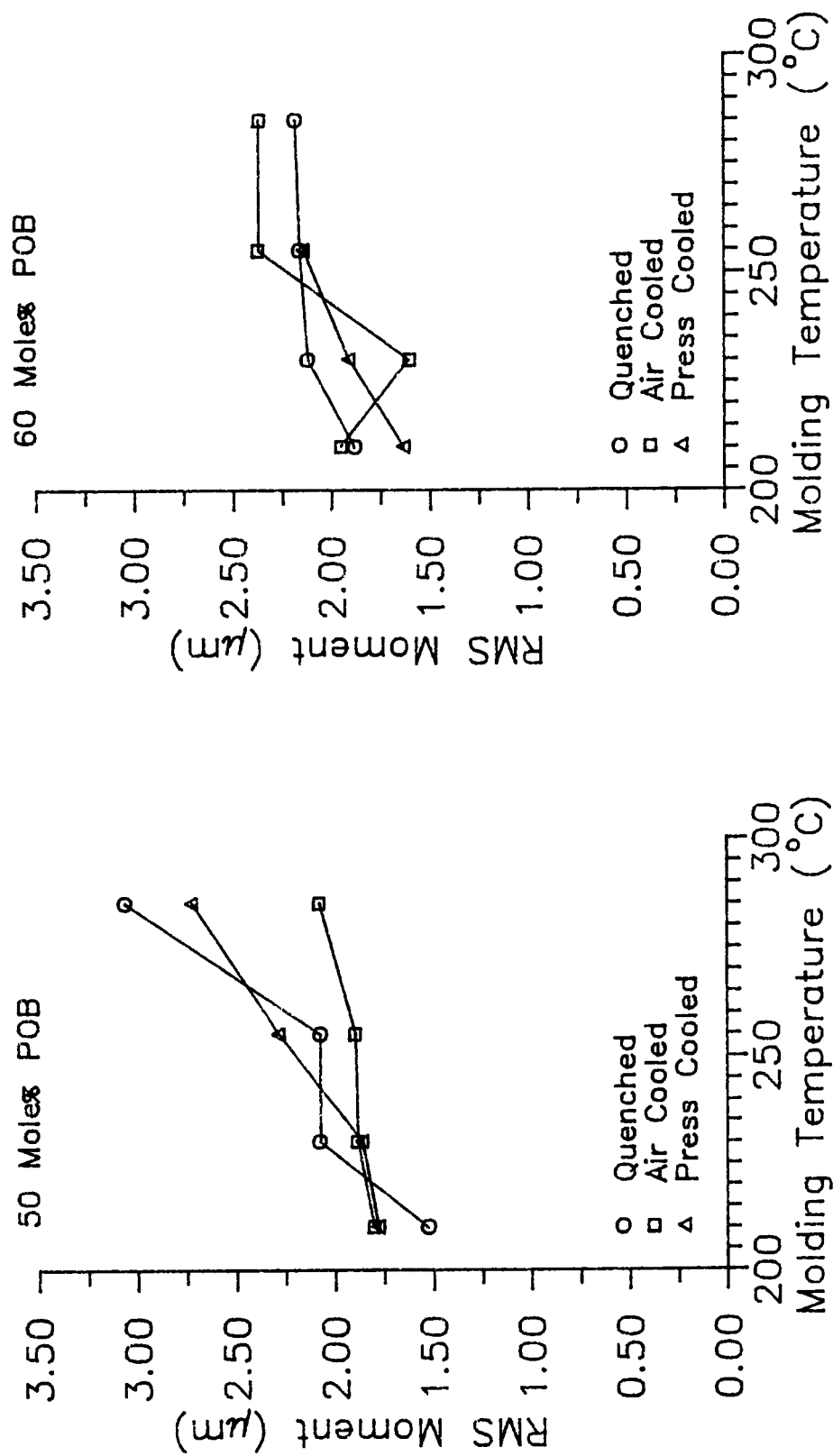


Figure 5.9 continued.

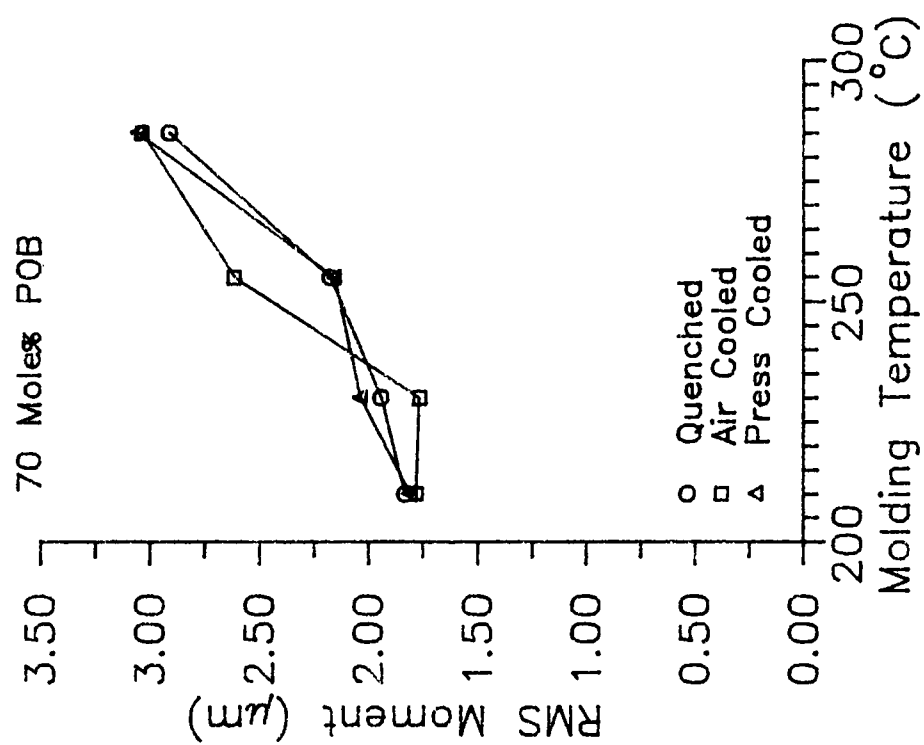


Figure 5.9 continued.

ORNL SAXS files analyzed using the second order polynomial method suggested by Stoll et al. [6]. Table 5.5 gives the RMS moments determined from selected files along with the R^2 value of the regression analysis. In the case of the 60 mole% quenched after molding at 255 °C, the RMS moment determined is 0.0214 μm with an R^2 value of 0.893. These sizes agree well with the fibrillar structure shown in the SEM micrographs contained in Figure 5.7, pages 78-81. The above results fit well into the microstructural model proposed by Sawyer and Jaffe. For the copolyesters the 2-4 μm domains correspond to Sawyer's and Jaffe's 5 μm macrofibrils. Likewise the 0.009-0.03 μm fibrillar structures are consistent with their microfibrils.

An initially surprising result was that the compression molded films' domain sizes are insensitive to the cooling condition employed. Figure 5.9 shows plots of the RMS correlation moment versus the mold-

Table 5.5: Results of SAXS RMS Moments for
PET/POB Compression Molded Films

Composition Mole% POB	Molding Temp. (°C)	Cooling Cond.	RMS Moment (μm)	R^2
60	210	air	0.009	0.990
60	210	quench	0.020	0.968
60	255	air	0.021	0.893
60	285	quench	0.019	0.996

ing temperature for all five compositions, and cooling conditions. It is apparent from these plots that there is no distinct trend or relationship between domain size and cooling condition. The quenched, air cooled, and press cooled curves cross and recross each other with no real separation or trends made evident. In fact, for the most part, at a given molding temperature the RMS correlation moments for the three cooling conditions are within 0.1-0.5 μm of each other. There does seem to be a trend for the domain size to increase with molding temperature, and appears to be the strongest for molding temperatures above 255 $^{\circ}\text{C}$. However, in no case for a given composition does the difference between the highest RMS moment and the lowest RMS moment exceed 1.5 μm . The only exception to this insensitivity to cooling rate is with the 28 mole% samples. All of the quenched films from this composition gave clear films, that yielded little scattering, and virtually no structure when viewed under crossed polars (Figure 5.6a). This indicates that the film is amorphous in nature. However, when more slowly cooled (air or press), the 28 mole% POB material yielded SALS patterns and optical microstructures similar to the other films (Figure 5.6b). If the copolyesters do not form liquid crystalline structures until after 30 mole% POB content, then the 28 mole% material is setting right on the edge between liquid crystalline and flexible coil behavior. In the melt it is a clear, disordered fluid. So if the cooling is rapid enough it forms an amorphous structure similar to quenched PET films. However, at slower cooling rates it has enough time to form an ordered structure similar to those observed for the higher POB compositions.

The insensitivity of domain size to the cooling condition suggests that the structure formed in the melt does not relax upon cooling or at least requires very long relaxation times. This interpretation would agree with Zachariades' and Logan's observation with the 80 mole% POB copolyester, that rotationally induced shear bands were not affected by subsequent annealing experiments [46]. Also, Wissbrun [51] reported long stress relaxation times for the 60 mole% POB material. The thermal insensitivity of the structure makes sense if we consider the copolyester chain as a semi-flexible rod. As shown by Flory [31], the equilibrium state is an ordered state below some critical degree of flexibility. With no externally induced field, there is no preferred orientation direction, so localized order prevails. The formation of larger domains would require the cooperative movement of large numbers of chain segments, which in turn need more thermal input and time. The amount of thermal input required for these copolyesters may be such that the solid to isotropic transition is reached before any cooperative reorganization can occur.

Stretched and Oriented Films

Stretching the Tennessee Eastman's 60 mole% POB copolyester, under the conditions achievable with the T.M. Long apparatus, yielded little, if any, orientation in the stretched film. Table 5.6 and 5.7 lists the results of the stretching experiments. From Table 5.6 it is evident that only two of the ten samples stretched did not fail in some manner. These two samples, U2 and U8, were stretched at temperatures of 110 °C and 90 °C. All of the samples stretched above the

Table 5.6: T.M. Long Stretching Results.
 Attempted Stretch Ratio: 2x1
 Stretch Rate: 750%/min.

Average Sample Code	Stretch Thick. (mm)	Temp. (°C)	Comments
U1	0.143	110	Ripped
U2	0.134	110	OK
U3	0.138	175	Ripped
U4	0.138	175	Ripped
U5	0.136	110	Ripped
U6	0.142	110	Ripped
U7	0.137	160	Ripped
U8	0.134	90	OK
U9	0.144	90	Ripped
U10	0.137	160	Ripped

Table 5.7: SALS Results for Stretched Films.

Sample	Str. Thick. (mm)	Exten. Ratio	Par. Mom. (μm)	Nor. Mom. (μm)	Mom. Ratio
U1	0.109	1.31	2.62	2.27	1.15
U2	0.078	1.72	2.69	2.64	1.02
U3	0.114	1.21	3.34	2.41	1.39
U4	0.121	1.14	2.99	2.36	1.27
U7	0.125	1.10	2.78	2.18	1.28
U8	0.065	2.06	4.79	2.81	1.70
U2 [*]		1.00	2.79	2.60	1.07

* Unstretched sample

145 °C endotherm (U3, U10, U7) failed. SALS was performed in the Hv mode on samples taken from U2, U8, U1, U3, and U7, as well as unstretched specimens from the films that U2, and U8 were cut out from. Figure 5.10 shows the resulting Hv SALS patterns for these films. As can be seen the resulting patterns are basically circular or only very slightly elliptical. This result suggests that stretching the films induced little orientation. Table 5.7 indicates the thickness of the scattering specimens, the extension ratio of the films (molded thickness/stretched thickness), the RMS moments parallel and normal to the stretching direction, and the ratio between the moments parallel, and normal to the machine direction (M.D.). As an example, sample U2 has a stretched thickness of 0.078 mm, for an extension ratio of 1.72, the RMS parallel moments is 2.69 μm , while the normal moment is 2.64 μm , for a moment ratio of 1.02. A comparison between the extension ratios and the moment ratios reveals no trends or correlation. In fact, the low moment ratios themselves indicate that little orientation is present in the films. The lack of well developed orientation is confirmed by the results of WAXD and SAXS experiments on the unstretched U2 specimen and the stretched U2 and U8 specimens.

The specimens for the X-ray experiments were sandwiches constructed from strips cut along the stretching direction as described in Chapter IV. The WAXD film patterns are shown in Figure 5.11. The resulting patterns for all three specimens are a series of concentric rings, indicating no orientation. Likewise, the SAXS patterns (Figure

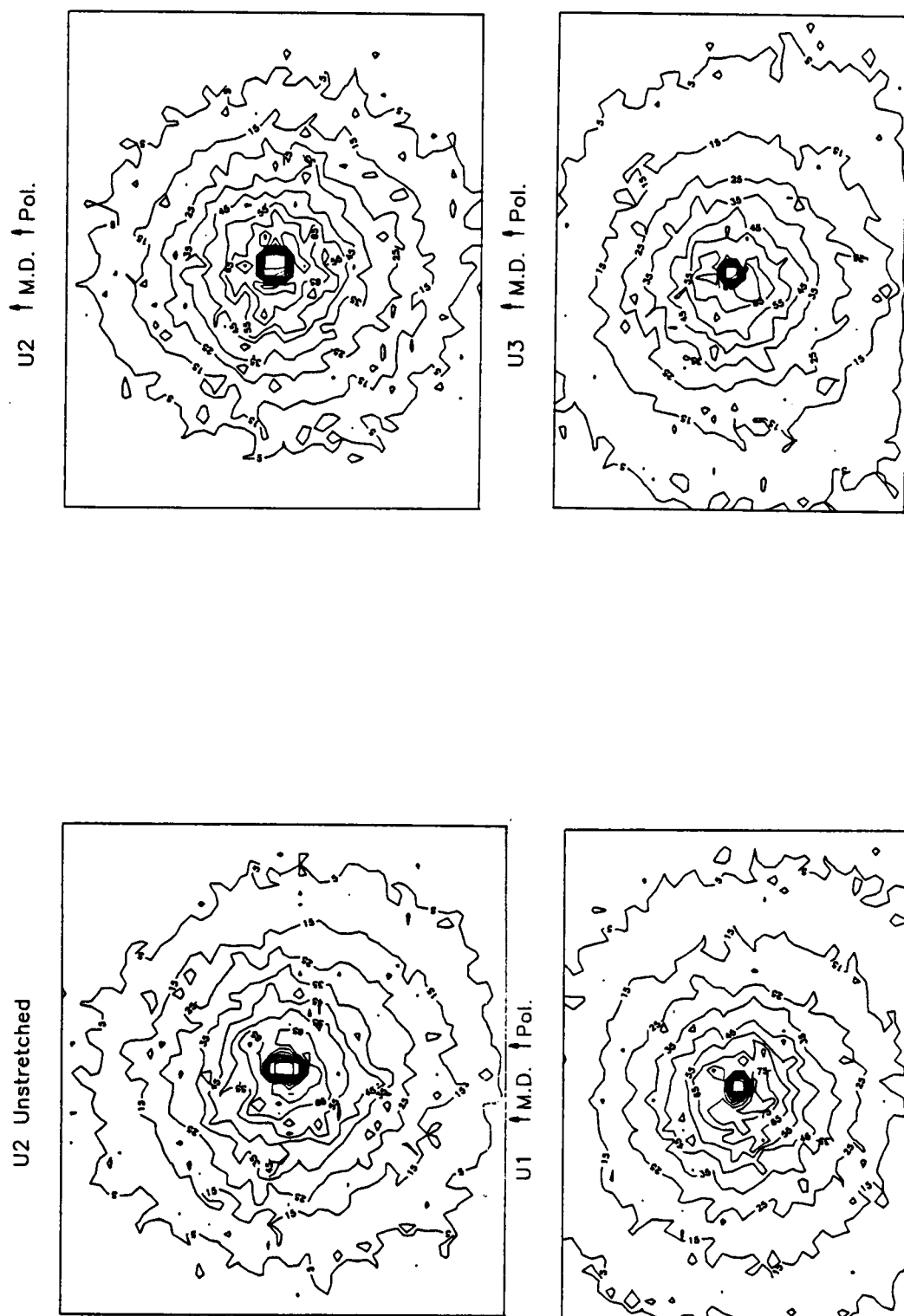


Figure 5.10: Hv patterns for stretched PET/POB films.

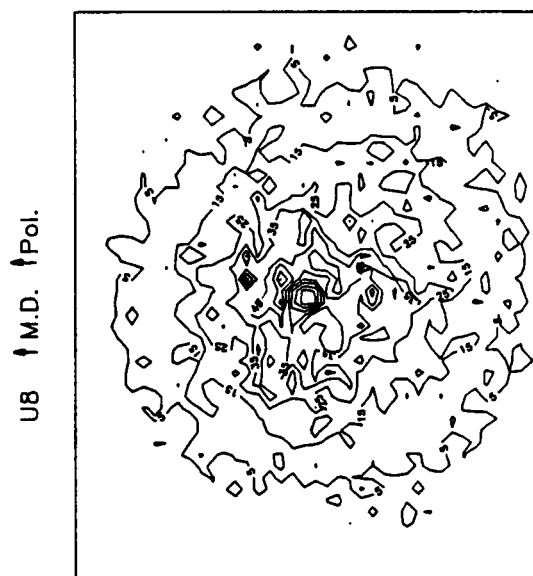
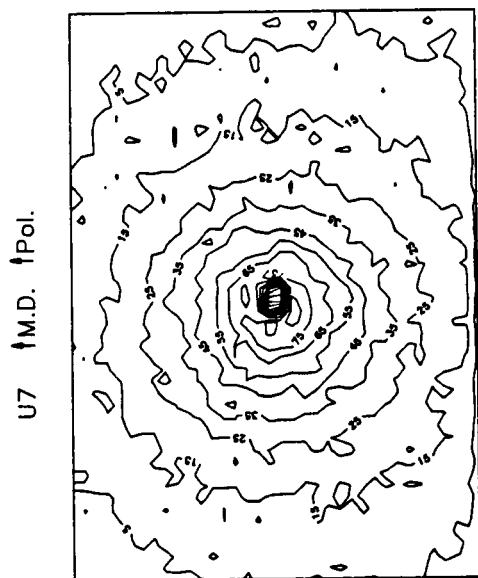
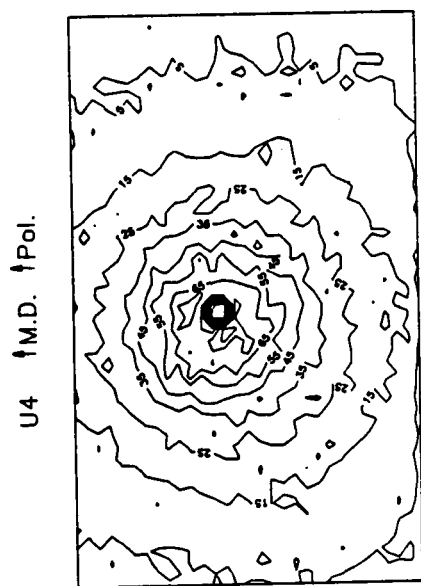


Figure 5.10 continued.

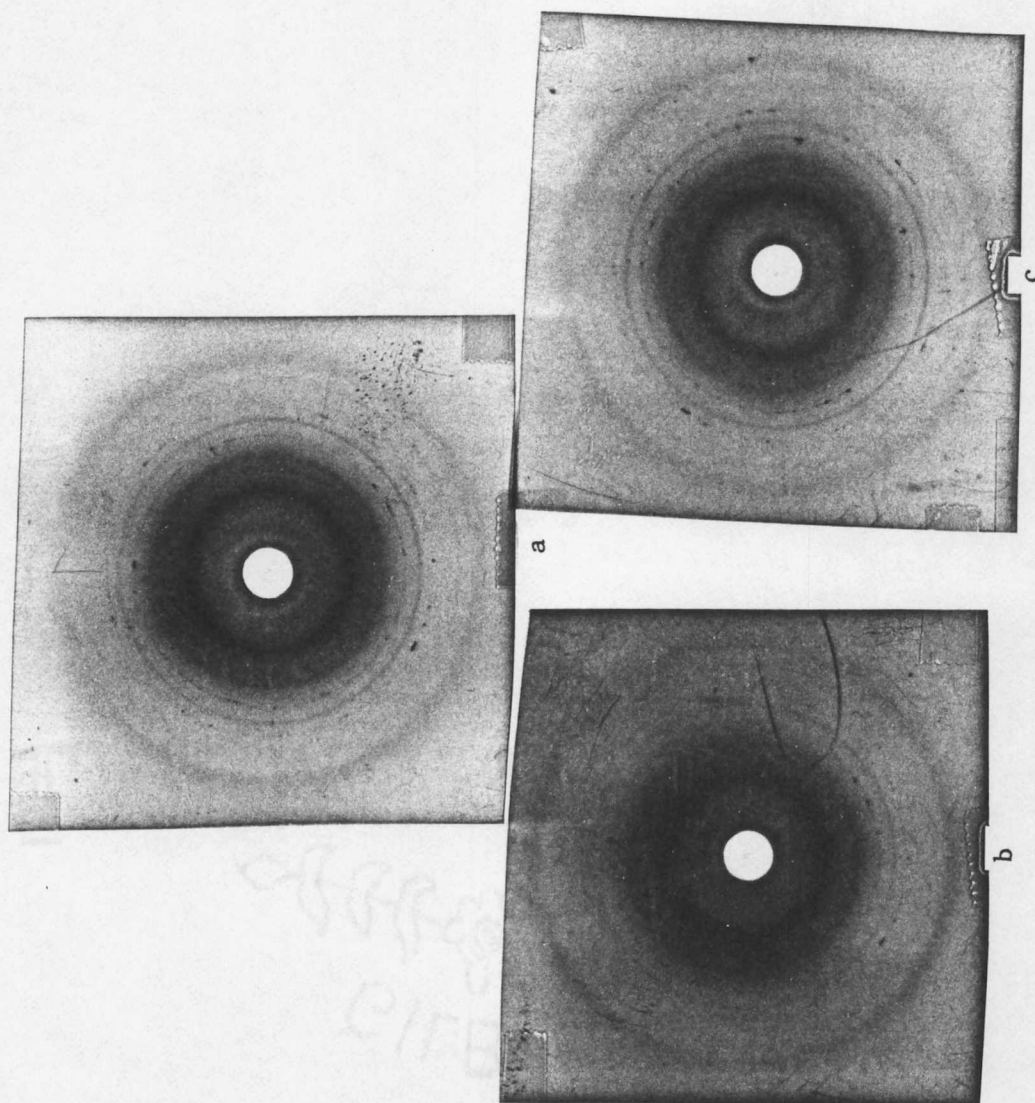


Figure 5.11: WAXD patterns of unstretched and 2x1 stretched PET/POB films. a) sample U2 unstretched, b) sample U2, c) sample U8.

5.12) show circular symmetry, again consistent with the lack of orientation in the films.

It was quite surprising to this researcher that stretching the films did not increase the orientation within the liquid crystalline films as it does for flexible coil films. However, the same rationale used to explain the relative insensitivity to cooling rate on domain size may also apply here. Again, to increase the internal order of the film, large scale cooperative motions of the chains are required. In flexible coil polymers two deformation mechanisms take place depending on whether the polymer is amorphous or crystalline. In crystalline polymers, the mechanical load typically orients the lamellae, hence deforming the spherulites, while the induced load straightens out chain segments in amorphous polymers. Both of these processes can occur by small localized motions, that is rotation about one or two bonds. In liquid crystalline polymers, large segments of the chain are already extended, thus any orientation requires motion on the scale of several bond lengths. Thus, if the surroundings of the chain are rigid enough, slippage or fracture may happen before orientation. Figure 5.13 shows the SEM micrographs of the stretched films of samples U2, and U8. Note the series of parallel bands running normal to the stretching direction of the films. These bands might be the result of slippage of parallel planar domains past one another while under load. So, instead of deforming domains, or aligning fibrils, the load may be causing dislocations of domains via slippage. These observations are consistent with the work of Shih, Hornberger, Siemens, and Zachariades [50], who report only amorphous orientation

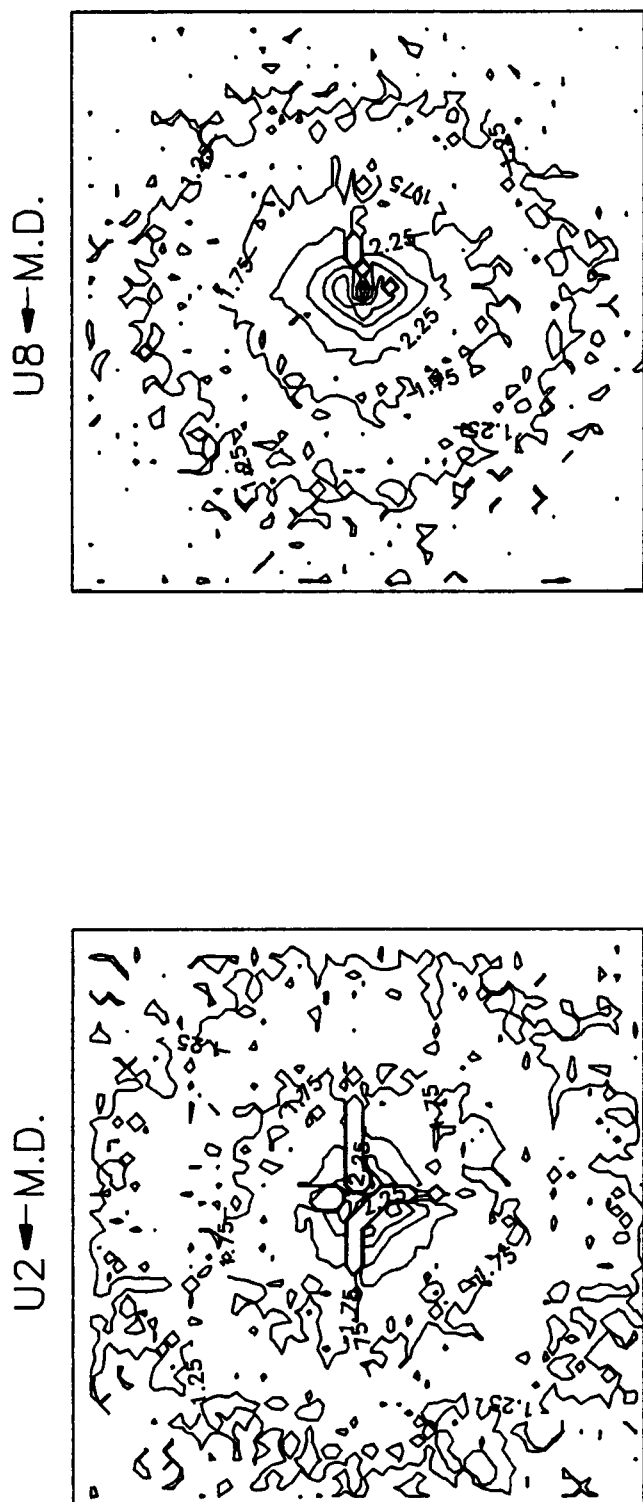
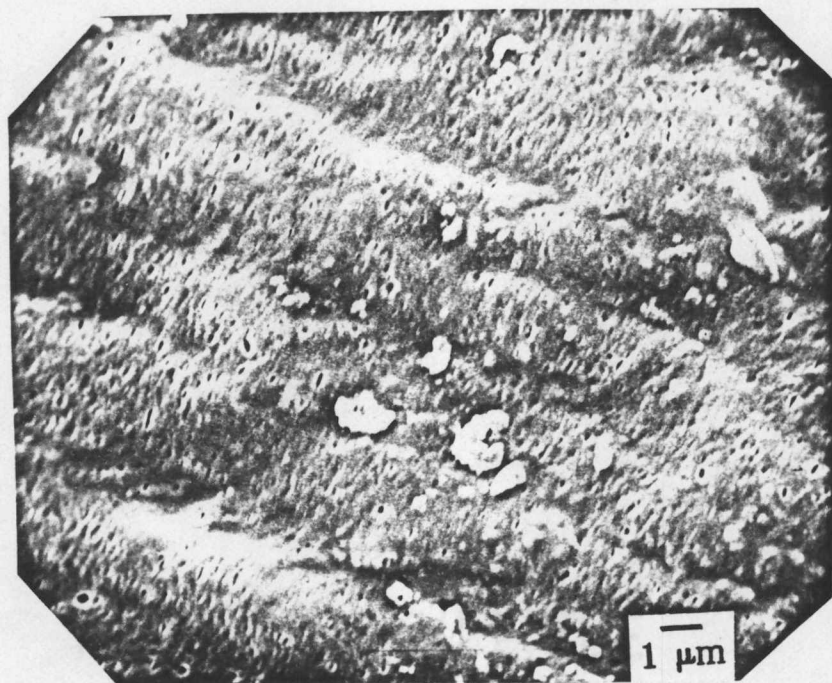
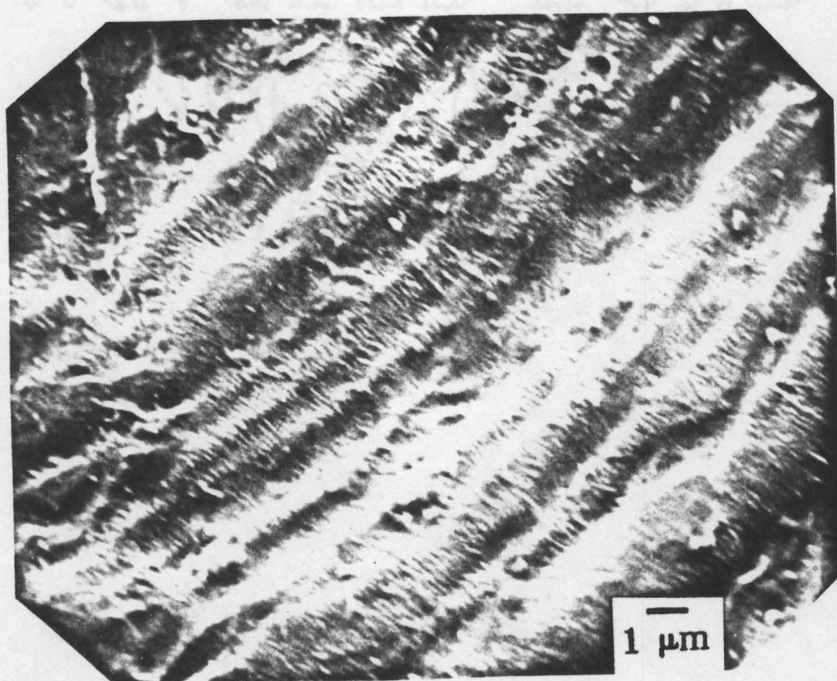


Figure 5.12: SAXS patterns of 2x1 stretched PET/POB films.



a



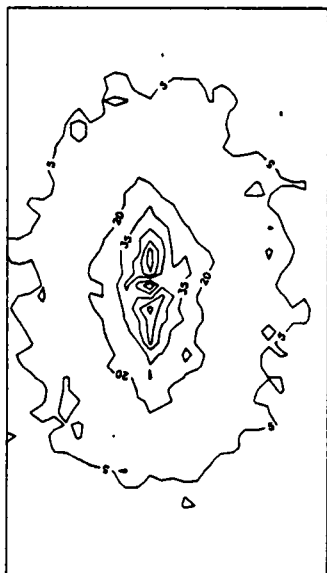
b

Figure 5.13: SEM micrographs of 2x1 stretched PET/POB films.
a) sample U2, b) sample U8.

for 2.7x1 stretched films of the 60 mole% POB copolyester plasticized with 1,1,1,3,3,3-hexafluoro-2-propanol, while no crystalline orientation is observed. So, if a highly oriented sample is required, it may be necessary to induce the orientation while the polymer is in the melt.

Support for being able to develop orientation while in the melt is given from the Hv SALS patterns of films drawn while extruded (Figure 5.14). These films were supplied by D. G. Baird and T. Wilson, at Virginia Polytechnic Institute (VPI). As indicated in Chapter IV, two liquid crystalline copolyesters were drawn: Tennessee Eastman's 40/60 PET/POB, and Celanese's Vectra®. Unlike the other patterns shown thus far, these patterns do not exhibit circular symmetry, but are essentially streaks, with the direction of the streak being normal to the machine direction (M.D.). This result is consistent with Rhodes' and Stein's [18] prediction for a scattering system composed of highly oriented rod-like particles. Further support for an oriented rod morphology comes from optical microscopy, where long fibrillar structures are shown (Figure 5.15). Also, while rotating the stage the field of view would become dark when the M.D. was parallel to either the polarizer or analyzer of the microscope, and was the brightest when situated at 45° to either one. Table 5.8 gives the RMS correlation moments for the directions parallel and normal to the M.D. and the ratio of the parallel moment to the normal moment. As an example for the Vectra® sample positioned such that the M.D. was at 45° to the polarizer, the RMS correlation moment parallel to the M.D. is $11.5 \mu\text{m}$, the normal RMS moment is $5.0 \mu\text{m}$, and the ratio of the two is

60 Mole% POB ↑ M.D. ↑ Pol.



60 Mole% POB ↘ M.D. ↑ Pol.



60 Mole% POB ← M.D. ↑ Pol.

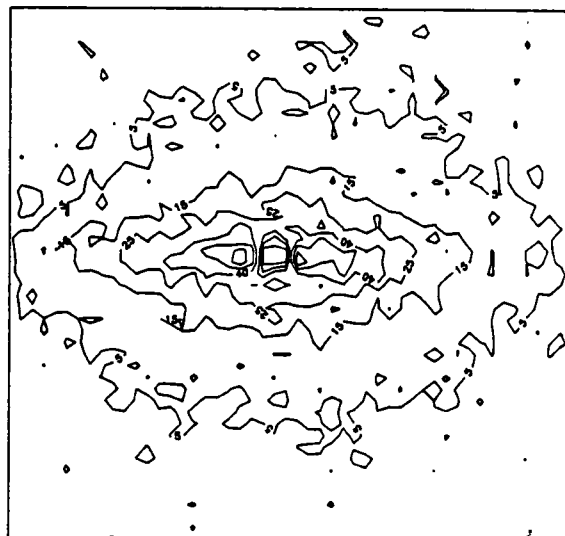


Figure 5.14: Hv patterns of extrusion drawn copolyester films.

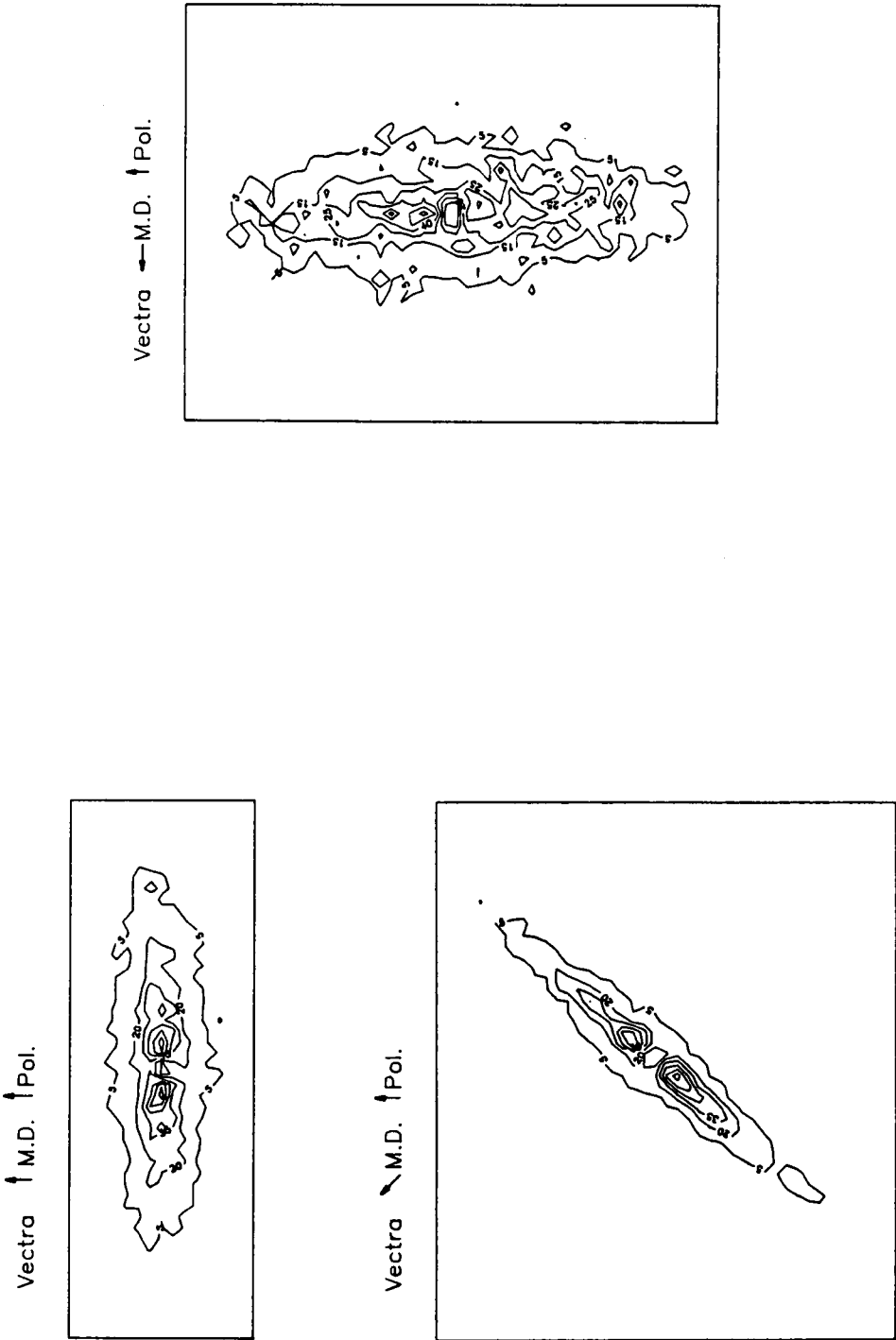
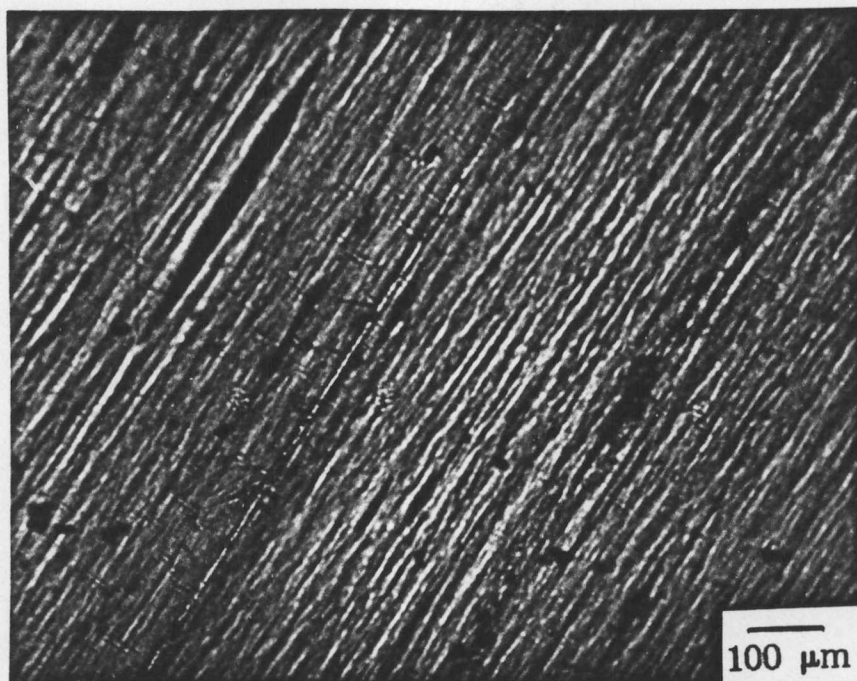
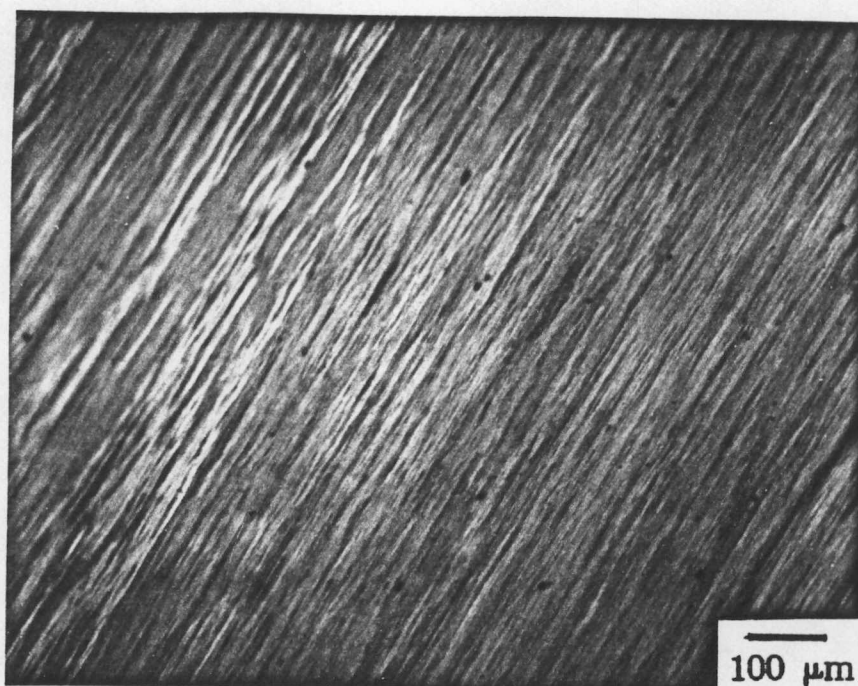


Figure 5.14 continued.



a



b

Figure 5.15: Optical micrographs of extrusion drawn copolyester films. a) 60 mole% POB, b) Vectra®.

3.79. The RMS moments obtained for the drawn film are of the same order of magnitude as those determined for the compression molded films, and agree well with the optical micrographs shown in Figure 5.15. The maintenance of a well develop streak for the Vectra® sample in all three M.D. to polarizer directions should be taken as a sign of highly enhanced orientation. In Table 5.8 the values given for the films with their M.D. at 45° to the polarizer are the most reliable since this orientation should permit the highest amount of transmittance through cross polars, while those given at 90° are the least reliable since this position provides the lowest level of transmittance. Further support fo developing orientation while in the melt comes from the work of Muramatsu and Krigbaum [49]. In their study of melt spun fibers of the 60mole% POB copolyester, they found that oriented structure could be produced through various combinations of draw ratio, and the die L/D ratio. However, to produce orientation, some drawing during the melt was always required.

Table 5.8: SALS Analysis of Extrusion Drawn Copolyester Films.

Sample	Orien. to Pol.	Parallel RMS Moment (μm)	Normal RMS Moment (μm)	Moment Ratio
Vectra	0°	23.8	7.13	3.34
Vectra	45°	11.5	5.01	2.30
Vectra	90°	9.03	5.43	1.66
PET/POB	0°	5.18	3.33	1.55
PET/POB	45°	5.07	3.29	1.54
PET/POB	90°	3.02	2.33	1.84

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The very effective video-SALS technique allows for the relatively rapid capture of quantitative scattering data. This technique allows for the timely capture of two-dimensional data, and subsequent analysis. The video method places SALS on a plane comparable to SAXS and SANS experiments using two-dimensional position sensitive detectors. Although, the spectral intensity range that can be covered is limited to 255 shades of gray, or approximately 2.5 orders of magnitude.

The information gained from the polynomial analysis gives insight into the average size of the scattering particles, but not as much to the distribution of sizes as was originally hoped. This may be due to higher order moments be derived from higher order regression terms that are strongly influenced by larger s^2 values. These s^2 values in turn tend to represent smaller particle sizes.

The compression molded films of the Tennessee Eastman's copolyester are composed of macrofibrils, which have localized order, but no long range order. The pockets of localized order, or domains, range from 1.5 μm to 3.5 μm in size. The domain size does increase slightly with molding temperature, but appear to be insensitive to the cooling condition employed. This indifference to cooling rate may be due to long relaxation times and the rod-like microstructure of the polymer,

which requires large scale cooperative motion in order to form oriented structures. Thus, it is necessary to form any desired orientation in the melt. This concept is reinforced by the fact the molded films proved difficult to stretch and often ripped before deforming. Also, an examination of the stretched films indicated little if any orientation. However, the extrusion drawn films of both the Tennessee Eastman's and the Celanese's copolyesters did exhibit highly ordered fibrillar structures.

Recommendations

In the area of the current SALS equipment, more work needs to be done on improving the resolution of the detection advice to take full advantage of the video camera's resolution. Currently software lags behind the hardware in this area. However, new imaging boards are available that will increase the image screen matrix from 249x236 to 512x512. Also these new boards are capable of acquisition rates up to 30 frames per second as opposed to the current 1 frame per 6 seconds. Additional work needs to be done to allow for thermal kinetic studies to be done using a heated stage. For this work, not only is a hot stage required but improved data acquisition rates and more software analysis. Ultimately, the capability of performing SALS experiments on an absolute intensity scale needs to be developed. To that end methods that will allow for the measurement of a material's transmission coefficient and for making background corrections need to be developed.

The future of the liquid crystalline copolyester project needs to include additional research into uniaxial films and new work into biaxial films. Understanding the nature of stretched films requires more work. However, if uniaxial orientation is desired extrusion drawing appears to be the promising technique. Methods that may prove fruitful in developing biaxial films include: extrusion blown films, sections of blow mold tubes, extrusion through a counter rotating annular die, extrusion of conical or hyperbolic mandrels, and extrusion through conical or hyperbolic annular dies.

Finally more work needs to be done in trying to understand the nature of the scattering function and the information to be gained from scattering. In this regard, computer simulated data sets might prove useful. In creating these files, larger data sets than those used in this work need to be investigated, and different distribution functions should be employed. Also, these data sets might prove useful in trying to understand other common scattering analyses such as the Debye analysis, or the Porod analysis.

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LIST OF REFERENCES

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APPENDICES

APPENDIX A

EQUIPMENT AND SOFTWARE SUPPLIERS

Item: IBM PC Model 5150-174, PC-DOS 2.00 (original), PC-DOS 3.2 (updated).

IBM (National Accounts Division)
9000 Executive Park Dr.
Knoxville, TN 37919

Item: Tecmar Captain Multifunction Board, with 384 KB Memory, Video Van Gogh Digitization Board and Support Software, Expansion Chassis, External 5 MB Cartridge Drive.

Tecmar Inc.
6225 Cochran Rd.
Solon, OH 44139-3377

Item: Dage-MTI Silicon Diode Camera, Model SC-66SX, with Silicon Vidicon Camera Tube.

Dage-MTI Inc.
208 Wabash St.
Michigan City, IN 46360

Item: He-Ne Laser (2 mW).

Aerotech Inc.
101 Zeta Dr.
Pittsburgh, PA 15238

Item: Optical Rail.

Oriel Corporation
P.O. Box 872
Stratford, CT 06497-0872

Item: Optical Table, and Rotatable Sample Holder.

Newport Corporation
P.O. Box 8020
Fountain City, CA 92728-8020

Item: 20 MB External Hard Disk.

Qubie Distribution
4809 Calle Alto
Camarillo, CA 93010

Item: VCR Video Tape Backup Board and Software.

Alpha Micro
P.O. Box 25059
Santa Ana, CA 92799

Item: QGRID, TOPO, AND GRAPHER, Graphics Software.

Golden Software Inc.
P.O. Box 281
Golden, CO 80402

Item: Plotrax Graphics and Statistics Software.

Engineering-Science Inc.
57 Executive Park South, N.E.
Suite 590
Atlanta, GA 30329

Item: 87Basic Compiler.

MicroWay Inc.
P.O. Box 79
Kingston, MA 02364

APPENDIX B

USER WRITTEN SOFTWARE

Description of Software

All the programs presented were wrtitten using IBM's BASICA, and compiled using Microway's 87Basic compiler. The system requires an 8087 math coprocessor ship, dual disk drives, or hard disk, PC-DOS 2.00 or higher, and 256 KB of RAM.

DES.BAS

```

10  ' ** Program: DES.BAS
20  ' ** Program Author: Larry Effler
30  ' ** Program Version 3.1   Date 12-11-1986
40  ' ** Purpose: This program creates a description of a Vid Van Gogh
datafile.
50  '           The .DES file created contains the following
pertinent infor-
60  '           mation: 1) Minimum coordinates of the scattering
pattern
70  '                   2) Maximum coordinates of the scattering
pattern
80  '                   3) Beam stop coordinates
90  '                   4) Sample to screen distance
100 '                   5) Screen to camera distance
110 '
120 PRINT "DES.BAS   Version 3.1"
130 SP=80!
140 BEEP
150 INPUT "Enter the name of the .DES file to be generated (w/o ext.)
";DES$
160 DES$ = DES$ + ".DES"
170 PRINT "Enter the minimum X,Y coordinates [";LX,LY;"]
180 INPUT LXI,LYI
190 PRINT "Enter the maximum X,Y coordinates [";UX,UY;"] "
200 INPUT UXI,UYI
210 PRINT "Enter the beam stop X,Y coordinates [";CX,CY;"] "
220 INPUT CXI,CYI
230 PRINT "Enter the Sample Position (in cm) [";SP;"] "
240 INPUT SPI

```

```

250 PRINT "Enter the Screen Position (in cm) [";IM;"] "
260 INPUT IMI
270 PRINT "Enter the Camera Position (in cm) [";CP;"] "
280 INPUT CPI
290 OPEN DES$ FOR OUTPUT AS #1
300 IF LXI<>0 THEN LX=LXI
310 IF LYI<>0 THEN LY=LYI
320 IF UXI<>0 THEN UX=UXI
330 IF UYI<>0 THEN UY=UYI
340 IF CXI<>0 THEN CX=CXI
350 IF CYI<>0 THEN CY=CYI
360 IF SPI<>0 THEN SP=SPI
370 IF IMI<>0 THEN IM=IMI
380 IF CPI<>0 THEN CP=CPI
390 SS = (IM+3.5#)-SP
400 SC = (CP-2#)-(IM+3.5#)
410 PRINT #1, LX, LY
420 PRINT #1, UX, UY
430 PRINT #1, CX, CY
440 PRINT #1, SS, SC
450 CLOSE
460 INPUT "Create another .DES file...(Y,N) ";Y$
470 IF Y$="Y" OR Y$="y" THEN 140 : END

```

POLYGEN.BAS

```

10 *** POLYGEN.BAS
20 *** Version 2.1      September 20, 1986
30 *** Larry Effler, Program Author
40 PRINT "POLYGEN.BAS      Version 2.1"
50 BEEP
60 PRINT "This program generates an output file for a first to eighth
order polynomial."
70 PRINT " "
80 INPUT "Enter the name of the outputfile";OUTF$
90 OPEN OUTF$ FOR OUTPUT AS #1
100 INPUT "Polynomial Order (1-8) ";PO
110 IF PO=1 GOTO 200
120 IF PO=2 GOTO 300
130 IF PO=3 GOTO 410
140 IF PO=4 GOTO 530
150 IF PO=5 GOTO 660
160 IF PO=6 GOTO 800
170 IF PO=7 GOTO 950
180 IF PO=8 GOTO 1110
190 GOTO 100
200 First order
210 PRINT "Enter the regression coefficients: "
220 INPUT "B0 = ";B0

```

```

230 INPUT "B1 = ";B1
240 INPUT "Enter initial and final h values and step size ";K0,K,SS
250 FOR H=K0 TO K STEP SS
260 LNI = B0 + B1*H
270 PRINT #1, H, LNI
280 NEXT H
290 GOTO 1270
300 ^Second order
310 PRINT "Enter the regression coefficients: "
320 INPUT "B0 = ";B0
330 INPUT "B1 = ";B1
340 INPUT "B2 = ";B2
350 INPUT "Enter initial and final h values and step size ";K0,K,SS
360 FOR H=K0 TO K STEP SS
370 LNI = B0 + B1*H + B2*H^2
380 PRINT #1, H, LNI
390 NEXT H
400 GOTO 1270
410 ^Third order
420 PRINT "Enter the regression coefficients: "
430 INPUT "B0 = ";B0
440 INPUT "B1 = ";B1
450 INPUT "B2 = ";B2
460 INPUT "B3 = ";B3
470 INPUT "Enter initial and final h values and step size ";K0,K,SS
480 FOR H=K0 TO K STEP SS
490 LNI = B0 + B1*H + B2*H^2 + B3*H^3
500 PRINT #1, H, LNI
510 NEXT H
520 GOTO 1270
530 ^Fourth order
540 PRINT "Enter the regression coefficients: "
550 INPUT "B0 = ";B0
560 INPUT "B1 = ";B1
570 INPUT "B2 = ";B2
580 INPUT "B3 = ";B3
590 INPUT "B4 = ";B4
600 INPUT "Enter initial and final h values and step size ";K0,K,SS
610 FOR H=K0 TO K STEP SS
620 LNI = B0 + B1*H + B2*H^2 + B3*H^3 + B4*H^4
630 PRINT #1, H, LNI
640 NEXT H
650 GOTO 1270
660 ^Fifth order
670 PRINT "Enter the regression coefficients: "
680 INPUT "B0 = ";B0
690 INPUT "B1 = ";B1
700 INPUT "B2 = ";B2
710 INPUT "B3 = ";B3
720 INPUT "B4 = ";B4
730 INPUT "B5 = ";B5
740 INPUT "Enter initial and final h values and step size ";K0,K,SS

```

```

750 FOR H=K0 TO K STEP SS
760 LNI = B0 + B1*H + B2*H^2 + B3*H^3 + B4*H^4 + B5*H^5
770 PRINT #1, H, LNI
780 NEXT H
790 GOTO 1270
800 ^Sixth order
810 PRINT "Enter the regression coefficients: "
820 INPUT "B0 = ";B0
830 INPUT "B1 = ";B1
840 INPUT "B2 = ";B2
850 INPUT "B3 = ";B3
860 INPUT "B4 = ";B4
870 INPUT "B5 = ";B5
880 INPUT "B6 = ";B6
890 INPUT "Enter initial and final h values and step size ";K0,K,SS
900 FOR H=K0 TO K STEP SS
910 LNI = B0 + B1*H + B2*H^2 + B3*H^3 + B4*H^4 + B5*H^5 + B6*H^6
920 PRINT #1, H, LNI
930 NEXT H
940 GOTO 1270
950 ^Seventh order
960 PRINT "Enter the regression coefficients: "
970 INPUT "B0 = ";B0
980 INPUT "B1 = ";B1
990 INPUT "B2 = ";B2
1000 INPUT "B3 = ";B3
1010 INPUT "B4 = ";B4
1020 INPUT "B5 = ";B5
1030 INPUT "B6 = ";B6
1040 INPUT "B7 = ";B7
1050 INPUT "Enter initial and final h values and step size ";K0,K,SS
1060 FOR H=K0 TO K STEP SS
1070 LNI = B0 + B1*H + B2*H^2 + B3*H^3 + B4*H^4 + B5*H^5 + B6*H^6 +
B7*H^7
1080 PRINT #1, H, LNI
1090 NEXT H
1100 GOTO 1270
1110 ^Eighth order
1120 PRINT "Enter the regression coefficients: "
1130 INPUT "B0 = ";B0
1140 INPUT "B1 = ";B1
1150 INPUT "B2 = ";B2
1160 INPUT "B3 = ";B3
1170 INPUT "B4 = ";B4
1180 INPUT "B5 = ";B5
1190 INPUT "B6 = ";B6
1200 INPUT "B7 = ";B7
1210 INPUT "B8 = ";B8
1220 INPUT "Enter initial and final h values and step size ";K0,K,SS
1230 FOR H=K0 TO K STEP SS
1240 LNI = B0 + B1*H + B2*H^2 + B3*H^3 + B4*H^4 + B5*H^5 + B6*H^6 +
B7*H^7 + B8*H^8

```

```

1250 PRINT #1, H, LNI
1260 NEXT H
1270 CLOSE
1280 INPUT "Do you have another file to be generated...(Y,N)";Y$
1290 IF Y$="Y" OR Y$="y" THEN 70
1300 END

```

SAXSGRD.BAS

```

10  ' ** SAXSGRD.BAS
20  ' ** Version 2.3      07-AP-87
30  ' ** Program Author: Larry Effler
40  '
50  ' ** This program takes a 2-dimensional data file generated by
60  '    the ORNL SAXS facility and manipulate in a form that is can
70  '    be read by Golden Software's TOPO or SURF software.
80  '
90  PRINT "SAXSGRD version 2.3"
100 DIM Z(5000)
110 DEFINT I-N
120 DR$ = "b:"
130 PRINT "Enter the input drive location...[";DR$;"]"
140 INPUT DRI$
150 IF DRI$ = "" THEN 160 ELSE DR$ = DRI$
160 N=1
170 C10 = LOG(10)
180 PRINT " "
190 INPUT "Enter the name of the ORNL file, w/o extension ";INFIL$
200 DOUT$=INFIL$
210 PRINT "Enter the name of the output file, w/o extension
[";DOUT$;"]"
220 INPUT OUTFIL$
230 INPUT "Output the intensity as log(I)...(Y,N)  [y]";YLOG$
240 IF YLOG$ = "" THEN YLOG$ = "Y"
250 IF OUTFIL$="" THEN OUTFIL$=DOUT$
260 OUTFIL$ = OUTFIL$ + ".GRD"
270 INFIL$ = DR$ + INFIL$ + ".D21"
280 OPEN INFIL$ FOR INPUT AS #1
290 PRINT " "
300 PRINT "Reading input file"
310 FOR K = 1 TO 8
320 INPUT #1, A$
330 NEXT K
340 PRINT A$
350 FOR I=1 TO 64
360 FOR J=1 TO 64 STEP 8
370 INPUT #1, Z(N), Z(N+1), Z(N+2), Z(N+3), Z(N+4), Z(N+5), Z(N+6),
Z(N+7)
380 N=N+8

```

```

390 NEXT J,I
400
'=====
=====190
410 ' MAKEGRID.BAS - Program to convert an ASCII file containing
regularly
420 '          spaced grid data to a [.GRD] file.
430 '
440 ' (C) Copyright Golden Software, Inc. 1985
450
'=====
=====
460 '
470 '   Program MAKEGRID.BAS reads in a file and writes it back out
in
480 '   the QGRID format so that TOPO.EXE or SURF.EXE may read it.
The
490 '   file that is read in must have regularly spaced points. The
500 '   order of the input file is important. The first line must
510 '   have the number of rows and columns, then from XMIN to XMAX
along
520 '   row YMIN, then XMIN to XMAX along the next row up, and so
forth
530 '   (i.e. sorted on the X column first and then the Y column).
540 '   For example:
550 '
560 '           2,3
570 '           0,0,1.986
580 '           1,0,2.292
590 '           0,1,1.986
600 '           1,1,3.696
610 '           0,2,2.333
620 '           1,2,2.292
630 '
640 '   Note that the first line states that the grid is 2 by 3.
650
'=====
===
660 NR = 64
670 NC = 64
680 MATLGTH = NR*NC
690 '
700 PRINT "Setting output parameters"
710 '
720 XMIN = 1: XMAX = 64
730 YMIN = 1: YMAX = 64
740 ZMIN = Z(1): ZMAX = Z(1)
750 '
760 FOR N = 2 TO MATLGTH
770     IF Z(N) < ZMIN THEN ZMIN = Z(N)
780     IF Z(N) > ZMAX THEN ZMAX = Z(N)
790 NEXT N

```

```

800 -
810 -
820 -
830 OPEN OUTFIL$ AS #2 LEN=4
840 FIELD #2, 4 AS VERIFY$
850 LSET VERIFY$ = "DSPM": PUT #2
860 FIELD #2,2 AS BYTE1$, 2 AS BYTE2$
870 LSET BYTE1$ = MKI$(NC) :
880 LSET BYTE2$ = MKI$(NR) : PUT #2
890 FIELD #2, 4 AS SP$
900 LSET SP$ = MKS$(XMIN) : PUT #2
910 LSET SP$ = MKS$(XMAX) : PUT #2
920 LSET SP$ = MKS$(YMIN) : PUT #2
930 LSET SP$ = MKS$(YMAX) : PUT #2
940 IF ZMIN <= 0 THEN ZMIN = 1E-10
950 IF YLOG$ = "Y" OR YLOG$ = "y" THEN ZMIN = LOG(ZMIN)/C10
960 LSET SP$ = MKS$(ZMIN) : PUT #2
970 IF YLOG$ = "Y" OR YLOG$ = "y" THEN ZMAX = LOG(ZMAX)/C10
980 LSET SP$ = MKS$(ZMAX) : PUT #2
990 -
1000 PRINT "Printing output file"
1010 -
1020 IF YLOG$ = "Y" OR YLOG$ = "y" THEN 1030 ELSE 1090
1030 FOR N=1 TO MATLGTH
1040 IF Z(N) <= 0 THEN Z(N) = 1E-10
1050 Z(N) = LOG(Z(N))/C10
1060 LSET SP$ = MKS$(Z(N)) : PUT #2
1070 NEXT N
1080 GOTO 1120
1090 FOR N = 1 TO MATLGTH
1100     LSET SP$ = MKS$(Z(N)) : PUT #2
1110 NEXT N
1120 -
1130 CLOSE
1140 PRINT " "
1150 PRINT " "
1160 INPUT "Is there another file to be converted ";Y1$
1170 IF Y1$ = "Y" OR Y1$ = "y" THEN 160
1180 END

```

SAXS1-D.BAS

```

10 - ** SAXS1-D.BAS
20 - ** Version 2.2      04-18-87
30 - ** Written by: Larry Effler
40 -
50 - ** This program takes an ORNL data slice file and converts it
into one of
60 -     four output options for data analysis.

```

```

70 -
80 PRINT "SAXSI-D      Version 2.2"
90 DIM S(500), I(500), DEVIAT(500)
100 PI = 3.1415926#
110 LA = 1.54
120 PRINT""
130 BEEP: :BEEP
140 PRINT "This program will take an ORNL data slice file and allows
for the"
150 PRINT "file to transformed into one of nine options.  This program
will"
160 PRINT "automatically strip the text header from the ORNL file."
170 PRINT ""
180 D$ = "b:";EXT$ = ".D44"
190 CNT=0
200 PRINT "Enter the input drive location...[";D$;"]"
210 INPUT DI$
220 PRINT "Enter the input extension...[";EXT$;"]"
230 INPUT EXTI$
240 IF DI$ = "" THEN 250 ELSE D$ = DI$
250 IF EXTI$ = "" THEN 260 ELSE EXT$ = EXTI$
260 IF EXT$ = ".D44" OR EXT$ = ".d44" THEN SIGN$ = "N"
270 IF EXT$ = ".D45" OR EXT$ = ".d45" THEN SIGN$ = "P"
280 IF EXT$ = ".D41" OR EXT$ = ".d41" THEN SIGN$ = "A"
290 PRINT SIGN$
300 INPUT "Enter the name of the input file, w/o extension";INPF$
310 INFIL$ = D$ + INPF$ + EXT$
320 OPEN INFIL$ FOR INPUT AS #1
330 OUTFIL$ = INPF$ + SIGN$ + ".DAT"
340 PRINT "Enter the name of the output file w/o ext. [";OUTFIL$;"]"
350 INPUT OUTF$
360 IF OUTF$ = "" THEN 370 ELSE OUTFIL$ = OUTF$ + ".DAT"
370 OPEN OUTFIL$ FOR OUTPUT AS #2
380 PRINT "Select output option..."
390 PRINT " 1. Intensity (I) vs. Scattering Angle (SA) (radians)"
400 PRINT " 2. I vs. s          s = 4*pi/la*sin(SA/2)"
410 PRINT " 3. ln(I) vs. ln(s)"
420 PRINT " 4. log(I) vs. log(s)"
430 PRINT " 5. I vs. s^2"
440 PRINT " 6. ln(I) vs. s^2"
450 PRINT " 7. log(I) vs. s^2"
460 PRINT " 8. ln(I) vs. ln(s^2)"
470 PRINT " 9. log(I) vs. log(s^2)"
480 INPUT "Option number";OPTNUM
490 FOR K = 1 TO 8
500 INPUT #1, A$
510 NEXT K
520 PRINT A$
530 FOR J=1 TO 300
540 IF EOF(1) THEN 580
550 INPUT #1, S(J), I(J), DEVIAT(J)
560 CNT=CNT+1

```

```

570 NEXT J
580 IF OPTNUM = 1 THEN 670
590 IF OPTNUM = 2 THEN 750
600 IF OPTNUM = 3 THEN 800
610 IF OPTNUM = 4 THEN 870
620 IF OPTNUM = 5 THEN 950
630 IF OPTNUM = 6 THEN 1020
640 IF OPTNUM = 7 THEN 1100
650 IF OPTNUM = 8 THEN 1180
660 IF OPTNUM = 9 THEN 1260
670 ^ Option 1, I vs. SA
680 FOR J=1 TO CNT
690 S(J) = ABS(S(J))
700 X = (LA/(4*PI))*S(J)
710 SA = 2*(ATN(X/SQR(1-X*X)))
720 PRINT #2, USING " _ ###.####^";SA,I(J)
730 NEXT J
740 GOTO 1340
750 ^ Option 2, I vs. s
760 FOR J=1 TO CNT
770 PRINT #2, USING " _ ###.####^";ABS(S(J)),I(J)
780 NEXT J
790 GOTO 1340
800 ^ Option 3, ln(I) vs. ln(s)
810 FOR J=1 TO CNT
820 IF ABS(S(J)) = 0 GOTO 850
825 IF I(J) <= 0 GOTO 850
830 SA = LOG(ABS(S(J)))
840 PRINT #2, USING " _ ###.####^";SA,LOG(I(J))
850 NEXT J
860 GOTO 1340
870 ^ Option 4, log(I) vs. log(s)
880 FOR J=1 TO CNT
890 IF ABS(S(J)) = 0 GOTO 930
895 IF I(J) <= 0 GOTO 930
900 SA = LOG(ABS(S(J)))/LOG(10)
910 IJ = LOG(I(J))/LOG(10)
920 PRINT #2, USING " _ ###.####^";SA,IJ
930 NEXT J
940 GOTO 1340
950 ^ Option 5, I vs. s^2
960 FOR J=1 TO CNT
970 SA = ABS(S(J))^2
980 PRINT #2, USING " _ ###.####^";SA,I(J)
990 ^ Option 7, log(I) vs. s^2
1000 NEXT J
1010 GOTO 1340
1020 ^ Option 6, ln(I) vs. s^2
1030 FOR J=1 TO CNT
1040 IF I(J)<=0 THEN 1080
1050 SA = ABS(S(J))^2
1060 I(J) = LOG(I(J))

```

```

1070 PRINT #2, USING "_ ###.####^";SA,I(J)
1080 NEXT J
1090 GOTO 1340
1100 ^ Option 7, log(I) vs. s^2
1110 FOR J=1 TO CNT
1120 IF I(J)<=0 THEN 1160
1130 SA = ABS(S(J))^2
1140 I(J) = LOG(I(J))/LOG(10)
1150 PRINT #2, USING "_ ###.####^";SA,I(J)
1160 NEXT J
1170 GOTO 1340
1180 ^ Option 8, ln(I) vs. ln(s^2)
1190 FOR J=1 TO CNT
1200 IF I(J)<=0 THEN 1240
1210 SA = LOG(S(J)^2)
1220 I(J) = LOG(I(J))
1230 PRINT #2, USING "_ ###.####^";SA,I(J)
1240 NEXT J
1250 GOTO 1340
1260 ^ Option 9, log(I) vs. log(s^2)
1270 FOR J=1 TO CNT
1280 IF I(J)<=0 THEN 1320
1290 SA = LOG(S(J)^2)/LOG(10)
1300 I(J) = LOG(I(J))/LOG(10)
1310 PRINT #2, USING "_ ###.####^";SA,I(J)
1320 NEXT J
1330 GOTO 1340
1340 CLOSE
1350 INPUT "Analyze another file...(Y,N)";Y$
1360 IF Y$="y" OR Y$="Y" THEN 190
1370 END

```

SLICE.BAS

```

10 ^ ** SLICE.BAS
20 ^ ** PROGRAM AUTHOR: Larry Effler
30 ^ ** ASSISTED BY: Stephen Stiner, David Lewis, and T. Levitte Cox
40 ^ ** PROGRAM VERSION 9.3 DATE 12-07-1986
50 ^ ** PURPOSE: THIS PROGRAM CONVERTS RECTANGULAR CO-ORDINATE DATA
60 ^                COLLECTED IN SMALL ANGLE LIGHT SCATTERING EXPERIMENTS
70 ^                TO A SELECTED SLICE ALONG A GIVEN AZIMUTHAL ANGLE.
80 ^
90 REM
100 REM  To execute this program you must know the beam stop
coordinates and
110 REM  the screen to camera distance.
120 REM

```

```

130 REM   The following section, lines 26 to 95, contains the Video
Van Gogh
140 REM   Software Support Module: VIDMOD.BAS
150 REM
160 REM           VIDMOD.BAS   (C) Copyright Tecmar, Inc.  1983
170 'This module must be included in any user-generated application
program.
180 'It's function is to retrieve the segment address of the library,
and
190 'to define the variable names used to call the library routines.
200 '
210 'First retrieve the segment of the library from 0:3ce
220 DEF SEG = 0:VSEG = PEEK (&H3CF):VSEG = (VSEG * 256) + PEEK
(&H3CE):DEF SEG
230 DEF SEG = VSEG:POKE &H13E,0:POKE &H13F,0      'CLEAR FORTRAN AND
COMPILED
240 DEFSNG X,Y,V
250 'Now define the function names, which are simply variables equal
to the
260 'offsets into VSEG of the respective subroutine.
270 VIDDIG = &H2E:VURDAT = VIDDIG + 19:DISPIC = VURDAT + 19
280 SAVDAT = DISPIC + 19:GETDAT = SAVDAT + 19:VUBDAT = GETDAT + 19
290 PRPIC = VUBDAT + 19:GETPIC = PRPIC + 19:GETPNT = GETPIC + 19
300 SETPNT = GETPNT + 19:MODBUFF = SETPNT + 19:HEXN = &H155
310 BD.ADDR = &H149:GM.ADDR = &H14D:GM.REGEN = &H14F:BUFF.ADDR = &H14B
320 REM
330 PRINT "SLICE.BAS Version 9.3"
340 BEEP:BEEP:BEEP
350 PRINT "WARNING!!! This programs assumes four-fold symmetry in your
pattern."
360 PRINT "This program will search for data along a specified
azimuthal angle"
370 PRINT "slice and at 90 degrees to the given angle.  The program
will then"
380 PRINT "average the intensity value for each scattering angle and
output as such."
390 PRINT "If your pattern does not contain four-fold symmetry then
you must"
400 PRINT "edit lines 1100-1500 as needed in the .BAS program, or use
2FOLD.EXE."
410 PRINT " "
420 INPUT " Enter the name of the image file w/o
ext...[file.IMG]";FSP$
430 INPUT" Entries correct (Y/N)";ENTCOR$
440 IF ENTCOR$ = "N" OR ENTCOR$ = "n" THEN 340
450 PRINT "Loading binary data file into memory...";FSP$
460 REM * Setup specified file for conversion process
470 REM * Load buffer in memory at address setup by Vidbuff routine
480 REM with binary data file created by VVG software.
490 FSPR$=FSP$ + ".IMG"
500 VALUE% = 0:ER% = 0
510 DEF SEG = VSEG

```

```

520 GOSUB 530
530 CALL GETDAT (FSPR$,ER%)
540 IF ER% < > 0 THEN PRINT "ERROR =";ER% : STOP
550 RETURN 560
560 BEEP
570 REM * Read memory locations specified by starting and ending
580 REM   X,Y coordinates and write X,Y,Z values to output file,
590 REM   where X is the x coordinate, Y is the Y coordinate, and
600 REM   Z is the intensity value (VALUE%) returned by the GETPNT
    routine.
610 INPUT "Is there a .DES file...(Y,N) [Y] ";Y3$
620 IF Y3$="" THEN Y3$="Y"
630 IF Y3$="N" OR Y3$="n" THEN 750
640 PRINT "Enter the name of the .DES file (w/o ext.) [";FSP$;"]"
650 INPUT DES$
660 IF DES$="" THEN DES$=FSP$
670 DES$ = DES$ + ".DES"
680 OPEN DES$ FOR INPUT AS #1
690 INPUT #1, LX, LY
700 INPUT #1, UX, UY
710 INPUT #1, CX, CY
720 INPUT #1, SS, SC
730 CLOSE #1
740 GOTO 830
750 ^ Keyboard input
760 INPUT "Enter starting X,Y coordinates ";LX,LY
770 INPUT "Enter ending X,Y coordinates ";UX,UY
780 INPUT "Enter the beam stop X,Y coordinates ";CX,CY
790 INPUT "Enter the sample to screen distance in cm ";SS
800 INPUT "Enter the screen to camera distance in cm ";SC
810 INPUT "Entries correct...(Y/N) ";ENCOR$
820 IF ENCOR$ = "N" OR ENCOR$ = "n" THEN 750
830 NR = UY-LY+1
840 NC = UX-LX+1
850 IMAX = 0
860 Y2 = 905.9071*SC^-1.044978
870 X2 = 712.6335*SC^-1.052816
880 DIM AA(4000),SA(4000),IN(4000),AN(1000),INTEN(1000)
890 PRINT " "
900 ^ * GET THE NAME FOR THE NEW FILE
910 INPUT "Enter the name of the new file, w/o ext. [.DAT]";B1$
920 B2$ = B1$ + ".DAT"
930 ^ * OPEN THE FILES TO BE USED
940 OPEN B2$ FOR OUTPUT AS #2
950 PRINT "The sample to screen distance for ";FSP$;" is ";SS;" cm."
960 INPUT "Enter the desired azimuthal angle (deg.) and error range
    (cm) ";TH,ERT
970 PRINT " "
980 PRINT "Select data output option:"
990 PRINT " 1. Intensity (I) vs. Scattering Angle (SA)"
1000 PRINT " 2. I vs. s,          s=4*pi/la*sin(SA/2)"
1010 PRINT " 3. I vs. h,          h=2*pi/la*sin(SA)"

```

```

1020 PRINT " 4. ln(I) vs. s^2      (Guinier plot)"
1030 PRINT " 5. I vs. s^2        (modified Guinier plot)"
1040 PRINT " 6. ln(I) vs. h^2    (Prud'homme & Stein Plot)"
1050 PRINT " 7. I vs. h^2        (modified Prud'homme & Stein Plot)"
1060 PRINT " 8. ln(I) vs. s  "
1070 PRINT " 9. ln(I) vs. h  "
1080 PRINT "10. ln(I) vs. ln(s) "
1090 PRINT "11. ln(I) vs. ln(h) "
1100 PRINT "12. I^-0.5 vs. s^2    (Debye Plot)"
1110 PRINT "13. I^-0.5 vs. h^2    (Debye Plot)"
1120 INPUT "Option number ";ANS
1130 INPUT "Output the data as a four quadrant average...(Y,N)
[Y]";Y1$
1140 INPUT "Normalize the data by the maximum intensity value...(Y,N)
[Y]";YNORM$
1150 INPUT "Suppress beam stop data...(Y,N)  [Y]";YBS$
1160 IF Y1$="" THEN Y1$="Y"
1170 IF YNORM$="" THEN YNORM$="Y"
1180 IF YBS$="" THEN YBS$="Y"
1190 IF YBS$="y" OR YBS$="Y" THEN BSCHK=.36 ELSE BSCHK=0
1200 J=0
1210 I=0
1220 L=0
1230 LA=.6328
1240 PI=3.1415926#
1250 TH = TH*PI/180
1260 ^ * BEGIN THE CONVERSION PROCESS
1270 PRINT " "
1280 PRINT "SCANNING FILE FOR DESIRED AZIMUTHAL ANGLE "
1290 IF TH = PI/2 THEN 1310
1300 TTH = TAN(TH)      ^set upper and lower limits
1310 UL = ERT
1320 LL = -ERT
1330 FOR Y1 = LY TO UY
1340 FOR X1 = LX TO UX
1350 ER% = 0
1360 X% = X1:Y% = Y1
1370 CALL GETPNT (X%,Y%,VALUE%,ER%)
1380 IF ER% < > 0 THEN PRINT" ERROR = ";ER% : STOP
1390 X0=X% : Y0=Y%
1400 IF VALUE%>IMAX THEN IMAX=VALUE%
1410 X0 = (X0-CX)/X2
1420 Y0 = (CY-Y0)/Y2
1430 IF TH=PI/2 OR TH=0 THEN 1540
1440 IF TH=3*PI/2 OR TH=PI OR TH=2*PI THEN 1540
1450 UL1 = Y0*TTH + ERT
1460 LL1 = Y0*TTH - ERT
1470 LL2 = -Y0/TTH - ERT
1480 UL2 = -Y0/TTH + ERT
1490 IF X0>=LL1 AND X0<=UL1 THEN 1580
1500 IF X0<=-LL1 AND X0>=-UL1 THEN 1580
1510 IF X0>=LL2 AND X0<=UL2 THEN 1580

```

```

1520 IF X0<=-LL2 AND X0>=-UL2 THEN 1580
1530 GOTO 1770
1540 ^ * Case for TH=0 or th=90
1550 IF X0<=UL AND X0>=LL THEN 1580
1560 IF Y0<=UL AND Y0>=LL THEN 1580
1570 GOTO 1770
1580 ^ * Convert to angular coordinates
1590 IF Y0=0 THEN 1700
1600 IF X0>=0 AND Y0>0 THEN C=0
1610 IF Y0<0 THEN C=PI
1620 IF X0<0 AND Y0>0 THEN C=2*PI
1630 CC = SQR(X0^2 + Y0^2)
1640 IF CC <= BSCHK THEN 1770
1650 J=J+1
1660 IN(J) = VALUE%
1670 SA(J) = ATN(CC/SS)
1680 AA(J) = ATN(X0/Y0) + C
1690 GOTO 1770
1700 IF ABS(X0) <= BSCHK THEN 1770
1710 J=J+1
1720 IN(J) = VALUE%
1730 SA(J) = ATN(ABS(X0/SS))
1740 IF X0=0 THEN AA(J)=0
1750 IF X0>0 THEN AA(J)=PI/2
1760 IF X0<0 THEN AA(J)=3*PI/2
1770 NEXT X1,Y1
1780 IF Y1$="N" OR Y1$="n" THEN 1950
1790 ^ * Average intensity values
1800 PRINT " "
1810 PRINT "Averaging Data"
1820 FOR N=1 TO J
1830 IF SA(N)=-1 THEN 1930
1840 CHK=SA(N):SUM=IN(N)
1850 K=1:L=L+1
1860 FOR M=N+1 TO J
1870 IF SA(M)<>CHK THEN 1900
1880 SUM=SUM+IN(M)
1890 K=K+1:SA(M)=-1
1900 NEXT M
1910 INTEN(L)=SUM/K
1920 AN(L)=SA(N)
1930 NEXT N
1940 GOTO 2010
1950 ^ * Straight data
1960 L=J
1970 FOR N=1 TO J
1980 INTEN(N) = IN(N)
1990 AN(N) = SA(N)
2000 NEXT N
2010 ^ * Normalize Data
2020 IF YNORM$="Y" OR YNORM$="y" THEN 2030:ELSE 2080
2030 PRINT " "

```

```

2040 PRINT "Normalizing Data"
2050 FOR N=1 TO L
2060 INTEN(N) = INTEN(N)/IMAX * 100
2070 NEXT N
2080 ^ * Output Data
2090 IF ANS=1 THEN 2220
2100 IF ANS=2 THEN 2500
2110 IF ANS=3 THEN 2570
2120 IF ANS=4 THEN 2320
2130 IF ANS=5 THEN 2640
2140 IF ANS=6 THEN 2410
2150 IF ANS=7 THEN 2720
2160 IF ANS=8 THEN 2800
2170 IF ANS=9 THEN 2890
2180 IF ANS=10 THEN 2980
2190 IF ANS=11 THEN 3070
2200 IF ANS=12 THEN 3160
2210 IF ANS=13 THEN 3250
2220 ^ * Option 1 I vs. SA
2230 CFDR = 180/PI
2240 INPUT "Output SA in Degrees or Radians...(D,R) ";DR$
2250 IF DR$ = "r" OR DR$ = "R" THEN CFDR=1
2260 FOR N=1 TO L
2270 AN(N) = AN(N)*CFDR
2280 PRINT #2, AN(N), INTEN(N)
2290 I=I+1
2300 NEXT N
2310 GOTO 3340
2320 ^ * Option 4 Guinier Plot
2330 FOR N=1 TO L
2340 IF INTEN(N)=0 THEN 2390
2350 H = ((4*PI/LA)*SIN(AN(N)/2))^2
2360 INTEN(N) = LOG(INTEN(N))
2370 PRINT #2, H, INTEN(N)
2380 I=I+1
2390 NEXT N
2400 GOTO 3340
2410 ^ * Option 6 Prud'homme & Stein Plot
2420 FOR N=1 TO L
2430 IF INTEN(N)=0 THEN 2480
2440 H = (2*PI/LA*SIN(AN(N)))^2
2450 INTEN(N) = LOG(INTEN(N))
2460 PRINT #2, H, INTEN(N)
2470 I=I+1
2480 NEXT N
2490 GOTO 3340
2500 ^Option 2 I vs. s
2510 FOR N=1 TO L
2520 S = 4*PI/LA*SIN(AN(N)/2)
2530 I=I+1
2540 PRINT #2, S, INTEN(N)
2550 NEXT N

```

```

2560 GOTO 3340
2570 ^* Option 3  I vs. h
2580 FOR N=1 TO L
2590 H = 2*PI/LA*SIN(AN(N))
2600 I=I+1
2610 PRINT #2, H, INTEN(N)
2620 NEXT N
2630 GOTO 3340
2640 ^ * Option 5  modified Guinier Plot
2650 FOR N=1 TO L
2660 IF INTEN(N)=0 THEN 2700
2670 SS = ((4*PI/LA)*SIN(AN(N)/2))^2
2680 PRINT #2, SS, INTEN(N)
2690 I=I+1
2700 NEXT N
2710 GOTO 3340
2720 ^ * Option 7  modified Prud'homme & Stein Plot
2730 FOR N=1 TO L
2740 IF INTEN(N)=0 THEN 2780
2750 HH = (2*PI/LA*SIN(AN(N)))^2
2760 PRINT #2, HH, INTEN(N)
2770 I=I+1
2780 NEXT N
2790 GOTO 3340
2800 ^ * Option 8  ln(I) vs. s
2810 FOR N=1 TO L
2820 IF INTEN(N)<=0 THEN 2870
2830 S4=4*PI/LA*SIN(AN(N)/2)
2840 LOGI = LOG(INTEN(N))
2850 I=I+1
2860 PRINT #2, S4, LOGI
2870 NEXT N
2880 GOTO 3340
2890 ^ * Option 9  ln(I) vs. h
2900 FOR N=1 TO L
2910 IF INTEN(N)<=0 THEN 2960
2920 H = 2*PI/LA*SIN(AN(N))
2930 IS = LOG(INTEN(N))
2940 I=I+1
2950 PRINT #2, H, IS
2960 NEXT N
2970 GOTO 3340
2980 ^ * Option 10  ln(I) vs. ln(s)
2990 FOR N=1 TO L
3000 IF INTEN(N)<=0 OR AN(N)<=0 THEN 3050
3010 H = LOG((4*PI/LA)*SIN(AN(N)/2))
3020 INTEN(N) = LOG(INTEN(N))
3030 PRINT #2, H, INTEN(N)
3040 I=I+1
3050 NEXT N
3060 GOTO 3340
3070 ^ * Option 11  ln(I) vs. ln(h)

```

```

3080 FOR N=1 TO L
3090 IF INTEN(N)<=0 OR AN(N)<=0 THEN 3140
3100 H = LOG((2*PI/LA)*SIN(AN(N)))
3110 INTEN(N) = LOG(INTEN(N))
3120 PRINT #2, H, INTEN(N)
3130 I=I+1
3140 NEXT N
3150 GOTO 3340
3160 ^ * Option 12. I^-0.5 vs. s^2 (Debye Plot)
3170 FOR N=1 TO L
3180 IF INTEN(N)<=0 THEN 3230
3190 S = ((4*PI/LA)*SIN(AN(N)/2))^2
3200 IOUT = 1/SQR(INTEN(N))
3210 PRINT #2, S, IOUT
3220 I=I+1
3230 NEXT N
3240 GOTO 3340
3250 ^ * Option 13. I^-0.5 vs. h^2 (Debye Plot)
3260 FOR N=1 TO L
3270 IF INTEN(N)<=0 THEN 3320
3280 H = ((2*PI/LA)*SIN(AN(N)))^2
3290 IOUT = 1/SQR(INTEN(N))
3300 PRINT #2, H, IOUT
3310 I=I+1
3320 NEXT N
3330 GOTO 3340
3340 CLOSE
3350 BEEP
3360 PRINT "SLICE.BAS is completed. Number of data sets in ";B2$;"
is...";I
3370 INPUT "Is there another file to be analyzed...(Y,N) [Y]";Y$
3380 IF Y$="" THEN Y$="Y"
3390 IF Y$="n" OR Y$="N" THEN 3440
3400 INPUT "Will the same input file be used...(Y,N) [N]";Y4$
3410 IF Y4$="" THEN Y4$="N"
3420 IF Y4$="n" OR Y4$="N" THEN 420
3430 GOTO 830
3440 END

```

2FOLD.BAS

```

10 ^ ** 2FOLD.BAS
20 ^ ** PROGRAM AUTHOR: Larry Effler
30 ^ ** ASSISTED BY: Stephen Stiner, David Lewis, and T. Levitte Cox
40 ^ ** PROGRAM VERSION 3.3 DATE 12-07-1986
50 ^ ** PURPOSE: THIS PROGRAM CONVERTS RECTANGULAR CO-ORDINATE DATA
60 ^                COLLECTED IN SMALL ANGLE LIGHT SCATTERING EXPERIMENTS
70 ^                TO A SELECTED SLICE ALONG A GIVEN AZIMUTHAL ANGLE.
80 ^
90 REM

```

```

100 REM   To execute this program you must know the beam stop
coordinates and
110 REM   the screen to camera distance.
120 REM
130 REM   The following section, lines 160 to 320, contains the Video
Van Gogh
140 REM   Software Support Module: VIDMOD.BAS
150 REM
160 REM           VIDMOD.BAS   (C) Copyright Tecmar, Inc. 1983
170 'This module must be included in any user-generated application
program.
180 'It's function is to retrieve the segment address of the library,
and
190 'to define the variable names used to call the library routines.
200 '
210 'First retrieve the segment of the library from 0:3ce
220 DEF SEG = 0:VSEG = PEEK (&H3CF):VSEG = (VSEG * 256) + PEEK
(&H3CE):DEF SEG
230 DEF SEG = VSEG:POKE &H13E,0:POKE &H13F,0      'CLEAR FORTRAN AND
COMPILED
240 DEFSNG X,Y,V
250 I=0
260 'Now define the function names, which are simply variables equal
to the
270 'offsets into VSEG of the respective subroutine.
280 VIDDIG = &H2E:VURDAT = VIDDIG + 19:DISPIC = VURDAT + 19
290 SAVDAT = DISPIC + 19:GETDAT = SAVDAT + 19:VUBDAT = GETDAT + 19
300 PRPIC = VUBDAT + 19:GETPIC = PRPIC + 19:GETPNT = GETPIC + 19
310 SETPNT = GETPNT + 19:MODBUFF = SETPNT + 19:HEXN = &H155
320 BD.ADDR = &H149:GM.ADDR = &H14D:GM.REGEN = &H14F:BUFF.ADDR = &H14B
330 REM
340 PRINT "2FOLD.BAS Version 3.3"
350 BEEP:BEEP:BEEP
360 PRINT "WARNING!!! This programs assumes two-fold symmetry in your
pattern."
370 PRINT "This program will search for data along a specified
azimuthal angle"
380 PRINT "slice and at 180 degrees to the given angle.  The program
will then"
390 PRINT "average the intensity value for each scattering angle and
output as such."
400 PRINT "If your pattern does not contain two-fold symmetry then you
must"
410 PRINT "edit lines 1100-1500 as needed in the .BAS program."
420 PRINT " "
430 INPUT " Enter the name of the image file w/o ext.
[file.IMG]";FSP$
440 INPUT" Entries correct (Y/N)";ENTCOR$
450 IF ENTCOR$ = "N" OR ENTCOR$ = "n" THEN 350
460 FSPR$=FSP$ + ".IMG"
470 PRINT "Loading binary data file into memory...";FSPR$
480 REM * Setup specified file for conversion process

```

```

490 REM * Load buffer in memory at address setup by Vidbuff routine
500 REM   with binary data file created by VVG software.
510 VALUE% = 0:ER% = 0
520 DEF SEG = VSEG
530 GOSUB 540
540 CALL GETDAT (FSPR$,ER%)
550 IF ER% < > 0 THEN PRINT "ERROR =";ER% : STOP
560 RETURN 570
570 BEEP
580 REM * Read memory locations specified by starting and ending
590 REM   X,Y coordinates and write X,Y,Z values to output file,
600 REM   where X is the x coordinate, Y is the Y coordinate, and
610 REM   Z is the intensity value (VALUE%) returned by the GETPNT
   routine.
620 INPUT "Is there a .DES file...(Y,N)   [Y]";Y3$
630 IF Y3$="" THEN Y3$="Y"
640 IF Y3$="N" OR Y3$="n" THEN 760
650 PRINT "Enter the name of the .DES file (w/o ext.) [";FSP$;"]"
660 INPUT DES$
670 IF DES$="" THEN DES$=FSP$
680 DES$ = DES$ + ".DES"
690 OPEN DES$ FOR INPUT AS #1
700 INPUT #1, LX, LY
710 INPUT #1, UX, UY
720 INPUT #1, CX, CY
730 INPUT #1, SS, SC
740 CLOSE #1
750 GOTO 840
760 ^ Keyboard input
770 INPUT "Enter starting X,Y coordinates ";LX,LY
780 INPUT "Enter ending X,Y coordinates ";UX,UY
790 INPUT "Enter the beam stop X,Y coordinates ";CX,CY
800 INPUT "Enter the sample to screen distance in cm ";SS
810 INPUT "Enter the screen to camera distance in cm ";SC
820 INPUT "Entries correct...(Y/N) ";ENCOR$
830 IF ENCOR$ = "N" OR ENCOR$ = "n" THEN 760
840 NR = UY-LY+1
850 NC = UX-LX+1
860 IMAX = 0
870 Y2 = 905.9071*SC^-1.044978
880 X2 = 712.6335*SC^-1.052816
890 DIM AA(4000),SA(4000),IN(4000),AN(1000),INTEN(1000)
900 PRINT " "
910 ^ * GET THE NAME FOR THE NEW FILE
920 INPUT "Enter the name of the new file, w/o ext.   [.DAT] ";B1$
930 B2$ = B1$ + ".DAT"
940 ^ * OPEN THE FILES TO BE USED
950 OPEN B2$ FOR OUTPUT AS #2
960 PRINT "The sample to screen distance for ";FSP$;" is...";SS
970 INPUT "Enter the desired azimuthal angle (deg.) and error range
   (cm) ";TH,ERT
980 PRINT " "

```

```

990 PRINT "Select data output option:"
1000 PRINT " 1. Intensity (I) vs. Scattering Angle (SA)"
1010 PRINT " 2. I vs. s,          s=4*pi/la*sin(SA/2)"
1020 PRINT " 3. I vs. h,          h=2*pi/la*sin(SA)"
1030 PRINT " 4. ln(I) vs. s^2      (Guinier plot)"
1040 PRINT " 5. I vs. s^2          (modified Guinier plot)"
1050 PRINT " 6. ln(I) vs. h^2      (Prud'homme & Stein Plot)"
1060 PRINT " 7. I vs. h^2          (modified Prud'homme & Stein Plot)"
1070 PRINT " 8. ln(I) vs. s"
1080 PRINT " 9. ln(I) vs. h"
1090 PRINT "10. ln(I) vs. ln(s)"
1100 PRINT "11. ln(I) vs. ln(h)"
1110 PRINT "12. I^-0.5 vs. s^2      (Debye Plot)"
1120 PRINT "13. I^-0.5 vs. h^2      (Debye Plot)"
1130 INPUT "Option number ";ANS
1140 INPUT "Output the data as a two quadrant average...(Y,N)
[Y]";Y1$
1150 INPUT "Normalize by the maximum intensity value...(Y,N)
[Y]";YNORM$
1160 INPUT "Suppress beam stop data...(Y,N)    [Y]";YBS$
1170 IF Y1$="" THEN Y1$="Y"
1180 IF YBS$="" THEN YBS$="Y"
1185 IF YNORM$="" THEN YNORM$="Y"
1190 IF YBS$="y" OR YBS$="Y" THEN BSCHK=.36 ELSE BSCHK=0
1200 J=0
1210 I=0
1220 L=0
1230 LA=.6328
1240 PI=3.1415926#
1250 TH = TH*PI/180
1260 ^ * BEGIN THE CONVERSION PROCESS
1270 PRINT " "
1280 PRINT "SCANNING FILE FOR DESIRED AZIMUTHAL ANGLE "
1290 IF TH = PI/2 THEN 1310
1300 TTH = TAN(TH)      ^set upper and lower limits
1310 UL = ERT
1320 LL = -ERT
1330 FOR Y1 = LY TO UY
1340 FOR X1 = LX TO UX
1350 ER% = 0
1360 X% = X1:Y% = Y1
1370 CALL GETPNT (X%,Y%,VALUE%,ER%)
1380 IF ER% < > 0 THEN PRINT" ERROR = ";ER% : STOP
1390 XO=X% : YO=Y%
1400 IF VALUE% > IMAX THEN IMAX=VALUE%
1410 XO = (XO-CX)/X2
1420 YO = (CY-YO)/Y2
1430 IF TH=PI/2 OR TH=0 THEN 1490
1440 IF TH=3*PI/2 OR TH=PI OR TH=2*PI THEN 1490
1450 UL1 = YO*TTH + ERT
1460 LL1 = YO*TTH - ERT
1470 IF XO>=LL1 AND XO<=UL1 THEN 1550

```

```

1480 GOTO 1740
1490 ^ * Case for TH=0 or th=90
1500 IF TH =PI/2 OR TH=3*PI/2 GOTO 1530
1510 IF XO<=UL AND XO>=LL THEN 1550
1520 GOTO 1740
1530 IF YO<=UL AND YO>=LL THEN 1550
1540 GOTO 1740
1550 ^ * Convert to angular coordinates
1560 IF YO=0 THEN 1670
1570 IF XO>=0 AND YO>0 THEN C=0
1580 IF YO<0 THEN C=PI
1590 IF XO<0 AND YO>0 THEN C=2*PI
1600 CC = SQR(XO^2 + YO^2)
1610 IF CC<=BSCHK THEN 1740
1620 J=J+1
1630 IN(J) = VALUE%
1640 SA(J) = ATN(CC/SS)
1650 AA(J) = ATN(XO/YO) + C
1660 GOTO 1740
1670 IF ABS(XO)<=BSCHK THEN 1740
1680 J=J+1
1690 IN(J) = VALUE%
1700 SA(J) = ATN(ABS(XO/SS))
1710 IF XO=0 THEN AA(J)=0
1720 IF XO>0 THEN AA(J)=PI/2
1730 IF XO<0 THEN AA(J)=3*PI/2
1740 NEXT X1,Y1
1750 IF Y1$="N" OR Y1$="n" THEN 1920
1760 ^ * Average intensity values
1770 PRINT " "
1780 PRINT "Averaging Data"
1790 FOR N=1 TO J
1800 IF SA(N)=-1 THEN 1900
1810 CHK=SA(N):SUM=IN(N)
1820 K=1:L=L+1
1830 FOR M=N+1 TO J
1840 IF SA(M)<>CHK THEN 1870
1850 SUM=SUM+IN(M)
1860 K=K+1:SA(M)=-1
1870 NEXT M
1880 INTEN(L)=SUM/K
1890 AN(L)=SA(N)
1900 NEXT N
1910 GOTO 1980
1920 ^ * Straight data
1930 L=J
1940 FOR N=1 TO J
1950 INTEN(N) = IN(N)
1960 AN(N) = SA(N)
1970 NEXT N
1980 ^ * Normalize Data
1990 IF YNORM$="Y" OR YNORM$="y" THEN 2000:ELSE 2050

```

```

2000 PRINT " "
2010 PRINT "Normalizing Data"
2020 FOR N=1 TO L
2030 INTEN(N) = INTEN(N)/IMAX * 100
2040 NEXT N
2050 ^ * Output Data
2060 IF ANS=1 THEN 2190
2070 IF ANS=2 THEN 2470
2080 IF ANS=3 THEN 2540
2090 IF ANS=4 THEN 2290
2100 IF ANS=5 THEN 2610
2110 IF ANS=6 THEN 2380
2120 IF ANS=7 THEN 2690
2130 IF ANS=8 THEN 2770
2140 IF ANS=9 THEN 2860
2150 IF ANS=10 THEN 2950
2160 IF ANS=11 THEN 3040
2170 IF ANS=12 THEN 3130
2180 IF ANS=13 THEN 3220
2190 ^ * Option 1 I vs. SA
2200 CFDR = 180/PI
2210 INPUT "Output SA in degrees or radians...(D,R) ";DR$
2220 IF DR$="r" OR DR$="R" THEN CFDR = 1
2230 FOR N=1 TO L
2240 AN(N) = AN(N)*CFDR
2250 PRINT #2, AN(N), INTEN(N)
2260 I=I+1
2270 NEXT N
2280 GOTO 3310
2290 ^ * Option 4 Guinier Plot ln(I) vs. s^2
2300 FOR N=1 TO L
2310 IF INTEN(N)=0 THEN 2360
2320 H = ((4*PI/LA)*SIN(AN(N)/2))^2
2330 INTEN(N) = LOG(INTEN(N))
2340 PRINT #2, H, INTEN(N)
2350 I=I+1
2360 NEXT N
2370 GOTO 3310
2380 ^ * Option 6 Prud'homme & Stein Plot ln(I) vs. h^2
2390 FOR N=1 TO L
2400 IF INTEN(N)=0 THEN 2450
2410 H = (2*PI/LA*SIN(AN(N)))^2
2420 INTEN(N) = LOG(INTEN(N))
2430 PRINT #2, H, INTEN(N)
2440 I=I+1
2450 NEXT N
2460 GOTO 3310
2470 ^Option 2 I vs. s
2480 FOR N=1 TO L
2490 S = 4*PI/LA*SIN(AN(N)/2)
2500 I=I+1
2510 PRINT #2, S, INTEN(N)

```

```

2520 NEXT N
2530 GOTO 3310
2540 ^Option 3 I vs. h
2550 FOR N=1 TO L
2560 H = 2*PI/LA*SIN(AN(N))
2570 I=I+1
2580 PRINT #2, H, INTEN(N)
2590 NEXT N
2600 GOTO 3310
2610 ^ * Option 5 modified Guinier Plot I vs. s^2
2620 FOR N=1 TO L
2630 IF INTEN(N)=0 THEN 2670
2640 SS = ((4*PI/LA)*SIN(AN(N)/2))^2
2650 PRINT #2, SS, INTEN(N)
2660 I=I+1
2670 NEXT N
2680 GOTO 3310
2690 ^ * Option 7 modified Prud'homme & Stein Plot I vs. h^2
2700 FOR N=1 TO L
2710 IF INTEN(N)=0 THEN 2750
2720 HH = (2*PI/LA*SIN(AN(N)))^2
2730 PRINT #2, HH, INTEN(N)
2740 I=I+1
2750 NEXT N
2760 GOTO 3310
2770 ^ * Option 8 ln(I) vs s
2780 FOR N=1 TO L
2790 IF INTEN(N)<=0 THEN 2840
2800 S4=4*PI/LA*SIN(AN(N)/2)
2810 LOGI = LOG(INTEN(N))
2820 I=I+1
2830 PRINT #2, S4, LOGI
2840 NEXT N
2850 GOTO 3310
2860 ^ * Option 9 ln(I) vs. h
2870 FOR N=1 TO L
2880 IF INTEN(N)<=0 THEN 2930
2890 H = 2*PI/LA*SIN(AN(N))
2900 IS = LOG(INTEN(N))
2910 I=I+1
2920 PRINT #2, H, IS
2930 NEXT N
2940 GOTO 3310
2950 ^ * Option 10 ln(I) vs. ln(s)
2960 FOR N=1 TO L
2970 IF INTEN(N)<=0 OR AN(N)<=0 THEN 3020
2980 H = LOG((4*PI/LA)*SIN(AN(N)/2))
2990 INTEN(N) = LOG(INTEN(N))
3000 PRINT #2, H, INTEN(N)
3010 I=I+1
3020 NEXT N
3030 GOTO 3310

```

```

3040 ^ * Option 11  ln(I) vs. ln(h)
3050 FOR N=1 TO L
3060 IF INTEN(N)<=0 OR AN(N)<=0 THEN 3110
3070 H = LOG((2*PI/LA)*SIN(AN(N)))
3080 INTEN(N) = LOG(INTEN(N))
3090 PRINT #2, H, INTEN(N)
3100 I=I+1
3110 NEXT N
3120 GOTO 3310
3130 ^ * Option 12  I^-0.5 vs. s^2  Debye Plot
3140 FOR N=1 TO L
3150 IF INTEN(N)<=0 THEN 3200
3160 S = ((4*PI/LA)*SIN(AN(N)/2))^2
3170 IOUT = 1/SQR(INTEN(N))
3180 PRINT #2, S, IOUT
3190 I=I+1
3200 NEXT N
3210 GOTO 3310
3220 ^ * Option 13  I^-0.5 vs. h^2  Debye Plot
3230 FOR N=1 TO L
3240 IF INTEN(N)<=0 THEN 3290
3250 H = ((2*PI/LA)*SIN(AN(N)))^2
3260 IOUT = 1/SQR(INTEN(N))
3270 PRINT #2, H, IOUT
3280 I=I+1
3290 NEXT N
3300 GOTO 3310
3310 CLOSE
3320 BEEP
3330 PRINT "2FOLD.BAS is completed.  Number of data sets in file
";B1$;" is ";I
3340 INPUT "Is there another file to be analyzed...(Y,N)  [Y]";Y$
3350 IF Y$="" THEN Y$="Y"
3360 IF Y$="n" OR Y$="N" THEN 3410
3370 INPUT "Will the same input file be used...(Y,N)  [N]";Y4$
3380 IF Y4$="" THEN Y4$="N"
3390 IF Y4$="n" OR Y4$="N" THEN 430
3400 GOTO 690
3410 END

```

VVGCNV.BAS

```

10 REM ** Program Name: VVGCNV.BAS
20 REM ** Program Author: Larry Effler
30 REM ** Assisted by: David Lewis, Steven Stiner
40 REM ** Program Version 9.0 Date 02-27-87
50 REM ** Purpose: This program converts a binary data file containing
60 REM    intensity data, which was saved by Tecmar's Video Van Gogh
70 REM    support software, into a binary data file converted from

```

```

80 REM      X,Y, Intensity notation where X,Y are in pixels to X,Y,
Intensity
90 REM      format where X,Y are in cm's by accounting for lens
magnification.
100 REM     Where the distance is measured from the beam stop (i.e. the
beam stop
110 REM     is location 0,0 cm).
120 REM
130 REM     To execute this program you must know the beam stop
coordinates and
140 REM     the screen to camera distance.
150 REM
160 REM     The following section, lines 26 to 95, contains the Video
Van Gogh
170 REM     Software Support Module: VIDMOD.BAS
180 REM
190 REM          VIDMOD.BAS (C) Copyright Tecmar, Inc. 1983
200 'This module must be included in any user-generated application
program.
210 'It's function is to retrieve the segment address of the library,
and
220 'to define the variable names used to call the library routines.
230 '
240 'First retrieve the segment of the library from 0:3ce
250 DEF SEG = 0:VSEG = PEEK (&H3CF):VSEG = (VSEG * 256) + PEEK
(&H3CE):DEF SEG
260 DEF SEG = VSEG:POKE &H13E,0:POKE &H13F,0      'CLEAR FORTRAN AND
COMPILED
270 DEFSNG X,Y,V
280 I=0
290 'Now define the function names, which are simply variables equal
to the
300 'offsets into VSEG of the respective subroutine.
310 VIDDIG = &H2E:VURDAT = VIDDIG + 19:DISPIC = VURDAT + 19
320 SAVDAT = DISPIC + 19:GETDAT = SAVDAT + 19:VUBDAT = GETDAT + 19
330 PRPIC = VUBDAT + 19:GETPIC = PRPIC + 19:GETPNT = GETPIC + 19
340 SETPNT = GETPNT + 19:MODBUFF = SETPNT + 19:HEXN = &H155
350 BD.ADDR = &H149:GM.ADDR = &H14D:GM.REGEN = &H14F:BUFF.ADDR = &H14B
360 REM
370 DIM INTEN(12000)
380 PRINT " Video Van Gogh Conversion Program, Version 9.0 "
390 PRINT "      "
400 REM * Prompt user for file information.
410 BEEP
420 INPUT " Enter image file name w/o ext.  [file.IMG]";FSPI$
430 INPUT " Entries correct (Y/N)";ENTCOR$
440 IF ENTCOR$ = "N" OR ENTCOR$ = "n" THEN 400
450 PRINT "Loading binary data file into memory...";FSPI$
460 REM * Setup specified file for conversion process
470 REM * Load buffer in memory at address setup by Vidbuff routine
480 REM with binary data file created by VVG software.
490 FSP$ = FSPI$ + ".IMG"

```

```

500 VALUE% = 0:ER% = 0
510 DEF SEG = VSEG
520 GOSUB 530
530 CALL GETDAT (FSP$,ER%)
540 IF ER% < > 0 THEN PRINT "ERROR =";ER% : STOP
550 RETURN 560
560 BEEP
570 REM * Read memory locations specified by starting and ending
580 REM   X,Y coordinates and write X,Y,Z values to output file,
590 REM   where X is the x coordinate, Y is the Y coordinate, and
600 REM   Z is the intensity value (VALUE%) returned by the GETPNT
routine.
610 INPUT "Is there a .DES file...(Y,N)      [Y]";Y1$
620 IF Y1$="" THEN Y1$="Y"
630 IF Y1$="n" OR Y1$="N" THEN 760
640 PRINT "Enter the name of the .DES file (w/o ext.) [";FSPI$;"]"
650 INPUT DES$
660 IF DES$ = "" THEN DES$=FSPI$
670 DES$ = DES$ + ".DES"
680 OPEN DES$ FOR INPUT AS #3
690 INPUT #3, LX, LY
700 INPUT #3, UX, UY
710 INPUT #3, CX, CY
720 INPUT #3, SS, SC
730 NR = UY-LY+1
740 NC = UX-LX+1
750 GOTO 840
760 ^ Keyboard entries
770 INPUT"Enter starting X,Y coordinates ";LX,LY
780 INPUT"Enter ending X,Y coordinates ";UX,UY
790 INPUT"Enter beam stop X,Y coordinates ";CX,CY
800 INPUT "Enter the sample to screen distance in cm ";SS
810 INPUT "Enter the screen to camera distance in cm ";SC
820 NR = UY-LY+1
830 NC = UX-LX+1
840 ^Begin conversion
850 TLNGTH = NR*NC
860 INPUT"Enter the output file name w/o ext. [.GRD]";ASCF$
870 PRINT "Current file length is ";TLNGTH;" datapoints with ";NR;"
rows, and ";NC;" columns."
880 INPUT "Enter the row divisor step size (1, 2, 3, etc.)";STEPV
890 INPUT "Enter the column divisor step size (1, 2, 3, etc.)";STEPH
900 INPUT "Normalize by the maximum intensity value...(Y,N)
[Y]";YNORM$
910 INPUT"Entries correct...(Y/N) ";ENCOR$
920 IF YNORM$ = "" THEN YNORM$ = "Y"
930 IF ENCOR$ = "N" OR ENCOR$ = "n" THEN 760
940 ^Begin Conversion
950 ASCF$ = ASCF$ + ".GRD"
960 OPEN ASCF$ AS #2 LEN=4
970 BEEP
980 PRINT" Writing data to conversion file...."

```

```

990 I=0:J=1
1000 XMAX = 0: XMIN = 0
1010 YMAX = 0: YMIN = 0
1020 IMAX = 0: IMIN = 0
1030 CNTR1=0:CNTR2=0
1040 Y2 = 905.9071*SC^-1.044978
1050 X2 = 712.6335*SC^-1.052816
1060 FOR Y = LY TO UY STEP STEPV
1070 CNTR1=CNTR1+1
1080 FOR X = LX TO UX STEP STEPH
1090 CNTR2 = CNTR2 + 1
1100 X% = X:Y% = Y
1110 CALL GETPNT (X%,Y%,VALUE%,ER%)
1120 IF ER% < > 0 THEN PRINT" ERROR = ";ER% : STOP
1130 X1=X% : Y1=Y%
1140 XX = (X1-CX)/X2
1150 YY = (CY-Y1)/Y2
1160 INTEN(CNTR2) = VALUE%
1170 IF XX > XMAX THEN XMAX = XX
1180 IF XX < XMIN THEN XMIN = XX
1190 IF YY > YMAX THEN YMAX = YY
1200 IF YY < YMIN THEN YMIN = YY
1210 IF INTEN(CNTR2) > IMAX THEN IMAX = INTEN(CNTR2)
1220 IF INTEN(CNTR2) < IMIN THEN IMIN = INTEN(CNTR2)
1230 NEXT X
1240 NEXT Y
1250 NFC%=CNTR2/CNTR1
1260 FIELD #2, 4 AS VERIFY$
1270 LSET VERIFY$ = "DSPM": PUT #2
1280 FIELD #2, 2 AS BYTE1$, 2 AS BYTE2$
1290 FIELD #2, 2 AS BYTE1$, 2 AS BYTE2$
1300 LSET BYTE1$ = MKI$(NFC%)
1310 LSET BYTE2$ = MKI$(CNTR1): PUT #2
1320 FIELD #2, 4 AS SP$
1330 LSET SP$ = MKS$(XMIN): PUT #2
1340 LSET SP$ = MKS$(XMAX): PUT #2
1350 LSET SP$ = MKS$(YMIN): PUT #2
1360 LSET SP$ = MKS$(YMAX): PUT #2
1370 LSET SP$ = MKS$(IMIN): PUT #2
1380 LSET SP$ = MKS$(IMAX): PUT #2
1390 FOR N=1 TO CNTR2
1400 IF YNORM$="Y" OR YNORM$="y" THEN 1410 ELSE 1440
1410 IF N>=2 THEN 1430
1420 PRINT "Normalizing Data"
1430 INTEN(N) = INTEN(N)/IMAX * 100
1440 LSET SP$ = MKS$(INTEN(N)): PUT #2
1450 NEXT N
1460 CLOSE
1470 BEEP
1480 PRINT "Conversion completed...ASCII data file ";ASCFS;" written."
1490 PRINT "Number of data points...";CNTR2;" Number of
rows...";CNTR1;"Number of columns";NFC%

```

```
1500 INPUT " Do you wish to create another ASCII data file...(Y/N)
[Y]";CNE$
1510 IF CNE$ = "" THEN CNE$ = "Y"
1520 IF CNE$ = "N" OR CNE$ = "n" THEN 1570
1530 INPUT " Will you use the same input datafile      [N]";Y2$
1540 IF Y2$="" THEN Y2$ = "N"
1550 IF Y2$="Y" OR Y2$="y" THEN 840
1560 GOTO 400
1570 END
```

APPENDIX C

SALS RMS MOMENTS FOR PET/POB FILMS

Comp. Mole% POB	Molding Temp. °C	Cool. Cond.	R ²	RMS Moment (μm)
28	230	press	0.997	1.90
28	230	air	0.996	1.95
28	255	press	0.995	3.24
28	255	air	0.987	2.55
28	285	press	0.978	2.38
28	285	air	0.951	2.96
40	210	press	0.994	1.81
40	210	air	0.996	1.73
40	210	quench	0.998	1.80
40	230	press	0.997	1.73
40	230	air	0.997	1.78
40	230	quench	0.995	1.96
40	255	press	0.994	1.90
40	255	air	0.996	1.67
40	255	quench	0.996	1.65
40	285	press	0.907	3.02
40	285	air	0.900	2.57
40	285	quench	0.942	2.99
50	210	press	0.997	1.78
50	210	air	0.996	1.80
50	210	quench	0.996	1.52
50	230	press	0.996	1.86
50	230	air	0.996	1.88
50	230	quench	0.994	2.08
50	255	press	0.986	2.28
50	255	air	0.985	1.89
50	255	quench	0.987	2.07
50	285	press	0.931	2.72
50	285	air	0.968	2.08
50	285	quench	0.947	3.06
60	210	press	0.996	1.63
60	210	air	0.997	1.95
60	210	quench	0.997	1.88
60	230	press	0.996	1.91
60	230	air	0.997	1.60
60	230	quench	0.993	2.12
60	255	press	0.985	2.14
60	255	air	0.987	2.37
60	255	quench	0.989	2.16
60	285	air	0.961	2.36
60	285	quench	0.946	2.18

Comp. Mole% POB	Molding Temp. °C	Cool. Cond.	R ²	RMS Moment (μm)
70	210	press	0.997	1.81
70	210	air	0.996	1.78
70	210	quench	0.998	1.83
70	230	press	0.996	2.04
70	230	air	0.997	1.76
70	230	quench	0.997	1.94
70	255	press	0.990	2.16
70	255	air	0.988	2.61
70	255	quench	0.991	2.17
70	285	press	0.966	3.05
70	285	air	0.979	3.04
70	285	quench	0.970	2.91

VITA

Lawrence J. Effler, Jr. was born in Cincinnati, Ohio on March 25, 1960. After attending elementary and high schools in the Cincinnati area, he attended General Motors Institute (GMI) in Flint, Michigan starting in 1978. While pursuing his bachelor degree, Larry was a cooperative education student with the Inland Division of General Motors.

Upon graduating from GMI in 1983 with a Bachelor of Mechanical Engineering, he was employed full time with Inland as an Associate Production Engineer. In this function, Larry was primarily responsible for the upgrade, maintenance, and quality control of five co-extrusion sheet lines. Larry left after working for General Motors for approximately one and a half years, and entered the Graduate School of the University of Tennessee to pursue a Master of Science in Polymer Engineering, which he received in August, 1987.

Larry is a member of the Society of Plastics Engineers, Tau Beta Pi, Phi Kappa Phi, Pi Tau Sigma, and Theta Xi Fraternity. His current plans are to continue his work at the University of Tennessee, in order to receive his doctorate.