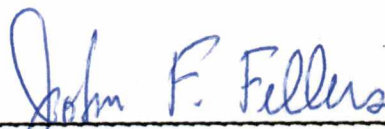


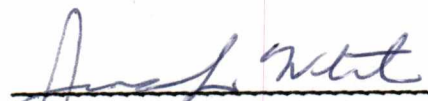
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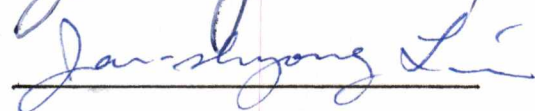


John F. Fellers, Major Professor

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Vice Chancellor
Graduate Studies and Research

MORPHOLOGICAL STUDY OF POLYSTYRENE CRAZES USING
SMALL-ANGLE X-RAY SCATTERING

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Paul A. Westbrook

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ABSTRACT

An extensive study of the crazing phenomenon in polystyrene with respect to molecular weight parameters and stress history has been performed. Experiments employed the small angle x-ray scattering camera in the National Center for Small Angle Scattering Research (NCSASR) at the Oak Ridge National Laboratory. Analysis was performed using reflection theory for the tensile axis scattering, and diffraction theory for the nontensile axis scattering from bulk crazed specimens. Results show that craze morphology is sensitive to structural characteristics of the polymeric glass, as defined by molecular weight parameters. Also, a fracture mechanism is developed from stress analysis based on void fraction and craze density measurements. Finally, the open-celled foam model of craze morphology is supported from diffraction patterns of crazes where reflection is not observed.

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1. INTRODUCTION

Crazing may be defined as a localized inhomogeneous strain response to a homogeneous tensile stress stimulus. The inhomogeneous deformation causes cavitation on the micro level, which causes several properties of the bulk material to change. A complete characterization of the morphology of crazed matter will lead to a better understanding of fracture mechanisms, optical properties, and permeability of crazed materials (eg. 24).

The phenomenon of crazing in polymers can be characterized using small - angle x-ray scattering (eg. 11,70), since there is a large difference in electron density between polymer and void. It is proposed that the morphology of crazed matter is dependent on the morphology of the bulk material from which the craze was formed (70). Therefore, molecular weight studies of crazing are justified. Since cracks are known to propagate through crazes (eg. 17), and the number of crazes generated in the polymer matrix is dependent on the stress history, dynamic stress measurements of craze morphology are justified.

The newly installed on-line dynamic deformation sample holder located at the NCSASR facility seems ideally suited for studies of this type (27,28). Also, this camera's pinhole collimation and two dimensional position sensitive detector (2DPSD) allow for absolute characterization of anisotropic x-ray scattering functions known to originate from polymeric crazes.

The basic structural features of crazes have been well established; however, the morphological details of crazed matter is still a subject of discussion. This disagreement may be a result of the different analysis techniques, sample geometries, compositions, and test conditions used for study. It is the purpose of the present research to characterize the polystyrene crazed matter for varying molecular weights and stress histories. The conclusions of this work will add insight to the understanding of craze morphology and suggest further experimental work.

2. REVIEW OF BACKGROUND AND LITERATURE

Two comprehensive reviews on the subject of crazing appeared in 1973, by Kambour (33) and Rabinowitz and Beardmore (56). Kausch (38) has reviewed the literature from 1973 to 1978 in his book "Polymer Fracture." There have been developments on the subject of crazing since the writing of Kausch, and they will be discussed in this chapter. First, a phenomenological description of crazing is given, followed by a review of major experimental techniques. Next the contributions to the craze literature since 1978 are reviewed. Lastly, the variables of interest in this research are discussed.

2.1 PHENOMENOLOGICAL DESCRIPTION OF CRAZING

Crazing, which occurs in amorphous and semi-crystalline polymers (38), appears to the eye as a series of tiny cracks (eg. 37,56). Crazes have many features in common with cracks: they grow perpendicular to the axis of principal stress (62,63), they reflect light in a manner similar to cracks (eg. 32,44), and they often precede fracture (eg. 17). It was not until the work of Sauer et al. (58,59), that crazes were differentiated from true cracks. Using wide-angle x-ray diffraction techniques and stress analysis, they (58,59) deduced that crazes must contain a network of oriented polymer connecting the bulk polymer interfaces. The oriented polymer, called fibrils, is able to support stress.

More recently, many electron microscopy studies of crazes have been performed (eg. 1,2,3,4,5,6,7,26,29,30,35,36,48,49,67), all of which support the conclusions of Sauer et al. (58,59). Generally, electron micrographs of crazed matter reveal a network of highly oriented fibrils and voids, whose dimensions are on the order of 10 to 20 nm.

Kambour (31) was the first to study the small-angle x-ray scattering behavior (SAXS) of crazes. His results revealed scattering centers of 7 to 10 nm, so he concluded that SAXS and electron microscopy experiments yielded comparable results. Since Kambour's initial SAXS experiment (31), many researchers have used SAXS techniques to characterize the morphology of crazes (eg. 23,44,45,61).

Despite the large number of experiments on crazing, no general agreement about specific craze morphology or craze initiation mechanisms has been reached. The confusion is probably a result of the wide range of experimental techniques and sample compositions that have been employed. However there are many characteristics of crazes which have been well established.

To the unaided eye, crazes appear similar to cracks, extending in a plane perpendicular to the axis of principal stress to cover almost the entire cross section. Like cracks, crazes tend to be wedge shaped with an angle between bulk polymer interfaces of less than five degrees (24). Crazing is considered to be a yield phenomenon (18); it is the process by which an elemental volume of polymer strains approximately 100 percent under lateral constraint, while bulk polymer strain remains

below two percent (34,62). The result is a sharply bound region of crazed matter, consisting of oriented fibrils and voids which connect regions of undeformed polymer (eg,2,3,4,5). This structure has been described as an open-celled foam in which the void and fibril dimensions are approximately 20 nm in diameter, and the void fraction is about 50 percent (eg. 45). The voided regions are interconnected such that liquids will diffuse throughout the crazed matter. The width of the craze (in the tensile direction) varies with distance away from the tip, and is usually less than one micron (eg. 2,3,4,5). Deformations associated with crazing are generally considered irreversible; however, some elastic recovery occurs upon unloading (eg. 34).

During fracture, cracks propagate through various paths inside the craze (43) which depend on the rate of strain. At low strain rates (43), cracks propagate through the central regions of the craze known as the midrib (43). The midrib is a section of the craze which contains a higher than average void fraction, and it extends the width of the craze perpendicular to the stress (eg. 2,3,4,5,43). High strain rates (43) produce cracks which propagate in a random manner, alternating between bulk polymer interfaces. In all cases, crazes or highly voided craze like material provides the crack propagation medium (eg. 14,15,16).

A glassy polymer must meet several criteria before it will exhibit the crazing phenomenon. First, its number averaged molecular weight must be greater than twice the entanglement molecular weight (20). Also, the applied tensile stress must be greater than the characteristic crazing stress of the polymer for the case of shock

loading (62,63). However, if the crazing stress is not exceeded, a fatigue phenomenon may occur. That is, crazing may occur over time under lower than critical stresses.

2.2 MAJOR INVESTIGATIVE TOOLS

For an instrument to be most useful in the study of the morphology of polymeric crazes, it must be able to resolve features in the range of 10nm to 1000nm. Two important tools most often used have been electron microscopy and small-angle x-ray scattering (SAXS). However, other experiments such as bulk density measurements of crazes are useful to correlate with SAXS data.

2.2.1 ELECTRON MICROSCOPY

Electron microscopy seems most desirable at first, because of the ability to view crazed matter directly, but there are experimental difficulties. Scanning electron microscopy (SEM) studies of craze morphology are possible because cracks are known to propagate through crazes (eg. 14,15,16). Thus, by studying fracture surfaces, important information about crazes may be obtained. However, SEM studies of fracture surfaces are limited by the assumption that craze structure is unaffected during fracture. Transmission electron microscopy studies (TEM) are possible only in thin films. Several types of studies are available: films microtomed from a crazed bulk sample (eg. 36), films microtomed from bulk uncrazed sample then strained to produce crazes (eg. 3), or solution cast films which are strained to produce crazes

(eg. 17). Studies of crazes in thin films (1000 nm) have been controversial, since there is doubt that the microstructure of crazes in films is the same as that in bulk samples (2,9).

Some researchers (eg. 36) have attempted to microtome films of crazes formed from the bulk. They reinforce the craze by diffusing a sulfur eutectic liquid into the voided regions, which solidifies before cutting, and the solid later sublimates in the atmosphere of a microscope. However, this technique has been criticised as aging the craze structure (eg. 2,3,4).

2.2.2 SMALL-ANGLE X-RAY SCATTERING

SAXS experiments have the distinct advantage in that they are able to examine bulk samples while leaving them undamaged. Since the electron density difference between polymer and void is large, crazes provide intense scattering media. However, the craze may not be viewed directly, and data analysis is not straightforward (51,70). So far, no one has clearly demonstrated the best way to handle the data. Therefore the results are controversial and sometimes contradictory.

This contradiction may be due to varying experimental methods, sample compositions, and sample preparation. The SAXS data have basically been treated in two ways, namely the Guinier (eg. 70) and the modified Porod analyses (eg. 11,52). Both methods attempt to characterize the size distribution function of scattering centers in the craze, but disagreement as to the nature of the scattering center exists.

Most of the SAXS studies of crazes have been done on the Kratky camera in the long slit geometry (eg. 11,44,45,61). Since scattering functions of crazes are known to be anisotropic, this method suffers from the difficulty of deconvoluting anisotropic functions (51).

Other SAXS experiments have been done in the pinhole geometry (eg. 45). Most of these results suffered from the use of photographic detectors and/or limited low angle resolution.

2.2.3 OTHER METHODS

There are other methods available which monitor bulk sample responses during crazing. One method used in this work was density measurement. By measuring the density of a sample before and after crazing, the void fraction of the polymer may be calculated. This information will be needed to help interpret SAXS results.

2.3 RECENT DEVELOPMENTS IN THE CRAZING LITERATURE

By far, the most utilized experimental technique of the past five years has been transmission electron microscopy (TEM) (13,14,15,16,17,39,66). Other important contributions have been made using diffraction techniques such as small-angle x-ray scattering (SAXS) (11,70) and small-angle electron diffraction (SAED) (9) in an electron microscope. Mechanical property experiments of crazing have also been performed (40,53). The most common material for study has been polystyrene (13,14,15,16,17,18,16,17), although other systems such as blends (61,67) etc. have been studied.

2.3.1 ELECTRON MICROSCOPY

Recently, the largest contribution to the crazing literature using TEM has been given by Kramer et al. (13,14,15,16,17,39,43). They developed a method by which crazes in thin films may be observed under load in an electron microscope (17). Basically, the technique (17) involves bonding a thin film onto a copper mesh. By straining the grid, a permanent deformation may be applied to the film.

Lauterwasser and Kramer(43) studied microscopic mechanisms of craze growth and fracture. They found that crazes thicken predominately by a surface drawing mechanism, rather than fibril creep. It was also noted that void fraction of crazed matter is proportional to the surface stress of the craze interface during formation. The midrib has a higher void fraction than other regions because it was formed at the craze tip, where stresses are high. The other regions are formed by surface drawing after the craze has developed; the void fractions of these regions are lower because the surface stresses are lower. Since their micrographs revealed no voids adjacent to the advancing craze tip, these authors support the Taylor meniscus instability mechanism for craze formation (64), since no precraze voiding is required for this model. For fracture mechanisms it was noted that some fibril creep must occur or fracture will never happen. It was postulated that slow disentanglement of polymer chains occurs at the midrib, which would nucleate a crack. At this time further surface drawing occurs near the interface at high surface energies. Thus, the crack may propagate near the midrib or interface depending on which is energetically more

favorable. Generally, at low strain rates cracks propagate at the midrib, while at high strain rates near the interface.

Farrar and Kramer (17) studied the microstructure of crazes in oriented polystyrene. They reported that crazes formed parallel to the axis of orientation have a higher void fraction than crazes formed in isotropic media, which in turn have a higher void fraction than crazes formed perpendicular to the axis of orientation. Similarly, craze thickness increases with increasing initial orientation parallel to the craze. Also, more crazes can be formed perpendicular to the orientation axis than parallel to it. These results are interpreted in terms of the tensile strength of the bulk polymer, and the ability to form fibrils.

Donald and Kramer (14) studied in more detail, the mechanisms of craze tip advance than did Lauterwasser and Kramer (43). They employed stereo microscopy and tilting techniques to view the craze tip from a three dimensional perspective. Regions of lower density ahead of the advancing craze tip were observed and classified as fingers. These fingers are predicted by the meniscus instability theory (64). As the meniscus between bulk polymer and craze breaks down, fibrils are formed. A stress analysis is performed using this meniscous instability theory, and the wavelength of the instability is shown to correlate well with the distance between fibrils.

Donald and Kramer (15) also studied the effect of strain history on craze microstructure. By straining thin films in a stepwise manner, they attempted to prove an earlier theory. That is, the characteristic

draw ratio of crazed matter is proportional to the surface stress of the craze, as influenced by the bulk stress. However, it was found that the applied stress to the sample had no effect on the draw ratio of thickened crazes. They concluded that relaxation of craze surface stresses occurs quickly after each deformation, so the values of the surface stresses are difficult to control.

Thirdly, Donald and Kramer (16) studied the effect of molecular entanglements on craze microstructure. They were able to study the effect of entanglement density using various polymers whose entanglement molecular weight varied from 43,000 (PTBS) to 2,500 (PC). There was observed a good correlation between entanglement density and fibril draw ratio. Those polymers having a large entanglement molecular weight (Me) also have a large extension ratio. Therefore void fraction increases with entanglement molecular weight.

King and Kramer (39) studied craze intersections of biaxially stretched polystyrene. They showed that volumes intersected by crazes contain a higher void fraction than normal crazed volumes. The secondary craze exposes interconnections between primary crazes fibrils, which exhibit load bearing capability normal to the secondary craze and parallel to the primary craze. Even though craze intersections can bear stress in any direction, the volume has been considerably weakened by the biaxial deformation. Thus, craze intersections provide line nucleation sites for cracks, and fracture occurs at a lower stress than in samples with no craze intersections.

Wellinghoff and Baer (66) classified polymeric glasses as to their deformation characteristics. Type one glasses craze at all temperatures below their glass transition temperature, and are characterized as vinyl polymers with bulky side groups. Type two glasses craze only at temperatures close to their glass transition temperature, and exhibit other deformation processes such as shear banding. These polymers are characterized as polymers with flexible main chains. It was found that all type one glasses can be transformed into type two glasses simply by forming blends of the two types. Type two polymers typically show less fibrillar strains than type one, and the presence of shear bands stop propagating crazes.

2.3.2 SMALL-ANGLE X-RAY SCATTERING

Brown and Kramer (11) performed SAXS experiments of crazes in bulk samples of polystyrene using the Kratky camera in the long slit geometry. They termed the scattering in the tensile axis as anomalous, and the scattering in the nontensile direction as normal, based on what one might expect from scattering of fibrils. Crazes were modelled as consisting of oriented fibrils spanning the width of the craze with no interconnections. This model, including fibril diameters calculated from SAXS results, was shown to be consistent with the Taylor meniscus instability theory (64) with stress analysis. They also cited results of TEM studies to support this model.

The work of Westbrook et al. (70) disagrees with the work of Brown and Kramer (11). Westbrook et al. reported on SAXS studies of polystyrene crazes done with pinhole geometry and a two-dimensional position-sensitive detector. They made issue of the anomalous streak; noting a more intense anomalous streak than did Brown and Kramer (11), Westbrook et al. claimed the oriented rod model contains no mechanism by which x-rays could be diffracted in the tensile direction. Westbrook et al. assumed the anomalous streak as diffraction from voids and interprets it as a result of distances between interconnections of fibrils. Therefore the open-celled foam model of Kambour (36) was reembraced. Brown later (8) suggested the anomalous streak results from reflections off the craze bulk polymer interfaces. Unfortunately, the reflection phenomenon was not considered in the papers of Brown and Kramer (11) or Westbrook et al. (70).

2.3.3 SMALL-ANGLE ELECTRON SCATTERING

Recently, Brown (9,10) resumed his crazing studies with small-angle electron scattering (SAES) in an electron microscope. In a preliminary paper (10) he outlined a general technique for studying SAES patterns in polymeric crazes and cracks using a tilting technique. Later, he (9) used this technique to compare the scattering patterns from thin films using SAES to scattering patterns from bulk samples using SAXS data obtained in a previous study (11). Brown showed from a theoretical standpoint, the scattering patterns from crazes using SAXS and SAES should be similar if the morphologies are identical. However,

the comparison of the data revealed that crazes in thin films had features about three times larger than crazes in bulk samples. He attributed this result to residual toluene acting as a plasticizer, and the lack of lateral constraint in the thin films.

2.3.4 OTHER STUDIES

A theoretical treatment for predicting craze features was developed by Fellers and Huang (19). They predicted the average size of a volume element which guarantees that a fluctuation associated with crazing will occur in it. This volume element depends on the applied stress, modulus of compressibility, and glass transition temperature. The calculated volume element for polystyrene is shown to be on the order of void sizes observed in crazes. An expression for the entanglement density versus molecular weight is also developed.

Wool and O'Connor (71) studied craze healing in polystyrene using optical microscopy. Molecular mechanisms of craze healing were treated analogously to crack healing. A healing envelope in temperature and time is developed. It was shown that even though a craze may appear healed, the region still exhibits poor mechanical properties, because molecules have not had sufficient time for complete interpenetration by reptation. Thus, craze reformation occurs faster than the original formation.

2.4 IMPORTANT VARIABLES

The variables of interest in this crazing study are: the amorphous structure as defined by the chemical composition, the level of applied stress, the time at which the stress has been applied. and the relaxation behavior under zero stress. These variables can be investigated using a dynamic SAXS experiment.

2.4.1 AMORPHOUS STRUCTURE

Amorphous polymers are so named because their molecules do not arrange themselves in an orderly way in the well annealed solid state. Typically, these polymers are transparent because no periodic structure on the order of the wavelength of light is present to cause scattering. Glassy polymers will not crystallize because they generally have large side groups or rigid main chains which prohibit orderly packing. This is the case for atactic polystyrene. Amorphous polymers in equilibrium adopt a random coil conformation, in which the location of the main chain is governed by a modified statistical excluded volume theory (21).

Even though amorphous polymers have no periodic structure, they do have heterogeneities (68,69). Some heterogeneities are known as entanglements and chain ends (19). Naturally, entanglements tend to strengthen the polymer matrix, because stress may be supported across an entanglement in directions other than the main chain direction. Unfortunately, there is no precise definition of an entanglement; however, an entanglement molecular weight can be determined from discontinuities in the rheological behavior of the melt. The

entanglement number density as a function of molecular weight has been calculated for polystyrene using statistical analysis. Conversely, chain ends tend to weaken the polymer matrix, because stress may not be supported in any direction across a defect. Chain ends are easily defined as the termination point of the main chain, and their number density may be directly calculated for unbranched polymers using molecular weight data. These features, along with impurities, cross links, chain mobility, etc., will be referred to as the intrinsic structure of the amorphous state.

The amorphous structure of a polymer seems to be the most important variable in determining the crazing behavior (70). Statistical fluctuations in the number density of chain ends and entanglements may ultimately lead to voiding and fibrillation. For example, volume elements consisting of a high number density of matrix strengthening components (entanglements, etc.), and a low number density of matrix weakening components (chain ends, etc.) may fibrillate at low stress levels and vice versa.

The easiest method of changing the number density of structural elements of the polymeric glass is to change the chemical composition. There are several ways to study craze structure as a function of chemical composition. The most characterizeable variables are: monomer unit, number averaged molecular weight, and molecular weight dispersity as defined by $\overline{M}_w/\overline{M}_n$.

2.4.2 CHEMICAL COMPOSITION

SAXS studies have shown that craze structures in polymers consisting of different monomer units are dramatically different (70). A comparison of polystyrene and polycarbonate craze scattering patterns reveal very few qualitatively similar features. The most obvious difference is the presence of a large intensity maximum in the transverse directions of the polycarbonate scattering pattern, where the polystyrene pattern has none. Therefore the two systems must have dramatically different craze morphologies.

Preliminary findings of molecular weight variables have been done for polystyrene (70). It was shown that all polystyrene crazes have similar morphological features, but vary quantitatively. For example, the scattering behavior of low molecular weight polymer crazes are qualitatively similar to that of high molecular weight polymer crazes, except lower scattered intensity. Therefore, larger scattering centers exist in crazes of lower molecular weight polymer, but other aspects of morphology such as shape, order, etc. must be the same.

No systematic study of craze morphology with respect to molecular weight or its dispersity has been reported; however, it seems intuitive that some dependence exists. It is possible, for example, that polydisperse samples whose number averaged molecular weight is close to $2M_e$ will craze, while a monodisperse sample with the same molecular weight will not. A disperse Polymer would have the opportunity to form a supportive structure of entanglements, while the monodisperse polymer would not. Similar arguments may be made for molecular weight

dependence on crazing behavior. Hence, crazing behavior may be a function of molecular weight parameters.

2.4.3 PROCESSING PARAMETERS

Two important processing parameters include temperature and strain rate during craze formation. To some extent, these parameters have already been investigated for polystyrene (70). The major conclusion of that work is that temperature and strain rate during craze formation have no quantifiable effect on the morphology in completely relaxed samples at room temperature. However, no kinetic data have been reported using on line stress, temperature or time variables in a SAXS craze formation experiment.

2.4.4 TRANSIENT BEHAVIOR

The behavior of the scattering functions with time and stress are the most important variables in the study of crazing kinetics. This can be done by using a stepwise increasing incremental stress function. Craze initiation may be observed in scattering patterns where the crazing conditions have not been exceeded. In the same manner, craze growth may be studied in scattering patterns where the crazing conditions have been exceeded. Another important phenomenon which has been discussed briefly in the literature, is the effect of sample unloading (11). Here, craze morphology is shown to be dependent on whether the stress on the sample is maintained during experimentation.

These three transient effects can be measured in one sample with the on line SAXS deformation sample holder at NCSASR.

3. EXPERIMENTAL

In this chapter, a discussion of the sample preparation and x-ray data analysis techniques will be given. Specifically, the constraints on sample dimensions will be discussed along with sample compositions and fabrication techniques. Also, a brief discussion of the NCSASR SAXS equipment will be given.

3.1 SAMPLE PREPARATION

Suitable samples for dynamic SAXS analysis of crazing must meet several specifications dictated by the limits of the systems. For a glassy polymer to craze, its number averaged molecular weight must be at least twice the theoretical entanglement molecular weight of the polymer. The cross sectional dimensions of the sample are limited by the breaking stress exceeding the tensile force limits of the pull rods in the dynamic device. Also, the optimum path length of the x-ray is governed by the reciprocal of the linear absorption coefficient of the polymer. Lastly, varying states of molecular orientation will effect the sample performance. Since orientation is not a variable of interest in this study, care must be taken to minimize internal stresses by annealing. With these limitations in mind, samples were prepared in the following way.

3.1.1 SAMPLE COMPOSITIONS

The parameters of interest in varying sample compositions are: number averaged molecular weight, molecular weight distribution as defined by $\overline{M}_w/\overline{M}_n$, and monomer unit. Because of their availability, (19) polystyrene samples were selected for the molecular weight and molecular dispersity experiments.

For the case of polystyrene, the dependence of craze morphology with respect to molecular weight will be studied using samples which vary in number averaged molecular weight but are nearly monodisperse. These polymers were specifically synthesized and characterized in small quantities by T.F. Chapman of the University of Tennessee, and Lu Ho Tung of Dow Chemical Company. The effect of molecular weight dispersity on craze morphology will be studied by comparing the results from the above set of samples to a series of commercial polymers obtained from Dow, U.S. Steel, and Shell Chemical Companies. A summary of the characterization of all polystyrenes used in this work is found in Table 3.1 (page 22). Figure 3.1 (page 23) shows a graphical interpretation of the variables of interest in Table 3.1.

3.1.2 SAMPLE DESIGN AND DIMENSIONS

The most important dimension of the sample is the thickness (the direction in which the x-ray travels). Since the linear absorption coefficient of polystyrene is 10.87 in^{-1} , the optimum thickness of the sample is about 0.1 in. Next, we desire the sample to be as wide as possible such that the sample is easily aligned in the x-ray beam, and

TABLE 3.1 CHARACTERIZATION OF POLYSTYRENE SAMPLES

POLYMER	$\bar{M}_w(E-05)$	$\bar{M}_n(E-05)$	$PD=\bar{M}_w/\bar{M}_n$
678U*	2.47	0.78	3.76
TC3-30*	2.83	0.61	4.64
USS*	3.39	1.14	2.97
S103**	1.25	1.18	1.05
S107**	1.53	1.42	1.05
685D*	2.06	1.59	1.91
PS4***	2.30	2.02	1.14
S108**	2.67	2.47	1.08
PS6***	4.02	3.67	1.09
S107A**	7.07	7.21	1.21
PS8A***	12.8	10.8	1.19
PS7***	15.1	12.3	1.23

* commercial samples

** samples synthesized and characterized by Lu Ho Tung
of Dow Chemical Company

*** samples synthesized and characterized by T.F.Chapman
of the University of Tennessee

Molecular weights determined by the gel permeation
chromatography method.

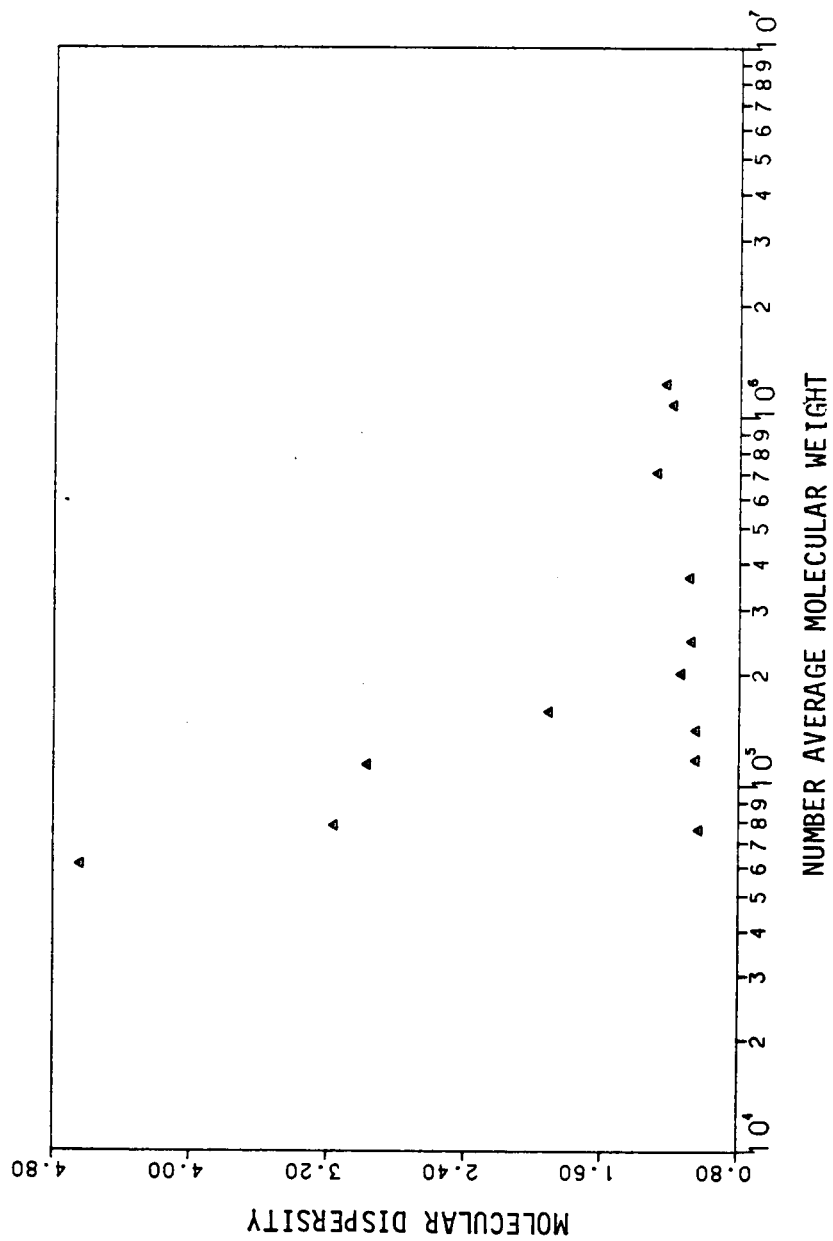


Figure 3.1 Polystyrene characterization.

the x-ray beam will be well away from the edges of the sample. Once the thickness is set (above), the width is determined from both the maximum loading force available to the sample, and the sample's breaking stress. For this calculation, a breaking stress of 4.83×100 Pa will be used, since no unoriented polystyrene fractures at a greater stress. The maximum force available to the sample by the existing hydraulic system is 533 N. Therefore, the width of the sample should be less than 0.5 cm. This dimension is tolerable since the width of the x-ray beam is 0.1 cm. The length of the sample is governed by what comfortably fits in the sample holders mounted on the pullrods. A tensile bar geometry which meets the above requirements is shown in Figure 3.2 (page 25).

3.1.3 TENSILE BAR FABRICATION

The tensile bars are made by cutting from sheets of molded polymer whose thickness corresponds to the the thickness of the tensile bar. The polymer sheets are compression molded in a picture frame mold. A schematic drawing of the molding operation is shown in Figure 3.3 (page 26). Pelletized polymer is placed inside the mold and processed in the following way:

1. Platens are heated to 180°C
2. Preheat polymer inside mold at 180°C for ten minutes, such that a molten state is achieved.
3. Increase force on mold to 20,000 lbs over a period of ten minutes, such that bubbles may escape.
4. Relieve pressure on mold and anneal for ten minutes

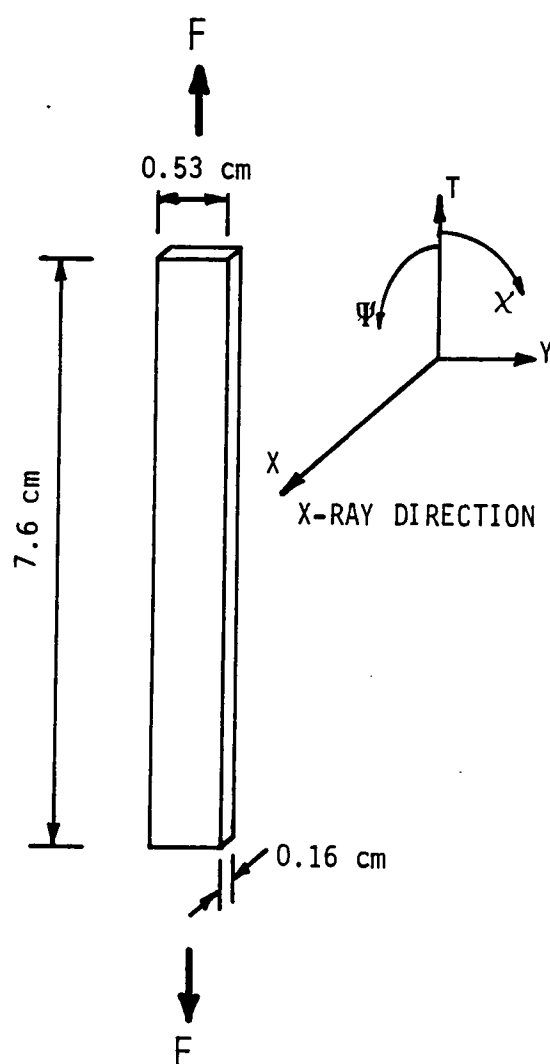


Figure 3.2 Sample geometry with respect to laboratory axes.

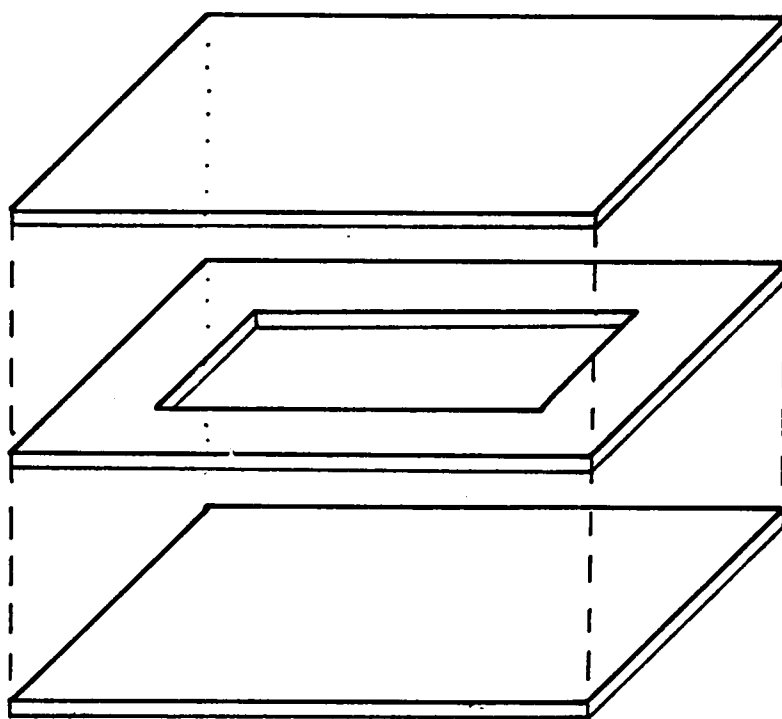


Figure 3.3 Picture frame mold apparatus for compression molding.

at 180°C, such that internal stresses are relieved.

5. Remove mold from hot press and cool to room temperature slowly in air.

Steps four and five are done so that an isotropic sheet is made. The birefringence of the material is checked to assure the isotropic character. Cutting the sheets into tensile bars of dimensions shown in Figure 3.2 is accomplished on a low speed water cooled diamond saw. Lastly the cut edges are polished by stroking in the tensile direction with 600 grit sandpaper.

3.1.4 LAMINATED SAMPLE FABRICATION

The interfaces between crazes and bulk polymer can be modelled by a laminated sample constructed of stacked thin films, where the planes of the films are parallel to the x-ray beam. These samples are used to help understand the nature of x-ray scattering from crazed samples, in terms of reflection phenomenon.

The thin films are obtained by biaxially stretching the polymers at 110°C. The thickness of these films are about 0.1 millimeter thick. They are then cut and stacked one on top of another, until the compounded thickness exceeds two millimeters. When clamped together, the films are placed in the x-ray beam such that the planes of the films are parallel to the x-ray beam. For interfacial variety, the thickness of the films can be changed (lowering the number of interfaces exposed to the x-ray beam), and the films can be glued together with epoxy (lowering the phase contrast in the interface).

3.2 NCSASR SAXS APPARATUS

The NCSASR SAXS apparatus, including the newly installed dynamic deformation device used in this work, has been described in detail in the literature (27,28). However, a summary of important characteristics is given here for clarity. The discussion will briefly cover how the hardware and software are used in the experimental methodology as applied to dynamic crazing studies.

3.2.1 HARDWARE

Here, the major components of the x-ray device are listed and defined. Most of the features described are represented in Figure 3.4 (page 29), a schematic representation of the SAXS device.

1. X-ray Generator The x-ray generator is a 6.0 kilowatt Rigaku-Denki rotating anode device. When operating at 40kv and 40ma with a source to sample distance of 1.6 meters, the copper K_{α} intensity can be as high as 2.5×10^6 photons per square millimeter per second with a polished anode and good alignment.

2. Monochromatization and collimation The characteristic K_{α} x-rays emitted by the copper anode are further separated into its alpha and beta components by reflection off a graphite pyrolytic single crystal. The monochromatization is further achieved with a sophisticated electronic detection system. The angle of the generator with respect to the collimation apparatus is set so that copper K_{α} (0.154 nm) radiation is used. The collimation is accomplished through two one square millimeter pinholes separated by 1.6 meters. The pinhole technique is used so that

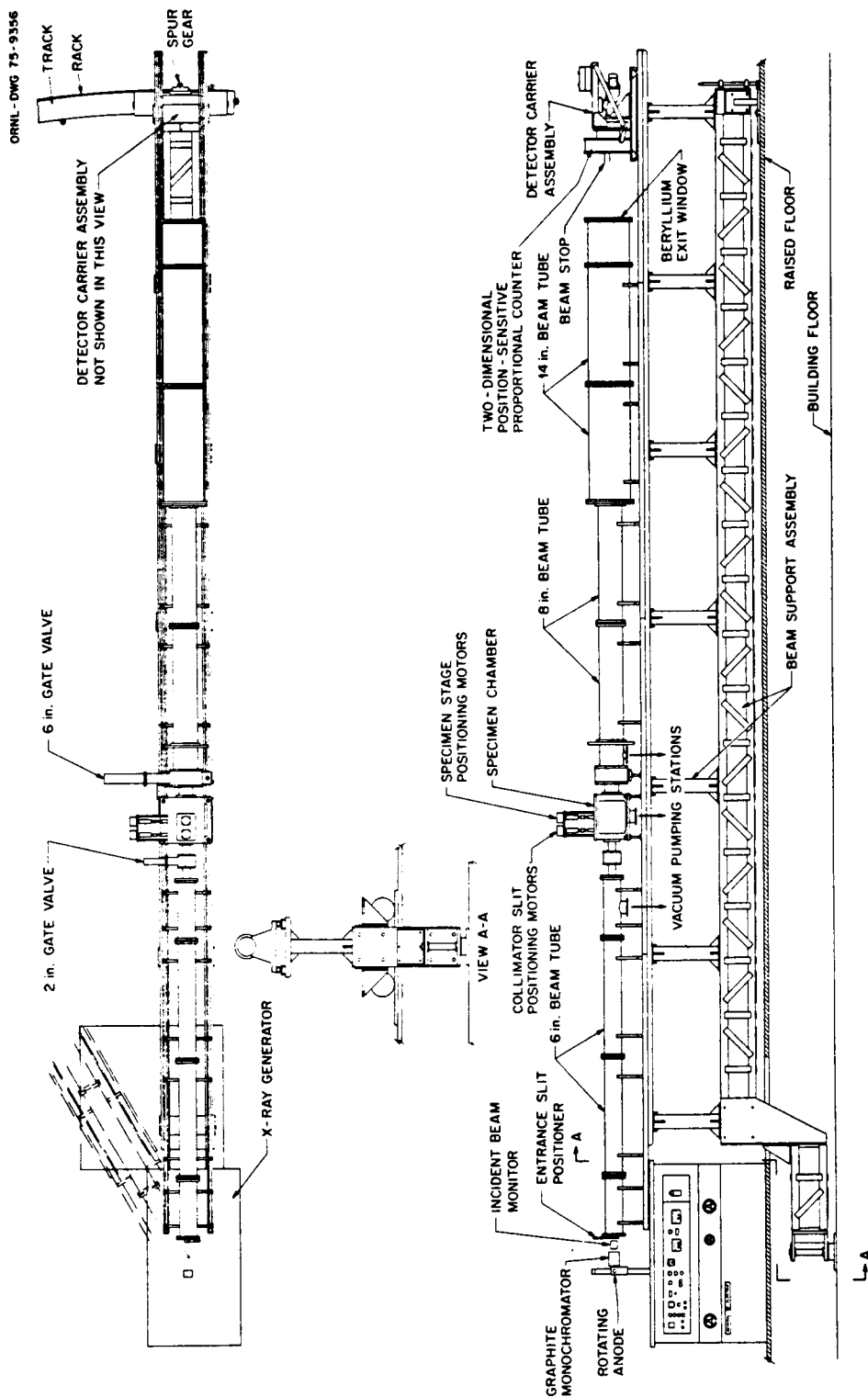


Figure 3.4 Schematic drawing of the new small angle x-ray scattering camera, showing locations of key alignment adjustments. (27)

smearing of scattered intensity can be avoided, and thus the deconvolution of data is not necessary.

3. Sample Holder The sample holder pullrods are equipped with a hydraulic system which will allow up to 120 pounds tensile force to be applied to the sample. The hydraulic system is operated by a function generator with servo control. It was designed to operate with sinusoidal or other cyclic deformations. Assuming the sample undergoes reversible deformation, the Mostec memory system in the associated data acquisition system is designed to cumulate scattered intensity data from the detector in up to 64 divisions of each repeated cycle (see Figure 3.5 page 31). Since the crazing phenomenon is not reversible with deformation, this process can not be employed. Either a ramp function with an extremely small slope with time, or a step function is needed. A step function is chosen for ease of operation; the details of which are illustrated in Figure 3.6 (page 32).

Deformation of the sample is accomplished by movement of the upper pullrod, while the lower pullrod remains stationary. This means the volume which the x-ray beam samples changes with deformation. However, glassy polymers deform less than two percent before fracture, so it is assumed volume irradiated by the incident x-ray beam is not changed during crazing.

4. Detector The detector, which monitors scattered intensity, is a compound detector known as a two-dimensional position-sensitive detector (2DPSD). It consists of two selected resistance wires which are meshed and arranged to form a cartesian grid. The grid is divided

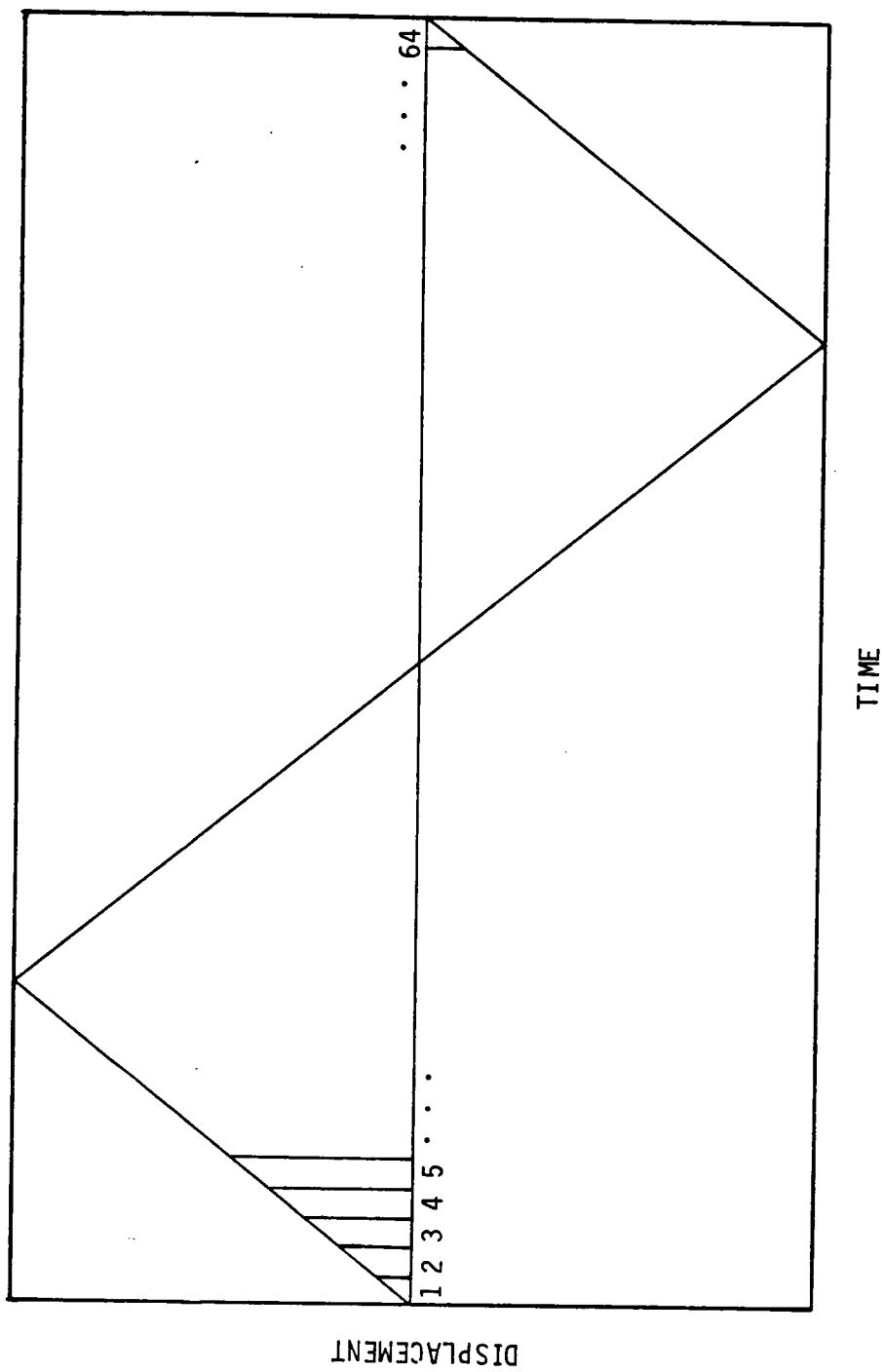


figure 3.5 Schematic of NCSASR SAXS sample deformation history for intensity measurement.

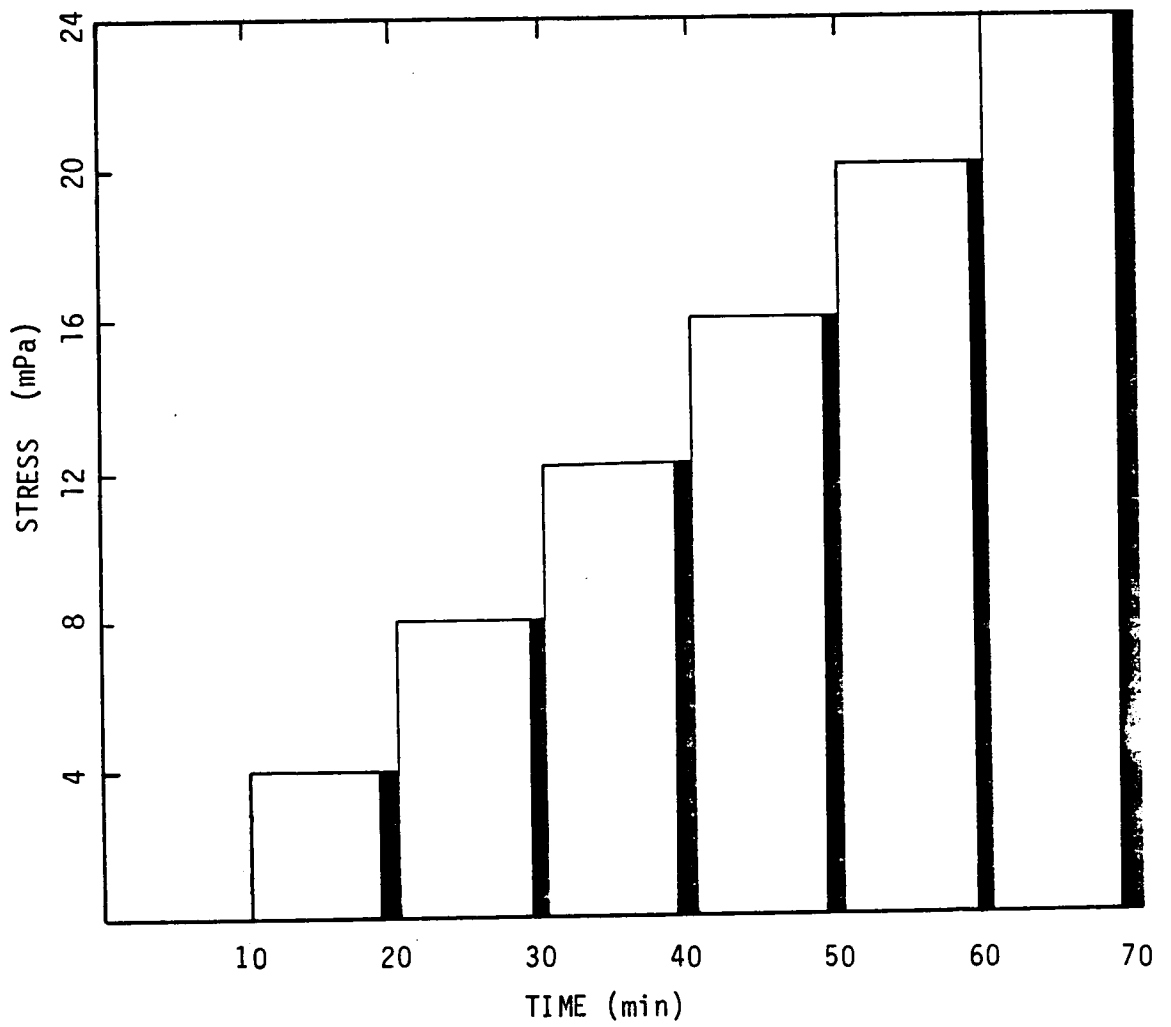


Figure 3.6 Sample deformation history for crazing studies.

into 64×64 elements, according to the detector resolution and the limitation of the mini-computer memory capacity. The size of each detector element is 0.324×0.324 cm. making the size of the 2DPSD 20.7×20.7 cm. The intensity measured by each detector element is position encoded and directed by the microprocessor to store in a unique address in the computer memory. Therefore a 64×64 matrix of scattered intensity in two dimensions exists for each experiment. The distance between sample holder and 2DPSD is variable in increments of one meter from about one meter to about five meters, which controls the available angular resolution. Since the scattering centers in crazes are anticipated to be in the range of five to 100 nm, the maximum small-angle resolution of the instrument is desired, and the sample to detector distance is set at 5.048 meters.

5. Computer The two major functions of the Modcomp computer system are to record and reduce data. The software which performs these functions are described qualitatively in the next section.

The first function of the computer is to record the scattered intensity as a function of detector location and stress (strain) level. It accomplishes this by allocating specific locations in memory for each detector and sample condition. For each experiment, a header record accompanies the data. The header record contains such information as: experiment number, equipment geometry, absolute intensity, sample constants, etc. The computer uses the header information when executing data correction and reduction routines. These routines comprise the second function of the computer. The intensity data are corrected by

subtracting background radiation and normalizing for detector sensitivity, transmission coefficient of the sample, etc. The computer will also reduce the contour plots to linearly averaged scattering intensity versus scattering angle plots by radial or slice averaging routines in the data analysis software.

3.2.2 SOFTWARE

As indicated in the last section, the computer software enables the gathering, correction and reduction of data. The computer is operated by simultaneous foreground and background programs. The major software is qualitatively described here.

1. Foreground Programs The major purpose of the foreground programs 'SAXS' and 'DSAXS' is to automate the hardware. Both programs operate stepping motors for the glassy carbon, 2DPSD position, sample stage, etc. They also prepare the header record and take data. DSAXS is designed to operate the hydraulic system, coordinate the Mostec memory system and register the stress and strain information.

2. Background Programs The purpose of the background programs is to correct and reduce the two dimensional intensity data. A summary of some important background programs for data reduction is given:

FILE To fetch and store two dimensional data from disc storage to working memory.

BKG, BKC Two routines for subtracting background intensity while normalizing for detector sensitivity, transmission coefficient, absolute intensity, etc. BKC is used for samples with low signal to noise ratios.

CONTOUR Displays the corrected two dimensional data in contour plot form with Tektronix cathode ray tube (CRT). Subroutine CEN lets one establish the center of the contour plot with a cursor in the CRT, and stores that position in the header record. Subroutines RAD and AVE reduce the two dimensional data to one dimensional form by performing circular or linear averages respectively.

MANAGER manipulates data sets in memory which are stored on disc; one can read from, or write to the disc, delete data, alter header records, etc.

3.3 ALIGNMENT AND CALIBRATION OF SAXS HARDWARE

Due to the large size of the SAXS instrument used, tolerances of location and/or orientation of collimation and monochromation equipment are low. Therefore great care must be taken to insure maximum performance of the device. Figure 3.4 (page 29) is a schematic representation of the SAXS machine, showing the locations of key adjustments involved in the alignment procedure. Table 3.2 (page 36) is a summary of descriptions of each adjustment. After alignment, the SAXS device is calibrated for detector sensitivity, absolute intensity, background intensity.

TABLE 3.2 SUMMARY OF SAXS HARDWARE ADJUSTMENTS

ADJUSTMENT #	FUNCTION
1	Change azimuthal angle of the crystal monochromator with respect to incident x-ray beam.
2	Position crystal monochromator in the center of incident x-ray beam.
3	Angle of crystal monochromator with respect to the incident x-ray beam.
4	Vertical coordinate of first pinhole.
5	Horizontal coordinate of first pinhole.
6	Vertical coordinate of second pinhole.
7	Horizontal coordinate of second pinhole.
8	Angle of detector with respect to the monochromator.
9	Vertical coordinate of detector.
10	Horizontal coordinate of detector.

3.3.1 ALIGNMENT

The most important diagnostic tool used in the alignment of the SAXS equipment is the 2DPSD. Contour plots obtained at strategic times during the alignment procedure will tell the experimenter in what direction and in some cases, how much to move each adjustment. Other important tools used in this procedure include an oscilloscope, the scaler counters and a fluorescent screen.

To begin with, both pinholes are removed from the machine. In this geometry, the diffracted x-ray beam is undefined such that tremendous intensity at the 2DPSD is possible. Therefore, extremely low power (10kV and 2Ma) is used, and the sample chamber air locks are closed whenever possible to prevent damage to the 2DPSD.

3.3.1.1 CRYSTAL MONOCHROMATOR

The alignment procedure begins with the removal of the crystal monochromator chamber from the attachment to the x-ray generator. Adjustment #2 is set visually by inspecting the location of the crystal with respect to the incident x-ray beam porthole. The projection of the crystal must occupy the maximum area of the porthole. After the crystal housing is replaced and attached onto the generator, adjustment #2 is no longer altered. The crystal is a graphite single crystal, which is cut such that the (hkl) diffraction plane is located 73.5 degrees away from its vertical (for copper K_α radiation). Therefore, the Bragg reflection occurs at $\theta=13.5$ degrees. Theta may be roughly set by visual inspection at first; however, the fine adjustment is made using a fluorescent

screen. Adjustment #3 is turned such that the copper K_{α} beam intensity is maximized. This operation is done cocurrently with adjustment #1 to obtain sharp focus. Once adjustment #3 is set in this step, it is never altered again.

Next, the exit slit of the monochromator chamber is aimed approximately in the center of the opening of the collimating tube. Since the generator/monochromator assembly is purposely not rigidly attached to the collimation devices, the generator may be moved slightly to accomplish the desired result. The height of the beam may be changed with the tilting screw (adjustment #1). The angle of the detector with respect to the crystal monochromator is set with the pivot crank (adjustment #8). Since the SAXS 10-meter device is pivoted under the monochromator housing, turning the crank will allow the collimation tube to intersect the generator at about 27 degrees. A more exact setting will be accomplished later.

3.3.1.2 PINHOLES

Now the 2DPSD is used to align the first and second pinholes. The second pinhole stage has a one inch diameter hole bored where the pinhole assembly is attached. The stage and pinhole assembly are machined such that when mounted together, the pinhole is located precisely in the center of the one inch hole. Therefore, the second pinhole stage may be accurately positioned without the pinhole assembly, simply by locating the position of the stage yielding the maximum count rate and symmetric contour pattern. If the dynamic sample holder is to

be used, there is one more restriction on the location of the second pinhole stage. That is, the x-ray beam must intersect the line of action of the pullrods. Since the pullrods are oriented vertically and are immobile, this restriction limits the horizontal position of the second pinhole. This position is accomplished by measuring the horizontal distance between the pullrods and a reference point, and equating it with the distance between the pinhole and the same reference point using adjustment #7. Next, the vertical position of the second pinhole is set simultaneously with the tilt monochromator and the pivot crank (adjustments #6, 1, and 8 respectively). Typically, several iterations of these settings are done to achieve the best compromise between the following criteria (listed in order of importance): symmetrical contour pattern, maximum count rate, and a centrally located pattern. The symmetrical contour pattern is most important because it insures the maximum intensity passes through the center of the pinhole stage, where the pinhole will ultimately be located. Maximum count rate is desired for maximum intensity, but we are willing to sacrifice a few percent for symmetry. Having the beam centrally located in the detector is more flexible, since the detector may be moved a few centimeters to achieve this goal (adjustments #9 and 10). When the stage alignment is complete, the second pinhole assembly is mounted onto its stage and another low intensity pattern is taken. It should be noted that the presence of the pinhole assembly dropped the transmitted intensity by a factor of about 300. If the x-ray intensity were uniform throughout the cross section in the one inch hole, then the pinhole assembly would have

dropped the transmitted intensity by a factor of about 507. This result indicates the intensity is greater in the center of the stage as desired. From the pattern of the last step, the position of the 2DPSD may be set. Adjustments #9 and #10 are used to set the beam midway between the 32nd and 33rd channel in both axes (use subroutine CEN to determine coordinates). This point being the center of the 64 by 64 grid.

After the second pinhole is positioned, the first pinhole may be installed. As a rough aid to alignment, an oscilloscope is used to monitor the signal generated by the 2DPSD. Adjustments #4 and #5 are used to locate the position of maximum transmitted intensity as indicated by the oscilloscope.

3.3.1.3 BEAMSTOP

The beamstop is attached with wax on the exterior of the beryllium window near the 2DPSD. For the sample to detector distance of five meters, and the distance between pinholes of 1.6 meters, one can calculate the divergence of the main beam and therefore, the size of the beamstop. For this geometry, a beamstop of eight millimeters square is sufficient. A crude approximation of the proper location for the beamstop may be obtained by measuring the center of the 2DPSD, then transferring this location to the beryllium window. A low power contour plot will now indicate which direction the beamstop must be moved to improve its position. Several iterations of this procedure are done until a perfectly symmetrical background pattern is obtained (see

Figures 3.7 A and B, pages 42 and 43 respectively). As the beamstop's location is improved, the x-ray power may be gradually increased to full power (eg. 40kV and 40mA). The background count rate corresponding to good alignment at full power is about 700 counts per second. The background contour pattern is shaped like a cross because of the square cross sectional collimation technique.

3.3.1.4 SHIELDING

The system is now completely aligned and ready for calibration; however, two other minor shielding operations are needed. First, a lead shield equipped with a small hole in the center, is placed in the sample holder just before the second pinhole to stop stray radiation. Second, a large lead shield is placed around the exterior of the 2DPSD. This shield cuts down the amount of cosmic radiation allowed to reach the 2DPSD.

3.3.2 CALIBRATION

Calibration of the SAXS apparatus is a multistep process. The following experiments need to be done before scattering data can be taken: absolute intensity, 2DPSD sensitivity, background intensity, dark current intensity, and transmission coefficient measurements.

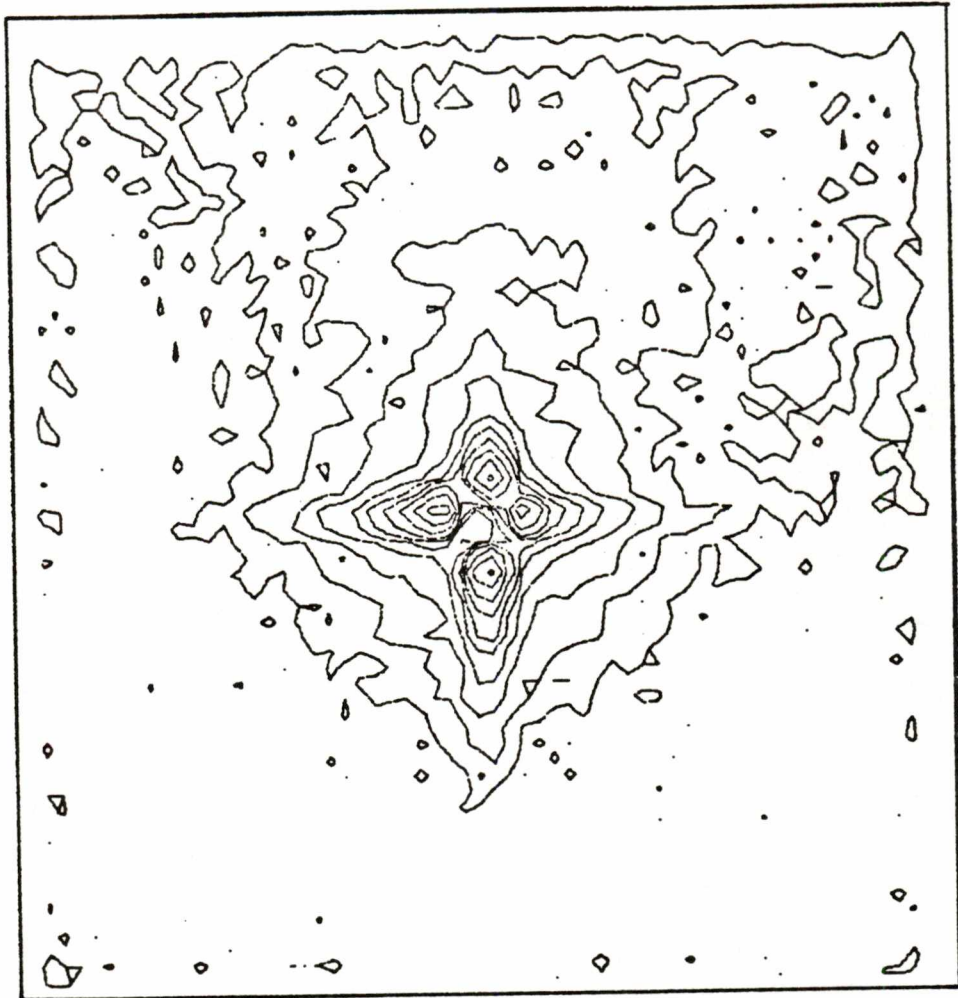


Figure 3.7 Empty beam background intensity. Exposure time is 500 sec.

A Contour plot.

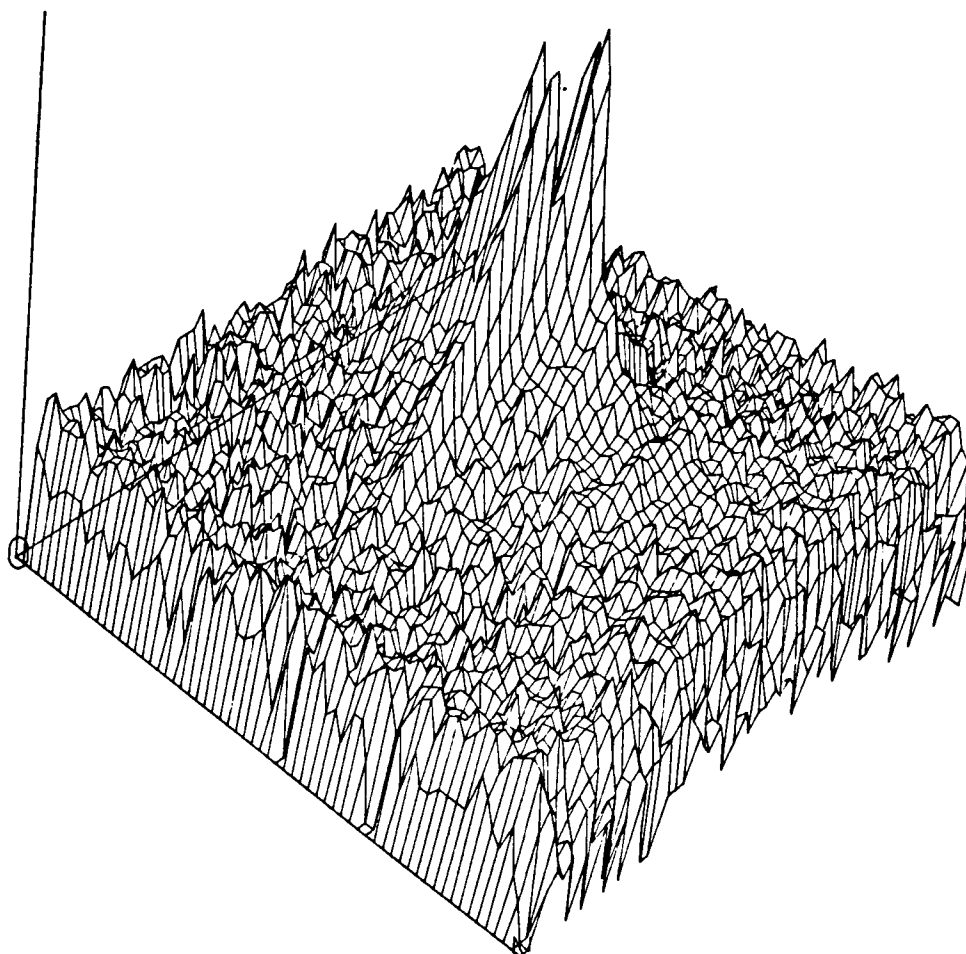


Figure 3.7 (Continued)

B Three dimensional logarithmic plot.

3.3.2.1 ABSOLUTE INTENSITY

The absolute intensity of a small-angle x-ray scattering experiment is the ratio of its intensity to that of the primary beam. The intensity of the primary beam is defined as the rate of photon bombardment per cross sectional area of the sample. This measurement is required for calculations involving the absolute determination of scattering center size distribution and volume fractions. Several methods are available for determination of absolute intensity (eg, 46,54,55); however, the multiple nickel foil and Lopolen methods (54,55) are used here because of their ease of application. (Lupolen is a heat treated polyethylene fabricated by Badische Anilin-und Sodafabrik, Germany.)

3.3.2.1.1 NICKEL FOIL METHOD

The nickel foil method involves attenuating the x-ray beam with layers of nickel foil, then plotting the transmitted intensity versus nickel thickness in a semi-logarithmic scale, and extrapolating to zero thickness. Various layers of nickel foil, each having the same thickness (about 0.01 in) are placed in the x-ray beam in the location of the sample with the beamstop removed. The 2DPSD is used here as a transmitted photon counter. Therefore the intensity value extrapolated at zero nickel thickness is the absolute intensity of the primary beam at the sample. This extrapolation is validated by the following equation:

$$I_{\text{trans}} = I_0 \left[\exp(-\mu t) \right]$$

where: I_{trans} = transmitted intensity
 I_0 = absolute intensity
 μ = linear absorption coefficient of nickel
 t = thickness of nickel

The true transmitted intensity, I_{true} , is calculated by:

$$I_{true} = [I_{obs} / (1 - t \cdot I_{obs})] - I_{dc}$$

Where $t = 7\mu s$ for the current detection system, and I_{obs} is the observed or measured intensity expressed in counts/sec.

The first term in the last equation is for the detector dead time correction, and the second term is for the dark current correction. Dark current primarily originates from cosmic radiation and electronic noise. Once the absolute intensity has been determined accurately by the nickel foil method, small variations in the absolute intensity can be measured quickly by the Lupolen method.

3.3.2.1.2 LUPOLEN METHOD

Lupolen is a carefully heat treated polyethylene whose microstructure is stable. Its SAXS pattern consists basically of an isotropic halo whose peak is at approximately 10 milliradians. The principle in this analysis is that the quantitative features of the scattering pattern vary only with the primary beam power. Therefore, radial average around the beamstop of the Lupolen scattering pattern is

taken, and the intensity at a specified angle is recorded. Given an initial absolute intensity, the absolute intensity at any time may be calculated by ratioing the values of the Lupolen intensities at the two times, and multiplying by the original absolute intensity. This method works best only when small variations of absolute intensity are present. Sources of these variations include: carbon deposits on the copper anode which diminish striking by thermal electrons, alignment variations due to changes in temperature or humidity in the laboratory, vibrations or other disturbances of the system.

3.3.2.2 DETECTOR SENSITIVITY

Each individual detector element in the compound 2DPSD may have a different sensitivity to radiation than others. Possible causes of this effect include: portions of the detector may be partially blocked by the beamstop or beryllium window support frame, variations in detector physics due to unequal aging rates, or nonuniform material processing properties. To calibrate the 2DPSD for this effect, a totally uniform radiation source is placed in the sample holder, such that the whole area of the detector has an equal opportunity to record radiation. Iron 55 is used as the source, and it is run until several million counts are recorded. These data will allow the computer software to normalize detector sensitivity by scaling up the measured intensity to an appropriate amount. Figures 3.8 A and B (pages 47 and 48) show a typical detector sensitivity function.

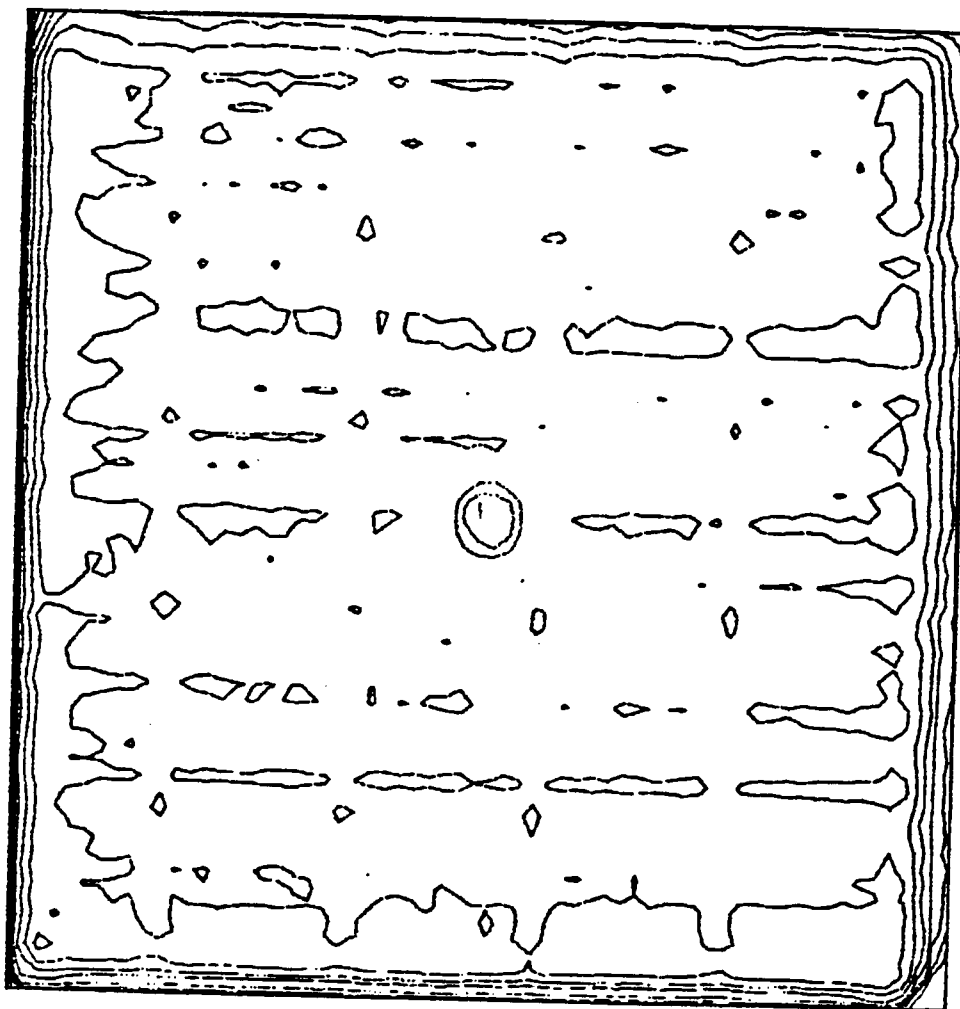


Figure 3.8 Detector sensitivity correction data.

A Contour plot.

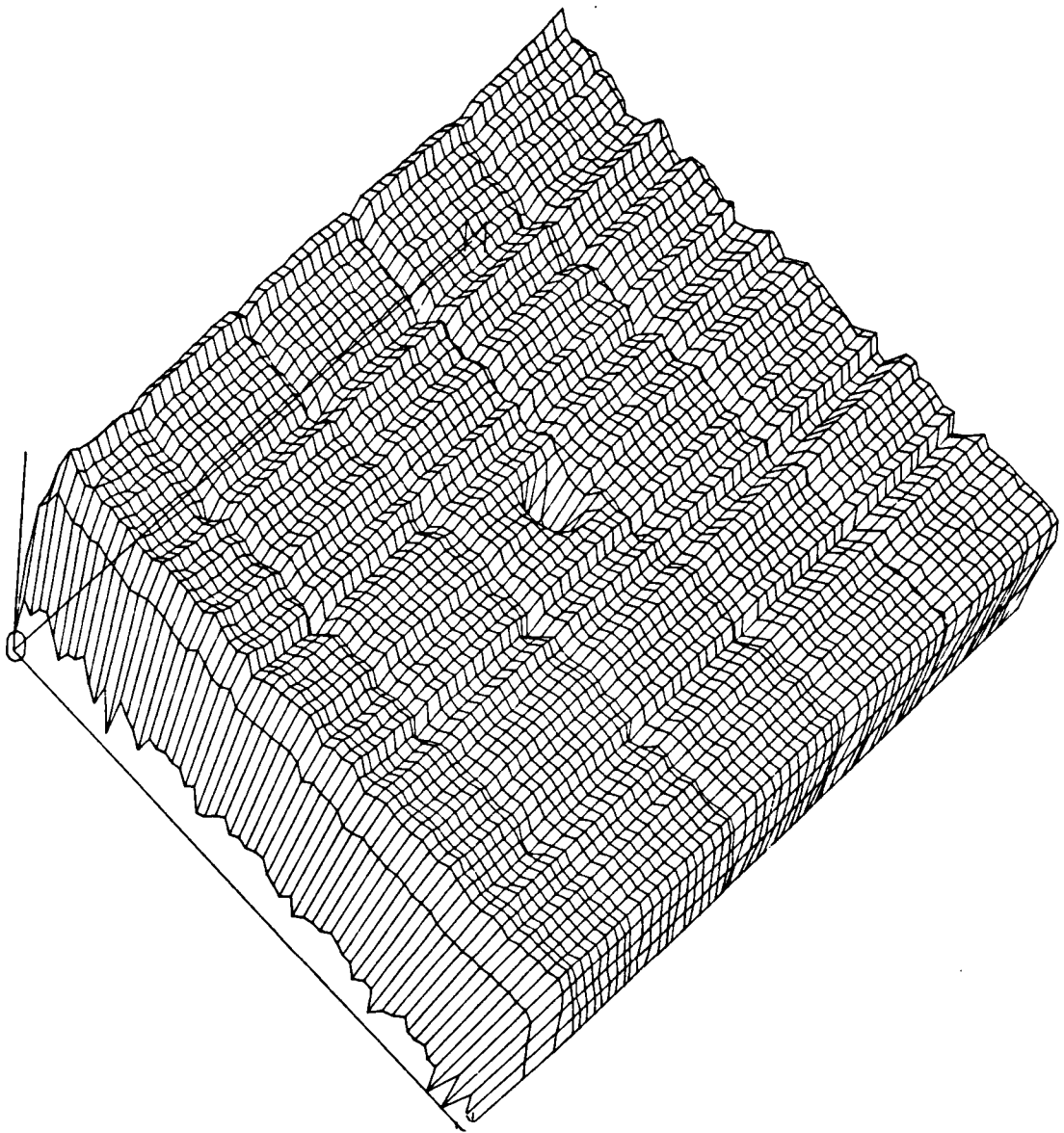


Figure 3.8 (continued)

B Three dimensional logarithmic plot.

3.3.2.3 DARK CURRENT INTENSITY

Dark current refers to the counts as registered by the detector when no x-rays are admitted to the detector. The dark current consists of radiation events that originate by cosmic radiation and electronic noise. This count rate is low (typically about 22 counts per second in a well shielded system) and must be subtracted from all scattering patterns. A dark current experiment is done by closing the sample chamber gate valves and recording stray intensity for an extensive period of time, normally not less than 1000 seconds. The experiment is done at full power so that the computer can record the beam monitor intensity for normalization purposes.

3.3.2.4 BACKGROUND CORRECTION

A significant background intensity exists due to the reflection off the second pinhole collimator (the major portion of the parasitic scattering). Since the pinhole has a square cross sectional area, the background pattern appears as a cross. The background intensity must also be subtracted from each scattering pattern (via subroutine BKC or BKG).

In some cases, the background intensity may be taken with a control sample in the beam. For the crazing studies, the scattering function of the polystyrene tensile bars with no stress history will be used as the background correction. In this way, the amorphous component of the scattering may be removed from the scattering from crazes.

3.3.2.5 TRANSMISSION COEFFICIENT

Lastly, the transmission coefficient of the sample must be measured. The transmission coefficient is a function of the sample thickness, intrinsic absorption coefficient and mass density; the optimum thickness is the reciprocal of the linear absorption coefficient, as suggested by Beer's law. The transmission coefficient may be calculated for any sample by the following equation:

$$T_m = I_t / I_o = [I_{gcs} - 0.5 I_s] / I_{gc}$$

where:

T_m = transmission coefficient of the sample

I_o = primary beam intensity

I_t = transmitted intensity through the sample

I_{gc} = scattered intensity by the glassy carbon

I_{gcs} = scattered intensity by the glassy carbon and sample

I_s = scattered intensity of the sample alone

And the factor 0.5 is the transmission coefficient of the glassy carbon itself. The purpose of the glassy carbon is to profusely scatter radiation away from the beamstop, and increase statistical confidence.

3.4 COLLECTION AND REDUCTION OF SAXS DATA

This section will describe the method by which the samples are analyzed in the SAXS instrument, and the data reduction techniques.

3.4.1 SCATTERING PATTERNS

The samples are gripped in the sample holders and stressed in a stepwise manner described in Figure 3.6 (page 32). In all cases, the stress is held constant during the scattering measurement, and incremented during the 15 second delay time the computer requires for storing one set of data, and initializing another set. The stress is raised by changing the setpoint on the servo controller to the hydraulic system.

The first scattering pattern for each sample is done under zero stress, and is used as the background scattering experiment. Therefore, any excess scattering originating in the samples under load is a direct result of the stress history of the sample, and not an artifact of the glass itself. By studying the excess scattering pattern as a function of the applied stress and time, precraze voiding, craze initiation and growth, and post failure relaxation may be evaluated.

3.4.2 DATA REDUCTION

Two dimensional contour plots are generated by the computer after it has corrected for background scattering and normalized the detector sensitivity etc. These contour plots are useful for qualitative comparison of the data with respect to the variables of interest. To help quantify the data, averaged intensity slices of specified azimuthal angles may be calculated. Figure 3.9 (page 53) is a schematic representation of this process (using subroutines CEN and AVE in the program CONTOUR). For isotropic scattering patterns, a radial average

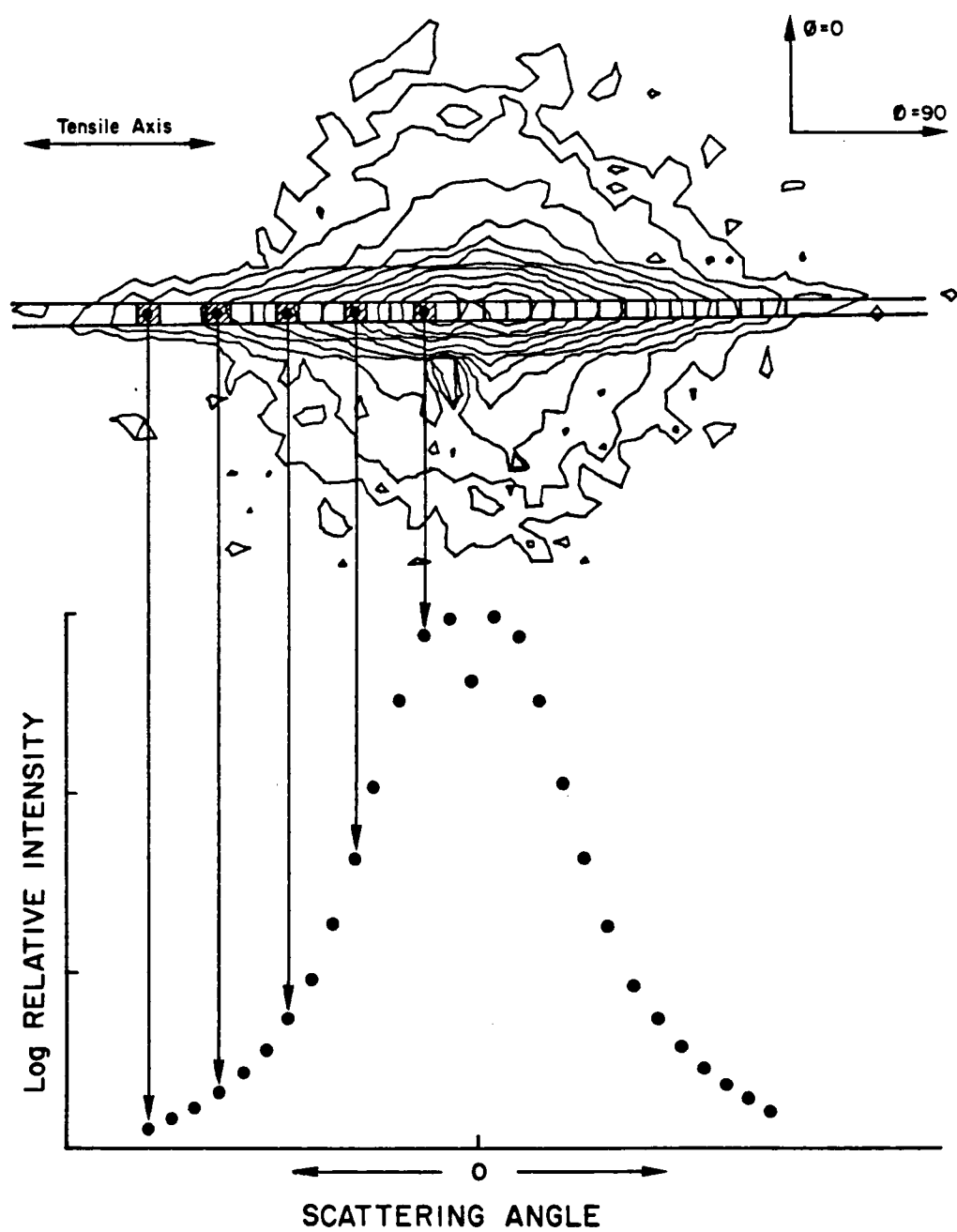


Figure 3.9 SAXS Data Reduction Technique.

around the beamstop may be done (subroutine RAD in the program RADIAL). The scattering patterns of crazes are highly anisotropic, so slices at $\theta=90$ and 0 degrees are taken to characterize the data. It is also assumed that the scattering pattern is symmetrical around the center of the scattering pattern. This allows the averaging of intensity data scattering angles on both sides of the beamstop. The result is a plot of intensity versus scattering angle for a specific angle in the scattering plane.

3.4.3 ANALYSIS

If the level of interparticle interference is judged low enough, the exponential approximation (eg. 22) may be applied to the linear data described above. From this procedure, an average dimension of scattering centers in each major axes may be obtained. With absolute intensity measurements, the volume fraction of scattering centers may be calculated. Other analysis techniques involving dilute systems include computer calculation through mathematic inversion of scattering data. One such routine is the method of Vonk (65). However, these analyses commonly assume a structure factor of a system with liquid like disorder. This is not true in the case of crazing. Therefore, the computer routine by Vonk requires alteration to handle anisotropic scattering patterns.

If interparticle interference prohibits the dilute approximation, then the analysis is reduced to a Bragg approach (eg. 22). That is, location and width of interference maxima of the reduced linear data.

4. RESULTS

This chapter mainly illustrates the dependence of the polystyrene craze scattering pattern as a function of applied stress level, molecular weight parameters and time. For the first two variables, the scattering pattern is analyzed in terms of the tensile and nontensile axis scattering. The latter variable is analyzed in terms of the scattering power of the sample as measured by the total scattered counts registered by the 2DPSD. First, however, the calibrations of transmission coefficient and absolute intensity are shown.

4.1 TRANSMISSION COEFFICIENT

Due to the speed of data acquisition, the transmission coefficient of the sample cannot be measured for each stress level. Therefore, some assumption about the behavior of the transmission coefficient as a function of craze density must be made. An experiment designed to determine this function was performed at low x-ray power. The sample was deformed with the same stress history as those in Figure 3.6 (page 32), and the transmission coefficient was measured twice at each stress level. The result, which is plotted in Figure 4.1 (page 56), indicates a constant transmission coefficient with respect to stress level and time. Therefore, the transmission coefficient calculated for each sample at the zero stress condition will be used for all stress and time levels reported in this work.

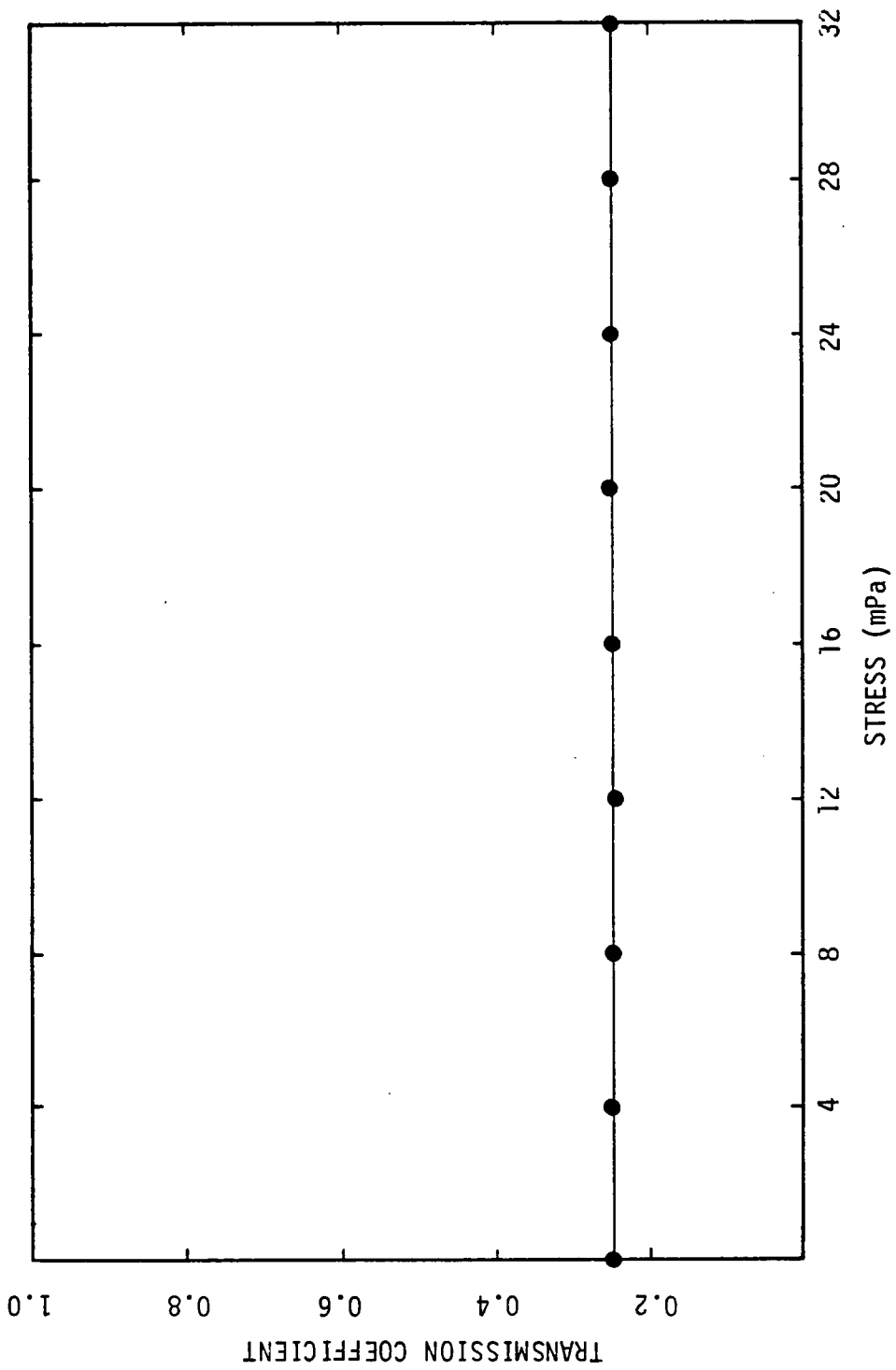


Figure 4.1 Transmission coefficient of a crazing sample as a function of stress.

4.2 ABSOLUTE INTENSITY

Absolute intensity measurements of the x-ray beam were made using the nickel foil and the Lupolen methods. The initial intensity was found to be 2.51 E6 photons per millimeter squared per second at an x-ray power of 40kV and 40mA by the nickel foil method. Subsequent calibrations of intensity were made using the Lupolen method after alignment or other instrumental changes. The summary of absolute intensities obtained during the experimentation is found in Figure 4.2 (page 58).

4.3 POLYSTYRENE SCATTERING RESULTS

Polystyrene SAXS results from this work can be divided into three general categories based upon the variables of interest. These categories investigate the character of the craze scattering pattern as a function of molecular weight parameters, stress level and time.

The basic qualitative features of the polystyrene craze scattering pattern remain constant over all values of molecular weight, stress and time, but their quantitative features may vary. It is these quantitative variables which are of interest. A review of the basic features of polystyrene craze scattering patterns, followed by their dependence on variables of interest is discussed in this section.

The basic polystyrene craze scattering pattern appears similar to Figures 4.3 A and B (pages 59 and 60). There exists a strong narrow streak of scattered radiation parallel to the tensile axis. This streak is approximately one order of magnitude more intense than nontensile

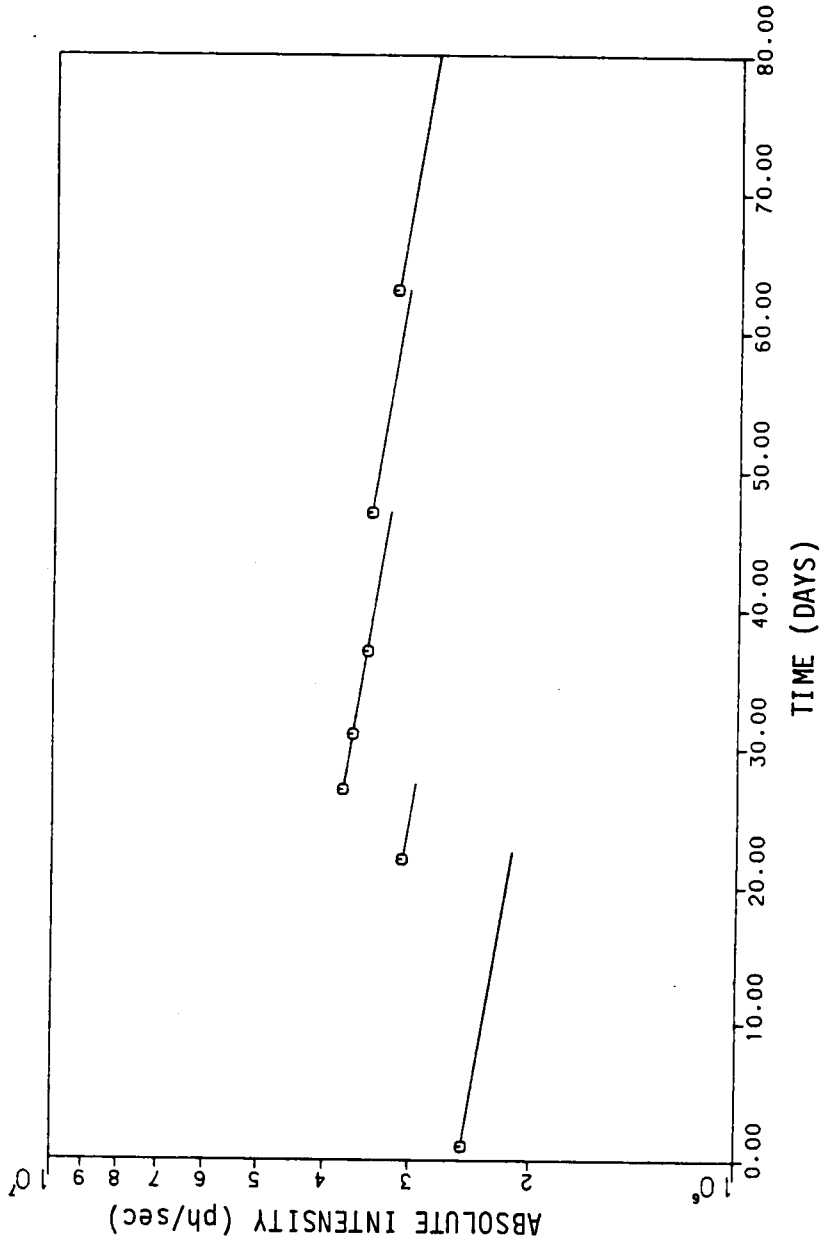


Figure 4.2 Absolute intensity of the SAXS instrument during experimentation.

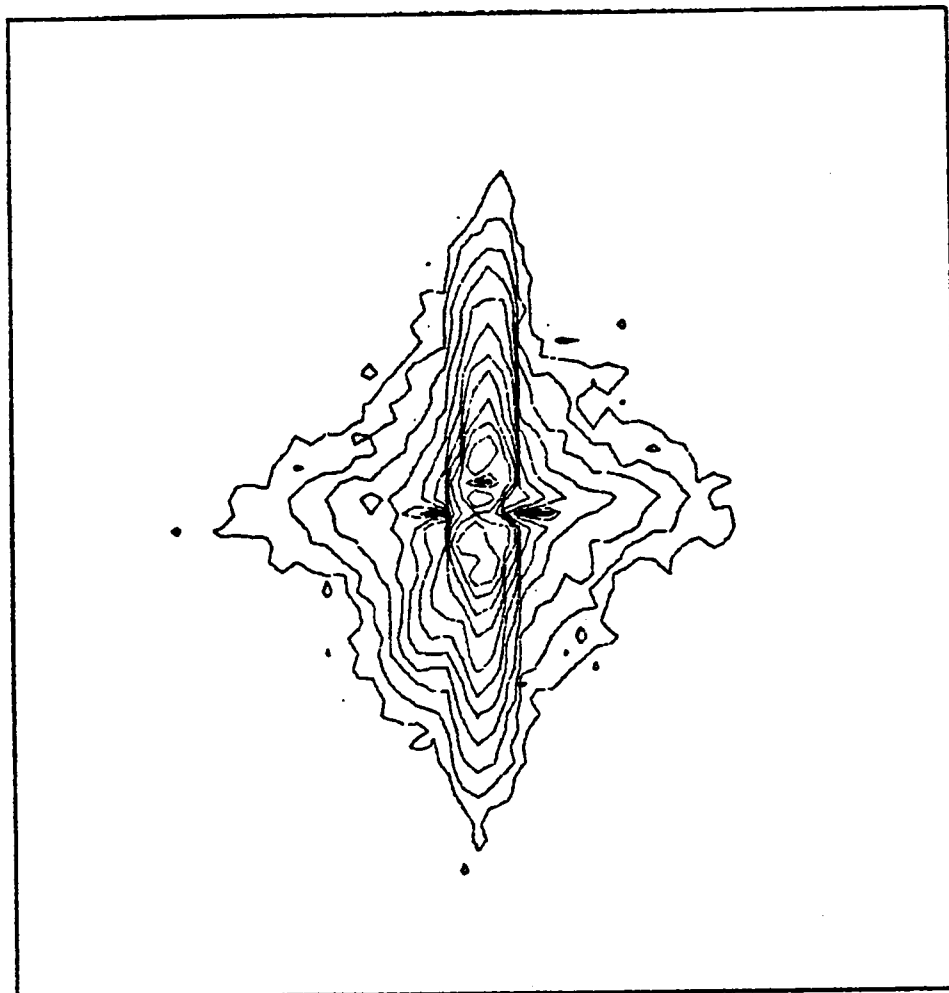


Figure 4.3 Typical polystyrene craze scattering pattern under a load of 4200 PSI. $\overline{M}_n=200,000$; PD=1.1.

A Contour plot.

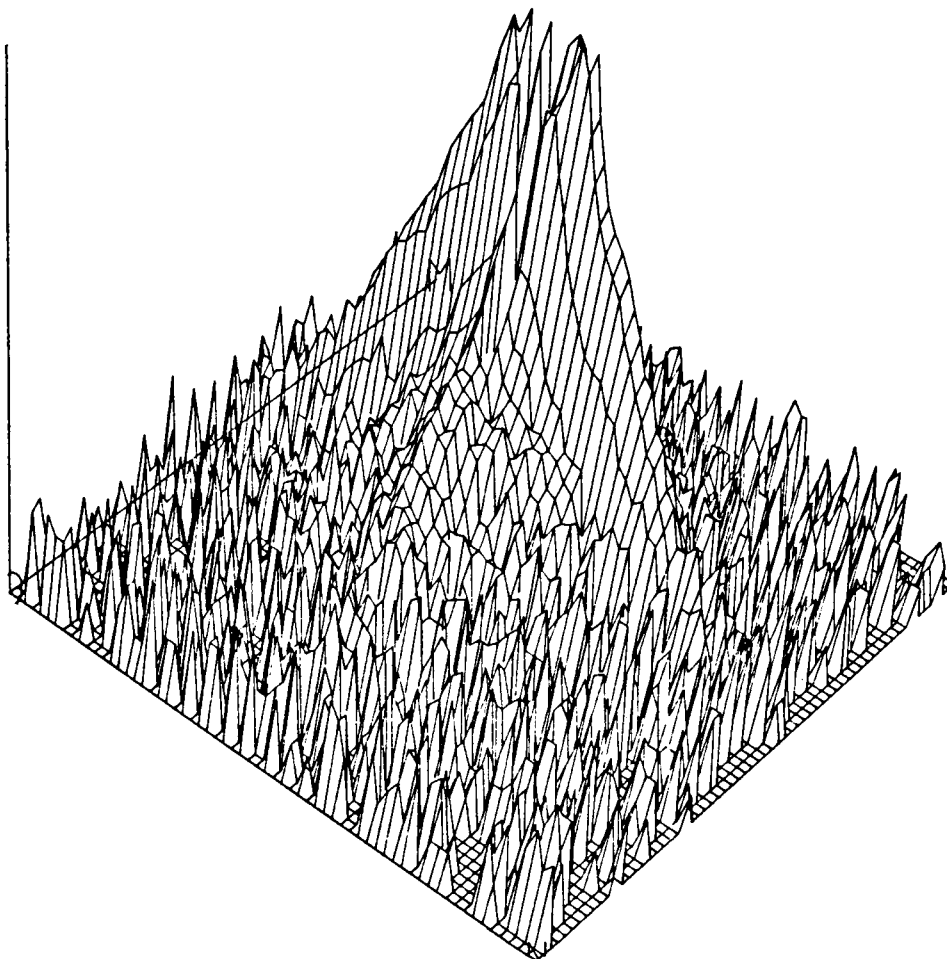


Figure 4.3 (continued)

B Three dimensional logarithmic plot.

scattering at comparable scattering angles. The nontensile axis scattering is also referred to as a streak for the purpose of discussion, but under relaxed conditions, the nontensile scattering can be isotropic (70). Other features of the polystyrene scattering pattern include the presence of an intensity maximum in the tensile axis streak, and an intensity minimum in the nontensile streak, both of which are less than five milliradians from the zero scattering angle.

4.3.1 MOLECULAR WEIGHT PARAMETERS

The two variables implied by molecular weight parameters are the number averaged molecular weight and the dispersity index as defined by $\overline{M}_w/\overline{M}_n$. There are therefore, two sets of results which deal with this issue. One set of results is obtained from samples with monodisperse but varying molecular weight, and another set of results from polydisperse commercial samples which can be compared to the monodisperse results in the low molecular weight range. As indicated before, the samples were elongated in the x-ray beam by a stepwise load increment manner at an average stress rate of about 100 psi/min.

The first result which becomes obvious upon experimentation is the molecular weight dependence on the rate at which x-rays are scattered. Here the 2DPSD is used simply as a device which sums all scattered radiation over a solid angle of 20 milliradians, with no emphasis on resolution. In other words, the 2DPSD measures the low angle scattering power of the sample as a function of stress and time. Figure 4.4 (page 62) shows these results for some polystyrene samples,

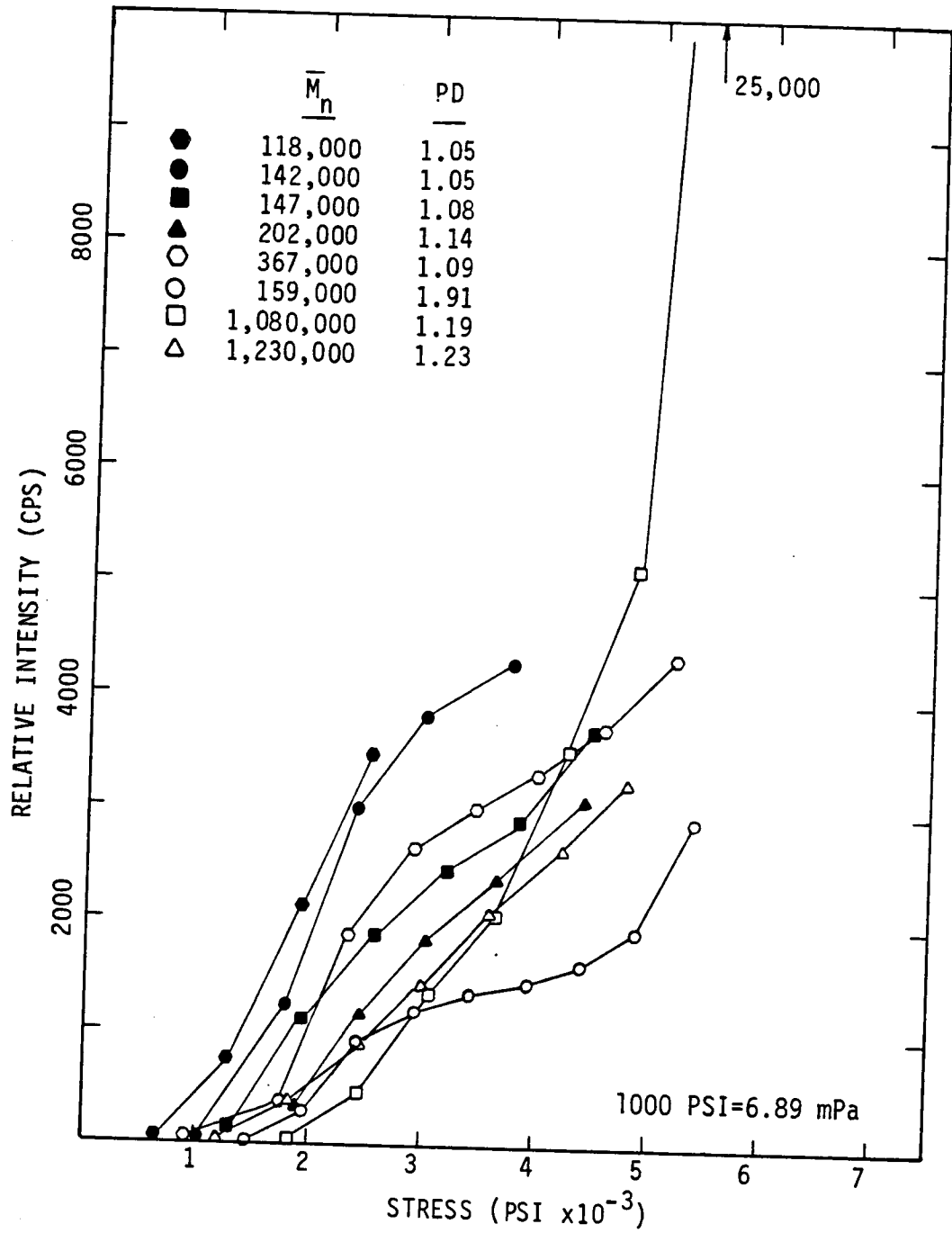


Figure 4.4 Total scattered intensity versus stress for several polymers.

except PS77 whose molecular weight is too low to be processed in the apparatus (others were left out for clarity). The intensity values shown in Figure 4.4 represent values corrected for background scattering and normalized for comparison. The general features of these curves include:

1. A slight increase in the scattering power below the crazing condition.
2. A sharp increase in scattering power upon crazing, followed by continued large increases of intensity until fracture.
3. In one case, tremendous increases of intensity are noted at fracture. This result occurred when the x-ray beam intersected the propagating crack.

If a few curves of Figure 4.4 are singled out for comparison, several notable molecular weight dependencies can be observed. Specifically, the higher molecular weight samples show an upturn in craze scattering intensity at a higher stress level than the lower molecular weight ones, and they always have a lower scattering power at equal stress and time levels. The same phenomenon is observed with the dispersity index, with highly disperse sample being analogous to high molecular weight samples and vice versa. This effect is illustrated more clearly in Figures 4.5 and 4.6 (pages 64 and 65). Figure 4.5 shows the scattering power versus stress level of two monodisperse samples which have widely different molecular weights. Figure 4.6 shows the scattering power versus stress level of two equal molecular weight samples having different molecular dispersity. It seems that increasing

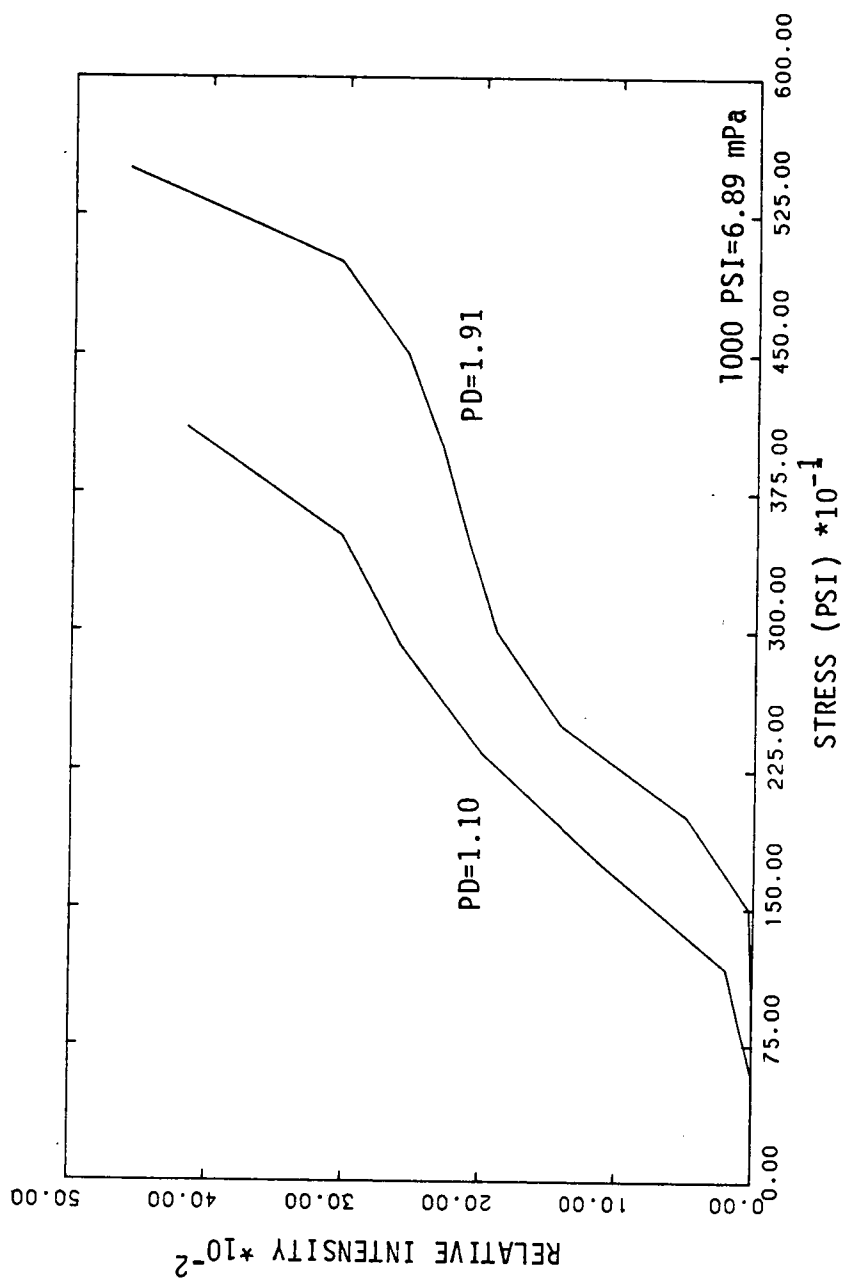


Figure 4.5 Total scattered intensity versus stress for two samples of different molecular dispersity.

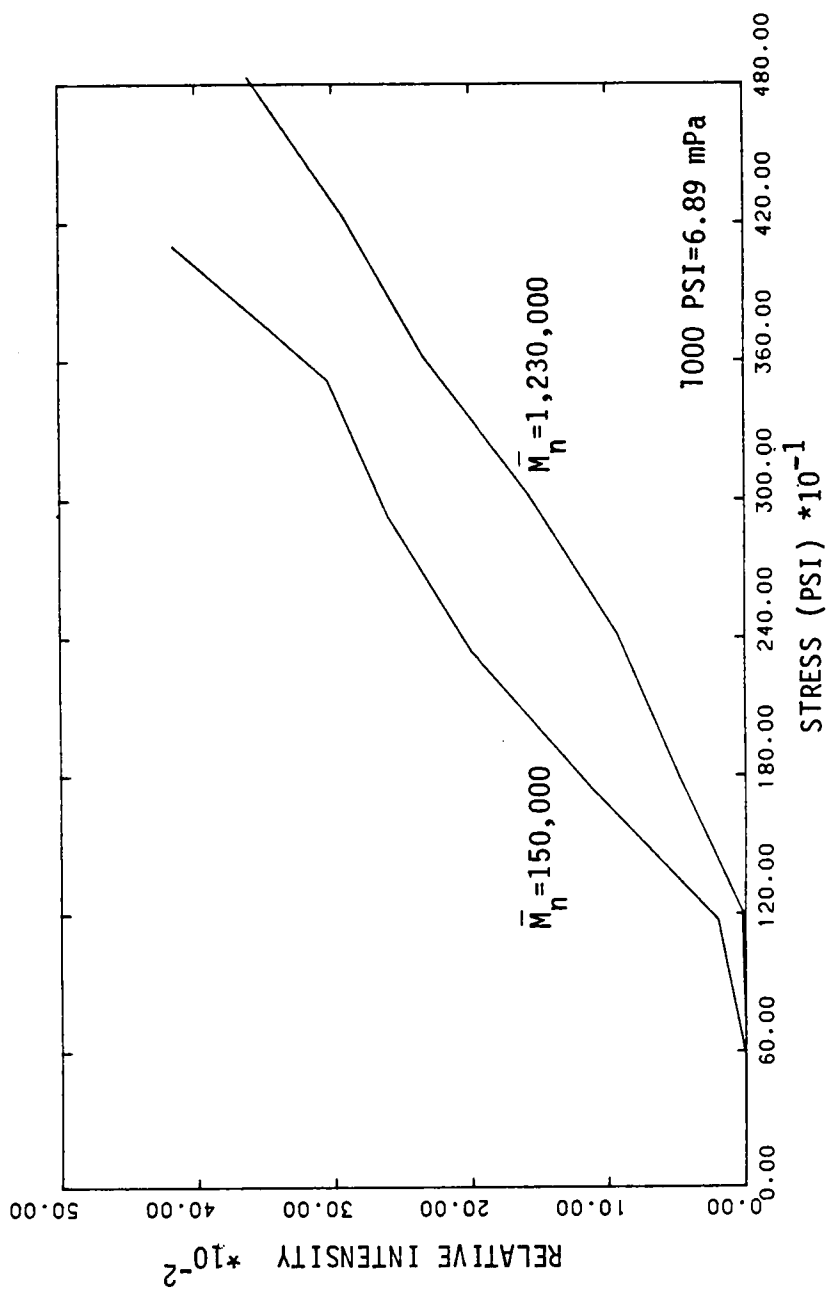


Figure 4.6 Total scattered intensity versus stress for two samples of different number averaged molecular weight.

samples having different molecular dispersity. It seems that increasing molecular weight has a similar effect as increasing molecular dispersity, as far as craze generation is concerned.

To investigate the detailed character of the scattering pattern as a function of molecular weight parameters, Figure 4.4 (page 63) indicates that the stress-time history of the samples must be constant. Therefore a stress level of 4000 psi was chosen because all samples reached this stress level before fracture, and the high stress ensures many crazes will be present. The contour plots of each sample are background corrected, and their tensile and nontensile axis slices are obtained by the procedure which was outlined in the last chapter. One more assumption is made at this point; that is, assume the scattering function is symmetric about the zero scattering angle such that intensities on opposite sides of the beamstop may be averaged to increase statistical confidence. These averaged intensity slices appear in Figure 4.7 (page 67) for the nontensile axis, and Figure 4.8 (page 68) for the tensile axis. Figure 4.9 (page 69) is an attempt to characterize the behavior of the tensile and nontensile axis scattering as a function of molecular weight, in terms of the intensity scattered at a single angle ($2\theta=5\text{mrad}$). More will be said about this procedure in Section 5.2.1 (page 99).

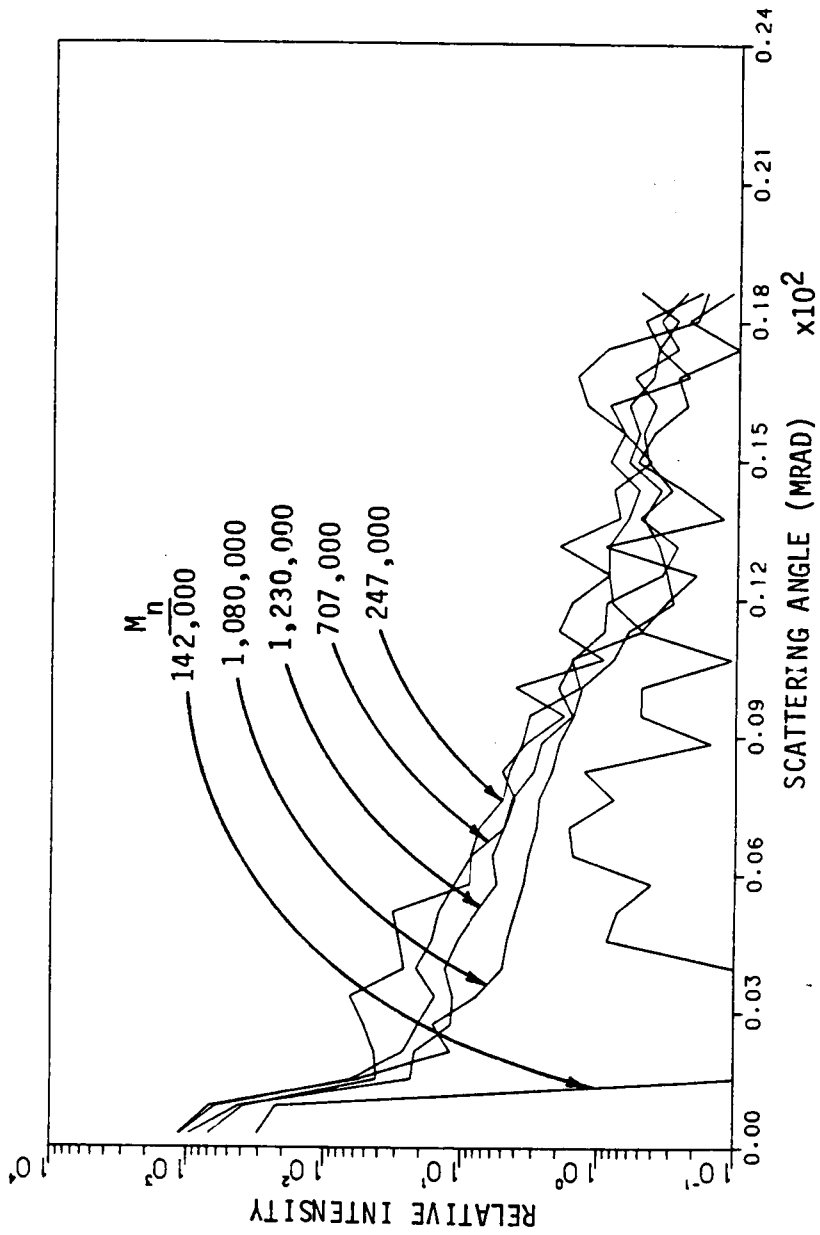


Figure 4.7 Nontensile axis diffracted intensity as function of molecular weight. Stress is 4200 PSI.

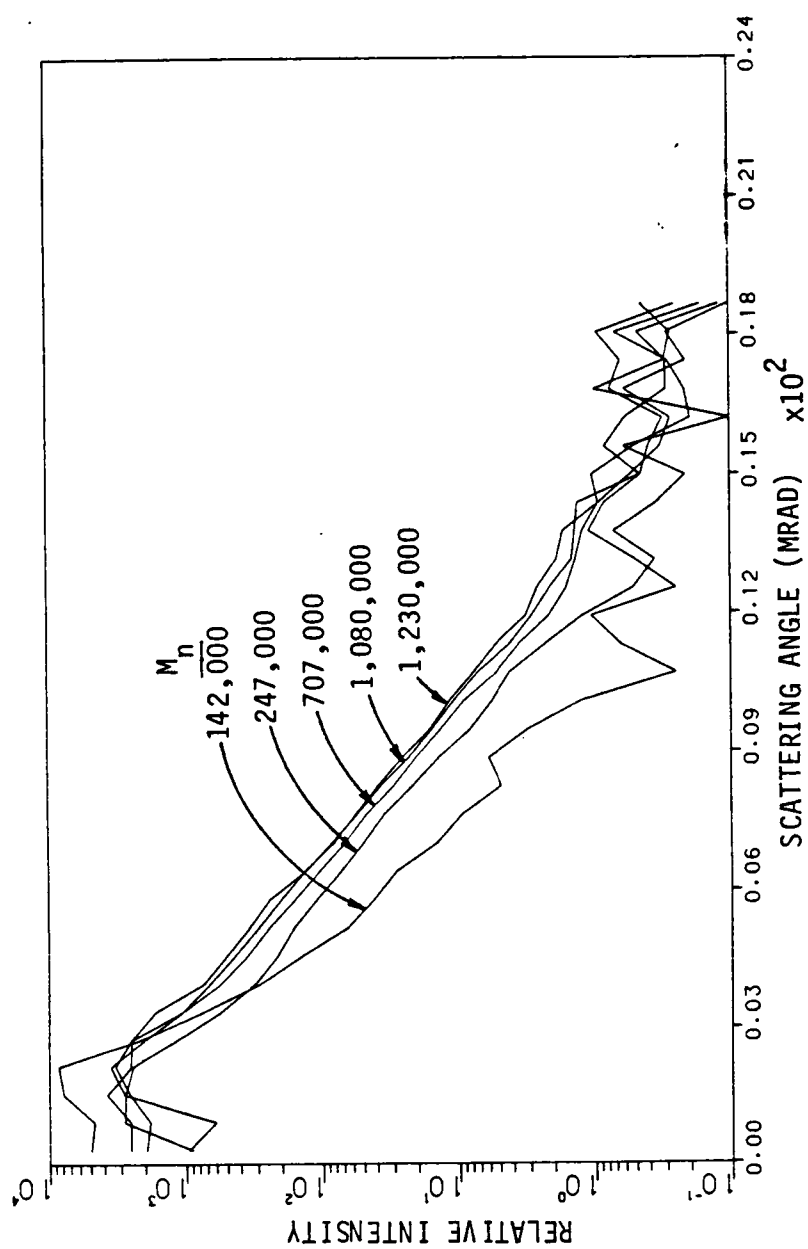


Figure 4.8 Tensile axis reflected intensity as a function of molecular weight. Stress is 4200 PSI.

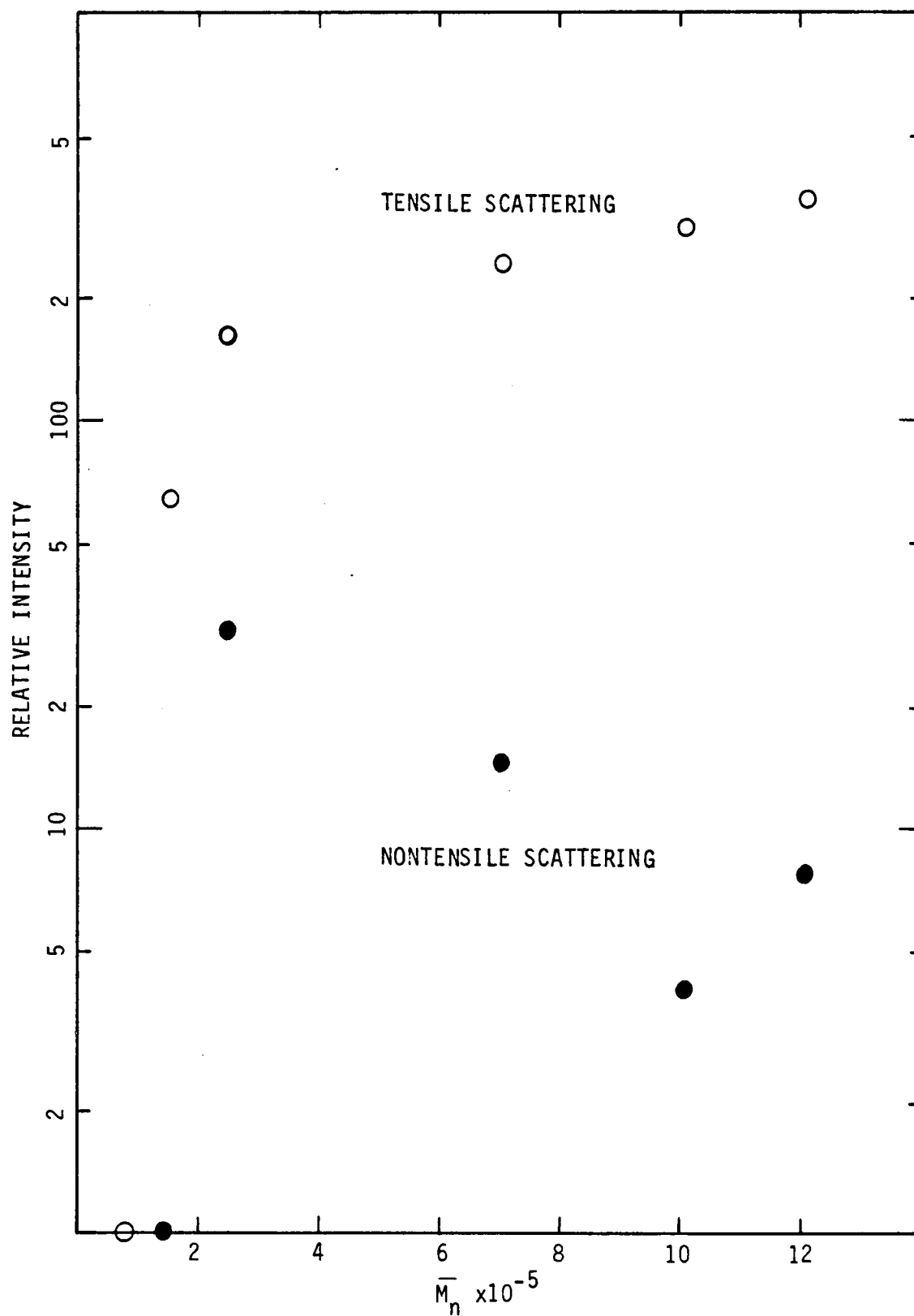


Figure 4.9 Relative intensity in the tensile and nontensile axes at 5mrad. Stress is 4200 PSI.

4.3.2 STRESS LEVEL

Again, Figure 4.4 (page 62) shows for all samples, as the applied stress increases the scattering power of the sample increases. However, to study the effect of stress level on the details of the scattering pattern, Figures 4.7 and 4.8 (pages 67 and 68) show the molecular weight parameters must be constant. To study the effect of stress level, the polystyrene PS4 was chosen ($M_n=202,000$ and $PD=1.14$). Using the same data reduction techniques and assumptions mentioned in the last section, the data were analyzed for all stress levels of PS4. These averaged intensity slices appear in Figure 4.10 (page 71) for the nontensile axis, and Figure 4.11 (page 72) for the tensile axis. Again, Figure 4.12 (page 73) is constructed to characterize the behavior of the tensile and nontensile axis scattering as a function of tensile stress, in terms of the intensity scattered at a single angle ($2\theta=5\text{mrad}$).

4.3.3 TIME

The prime interest of this variable is to study how the craze structure ages under conditions of constant stress. To accomplish this, two basic experiments were performed. First, craze relaxation studies as a function of time after fracture were done. Second, craze generation studies as a function of time at constant loads of 3000 psi and 4000 psi were done.

For the first experiment mentioned above, the scattering power as a function of time after fracture is plotted for a few polymers in Figures 4.13 and 4.14 (pages 74 and 75). Some samples are not shown

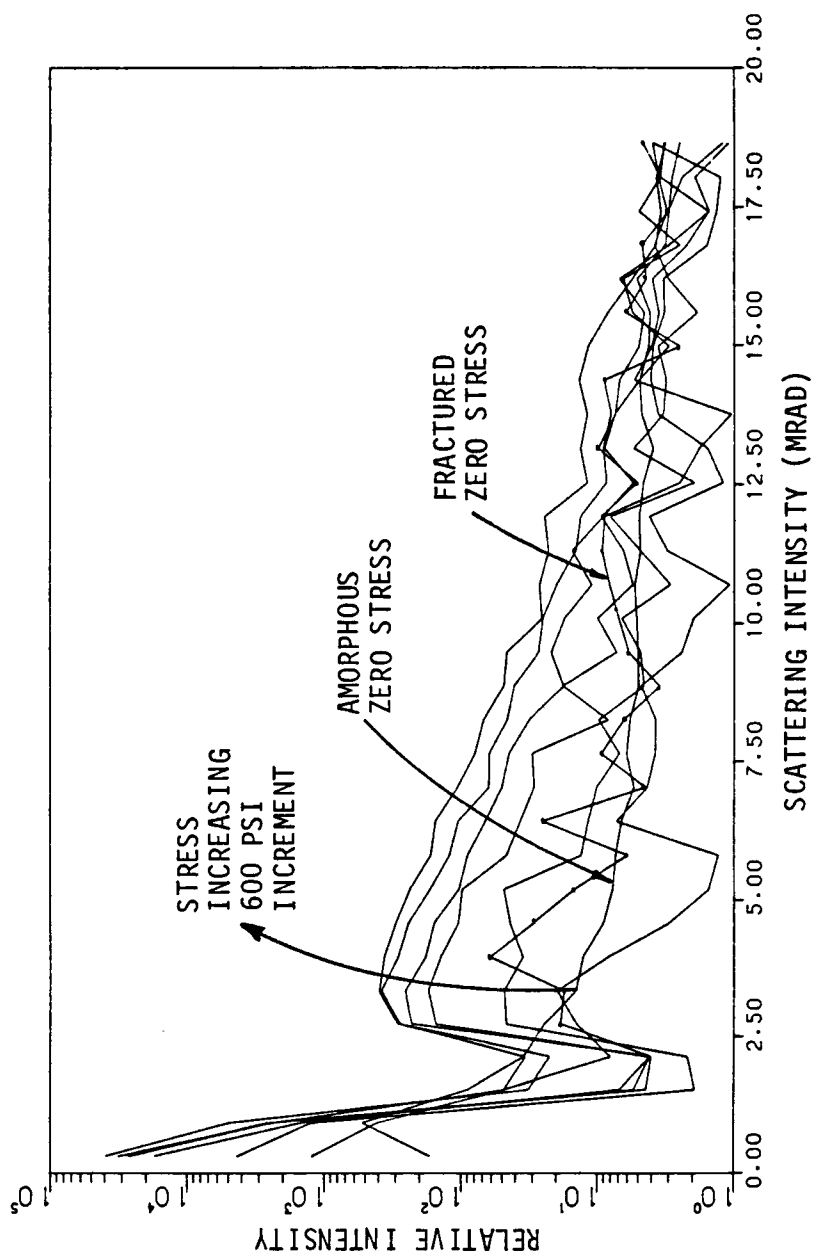


Figure 4.10 Nontensile axis diffracted intensity as a function of stress. ($\bar{M}_n=200,000$; PD=1.1).

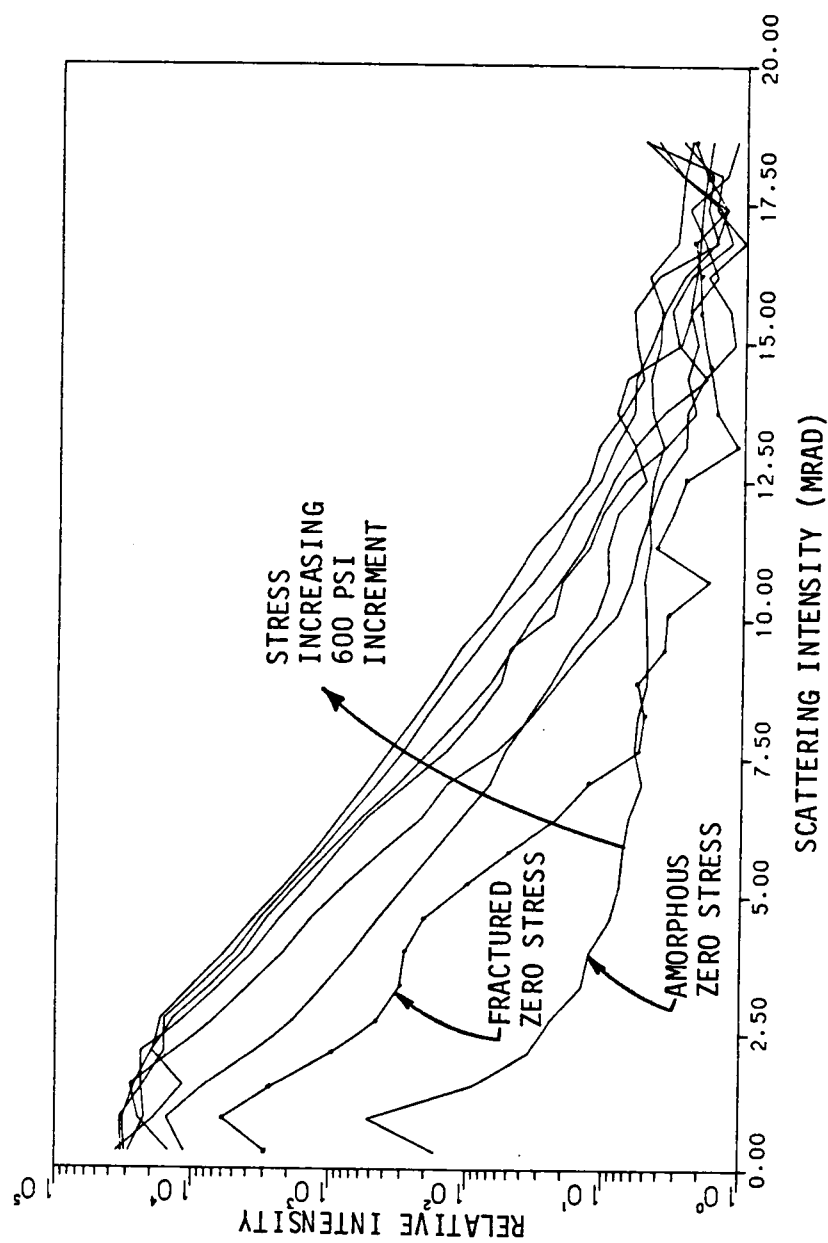


Figure 4.11 Tensile axis reflected intensity as a function of stress
 ($\bar{M}_n=200,000$; PD=1.1).

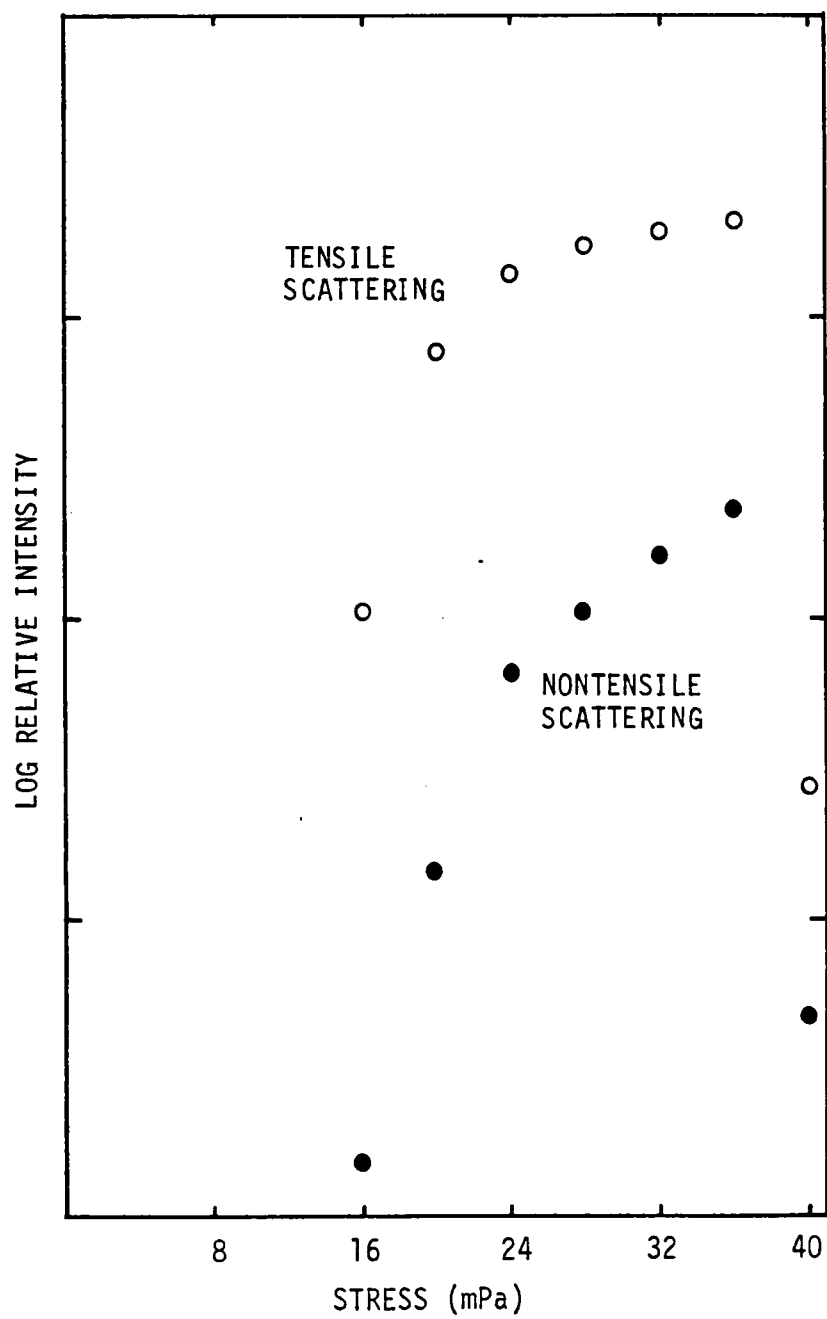


Figure 4.12 Scattering intensity at five milliradians as a function of stress ($\bar{M}_n=200,000$; PD=1.1).

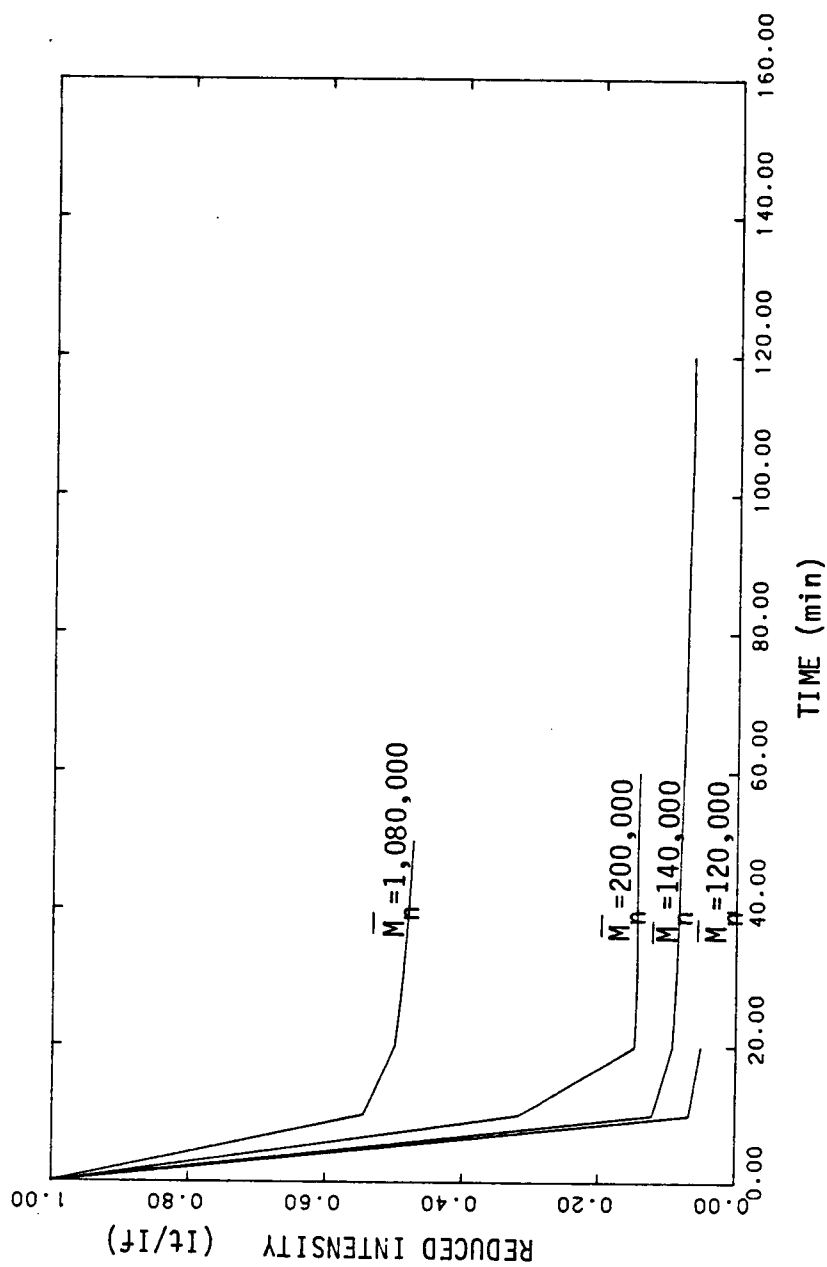


Figure 4.13 Craze relaxation after fracture as a function of molecular weight. (PD=1.1).

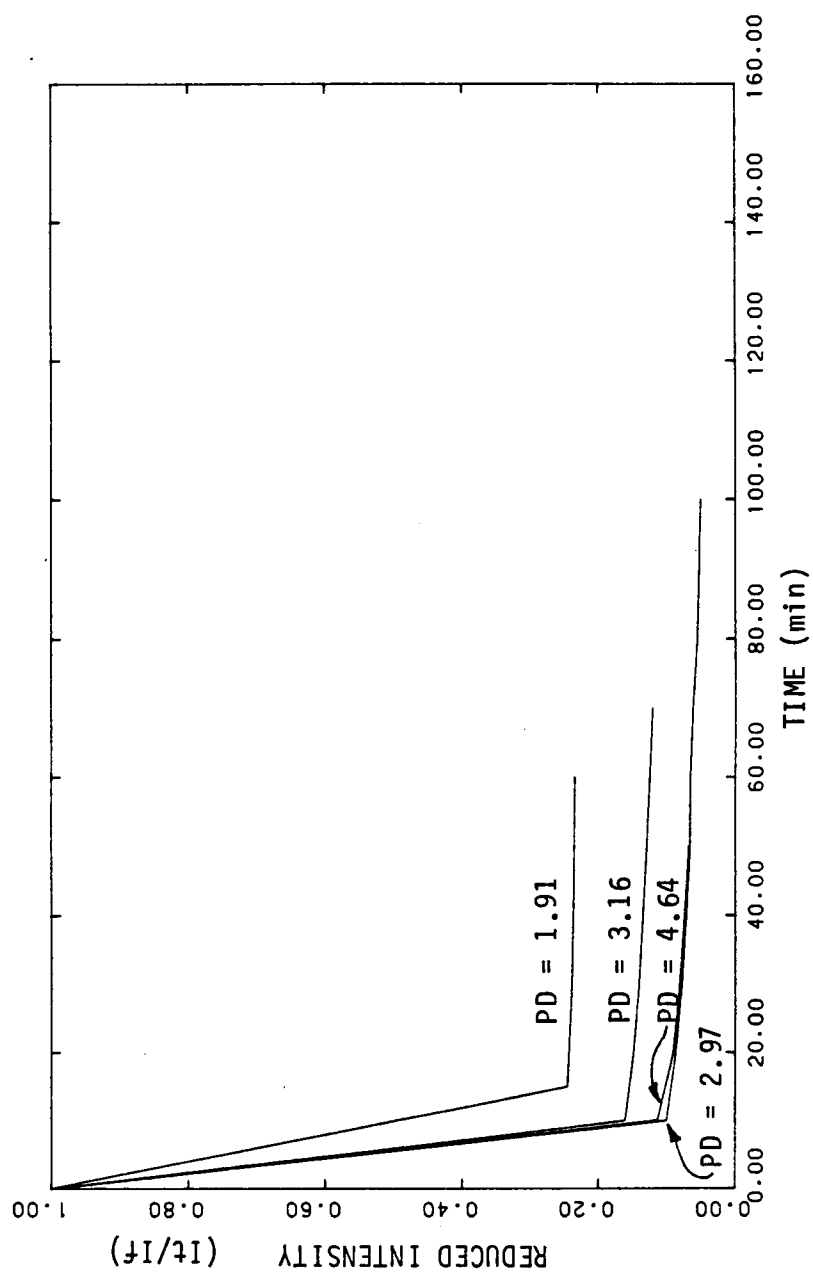


Figure 4.14 Craze relaxation after fracture. ($78,000 < \overline{M}_n < 159,000$).

because they broke in a manner which made the measurement impossible. The intensity in these plots is normalized by the intensity which each sample had as it fractured. Figure 4.13 shows this intensity as a function of time for the monodispersed samples, while Figure 4.14 is for the polydisperse samples. In each case the reduced intensity (intensity at the relaxation time divided by the intensity at fracture) initially drops by about one order of magnitude, then drops gradually with time. For the case of monodisperse samples, the ultimate reduced intensity correlates linearly with log number averaged molecular weight as shown in Figure 4.15 (page 77). It is interesting to note the line generated in Figure 4.15 extrapolates back to near twice the entanglement molecular weight, the condition for fracture without crazing. The ultimate reduced intensity does not correlate well with dispersity index in Figure 4.14, probably because there is some molecular weight dependence superimposed on the data.

For the second experiment mentioned above, the scattering power as a function of time at constant stress is plotted for two different stresses in Figure 4.16 (page 78). Here it is observed that a higher stress level produces a sample with a larger scattering power at comparable times. Also, no clear indication is given as to when the sample crazed as was the case in Figures 4.4 through 4.6 (pages 53 through 55). Lastly, the continuous increase of scattering power with log time indicates the system has not been able to stabilize the energy storage. Furthermore, the concave up character of Figure 4.16 indicates the system has not reached steady state.

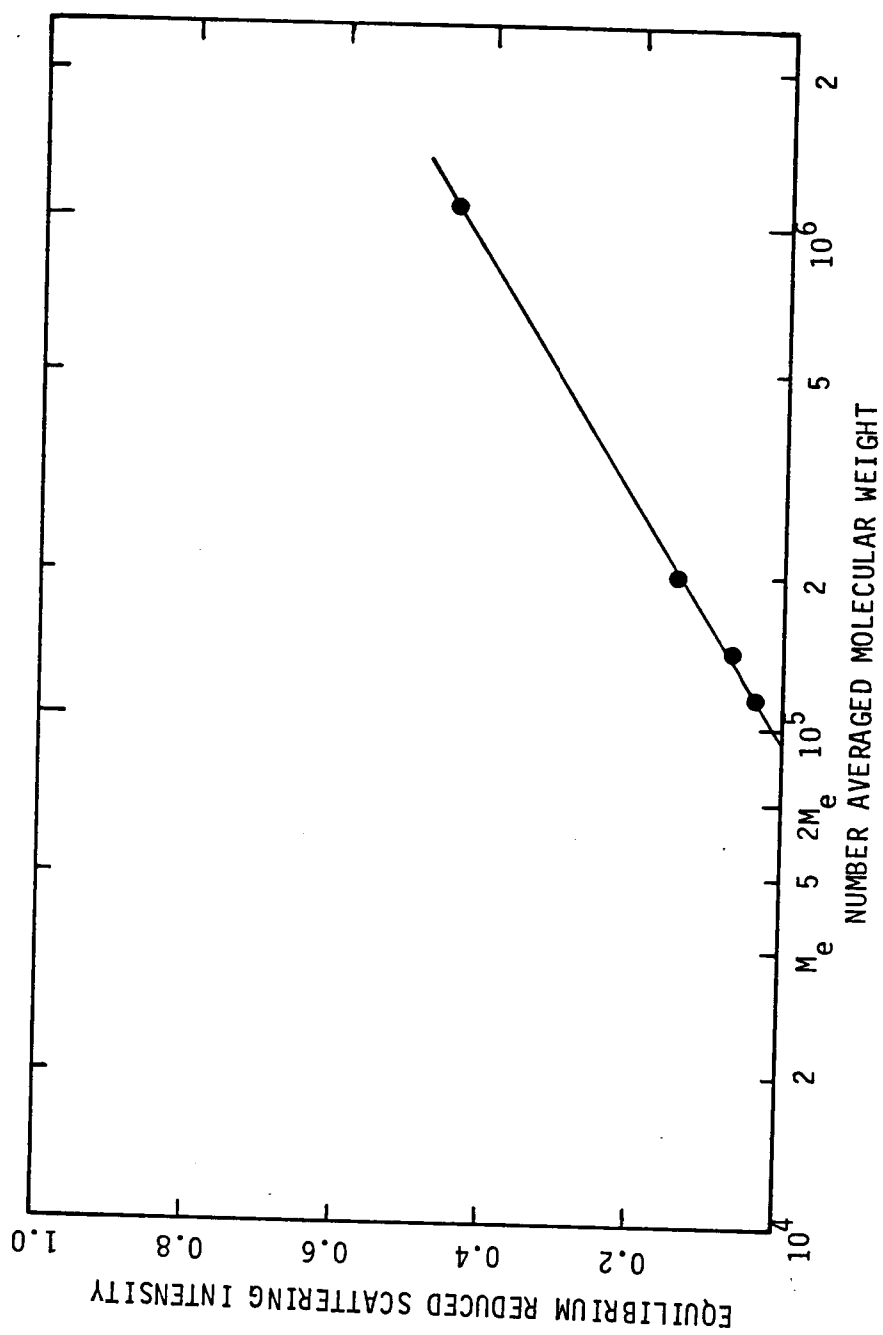


Figure 4.15 Reduced scattering intensity of long term relaxed crazes in fractured samples as a function of molecular weight.

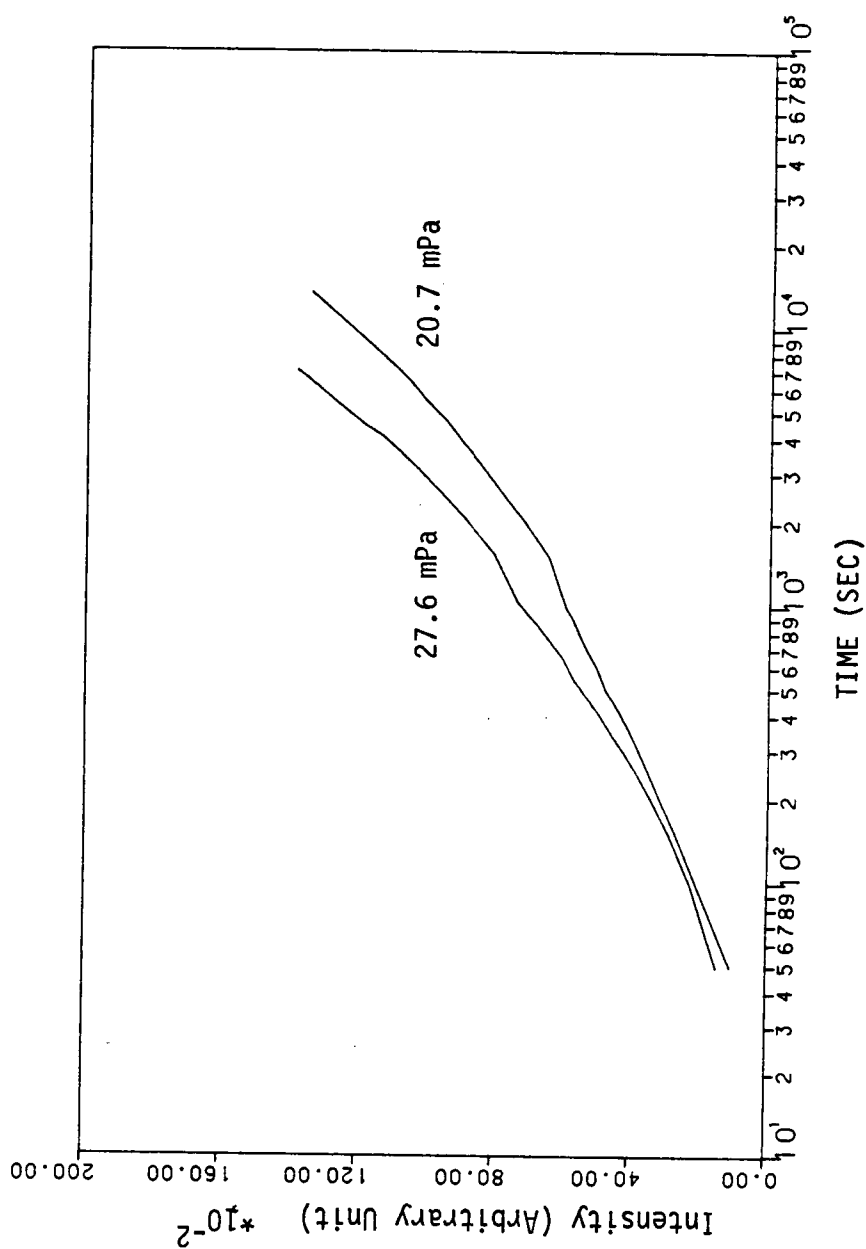


Figure 4.16 Craze generation at constant stress. ($\bar{M}_n=247,000$).

4.4 REFLECTION PHENOMENON

To determine what extent reflection contributes in the total scattered intensity of crazes, two experiments were performed. In the first experiment the crazes are modeled as a laminated sample consisting of stacked polystyrene films. In the second experiment the void fraction of a bulk crazed sample is calculated by both x-ray and density gradient column techniques, and then compared to each other to test for reflection in the scattering pattern.

4.4.1 LAMINATED SAMPLES

The effect of scattering intensity as a function of lamination was studied by varying the number of films (reflective interfaces), the phase contrast between films, and the orientation angle of the films with respect to the incident beam.

Figures 4.17 A and B (pages 80 and 81) are the scattering patterns obtained from a sample having an interface density of about ten films per millimeter. A striking resemblance to the craze scattering function is noted both in qualitative features and relative intensity. Figure 4.18 (page 82) shows the effect of lowering the interface density to about two layers per millimeter, while Figure 4.19 (page 83) shows the effect of lowering the phase contrast between films by putting epoxy between them. Both Figures 4.18 and 4.19 show the scattering power of the sample is reduced as compared to Figures 4.17 A and B. Finally, the vertical streak can be completely removed by tilting the sample a few degrees in the chi direction. This experiment was actually performed on

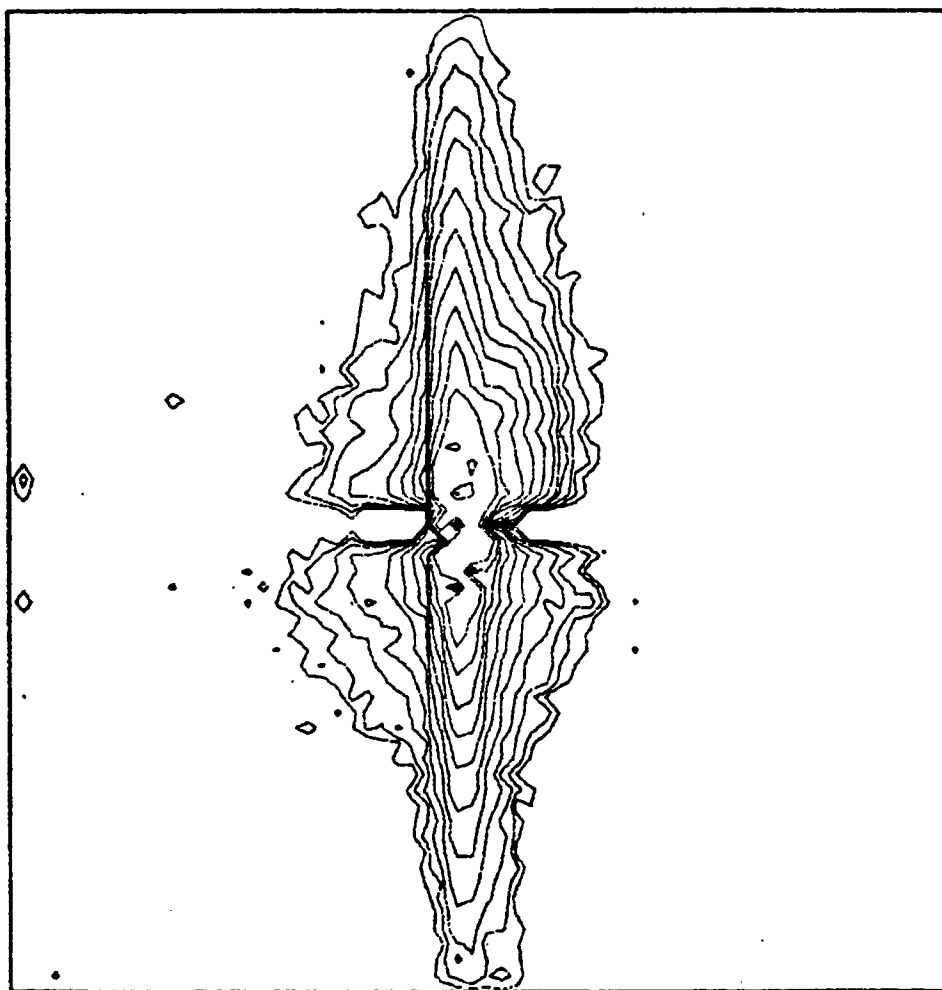


Figure 4.17 Polystyrene laminated sample scattering pattern. Sample contains approximately 10 interfaces per millimeter. Exposure time is 100 sec.

A Contour plot.

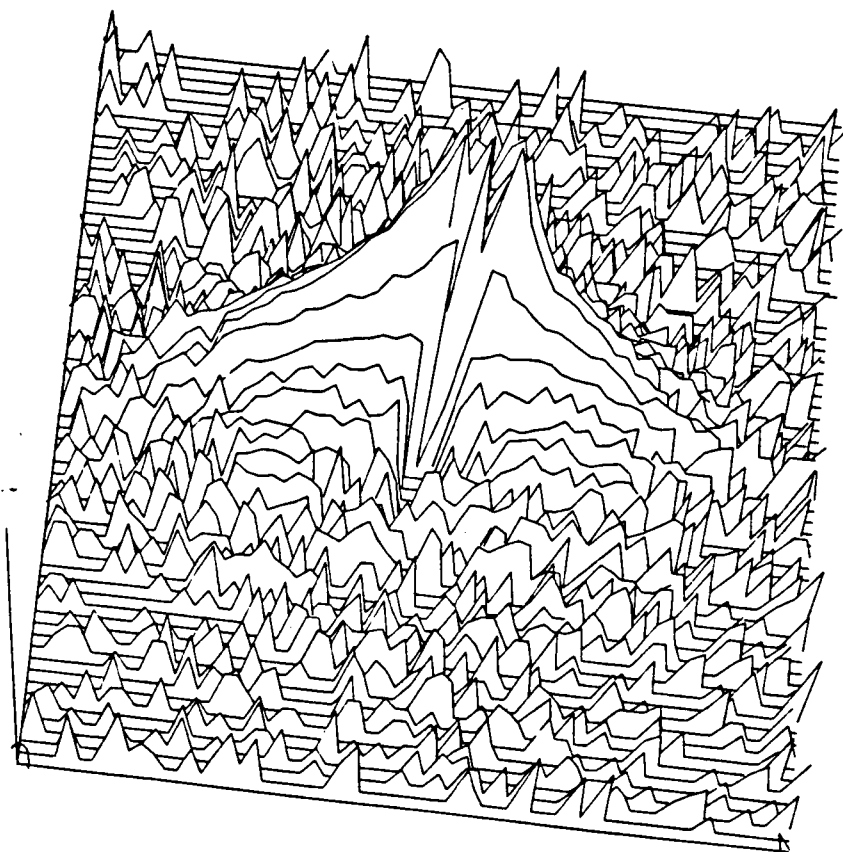


Figure 4.17 (continued)

B Three dimensional logarithmic plot.

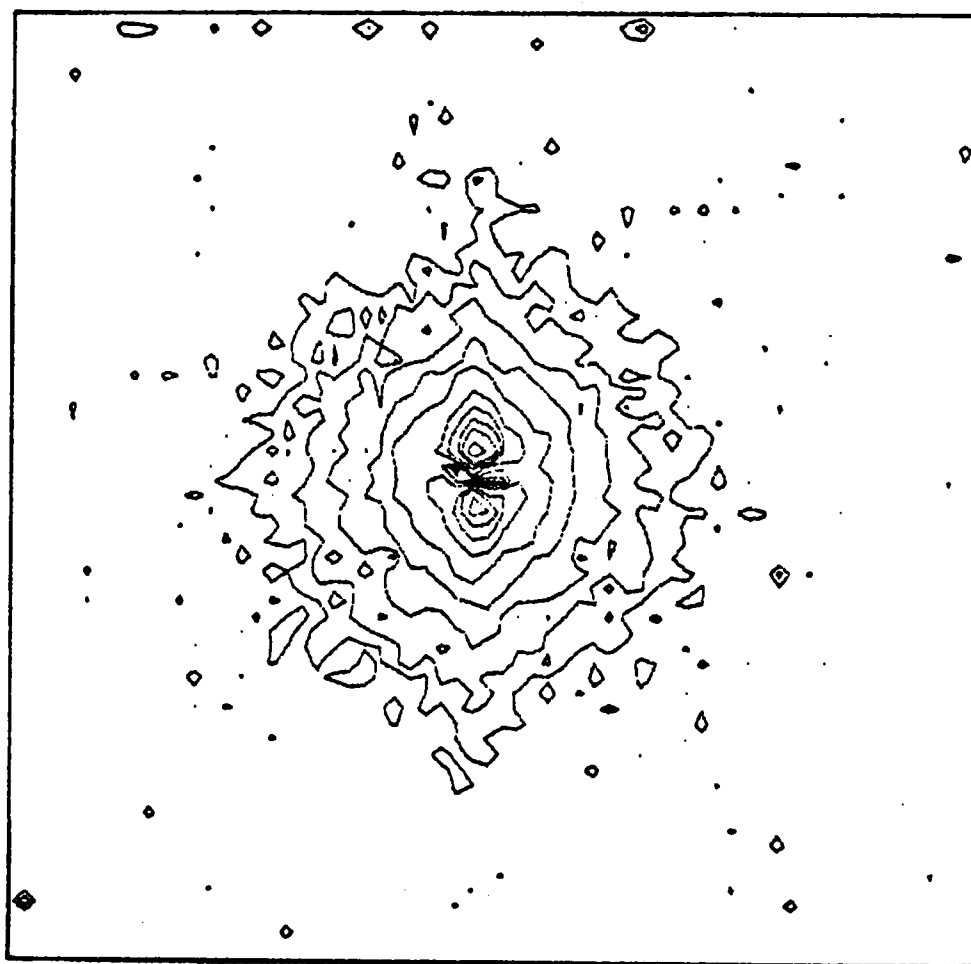


Figure 4.18 PET laminated sample scattering pattern. Sample contains approximately 2 interfaces per millimeter. Exposure time is 100 sec. (Contour plot).

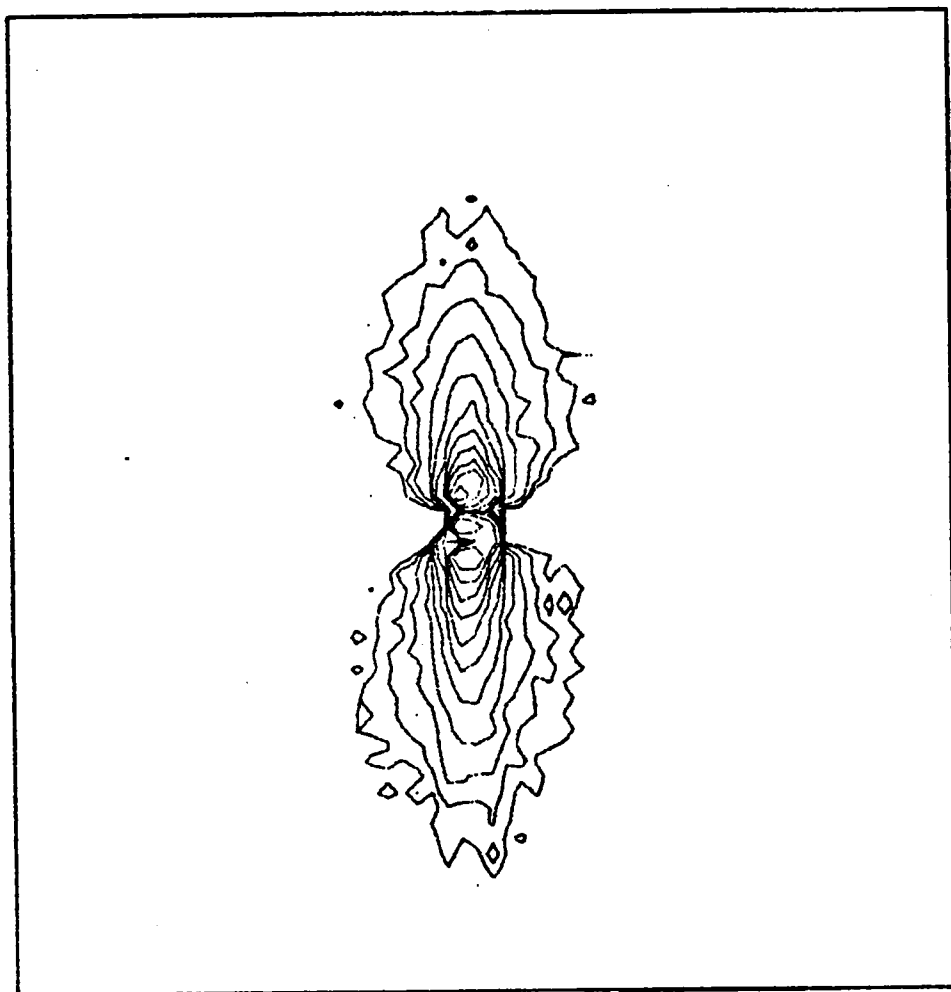


Figure 4.19 Polystyrene laminated scattering pattern. Sample contains epoxy interfaces. Exposure time is 100 sec. (contour plot).

a highly crazed sample which is discussed in the next section. The scattering pattern for tilted crazes appears in Figures 4.20 A and B (pages 85 and 86). These figures show a nearly circular scattering pattern, which corresponds to a nearly circular void cross section in real space. There is no evidence of the strong anomalous streak.

4.4.2 VOID FRACTION DETERMINATION

A sample of highly crazed polystyrene was made by loading it to 3000 PSI for one week. The sample was also allowed to relax for one week such that the morphology changed very slowly during the time of experimentation. Some assumptions which are made at this point are:

1. The craze density is large enough that a one millimeter square x-ray beam will sample a representative average volume of the sample.
2. The average microstructure of the sample is unaffected by cutting in the sample preparation.
3. The average microstructure of the sample is not changing with time.
4. The scattering centers of the craze are microvoids, such that void fraction may be calculated by x-ray analysis.
5. No water or glycol molecules diffuse into the craze in a density gradient column, such that void fraction may be calculated (8).

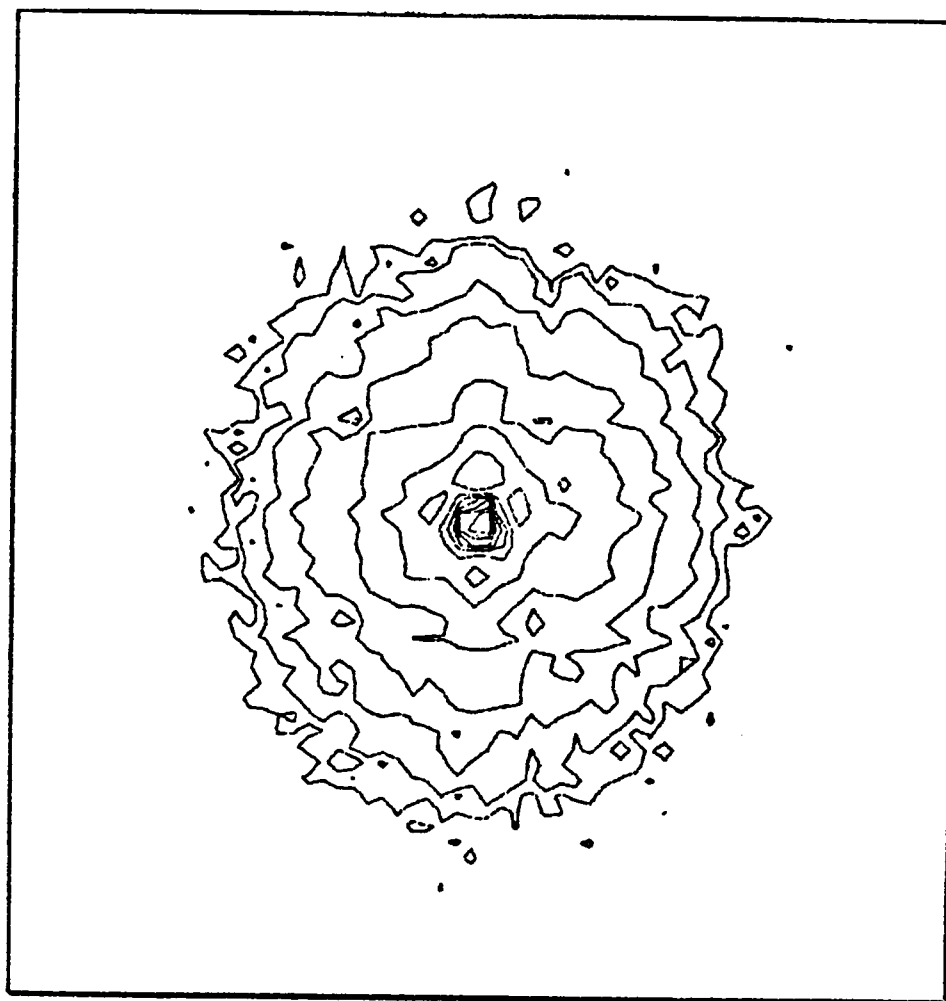


Figure 4.20 Polystyrene craze scattering pattern. Sample is tilted eight degrees in the chi direction to remove the reflection streak. Exposure time is 2000 sec.

A Contour plot.

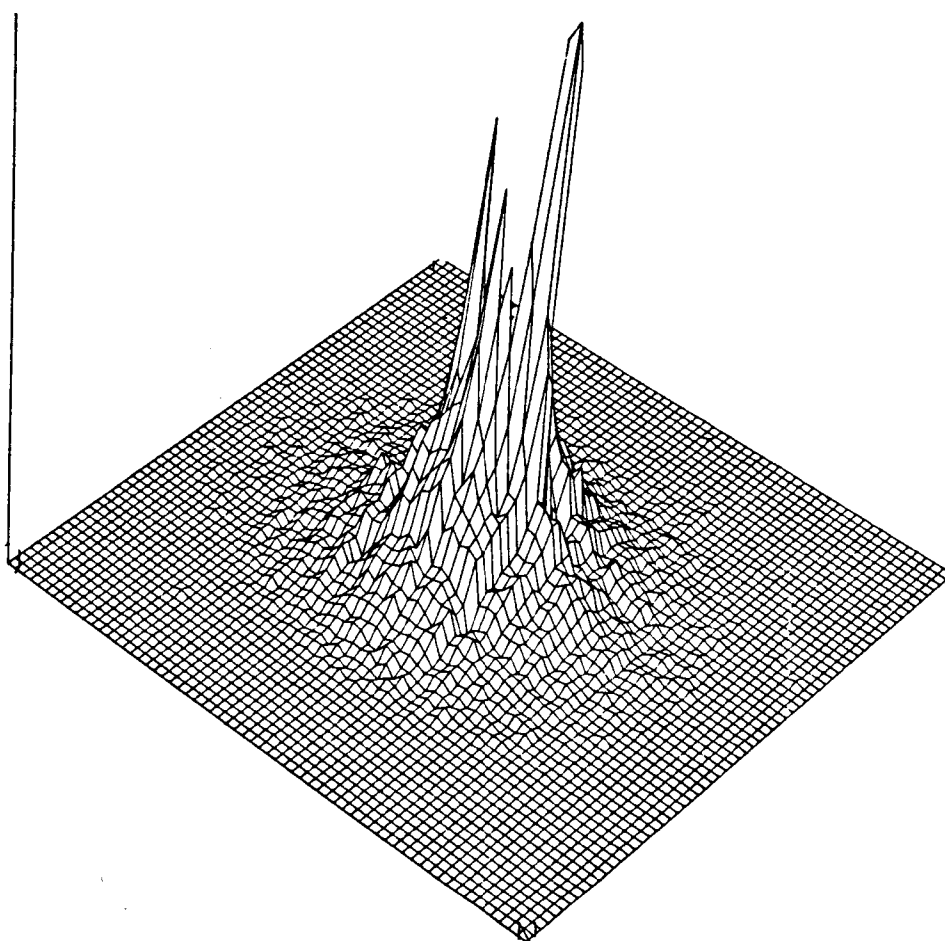


Figure 4.20 (continued)

B Three dimensional logarithmic plot.

The void fraction of a two phase material may be calculated by x-ray analysis according to the arguments of Kratky and Miholic (41). The mean square fluctuation of the electron density is given by:

$$(\rho_p - \rho_v) = K \cdot Q_d$$

where:

ρ_p = electron density of the polymer

ρ_v = electron density of the void

$$K = 1 / (ie N_a^2 \cdot d \cdot a \cdot \lambda^3)$$

ie = charge of an electron

N_a = Avagadro's number

d = specimen thickness in centimeters

a = specimen to detector distance in centimeters

λ = wavelength of radiation (0.154 nm)

Q_d = Invariant of the scattering function. Q_d can be calculated from the following integral:

$Q_d = \int I(s) \cdot dV_s$, For cylindrically symmetric distribution of scattered intensity, Q_d is given as:

$$Q_d = \left[\pi \iint S_2 \cdot I(S_1, S_2) \cdot dS_1 \cdot dS_2 \right] / I_0 \cdot CT \cdot TM$$

where:

I_0 = primary intensity

CT = counting time

TM = transmission coefficient

S_i = directionally dependent scattering vectors

Thus, the void fraction of a sample may be calculated from:

$$(\rho_1 - \rho_2)_{x\text{-ray}} = (\rho_1 - \rho_2)_{\text{theo}} \cdot W_1 \cdot W_2$$

$(\rho_1 - \rho_2)_{x\text{-ray}}$ is the electron density difference between phases as predicted by invariant analysis. $(\rho_1 - \rho_2)_{\text{theo}}$ is the calculated electron density difference between phases. W is the volume fractions of the phases. For a two phase system $W_1 + W_2 = 1$ such that a quadratic equation for void fraction can be solved.

This procedure was done for the crazed sample mentioned above for two cases, one where the anomalous streak was present, and one where it was not. The volume fraction calculated for the first case was 3.27 percent, while the volume fraction for the second case was 0.714 percent. Clearly a discrepancy exists. To investigate the problem further, a density gradient column measurement was performed.

The void fraction of a two phase material in a density gradient column is given by the equation:

$$W_1 = (\rho_{\text{bulk}} - \rho_{\text{craze}}) / \rho_{\text{craze}}$$

The void fraction of the crazed sample was found to be 0.31 percent by this method.

Clearly, the density gradient column agrees more with the tilted scattering pattern than the untilted (with the presence of the anomalous streak) one. The density gradient column value agrees with the x-ray analysis of the tilted pattern, when one considers that all of the assumptions mentioned above are not completely valid, and each tends to make the density gradient column experiment underestimate the true void fraction of the sample.

5. DISCUSSION

To formulate a meaningful interpretation from the SAXS data of polystyrene crazes, a characterization of both the reflection and diffraction phenomena of this system must be performed. Therefore, the first section of this chapter deals with interpretation of the results of Section 4.4 (page 79) on reflection. The origin of reflection of x-rays from crazes and laminated samples is developed, followed by a discussion of the significance of the craze scattering pattern. Lastly, the method of data analysis to be used in this work is described.

The second section of this chapter will discuss the molecular weight effects on crazing behavior, and will interpret results in terms of amorphous structural characteristics. Likewise, the third section discusses the effects of time dependent variables on the crazing behavior.

Finally, in the fourth section, a generalized model of the craze morphology of polystyrene will be developed from the available observations of Sections two and three, which are subject to the limitations discussed in Section one. The model will be compared and contrasted to conclusions of other researchers.

5.1 REFLECTION PHENOMENON

The observation of Section 4.4.2 (page 84) is that the x-ray technique grossly over predicts the void fraction of a crazed sample based on mass density measurements and theoretical considerations. It

is the opinion of the author, that even if the assumptions of section 4.4.2 were poor, the over prediction is too significant to ignore. Therefore, some scattering phenomenon other than diffraction must be occurring in the system.

The purpose of the laminated sample experiments of Section 4.4.1 (page 79) is to model craze planes in a sample where the only scattering event present is reflection; the diffraction from amorphous polystyrene is negligible (and background corrected). By showing the scattering pattern of the laminated sample is overwhelmingly dependent on the character of the interfaces, it is proven that reflection can be present in samples whose two phase structure is planar and parallel to the x-ray beam.

Finally, the striking resemblance of the laminated sample scattering pattern (Figures 4.17 A and B pages 80 and 81) to the crazed polystyrene scattering pattern (Figures 4.3 A and B pages 59 and 60) is noted. The major characterizeable difference is that the craze scattering pattern contains intensity parallel to the craze planes, where the laminated sample pattern contains no intensity parallel to the plane of lamination. Therefore, it is deduced that the nontensile scattering (at $\theta=90$ degrees) is by diffraction, and all classical diffraction theory may be applied to this region. Diffraction may indeed occur in the tensile direction, but its intensity is dwarfed by the reflection component of the scattering, and makes that correction of the data impossible.

Even though classical diffraction theory may not be applied to the tensile axis scattering from crazes, some useful analysis of the data may be possible. To characterize reflections in this system, an analysis of the total reflection must be performed.

5.1.1 ORIGIN OF REFLECTION OF X-RAYS

Refraction or reflection of x-rays has not received extensive attention in the literature, since the index of refraction of most substances for x-rays is close to unity. This means the velocity of x-rays is nearly unchanged when passing between vacuum and dense media. By definition, the index of refraction of a material is given by the equation:

$$n = C/V$$

where:

C=Velocity of electromagnetic radiation in a vacuum.

V=Velocity of electromagnetic radiation
in dense media.

To determine the index of refraction of a given pure material, one can use the following theoretical formula (12):

$$n = 1 - d = \left[1 - N(e \cdot \lambda)^2 \right] / 2\pi \cdot m \cdot V^2 \quad (\text{let } V=C)$$

where:

d=deviation of the index of refraction from unity.

e =Charge of an electron= 4.803 E-10 ESU

m =Mass of an electron= 9.109 E-28 gm

V =Velocity of x-rays = 2.998 E10 cm/sec

$N = N_A \cdot Z \cdot \rho / A$

Z =Number of electrons per unit volume of material.

A =Atomic mass of unit volume of material.

λ =wavelegnth of electromagnetic radiation.

ρ =bulk density of material.

N_A =Avagadro's number (6.0238×10^{23}).

For polystyrene:

$Z=56$ electrons/monomer

$A=104$ gm/mol monomer

ρ (typical polystyrene)= 1.05 gm/cm^3

now: $N=3.400 \text{ E23 electrons/cm}^3$

and: $d(\text{PS})=3.625 \text{ E-06}$

therefore: $n(\text{PS})=0.9999963746$

From optics, the general formula for the critical angle for total reflection is given by:

$$n = \sin(\pi/2 - \theta_c)$$

where θ_c is defined by: $\theta_c = \sqrt{2} d$

Then for polystyrene, the critical angle for reflection is 0.08840 mrad. This angle is well within the resolution of the small angle x-ray device. Assume that below θ_c , few reflections occur, while above θ_c , total reflection occurs.

5.1.2 CHARACTERIZATION OF REFLECTION OF X-RAYS

The reflection of x-rays off a craze-bulk polymer interface can originate from three categorical possibilities. Firstly, uncollimated x-rays can reflect off parallel interfaces (central region of the craze). Secondly, parallel x-rays can reflect off unparallel interfaces (craze tips). And thirdly, unparallel x-rays can reflect off unparallel surfaces.

There are two sources of uncollimated x-rays. One is divergence of the main beam through the pinholes; another is reflection off the second pinhole surfaces. For the case of the diverging beam, the reflected x-rays off parallel surfaces would be absorbed by the beamstop since the sample is placed between the second pinhole and the beamstop. Figure 5.1 (page 94) schematically illustrates this geometry. For the case of reflection off the second pinhole, the analysis is less trivial but the scattered intensity is still negligible. As was mentioned in Chapter 3, the empty beam background intensity is shaped like a cross because of the square pinhole geometry. Figures 3.7 A and B (pages 42 and 43) are the function of uncollimated x-rays caused by this effect. If these uncollimated x-rays are reflected off parallel surfaces, then the function of reflected x-rays will be either precisely the background

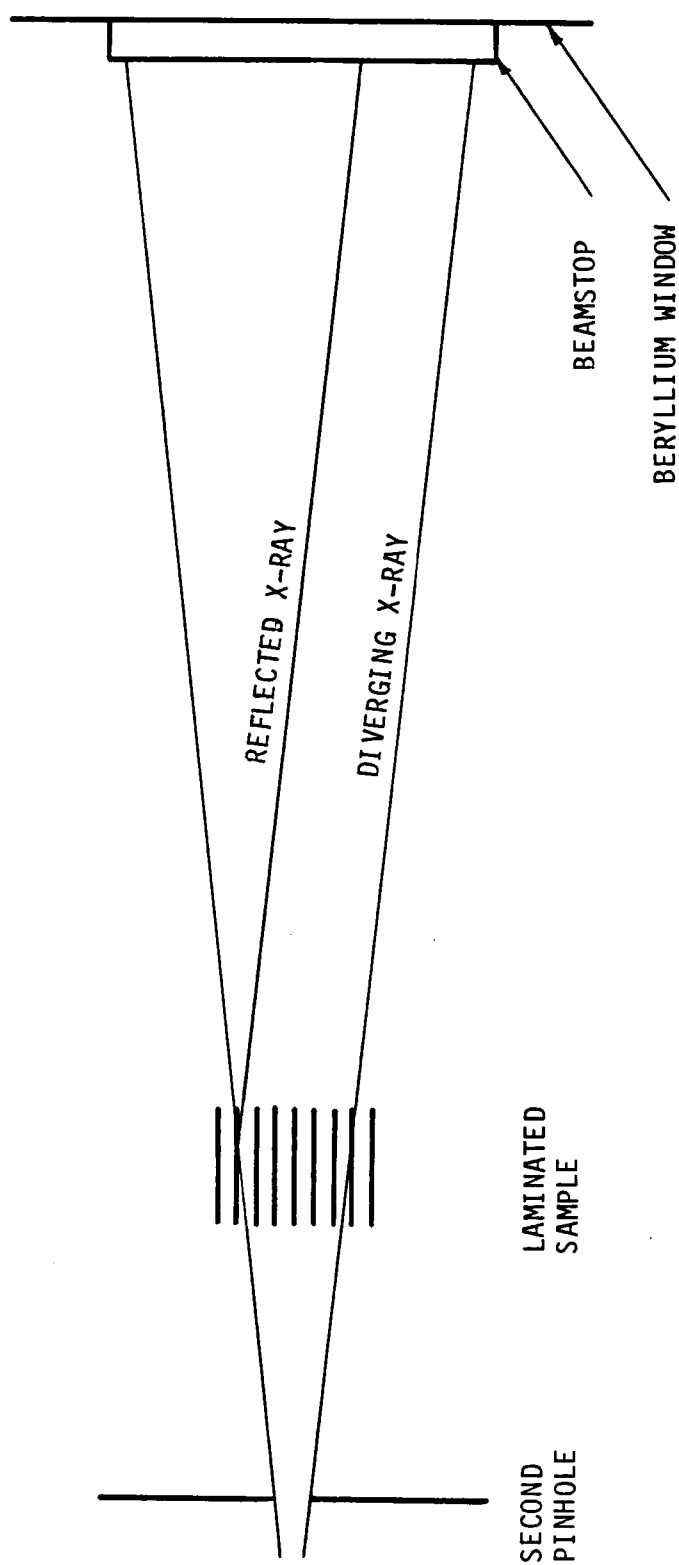


Figure 5.1 Schematic drawing of the SAXS geometry with laminated sample.
 Reflections of the diverging x-ray beam off parallel interfaces are caught by the beamstop.

intensity or the inverted background intensity, depending on whether the x-rays are reflected an even or odd number of times in the sample. This is true because the sample to detector distance is much greater than either the sample thickness or the pinhole to sample distance. So the background correction experiment will subtract all contributions of reflection off unparallel surfaces. Therefore, the contribution of the first case is negligible.

The second case gives the most important contribution to the reflected x-rays. That is, reflection of parallel x-rays off converging or diverging craze tips (the reflection off unparallel crazes is not considered). These reflections will not be corrected with the background, or caught by the beamstop. Therefore, the reflection streak is some function of the angular increase (decrease) in thickness of the crazes near the tips.

The third case is difficult to quantify because of the number of variables inherent to the problem. However, the cross shaped background can be used to advantage, since the density of uncollimated x-rays is lowest at 45 degrees to the vertical (see Figure 3.7 A and B, pages 42 and 43). If the sample is mounted such that the craze planes are 45 degrees to the vertical, then it can be assumed the reflections occurring from case three are minimal, and occurs mainly as a result of case two reflections. Figure 5.2 (page 96) shows the result of this experiment as compared to the case of horizontally mounted crazes. The reflected streak is less intense, especially at higher angles, for the case of crazes mounted at 45 degrees. Therefore, the low angle reflections are

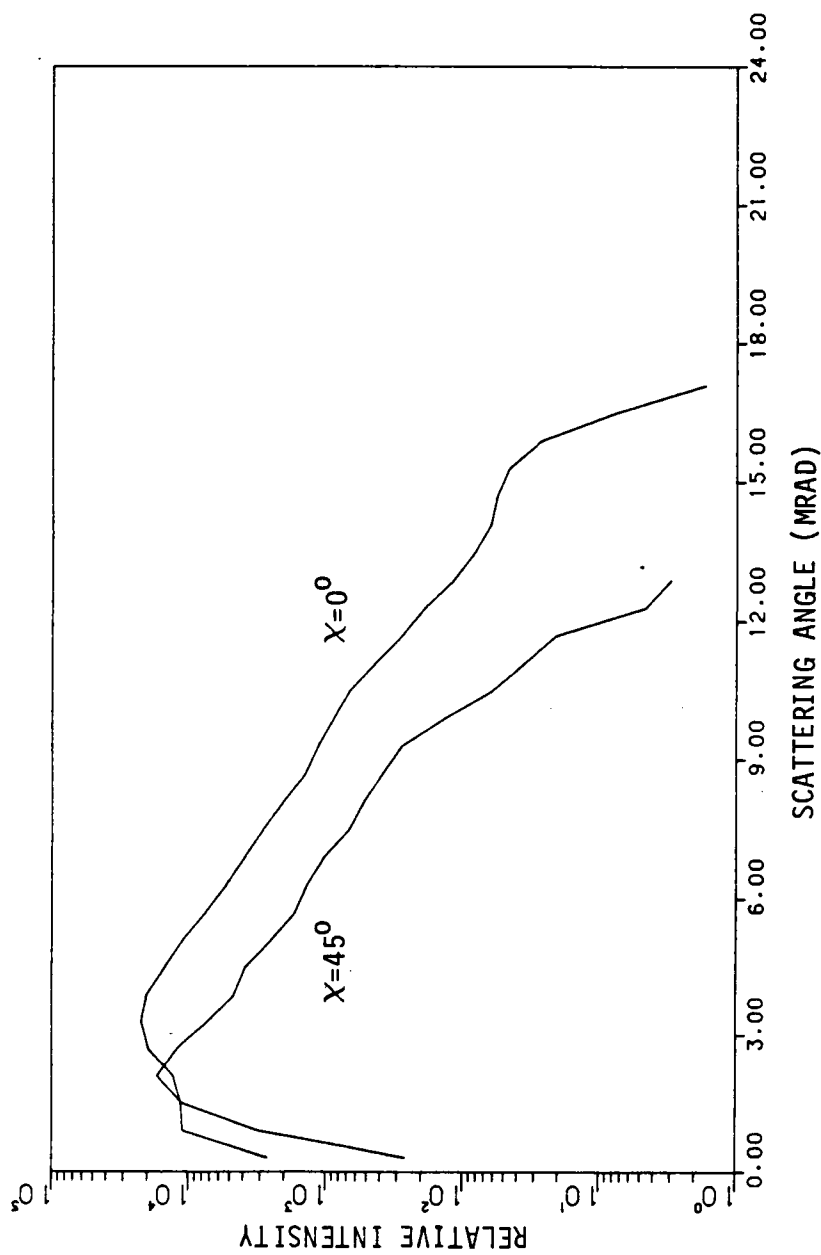


Figure 5.2 Effect of sample rotation about psi angle to reduce the reflective component of case three.

a direct function of the angular craze tip morphology, and the high angle reflections are a complicated function of the same.

The above discussion shows that at low angles of craze scattering patterns, reflections occur which result mostly from parallel x-rays reflecting off craze tips; while at high angles, reflections occur due to nonparallel x-rays reflecting off craze tips. Thus, the low angle reflection may be useful in characterizing craze tip angles.

The model of scattering from crazes presented in the last paragraph predicts that no uncorrected background reflections should occur in laminated samples of parallel interfaces. This prediction of course, is for the ideal case which can not be constructed experimentally. The intense scattering pattern observed for the laminated sample (Figures 4.17 A and B, pages 80 and 81) must therefore be a result of the inability to construct perfectly parallel planes of thin films. The most obvious origins of defects are edge effects, and nonuniform thickness of films and interfaces.

The contribution of nonparallel x-rays reflecting at large scattering angles explains the discrepancy between the previous results of Kramer and Brown (11) and Westbrook et al. (70). Kramer and Brown used a Kratky camera in the long slit geometry, where nonparallel x-rays are minimized, so they had small contributions from reflections of case three. Therefore, they reported the anomalous streak (tensile axis scattering) to be short compared to the normal streak (nontensile axis scattering). Westbrook et al. (70) report the anomalous scattering streak strong and extended compared to the normal streak, because of the

contributions of case three reflections at high angles due to pinhole collimation.

5.1.3 INTERPRETATION OF CRAZE SCATTERING PATTERNS

As was indicated in the last section, the scattering intensity in the tensile direction (normal to the craze plane) results mainly from parallel x-rays reflecting off nonparallel craze surfaces located near craze tips. Also, the scattered intensity in the nontensile direction results solely by diffraction from scattering centers inside the craze.

The nature of scattering centers being thought of as voids and/or fibrils has been the subject of some controversy in the literature. However, it is the opinion of the author that scattering center dimensions of polystyrene crazes correspond to microvoid dimensions inside the craze. The arguments leading to this conclusion have been developed elsewhere (70). Therefore, classical scattering theory will be applied to the nontensile axis scattering, and the result is interpreted as void dimensions.

The reflected intensity occurring in the tensile axis can be usefully interpreted in two ways. First, it provides a measure of craze tip angles; and second, the total scattered intensity is proportional to the number of crazes present in the sample. Therefore, craze growth rate and shape analysis are possible.

5.2 MOLECULAR WEIGHT EFFECTS ON CRAZING BEHAVIOR

In this section, the craze morphology as a function of molecular weight parameters will be developed according to the analysis technique outlined in the previous section. First, diffracted scattering will be considered, then reflected scattering will be treated separately. Both sets of results will be interpreted in terms of the amorphous structural characteristics of the polymeric glass.

5.2.1 DIFFRACTED SCATTERING IN THE NONTENSILE AXIS

The diffraction of x-rays from crazes has been attributed to scattering from microvoids. The nature of this scattering appears in Figure 4.7 (page 67) as a function of molecular weight. It can be seen by inspection that the general shape of these curves does not change with molecular weight, indicating the nontensile axis morphology is constant. However, the relative magnitude of these scattering curves changes with molecular weight. The molecular weight dependence on the magnitude of the curves was not clear from Figure 4.7, so Figure 4.9 (page 69) was constructed. Here it is assumed that the whole nontensile scattering curve can be adequately represented in terms of relative magnitudes by the intensity at a single specified point along the nontensile axis.

For this analysis, it would be more satisfactory to calculate the invariant of the scattering intensity, and plot it versus molecular weight. But the reflected component of the scattering is a significant contribution to the total scattered intensity and would seriously

distort the behavior of the invariant. Thus, it is assumed the invariant of the scattering curve and the intensity measured at a specific scattering angle are proportional to each other. Since the shape of the scattering curves are all similar with respect to molecular weight, this is not a bad approximation. The approximation allows for the relative void fraction comparisons between polymers.

Figure 4.9 (page 69) shows the nontensile diffracted intensity goes through a maximum close to $2M_e$, and decreases slowly at higher molecular weights. This intensity decrease indicates the number of voids is decreasing. Since the shape of the voids is approximately constant, the void fraction is decreasing with molecular weight.

It is postulated that a void in crazed matter originates from a region in the bulk material containing a higher than average density of matrix weakening elements. Since chain ends are weakening elements whose density depend on molecular weight, the equation describing this density should predict the intensity behavior. An equation for chain end density as a function of molecular weight is easily derived by dimensional analysis.

It is assumed:

1. unbranched polymer
2. constant mass density

$$P_{ce} = 2 \cdot \rho_{bulk} / DP \cdot M$$

[=] number of moles of chain ends per cubic centimeter.

where:

DP = degree of polymerization of the polymer

M = molecular weight of the monomer

ρ_{bulk} = mass density

This equation suggests the defect density goes as the reciprocal of the molecular weight of the polymer. The values of P_{ce} can be calculated absolutely, and they appear as the solid line in Figure 5.3 (page 102). Here, it is assumed that the magnitude of the diffracted intensity is proportional to the void fraction of the polymer craze. Therefore to test the hypothesis that void fraction is proportional to defect density, the intensity data are arbitrarily shifted (normalized), such that one datum point lies on the theory.

Figure 5.3 shows the high molecular weight scattered intensity is linear on this plot, and agrees with the theoretical development. The datum point for the lowest molecular weight polymer appears at extremely low intensity. This results from a maximum in scattered intensity caused by a competition of two effects. At the low molecular weight limit (2Me), no crazes form, so the void fraction of nonexistent crazes is naturally zero. At the high molecular weight limit (infinite), theory states that void initiator density is zero, so void fraction will be zero (This may not be the case at ultra high molecular weights, since other defects besides chain ends may initiate crazes). Thus, for voided crazed matter to exist between these extremes, the void fraction must pass through a maximum.

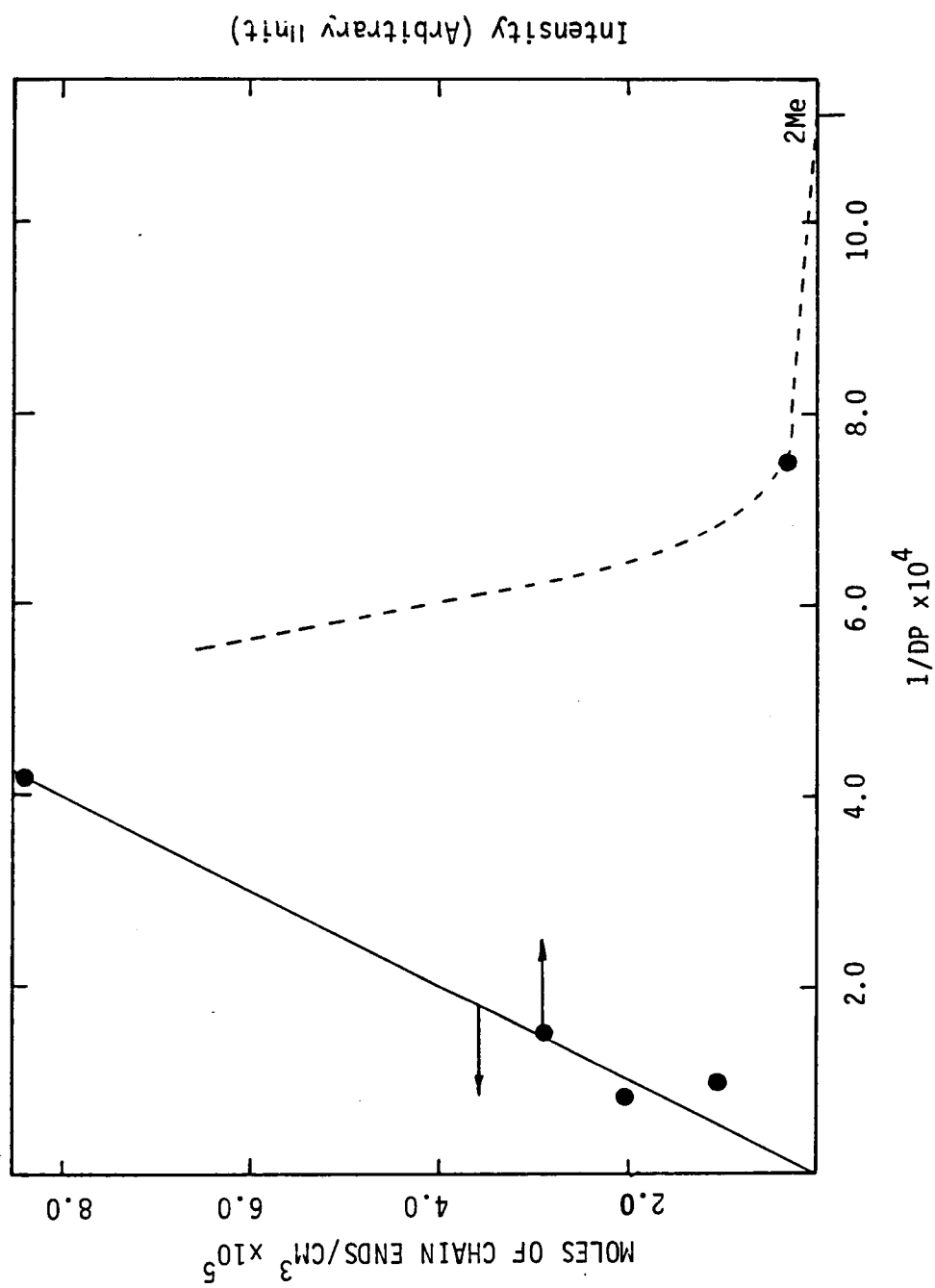


Figure 5.3 Comparison of diffracted intensity to concentration of defects as a function of inverse molecular weight.

The solid line in Figure 5.3 is the theoretical behavior substantiated by the indicated data. The dashed line is the hypothesized behavior based on the location of one datum point, the predicted behavior at 2Me, and the location of the theory.

5.2.2 REFLECTED SCATTERING IN THE TENSILE AXIS

The reflection of x-rays from crazes has been attributed to scattering from unparallel surfaces of the craze-bulk interfaces. The nature of these scattering curves appear in Figure 4.8 (page 58) as a function of molecular weight. The intensity at $2\theta=5\text{mrad}$ is also plotted in Figure 4.9 (page 69), using the same assumptions as in the last section. Again, the relative magnitudes of these scattering curves changes with molecular weight, indicating the number of crazes generated is a function of molecular weight. Likewise, the nature of the intensity peak changes with molecular weight, indicating the shape of the craze tips is a function of the same.

If we assume crazing is a yielding phenomenon which is characteristic of brittle polymers, and entanglement density affects the brittleness of the glass, then the entanglement density should affect the craze generation rate. Further, assume the intensity evaluated at a single angle is representative of the whole tensile axis streak, and is proportional to the number of crazes sampled by the x-ray beam. Now the entanglement density may be related to the tensile axis intensity as a function of molecular weight.

The equation developed by Fellers and Huang (19) for the entanglement density is given as:

$$N_e = (\sigma \cdot N_a / M_e) (1 - 2M_e / \bar{M}_n)$$

where:

N_e = entanglement density per cubic centimeters

σ = material density

N_a = Avagadro's number

M_e = Molecular weight between entanglements

$\bar{M}_n$ = Number averaged molecular weight

Here, a constant M_e obtained from rheological data is assumed. The entanglement density is therefore bounded at infinite molecular weight by the term: $(\sigma \cdot M_a / \bar{M}_n)$; and the slope of a N_e vs $1/\bar{M}_n$ plot is $-2\sigma \cdot N_a$. Now we should be able to plot the scattered intensity vs $1/\bar{M}_n$ on the same plot as N_e vs $1/\bar{M}_n$ and get a reasonable test of the Fellers and Huang equation. This plot appears in Figure 5.4 (page 105). In this figure, a value of 94,000 instead of 70,000 is used for $2M_e$ because of the craze relaxation data obtained in this work (Figure 4.14, page 75 predicts this value).

Figure 5.4 shows the entanglement density theory is not a bad prediction of the reflected intensity behavior at low DP values. The dashed line represents a translation of the theory based on a higher value for M_e , and represents a best fit of the theory to the two lowest

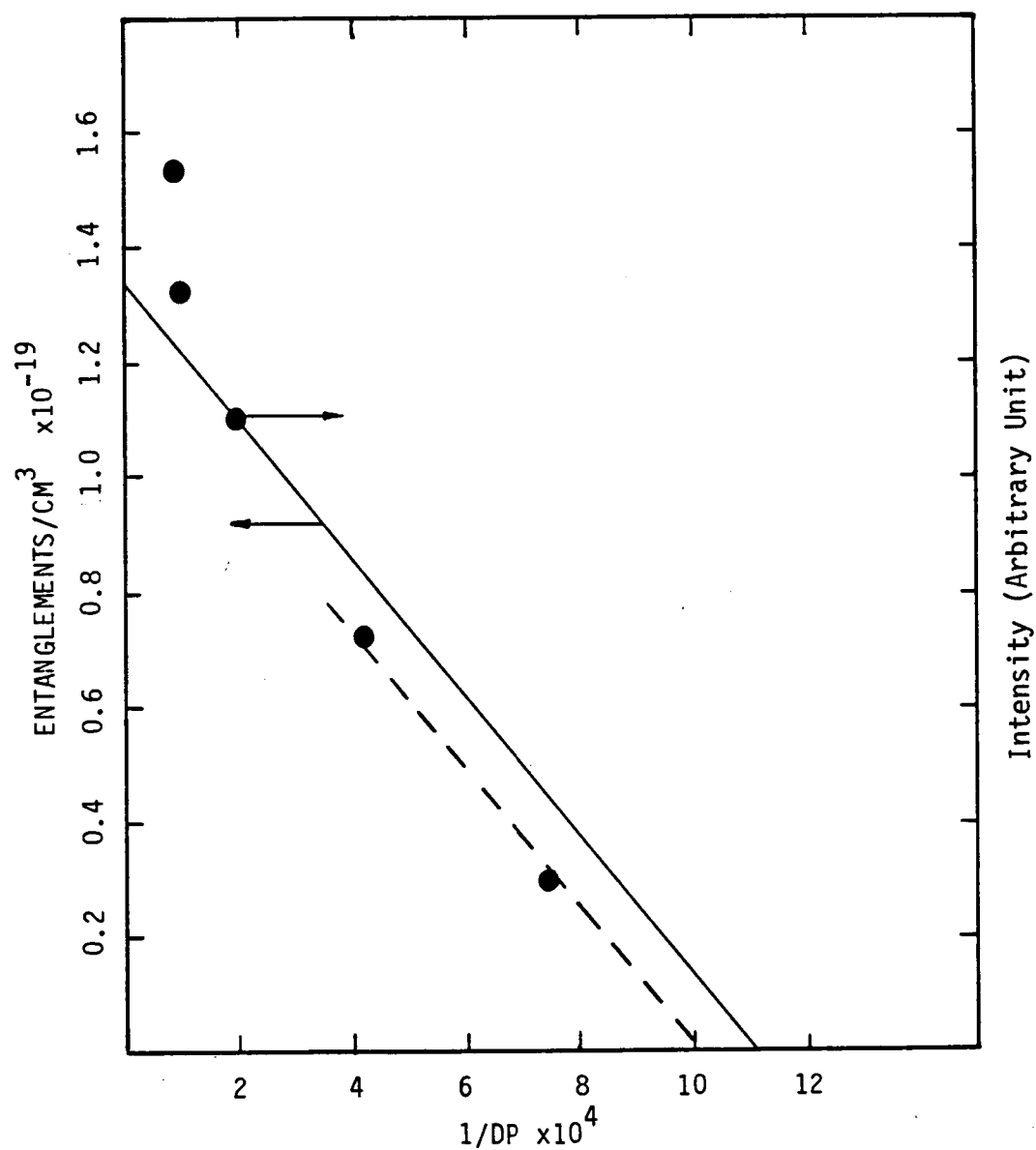


Figure 5.4 Fellers and Huang equation fit to the reflected intensity data.

molecular weight polymers. Never-the-less, the higher molecular weight data deviate sharply from the theory.

Thus, either the assumptions stated above are wrong, or the theory of Fellers and Huang is not general. Proceeding with the latter idea, the data indicate the distance between entanglements is not a constant. Rather, it is inversely proportional in some way to the molecular weight. Physically speaking, this result implies that the molecules are becoming more intertwined with each other as they get longer. In other words the concentration of the polymer in itself gets larger as the molecular weight increases. This hypothesis has support from experimental results (57). Namely, the density of polystyrene increases as the molecular weight increases.

From the behavior of the high molecular weight intensity data of Figure 4.9 (page 69), the entanglement molecular weight function is proposed to be of the following form:

$$M_e = M_{e0} \cdot \exp(-\text{const} \cdot \bar{M}_n)$$

where:

M_{e0} = entanglement molecular weight based
on rheological data (low $\bar{M}_n$).

$\bar{M}_n$ = number averaged molecular weight.

Now the Fellers and Huang equation is modified to the following form:

$$N_e = (\rho \cdot N_a / M_e) \left[1 - (2M_e / \bar{M}_n) \exp(-C \cdot \bar{M}_n) \right] \exp(C \cdot \bar{M}_n)$$

Where C is a constant.

Therefore, in the limit of high molecular weight, the new equation reduces to:

$$N_e = (\rho \cdot N_a / M_e) \exp(C \cdot \bar{M}_n)$$

If the data are plotted in the form of the last equation, Figure 5.5 is the result. It is unreasonable to expect this equation to continue to predict reflected intensity behavior of crazes from ultra high molecular weight polymers. The unfortunate consequence of the exponential function is that N_e will grow unbounded with molecular weight. Since the entanglement density must approach some limiting value, this equation will over predict the reflected intensity at a finite molecular weight. However, the usefulness of the improved equation for entanglement density is in the range of one order of magnitude above $2M_e$, the molecular weight region of most important polymers.

5.3 STRESS EFFECTS

The dependence of craze morphology as a function of stress was studied at constant chemical composition. The polystyrene chosen has a number averaged molecular weight of 202,000 and molecular dispersity of

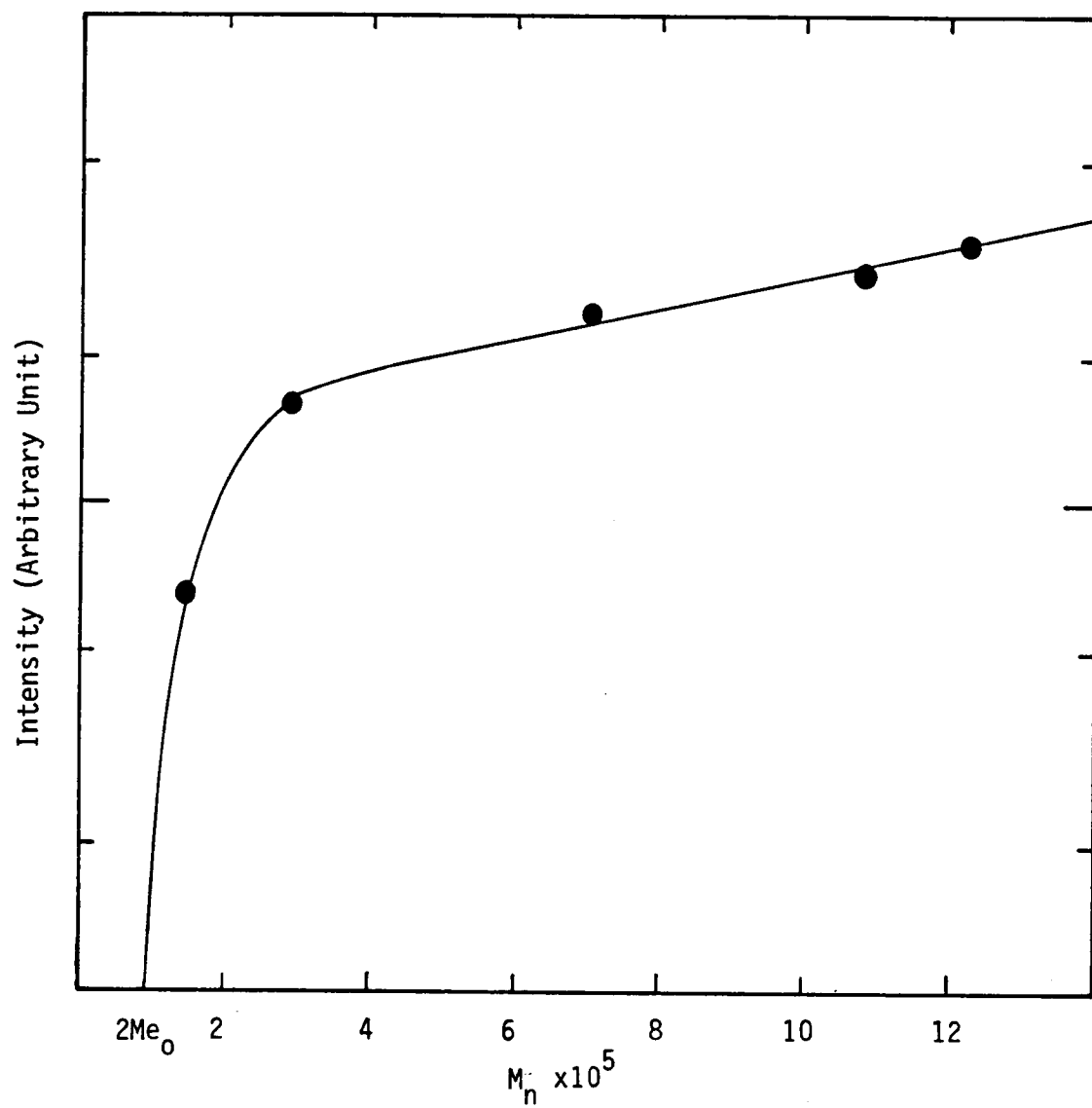


Figure 5.5 Modified Fellers and Huang equation fit to the reflected intensity data.

1.1. Experiments were conducted at a constant strain rate. Results are interpreted as outlined in Section 5.1 (page 89).

5.3.1 DIFFRACTED INTENSITY IN THE NONTENSILE AXIS

The main reason this polymer was chosen for discussion is the presence of a large scattering minimum in the nontensile axis scattering curve (see Figure 4.10, page 73). All polystyrene crazes under load exhibited this behavior to a varying extent; however, many were so small that the averaging technique for slicing smoothed over this minimum (see Figure 4.7, page 67).

The location of the Bragg maximum in Figure 4.7 is $2\theta=3.375$ mrad. Using Bragg's law, this angle corresponds to a d spacing of:

$$d=\lambda/(2\cdot\sin\theta)=45\text{ nm } (\lambda=0.154\text{ nm})$$

Since the diffracted intensity is attributed to scattering from voids, the average distance between voids is 45 nm.

Figure 4.10 also shows that the angle at which the peak occurs does not change with stress. Therefore, the distance between fibrils is not a function of stress. This result is undoubtedly due to the force not acting along the nontensile axis, and the presence of lateral constraint. The relative magnitudes of the diffracted intensity increases with stress, which indicates the generation of new voids.

As in Section 5.2.1, it is assumed the behavior of the whole diffracted intensity curve can be approximated by the intensity at one angle. For this analysis, the intensity at $2\theta=5$ mrad is plotted versus stress in Figure 4.12 (page 73). It is seen that the void fraction,

which is proportional to diffracted intensity, increases linearly (on cartesian coordinates) in the range where crazes exist. This linear result is entirely consistent with the predictions of Hooke's law with Poisson's ratio being less than one half. That void fraction of a deforming glass is linearly dependent on the strain. Since the strain rate is constant, the rate of void formation is constant.

The reason significant intensity is not recorded at stress levels below 2400 PSI, is because the sample is deforming homogeneously. Scattering centers of precrazed voids located around chain ends are of the order of 1 nm or so. These voids would not scatter x-rays onto the detector in the resolution used for these experiments. The voids associated with inhomogeneous deformations are on the order of hundreds of angstroms, for which the experiment was designed.

5.3.2 REFLECTED INTENSITY IN THE TENSILE AXIS

The tensile axis reflected scattering curves as a function of stress appear in Figure 4.11 (page 72). Following the analysis of Section 5.1, this scattering is proportional to the shape of the craze tip. Since contributions from case two and case three reflections are included in these curves, absolute shape analysis is difficult. Figure 5.2 (page 96) shows the intensity maximum at low angles is mostly unaffected by case three reflections, so the location of this maximum will be the most probable angle of craze divergence. Larger angles imply thicker crazes.

The maximum intensity values of Figure 4.11 are plotted against stress in Figure 5.6 (page 112). The point for 4200 PSI is omitted because its peak is difficult to resolve. Again, no reflection occurs below 2400 PSI because the deformation is homogeneous and no crazes exist.

The angle of divergence of a craze tip whose length is constant, is proportional to the thickness of the craze. Figure 5.6 shows the craze thickness increasing toward an asymptote before fracture. It seems the polymer matrix is saturating itself with crazed matter, such that at high stress levels, crazes are no longer able to grow by thickening.

The total reflected intensity is related to the number of crazes present in the sample. Here again, it is assumed the behavior of the entire reflection curve may be represented by the intensity at a single angle ($2\theta=5$ mrad). Figure 4.12 (page 73) shows this intensity versus stress. Unlike the diffracted intensity, the reflection intensity increases to an asymptotic value before fracture. This result is another indication that the bulk matrix is saturating itself with crazes.

5.3.3 FRACTURE MECHANISM BASED ON STRESS ANALYSIS

From the discussions of the last two sections, the fracture mechanism for polymeric glasses seems clear. For the case of elongation of a compressible material, Hooke's law states that the specific volume increases linearly with strain. For a polymeric glass, cavitation

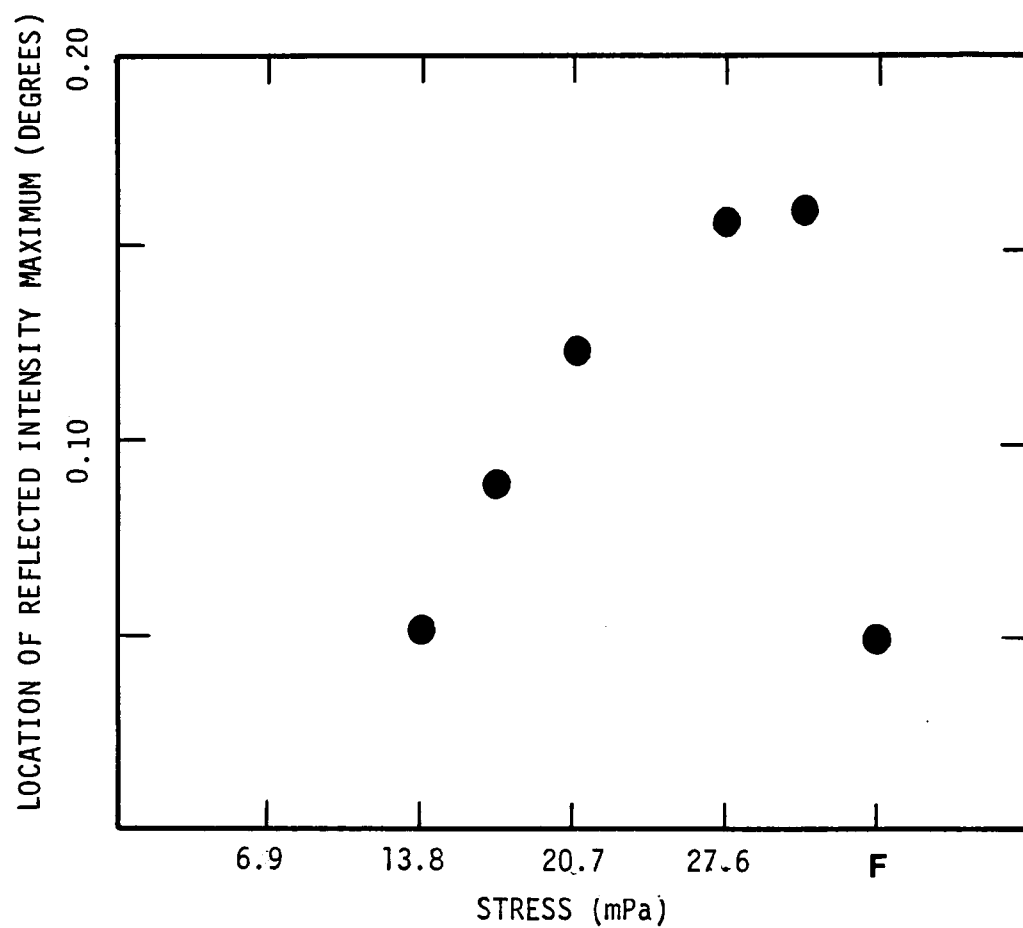


Figure 5.6 Craze thickening versus stress as indicated by the location of the reflected intensity maximum.

occurs inhomogeneously in the form of a craze, and the bulk material can support only a finite amount of crazed matter. When this limit is reached, further cavitation manifests itself in the form of fibril cessation and bulk fracture.

The saturation limit of the bulk polymer may be a function of molecular weight and rate of strain. The molecular weight dependence has already been indirectly treated in Section 5.2 (page 99). There it was shown that the number of crazes generated at a specific stress increases with molecular weight. It can be assumed, therefore, that the number of crazes present at fracture also increases with molecular weight. Thus, the saturation limit of a highly entangled matrix is higher than that of a less entangled matrix.

To increase the entanglement density of a polymer, means that the material becomes more ductile. Another way to enhance the ductile response of a polymer is to decrease the strain rate of deformation. This effect is partially investigated in the next section.

5.4 TIME EFFECTS

In this section the effects of craze generation under constant load and craze relaxation after fracture will be considered. Here, no detailed analysis of scattering patterns is provided. Rather, analysis of kinetic phenomena as indicated by total scattered intensity is performed.

5.4.1 CRAZE GENERATION UNDER CONSTANT LOAD

A glassy material bearing a constant load over a period of time experiences a negligible increase in stress. In the case of a viscoelastic solid, the strain will increase due to creep phenomenon. The key point used in this analysis is that one can approximate the behavior of a material in many experiments of varying strain rate with a few experiments at constant load. Figure 5.7 (page 115) attempts to illustrate this coordinate transformation from the data of Figure 4.16 (page 78).

The constant load experiments described above were performed on polystyrene characterized as $\overline{M}_n=250,000$ and $PD=1.1$ under loads of 3000 and 4000 PSI. The total scattered intensity as a function of time for these experiments is shown in Figure 4.16 and schematically in Figure 5.7. Two important observations can be made about these data.

First, the lower stress experiment has lower scattered intensity at equal times (points A and B). Obviously, stress is the driving force for craze generation and less stress for equal time produces fewer crazes. It is noted that the two curves appear to be related by a shift factor in strain rate.

Points A and B in the constant load experiments are analogous to points X and Y in the hypothetical constant strain rate experiments. That is, a higher strain rate will produce higher stresses at equal times than the lower strain rate experiment. Thus, the scattered intensity is higher at point X. However, if the lower strain rate experiment is allowed more time to reach the stress of point X at point

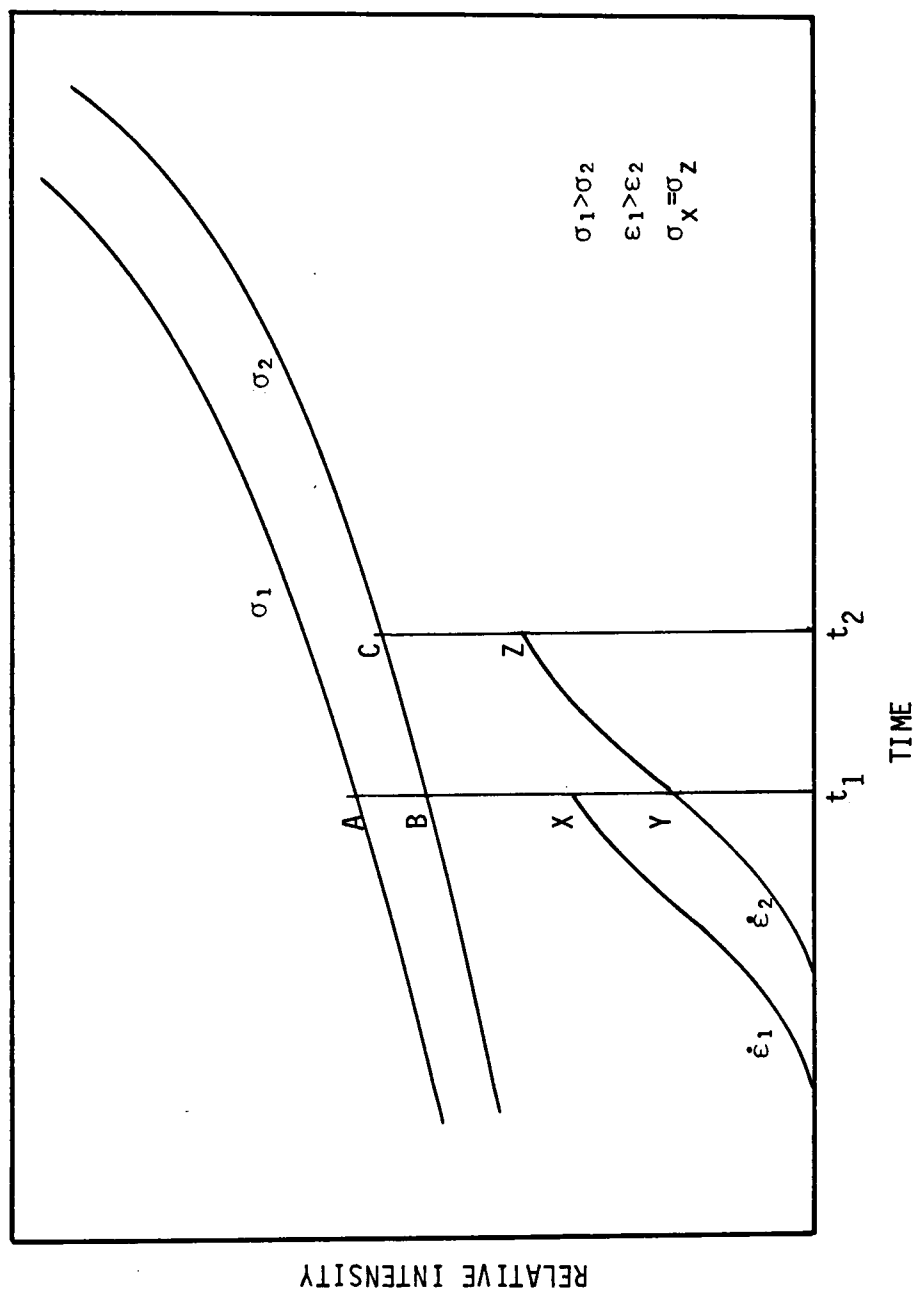


Figure 5.7 Schematic of the analogy between constant stress and constant elongation rate experiments.

Z, then the scattered intensity at point Z will be greater than that of point X. This result is analogous to points B and C of the constant load experiment where longer times produces higher scattered intensity at the same stress.

From this analogy, it has been shown that lower strain rates increase the number of crazes a matrix will support at a given stress. Therefore the number of crazes present at fracture will also increase with decreasing strain rate, and the saturation limit of the matrix is rate dependent.

Of course, the best way to verify these results is to continue the experiments of Figure 4.16 until fracture, then compare the scattering powers. This experiment was not done because fracture would occur at prohibitively long times.

5.4.2 CRAZE RELAXATION AFTER FRACTURE

The scattering power of relaxed samples as a function of molecular weight and time after fracture is plotted in Figure 4.13 and 4.14 (pages 74 and 75). The reduced intensity ordinate is necessary for direct comparison because the scattering power at fracture is a function of molecular weight. It is observed the scattering power initially drops about an order of magnitude, which illustrates the elastic character of the crazed matter. The scattering power then drops slowly with time, indicating the viscous (time retarded) character of the crazed matter.

Thus the elastic character of the craze is a strong function of molecular weight. This result is due to varying degrees of void fraction of the craze. It was shown in Section 5.2.1 (page 99) that fibril fraction increases with molecular weight. Therefore, the increase of viscous response of crazed matter with molecular weight, due to the greater fraction of viscoelastic material, is expected. These results also agree with the work of Donald and Kramer (15,16), who observed that the void fraction of crazes increases with entanglement density.

It is interesting to plot the long term relaxed scattering power of crazes versus molecular weight as in Figure 4.15 (page 77). An extrapolation back to zero intensity (corresponding to totally elastic recovery and zero fibril fraction), predicts a value for twice the entanglement molecular weight which is close to the value obtained from rheological measurement. The discrepancy may be due the considerations of Section 5.2.3 (page 103), arguing the distance between entanglements is molecular weight dependent.

Figure 4.14 is the analogous plot of Figure 4.13 for the molecular dispersity parameter. The general characteristics of the two plots with respect to elastic and viscous recoveries are similar; however the function of these parameters with respect to molecular dispersity is unclear. Unfortunately, all of the polymers in Figure 4.14 have significantly different number averaged molecular weights. Therefore, the function for molecular weight shown in Figure 4.13 must be somehow buried in the data of Figure 4.14.

5.5 A GENERAL MODEL FOR CRAZE MORPHOLOGY OF POLYSTYRENE

There are currently two basic models used in the literature to describe the morphology of crazes. One model describes crazed matter as perfectly oriented rods of polymer spanning the length of the craze with no interconnections. The other model qualitatively describes craze matter to be like an open celled foam, whose fibrils are interconnected to form voids. Voids are interconnected such that liquids will diffuse throughout the craze, but independent enough to respond individually to radiation. From the evidence present in this work, an argument is developed which supports the open celled foam theory.

First, consider the case of oriented rods. TEM data (eg. 39) suggest the width of the craze in the tensile direction is approximately one micron. Also, evaluation of Bragg peaks of diffracted radiation in the nontensile axis indicates the average distance between fibrils is about 45 nm. Assuming fiber symmetry, the average void volume described by this model is:

$$V = \pi (450/2)^2 \cdot (10,000) = 1,600,000,000 \text{ \AA}^3$$

Figure 5.3 (page 102) indicates a representative value for the concentration of entanglements in a polymer matrix is about 10^{-5} entanglements/ $\text{\AA}^3$. Thus, the number of entanglements originally present in the bulk matrix, which have been disentangled to form a void is approximately 16,000. It seems unlikely to this author that 16,000 entanglements per void can be removed in the instantaneous time associated with craze formation in an ultra high viscosity system.

More importantly, the oriented rod model contains no mechanism by which x-ray diffraction can occur in the tensile axis. Therefore, The importance of the scattering pattern of Figures 4.20 A and B, pages 85 and 86) can not be overemphasized. Figures 4.20 A and B are the scattering pattern of a craze with no reflected component from interfaces. Since the sample was only tilted eight degrees away from its vertical, the component of nontensile scattering in the tensile axis is small. Thus, the tensile axis diffraction of polystyrene crazed matter is significant, and the oriented rod model of craze morphology is shown to be inadequate.

On the other hand, the open celled foam model of craze morphology includes the existence of interconnections between fibrils. These interconnections are evidently formed as a result of entanglements present in the bulk which remained entangled after the crazing event. Therefore, the open celled foam model predicts significant diffraction in the tensile axis arising from dimensions between interconnections. This prediction is verified by Figures 4.20 A and B.

TEM studies of perpendicular craze intersections in polystyrene (39) also support the open celled foam model. If there are no interconnections among fibrils in a preexisting craze, then the volume intersected by the secondary craze would completely cavitate. But this result is not the observed behavior. The intersected volume reveals vast numbers of fibrils perpendicular to the primary craze fibrils. The ability of crazed matter to support stress in any direction proves the significance of interconnections.

The average void shape generated by the diffraction pattern in Figures 4.20 A and B is roughly spherical; therefore, the aspect ratio is roughly one, so the average volume these voids is three orders of magnitude less than that predicted by the oriented rod model. The vacancy of sixteen molecular entanglements per void may be more easily rationalized in terms of mass transfer during fibril and interconnection formation, and the concept of statistical distributions of molecular features.

6. CONCLUSIONS

The conclusions obtained in this work may be divided into four categories: scattering mechanisms, morphological description with respect to molecular weight and applied stress, craze generation as a function of ductility and relaxation, and a general model for morphology.

6.1 SCATTERING MECHANISMS

1. The x-ray scattering from a sample whose two phase structure forms parallel interfaces which are themselves parallel to the beam direction, exhibits considerable reflection scattering at small angles perpendicular to the plane of interface.

2. Crazes formed in a polymeric glass are one example of a system described above. Scattering in the tensile axis is predominately a result of reflection, while the nontensile scattering is by diffraction only.

3. Analysis of craze scattering follows two techniques. Diffracted nontensile scattering can be treated with classical diffraction theory, while the reflected tensile scattering is used for craze tip shape analysis. In both cases, the relative magnitude of scattered intensity is proportional to the number of scattering centers present in the sample.

6.2 MORPHOLOGICAL DESCRIPTION

The parameters of interest here include molecular weight parameters and level of applied stress.

6.2.1 MOLECULAR WEIGHT PARAMETERS

1. Diffracted intensity indicates the number of voids, and therefore void fraction reaches its maximum value at a molecular weight slightly above twice the entanglement molecular weight, then decrease linearly with inverse degree of polymerization.

2. In the same manner, it is shown the defect density associated with chain ends also decrease with increased degree of polymerization. Thus, a volume containing a higher than average density of defects (due to statistical fluctuation) will ultimately cavitate in crazed matter.

3. Reflected intensity dictates the number of crazes which the polymer will support increases with molecular weight. This function has been attributed to the ductility of the glass, and therefore the density of molecular entanglements. The reflected intensity can be made to fit a modified Fellers and Huang equation for entanglement density (in the range $2M_e < \bar{M}_n < 20M_e$), in which the molecular weight between entanglements is an exponential function of molecular weight.

6.2.2 APPLIED STRESS

1. Diffracted intensity indicates the distance between fibrils in the nontensile axis is constant with respect to the applied stress.

2. Diffracted intensity also shows the void fraction of the craze increases approximately linearly with stress in a constant strain rate elongation. This conclusion is consistent with the deformation of a compressible Hookean solid.

3. Reflected intensity measurements indicate the number of crazes in the sample reaches a maximum value before fracture. Thus, fracture occurs when no more crazes can be formed in the bulk matrix, under conditions of increasing specific volume.

6.3 DUCTILITY AND RELAXATION

1. The ductility of a polymeric solid can be enhanced by increasing the density of molecular entanglements or decreasing the rate of strain (stress) of the material. Both of these mechanisms increase the characteristic limit for craze density of the material.

2. Craze relaxation after fracture shows decreasing elastic response with increasing molecular weight. Therefore, the void fraction of crazed matter decreases with molecular weight. This identical conclusion is observed by independent results summarized in Section 6.2.1.

6.4 MORPHOLOGICAL MODEL

1. The observation of a significant component of diffracted intensity in the tensile axis renders the oriented rod model for craze morphology inadequate, since no mechanism exists by which this intensity is generated.

2. The open celled foam model predicts tensile axis diffraction, therefore it is more descriptive of craze morphology. Significant interaction between fibrils have also been observed by independent TEM studies of craze intersections.

7. RECOMMENDATIONS

1. The existing data generated in this work should be completely analyzed. For each polymer listed in Table 3.1, a complete set of scattered intensity versus stress data exists. Likewise, for each stress increment a complete set of scattered intensity data versus molecular weight exists. For the purpose of brevity, this work only analyzed and developed one axis for stress and molecular weight. The data of the whole matrix exists and can be analyzed according to the techniques outlined in this work.

2. The dynamic stress versus intensity measurements can be repeated using a short sample to detector distance (eg. one to two meters), such that precrazed voiding measurements may be made with respect to the variables of interest.

3. The dynamic stress versus intensity measurements can be repeated using an apparatus which allows for the deformation of a sample at slight Chi angles such that all reflections are suppressed. This allows for the characterization of microvoid dimensions in the tensile axis as a function of applied stress and molecular weight parameters.

4. More sophisticated craze tip shape analysis can be performed if the reflections of case three (reflection of unparallel rays off unparallel surfaces) can be greatly suppressed as in the Kratky camera in the long slit geometry. This result may be accomplished by a modification of the second pinhole collimator.

Reflections of case three are a direct result of the second pinhole being an orifice. If the second pinhole were a column of high length/diameter ratio, most edge effects are suppressed. A schematic of the proposed second collimator is shown in Figure 7.1 (page 127).

This design will also improve those scattering experiments whose reflection is not a problem. The background intensity due to unparallel X-rays will be greatly reduced; therefore, the signal to noise ratio of weak scatterers will be increased.

5. An investigation of the crazing phenomenon with respect to temperature would be interesting. Temperature must be an important variable in the system since crazing will not occur above the glass transition temperature.

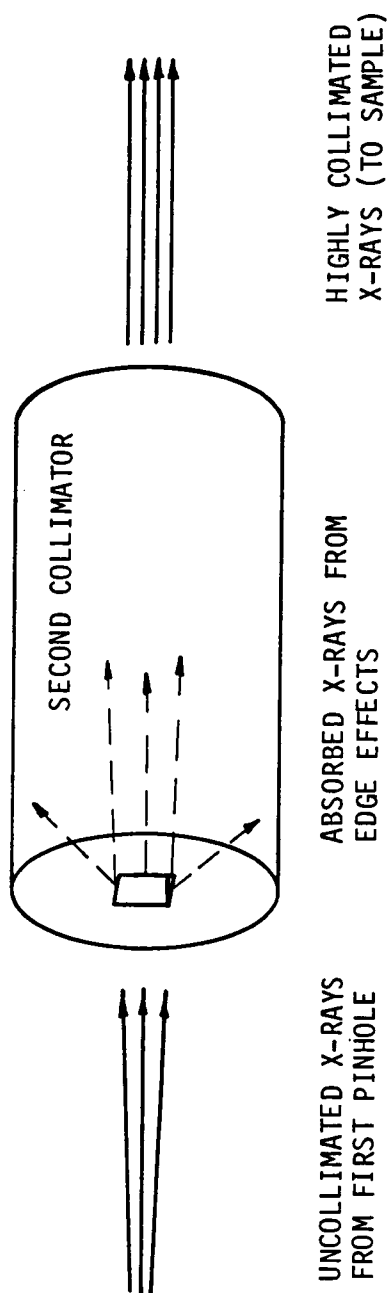


Figure 6.1 Schematic of second collimator proposed to replace pinhole.

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VITA

The author, Paul A. Westbrook, was born in Cleveland, Ohio on January 18, 1958. He attended elementary schools in Cleveland and Oak Ridge, Tennessee, where he moved in 1966. Upon graduation from Oak Ridge High School in 1976, he enrolled at The University of Tennessee, Knoxville. After graduating with honors in 1981 with a B.S. degree in Chemical Engineering, he was awarded a research assistantship in the Polymer Engineering program at the same university. After receiving a masters degree in August 1982, he is continuing his education at the doctoral level in the same department.