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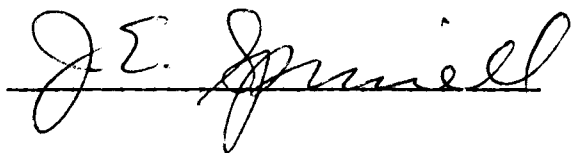
I am submitting herewith a thesis written by Mukerrem Cakmak entitled "The Effects of Drawing Polyethylene in the Solid State on Crystallographic, Morphological and Mechanical Properties." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.



E. S. Clark, Major Professor

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THE EFFECTS OF DRAWING POLYETHYLENE IN THE SOLID STATE
ON CRYSTALLOGRAPHIC, MORPHOLOGICAL AND
MECHANICAL PROPERTIES

A Thesis

Presented for the

Master of Science

Degree

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Mukerrem Cakmak

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ABSTRACT

The major purpose of this experimental research was to investigate the effects of drawing condition on the microstructure of high density polyethylene (HDPE) and its influence on the mechanical properties. A number of experiments on the mechanical properties of low density polyethylene (LDPE) were also carried out.

The microstructures of the samples were studied by a range of experimental techniques, including wide angle and small angle x-ray diffraction, scanning electron microscopy, thermal analysis and dynamic mechanical measurements. The macroscopic mechanical properties were also investigated.

The Warren-Averback Fourier analysis and the Guinier-Warren-Hoseman paracrystal analysis were used to determine crystal sizes and their perfection in a series of drawn filaments.

The polyethylene filaments were drawn both by a one-stage draw (100 percent/min) and by a two-stage method which utilizes 100 percent/min draw rate in the first stage and a 1 percent/min draw rate in the second stage (superdraw). The structural differences resulting from drawing by both methods and their relationship to the mechanical properties were studied.

The superdrawn HDPE samples showed a great increase of modulus with draw ratio (10 GPa for natural drawn, 25 GPa for superdrawn). The density, crystallinity and melting temperature measurements also increased with draw ratio. These changes are interpreted as an increase of order in the structure of HDPE filaments with increasing deformation. An increase in drawing temperature results in a decrease

of moduli at high draw ratios above the optimum temperature which corresponds to that of the α -transition.

A comparison of HDPE samples drawn by the one-stage and two-stage methods showed a rate effect in the one-stage method above 22X beyond which the increase of macroproperties of samples with draw ratio were lessened (i.e., modulus, crystallinity melting temperature).

The viscoelastic properties of HDPE samples showed a remarkably high storage modulus at high draw ratios (87 GPa). The distinction between the effects of one-stage and two-stage drawing methods on the properties of the samples is apparent in the dynamic mechanical measurements, although not readily discernible in the Young's modulus.

The SEM studies on strained superdrawn samples showed lateral cracks for which the number average size decreased with draw ratio.

X-ray integrated breadth studies of HDPE filaments showed that drawing results in an increase of weight average crystal sizes in the radial and also in the fiber direction. The Fourier analysis of these x-ray data also showed an increase in the number average crystal size in the radial direction with draw ratio. In addition, the root mean square strain in the samples was reduced; correspondingly, the a,b unit cell dimensions were decreased with draw ratio.

The application of paracrystallinity theory to the WAXS patterns showed that the number average size of microfibrils was not affected by deformation. On the other hand, the number average size of fibril clusters increased. While the microfibril perfection increased, the interfibrillar and intracluster paracrystalline domains originating from disordered amorphous regions showed a decrease of perfection due to the increase of sizes of paracrystalline domains.

The above findings indicate that the optimum drawing temperature for LDPE and HDPE is directly related to the chain mobility within the crystallites (α -transition). The HDPE samples showed that at the α -transition temperature, the "friction" between and within the microfibrils resulted in unfolding and orientation of chains in the draw direction. However, this friction decreased as the drawing temperature increased and was greatly reduced at 110°C. At this temperature, the refolding process dominates in the structure, resulting in a lowering of modulus values. Higher draw rates above the draw ratio of 22 resulted in greater crystal imperfections.

The HDPE samples drawn by the two-stage method show an increase of perfection and size with draw ratio. The crystallites comprise the main backbones of the drawn polymer, thus an increase in size and perfection results in improved mechanical properties. The results of the Fourier analysis and the Guinier-Warren-Hosemann analysis are found to be complementary in supporting these interpretations.

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CHAPTER I

INTRODUCTION

The polyethylenes (low and high density) are being widely used throughout industry due to their low cost and useful properties. Like most materials, the mechanical macroproperties (modulus, tensile strength, etc.) of polymers are primarily determined by the microstructure. Thus, the internal microstructure of polymers has been investigated extensively in the last two decades. However, the structure of polymers is still subject to controversy.

The main object of this thesis is to correlate the macroproperties (i.e., modulus, density) with the microproperties (i.e., crystal size, crystal perfection) of HDPE filaments. In this research, one-stage and two-stage uniaxial drawing methods were used to modify the microstructure, particularly with respect to unfolding and alignment of the covalently bonded chains. In the limit, the ultimate mechanical and physical properties will be achieved in a completely unfolded chain, perfectly crystalline filament. The degree to which the goal may be achieved by drawing methods, and the nature of the microstructure produced, is investigated in detail.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

A. MORPHOLOGY OF SEMI-CRYSTALLINE POLYMERS

Ever since the mankind began to use materials, scientists have tried to improve the properties of materials. One way to understanding of this properties is to study the internal structure, that is, micro-structure of the materials. In polymeric materials, generally properties strongly depend on the microstructure.

There have been models, in polymer science history, to elucidate the structure of semi-crystalline polymers. The earliest model known is the "Fringed Micelle" (13) which was later modified by many scientists. In this model, one section of a long polymer chain could pass through a crystalline phase, while remaining sections could pass through amorphous regions and then enter other crystalline regions. This model helped the scientists understand the Infra red and X-ray data of polymers and many macroscopic properties. The fringed micelle model is consistent with drawing behavior of polymers--to some extent; but, it was proven to be much too simple to represent the actual morphology of polymers. However, this model is still useful to analyze certain gross properties of polymers.

In 1957, Till, Keller and Fischer (33, 61, 125) proposed the folded chain structure in single crystals. In 1966 Dismore and Statton (29) combined the two theories for drawn nylon-66 fibers; but it was also inadequate to explain some of the mechanical properties.

Till, Keller and Fischer (33, 61, 125) found that chain folding in single crystals forms the so-called lamellae whose thicknesses of the order of 100-200Å and widths extending into micron range.

Later, Geil (36) and Peterlin and co-workers (89) studied complex single crystal structures. The lamella growth from solution and melt has been studied extensively by electron microscopy and small angle X-ray scattering methods. Several different folded chain structures may arise in crystallization depending on the environment as well as on the molecular weight and tacticity of the molecules (40, 74).

There are the three basic folded chain models,

1. Regular adjacent re-entry
2. Irregular adjacent re-entry (Loose loop)
3. Switch-board structure.

In the first two models, the chain re-enters the crystal adjacent to itself while in switch-board model the chain re-entry is random. The second model shows variations in the length of chain sections which are not in the crystal, and chain ends lie loosely on the surface (Loose loop). The first regular re-entry model represents the lowest free energy in a lamella crystal (Figure 1).

Achievement of regular adjacent re-entry structure of chains is restricted by nonuniform molecular weight and by the difficulty in controlling the crystallization environment. Inadequate chain mobility probably prevents the polymer from reaching the lowest energy level (Regular re-entry). The regular adjacent re-entry structure may be obtained by crystallization of polymer from dilute solutions under carefully controlled conditions. Generally, commercial semi-crystalline

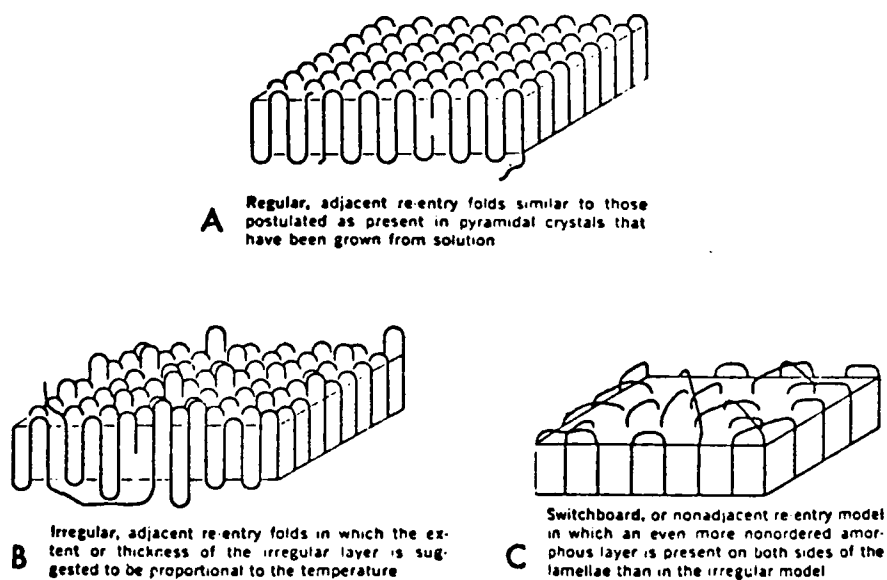


Figure 1. Models proposed for chain folding in single crystals of polymers.

polymers are produced in dense media by rapid crystallization; thus, it is speculated that the loose loop model is closest to the structure of these polymers. It was suggested (36) that the switch-board structure may be found in polymers which have very high molecular weight. The lamella structure plays a significant role on control of mechanical properties and deformation mechanisms.

Spherulite Structure

When the thin films of polymers are crystallized under a quiescent environment, they exhibit a characteristic structure called spherulitic. These spherulites consist of chain folded lamellae of narrow widths (ribbons) growing radially. The growth of spherulites takes place by a two stage mechanism (60, 127). In the first stage, lamellae grow but their diffusion into the surroundings is restricted by the high viscosity of melt. Thus, crystallization on the lateral surfaces of growing lamellae is restricted by the trapped segregated molecules. In the second stage of crystallization these segregated molecules crystallize between original fibers (lamellae), showing that the diffusion in spherulitic growth is important only on a localized level. These spherulites exhibit characteristic features--Maltese cross--under polarized light. These features help understand the internal structure of the spherulites.

B. DRAWING EFFECTS ON THE STRUCTURE OF POLYMERS

The structure changes during drawing of semi-crystalline polymers have been studied by many scientists. Peterlin et al. (90) suggest

that three stages of plastic deformation occur during drawing.

1. Plastic deformation of spherulitic structure,
2. Transformation of spherulites into fibrous structure by fracture of lamellae and formation of microfibrils,
3. Plastic deformation of fibrous structure.

Because of the composite amorphous and crystalline structure of semi-crystalline polymers, the stress and strain fields are inhomogeneous and anisotropic during deformation. In this composite structure the crystal lamellae act as force transmitters and amorphous layers between them are the main contributors to strain (90).

The plastic deformation of spherulites begins with lamella slip (95) and proceeds by rotation of stacked lamellae from perpendicular towards more parallel orientation with tensile stress (112). This early stage of plastic deformation of lamellae may involve twinning and phase transformation (37). The ability to deform a spherulitic structure depends on the conditions under which the sample is prepared. Large spherulites with coarse structure tend to promote brittleness as compared to finer structure when samples are drawn at temperatures which are too low for appreciable molecular motion during the experiment (Cold drawing). This behavior, presumably, is due to a greater number of tie molecules which interconnect both the lamellae and spherulites in finer structures. The transition from spherulitic to micro-fibrillar structure begins with tearing of the folded chain blocks about 90° and ends with rotation of these blocks into final fibrillitic structure.

The higher extensional strength and modulus of fibrillitic structure are due to increased number of tie molecules in the structure. Peterlin

and Meinel (77) suggested that interfibrillar tie molecules most likely originate from tie molecules connecting adjacent lamellae in the undeformed spherulitic structure. Since the number of tie molecules plays an important role on tensile strength of polymer. Perkins, Capiati and Porter (87) speculated that the higher the molecular weight, the greater the number of tie molecules is and thus the higher the tensile strength is.

The third stage of plastic deformation does not change the fibrous morphology (Peterlin's model (90)). Either microfibrils or the bundles of microfibrils slide past each other up to a point where the rapidly growing voids at the ends of macrofibrils and between the macrofibrils create sufficiently large critical cracks leading to sample failure. In the microfibrillar structure the lateral cohesion is relatively poor, so, in deformed thin layers of polypropylene (99) for example, one notices great many longitudinal voids created by separation caused by incomplete lateral coalescence of adjacent microfibrils or by separation caused by nonuniform straining of microfibrils. On the other hand, on the boundary between adjacent microfibrils, the van der Waal's forces are stronger with a crystal contact than with a crystal-amorphous layer contact. This, in the case of PP and PE, favors fit of crystal blocks of adjacent microfibrils to produce fairly well defined crystal lamellae more or less perpendicular to draw direction (90). In contrast, it seems that in PET structure, crystal blocks of adjacent microfibrils do not fit together. (97).

In 1973, Prevorsek et al. (96) proposed a new model for drawing behavior of nylon-6 and PET. This model is called the "SWISS CHEESE."

In the swiss cheese model, in contrast to the microfibrillar model of Peterlin, the fiber properties such as strength, diffusion and shrinkage force are determined by the matrix (extended chain domains) not by the dispersed phase. The microfibrils and dispersed phase primarily provide dimensional stability. The differences between the swiss cheese and the microfibrillar models are,

1. in the origin of interfibrillar tie molecules and their volume fraction change during drawing,
2. in the role played by the structure of microfibrils and the matrix in determining the fiber properties.

The microfibrillar model is based on the assumption that the interfibrillar tie molecules are formed primarily from the interlamellar tie molecules of spherulites, and that the mass of microfibrils does not change significantly during drawing. But, studies of Prevorsek et al. (96) indicate that with fibers of nylon-6 and PET drawn from amorphous or from low crystallinity precursors, the volume fraction of interfibrillar tie molecules increase with increasing draw ratio. The swiss cheese and microfibrillar models seems to be partly the result of the difference in the intermolecular binding forces. In the case of PE and PP, there are only Van der Waals' forces, but in nylon-6 there are hydrogen bonds between adjacent chains. In both models the tie molecules play a primary role in determining the tensile strength of fibers. Ward et al. (123) and Sheehan and Cole (104) determined that the higher the molecular weight, the greater the tensile strength. Extensional modulus seems to be independent of molecular weight above a critical value. Thus, to achieve high tenacity fibers, high MW is required. But, high MW is not

necessary for obtaining "Continuous Crystal" structure as discussed by Taylor (82); instead, narrow MW distribution seems to be necessary to achieve high modulus fibers.

C. VOID FORMATION DURING DRAWING

During cold drawing of synthetic fibers, void formation was observed by many investigators (99, 135, 124, 104). The void formation causes a density decrease in the fibers. It was concluded that the higher the draw ratio the greater the number of voids. Elongation of voids, caused by increased draw ratio, was interpreted from small angle X-ray scattering (SAXS) patterns by some authors (35, 91). In a recent study of Gorton et al. (35) on drawing of PP fibers, the extent of void formation was estimated from the overall volume increase which was calculated from diameter variations. They found that little volume change occurs at low strains for PP filaments having low orientation, but that increasing initial orientation is associated with increased void formation during drawing.

D. ANNEALING EFFECTS ON POLYMER STRUCTURE

The studies of Calleja and Peterlin (13) on PP showed that the long period in fibers increases with annealing temperature, and that the long period is not a function of the draw ratio (λ) or the initial long period of the microspherulitic structure. The effect of thermal contraction on structure and properties of PET fibers was investigated by Prevorsek et al. (97). They concluded that there are two types of amorphous domains; those separating the microfibrils and those separating

the adjacent crystallites in the microfibril. They speculated that molecules in these two domains respond differently to thermal effects and stress. Annealing of drawn fibers helps heal the voids in the structure resulting in higher tensile strength in the fiber (104). Anderson et al. (1) and Holden (46) reported that the melting point increases upon annealing of melt crystallized polymers.

E. EXTENDED CHAIN STRUCTURE

In the early years of polymer science, Carothers and Hill (17) proposed an extended chain structure to achieve high tensile properties in polymers. Later, many scientists tried to obtain this "CONTINUOUS CRYSTAL" structure by using several techniques some of which are presented in the following section. Thus far, no one has been able to achieve this structure by drawing because of chain folding phenomenon. Polymer scientists were attracted to this extended chain structure because of the outstanding potential tensile properties. Later, theoretical studies of linear straight chain hydrocarbon polymer were done by some scientists included Mark (75). He calculated the forces required to stretch the bonding angles between carbon-carbon bonds. The theoretical extentional modulus was found 244GPa (3.25×10^6 psi) lateral modulus $E=4$ GPa. Later, Sakurada and co-workers (101) used an X-ray diffraction method to obtain the limiting modulus experimentally. They also showed that the chains with helical conformation (PP) have lower extensional modulus than the chains with planar zig-zag conformation (PE).

F. TECHNIQUES FOR MAKING HIGH MODULUS FIBERS

The major goal of these various techniques is to unfold as many chains as possible and align them along one direction. Some of these methods are,

1. Solution spinning
2. Liquid crystal methods
3. Pressure extrusion of polymer melts
4. Drawing

Solution Spinning

This method has been used by Pennings et al. (140) for linear PE. A solution of PE in xylene is sheared to a critical level in a couette device at elevated temperatures. The critical speed was defined as a speed at which Taylor vortices occur in solution causing the formation of elongated crystals. The critical conditions are associated with extensional flow from a dead point at the growing fiber end (141).

Liquid Crystal Methods

In recent years, optically anisotropic dopes of polymers have become very important in the production of the high modulus fibers (136). This optically anisotropic dopes of liquid crystal nature are mostly aromatic, p-linked molecules which are rigid planar and polarizable.

The first process for producing fibers using polypeptide liquid crystals was developed by Ballard et al. (2). In this process the monomer, typically an amino acid and N-carboxy anhydride would be dissolved in a suitable solvent and polymerized. The resulting polymer

molecules would be in the form of the alpha-helix. The polymerization medium would then be wet spun into a coagulation bath to form a fiber which has the alpha-crystalline form. Then, drawing of these fibers converts the crystalline structure from alpha form to beta-extended chain form.

In 1968 Kwolek (68) discovered that p-liked aromatic polyamide solutions were nematic mesophases. She prepared an optically anisotropic poly(p-phenyleneterephtalamide) solution. This solution was then wet spun into a coagulation bath. Then fibers were washed and dried. These fibers had initial modulus of 171 g/den. and tenacity 5.3 g/den. It was found that fibers spun from optically isotropic solutions do not have high tensile properties. Later, Morgan and Pletcher (80) prepared optically anisotropic solutions of polyamides from fumaric and mesaconic acid. These fibers were produced by wet spinning into a coagulation bath. These fibers had 20.6 g/den. tensile strength, 4.6 percent elongation and 594 g/den. initial modulus. A heat treatment of the spun fiber greatly enhances the mechanical properties of aromatic polyamides.

Some aromatic polyesters also form mesophases (65,67). But, the properties of these fibers are not remarkable when compared to aromatic polyamides (i.e., PET (67) 196 g/den. modulus, 3.3 g/den. tensile strength, 5 percent elongation). In preparation of liquid crystals the concentration is very critical (68,2).

Pressure Extrusion of Polymer Melts

Highly oriented extrudate from the melt was discovered by Bowman (8) in 1968. In this method, capillary rheometer with conical entry

zone was used. While passing through the conical entry zone polymer chains become elongated. From investigations it was found that uniform elongational velocity gradient is difficult to achieve at high die angles specifically at the surface layer of the extrudate which limits the highest draw ratio in extrusion (6).

Porter and co-workers (15, 110, 134), later, modified the extrusion process. In one variation of this process, linear PE is extruded between 132°C and 136°C above critical shear rate. As extrusion proceeds, the driving pressure builds up and creates a significant amount of supercooling. Supercooling combined with the high elongational velocity promotes massive crystallization of the polymer in the capillary entrance. With this process PE fibers were produced having 70 GPa. modulus. This process is, however, not a continuous process and requires high pressure and temperature control.

At high degrees of orientation, the extrusion process provides better control over the final product dimensions than does drawing (138). The morphological structure of pressure extruded fiber is quite different from the superdrawn fibers. The center of pressure extruded fiber was found to be composed of more highly oriented material than is the skin of the fiber (93). In superdrawn fibers the orientation seems uniform throughout the crosssection (19, 85, 56, 124).

Drawing Methods

The tensile properties of polymers upon drawing because of the increased number of tie molecules between lamella blocks. The fully necked crystalline polymer which has microfibrils in the structure, is

still an order of magnitude below its ultimate strength; however, although the molecules are almost completely oriented, there are an appreciable number of chain folds in the structure (in lamella blocks) which function as built in defects.

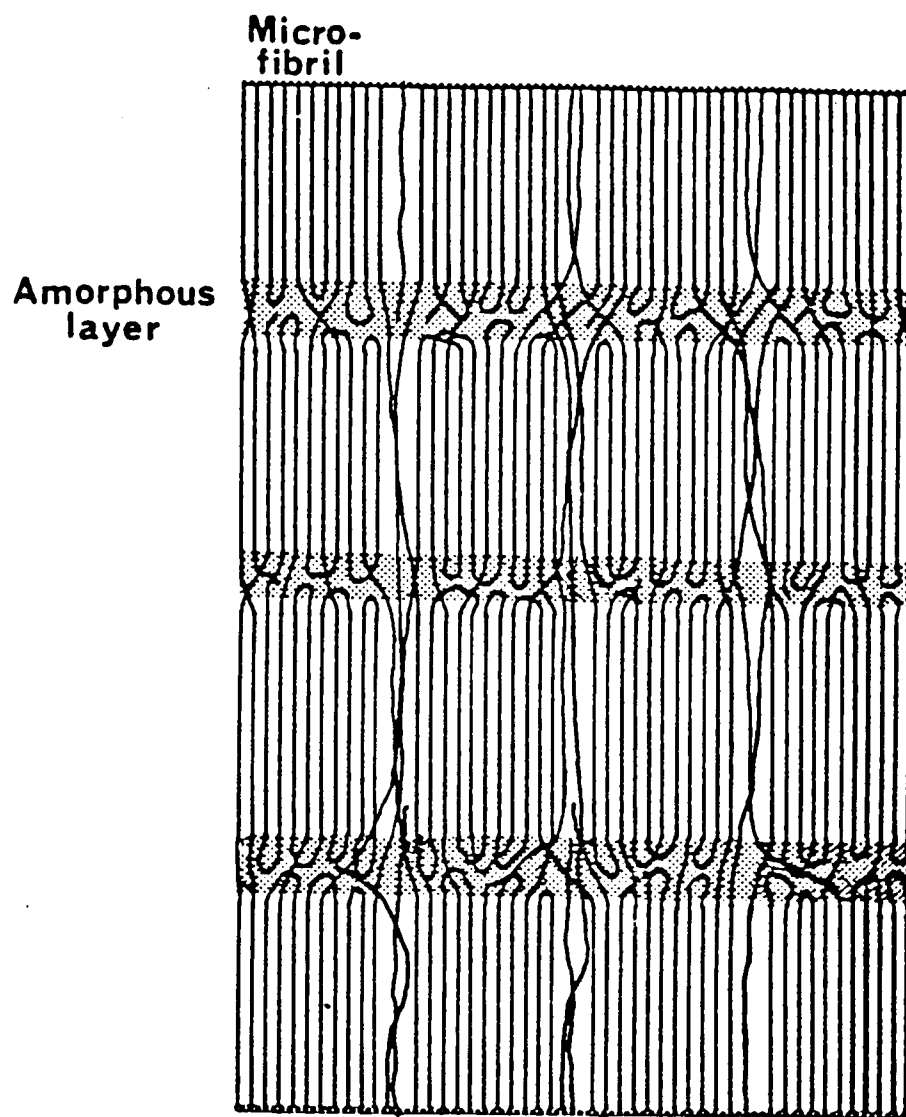
In 1964, Sheehan and Cole (104) obtained PP filaments with tenacities up to 0.95 GPa. by using single stage drawing. Some of their findings are as follow: At a given draw ratio the higher the MW the higher is the tenacity. Filaments with very narrow MW distributions have unusually high modulus values. The more the filaments are oriented during spinning, the lower are the tenacities of filaments.

In 1974, Clark and Scott (19) proposed a two step drawing process to eliminate the folded chains in the final fiber structure. Initially, the sample is drawn to its natural draw ratio (The draw ratio at which the neck fully disappears), then, the sample is slowly drawn to a final draw ratio at carefully controlled temperature and draw rate. They found that there is an optimum drawing temperature (α_c) (Crystalline dispersion temperature). It was suggested that at this temperature crystal properties change from purely elastic to viscoelastic (28, 53). Below this temperature the movement between chains will be, in effect, a creep phenomenon with finite strain rates resulting in fracture. At temperatures above (α_c) cohesion between adjacent microfibrils will be smaller and stress transfer for chain folds will be lessened. Clark and Scott (19) found that superdrawn acetal fibers have tensile strength of 1.7 GPa. and modulus of 35 GPa. Recently Joshi and Clark (56) were able to achieve 25 GPa. modulus and 1.2 GPa. tensile strength in superdrawing of acetal fibers of different molecular weight.

Ward and Andrews (129) found little evidence of sample temperature influencing the draw ratio. Their data indicate that for HDPE the draw ratio is minimum near alpha crystalline transition temperature. Cansfield, Capaccio and Ward (14) also used two-step drawing to produce high modulus films and fibers. They also found that there is an optimum drawing temperature to obtain high modulus for PP films and filaments. Their results show that final product (film) have 19 GPa. modulus at draw ratio of 18. It was suggested that modulus is independent of rate of deformation for PP films and filaments. Recently, Taylor and Clark (124) obtained PP filaments with 22 GPa. modulus and 0.92 GPa. tensile strength. They suggested that there are two competing mechanisms in superdrawing: a) Shearing displacement of microfibrils, b) Unfolding of chain fold blocks. Which mechanism will dominate is determined by temperature and draw rate.

The superdrawn fibers show a unique "Dead bend" property. Unlike most polymeric materials, under transverse force these fibers form a permanent bend (irreversible deformation) under high magnification, kink bands were observed in the deformed of the fibers. This dead bend reduce the modulus and tensile strength drastically (19,56,124). Finally, superdrawn polymer is characterized by a unique morphology in which a clear distinction between the crystalline and non-crystalline phase has disappeared ("CONTINUOUS CRYSTAL STRJCTURE") (Figures 2,3)

The effect of MW on tensile properties of superdrawn PE was investigated by Perkins et al. (87). They concluded that MW has little effect on modulus. The melting point, strain to break and tensile strength increased with the increase of MW. The thermal behavior of



NATURAL DRAW FIBER

Figure 2. Natural drawn fiber structural model.

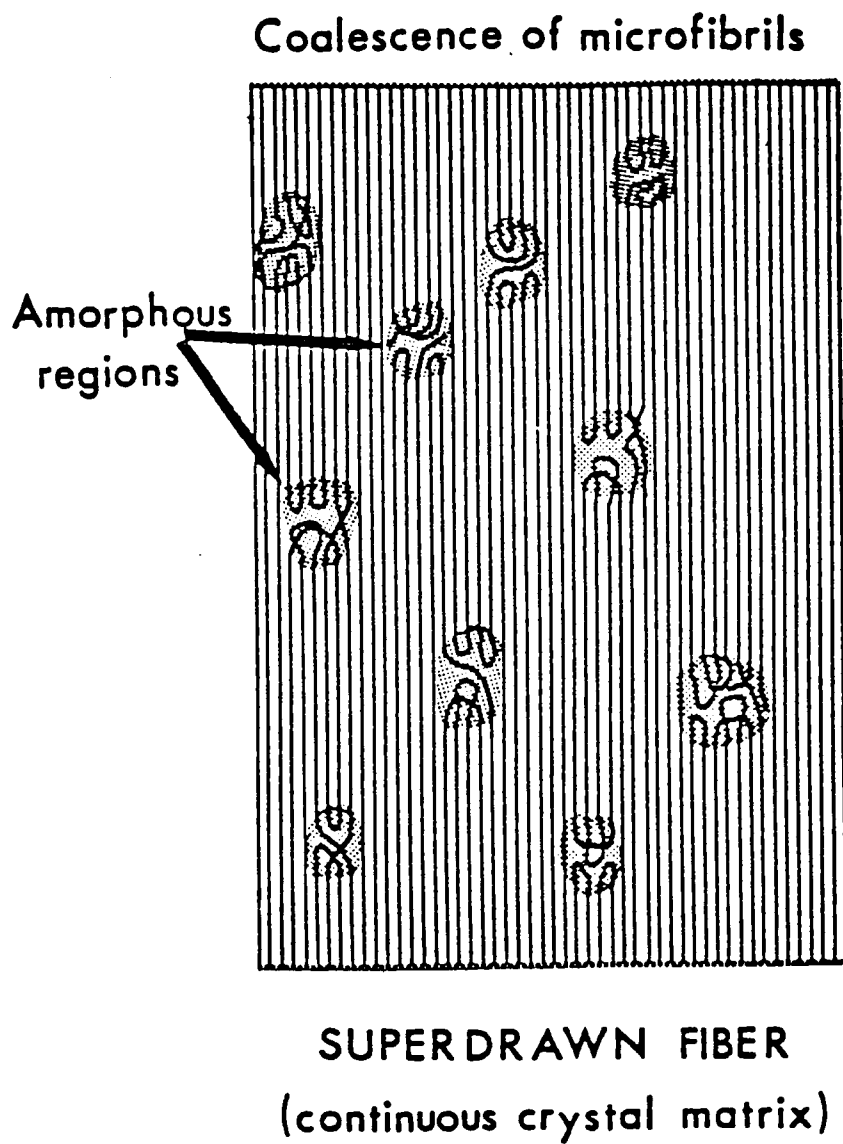


Figure 3. Superdrawn fiber structural model.

superdrawn PE was examined by Porter et al. (15). They found negative thermal expansion coefficient along c-axis which is consistent with extended chain structure. They also observed a magnitude change in thermal expansion coefficient between -35 C and -45 C for superdrawn polyethylene. Porter, Weeks, Capiati and Krzewski (94) observed this transition at -49 C, -52 C, -53 C for three less perfect polyethylene strands. Kim and DeBatist (64) found the break in expansion curve at -50 C for similar materials. This transition, as Porter and Capiati (15) suggested, might be attributed to the crystalline phase since it is also observed in related single crystals. Furthermore, they suggested that the thermal expansion be used to evaluate structural perfection in highly oriented PE fibers.

Transitions in Crystalline Polymers

Most organic polymers show a complex array of transition and/or multiple relaxation phenomena in addition to the classical glass transition and melting point. Isochronal measurements of complex modulus of crystalline polymers usually show the multiple transition such as the primary dispersion (α_a absorption) caused by initiation of microBrownian motion of molecular chains belonging to amorphous regions, the crystalline dispersion (α_c absorption) caused by internal friction within the crystalline region in highly crystalline polymers, and low temperature secondary dispersions. These dispersions change their relative intensities depending on the mechanical coupling of the crystalline region and amorphous region (A-C model) (120). Molecular chains under less restraint in the crystalline regions initiate their thermal motions at a lower temperature or at a shorter time (Higher frequency), while thermal motions

at a higher temperature or at a longer time. This means that the difference in the state of aggregation of molecules could be discussed by measuring the change of dispersion behavior. The temperature dependence of relaxation time or activation energy for relaxation and the shape of relaxation spectrum give us the basis for a more detailed discussion on the state of aggregation of molecules.

Transitions in Isothermally Prepared Single Crystals. Crystalline absorption of a single crystal mat is affected by the morphological features of the crystal and its perfection. Takayanagi (121) et al. prepared single crystals of PE of different long period (L) under isothermal crystallization. It was found that intensity of crystalline absorption increases systematically with L and dispersion temperature shifts towards the high temperature side with increasing lamellar thickness. The average relaxation time ($\bar{\tau}$) shifts towards longer relaxation times with increasing lamellar thickness. This tendency will be qualitatively understood by considering the corresponding modes of torsional motion of molecular segments constituting different lamellar thickness. A more elaborate theory based on the above considerations has been developed by Okano (84).

Transitions in Annealed Single Crystals. It is well known that single crystals of PE thicken by heat treatment above their crystallization temperature (36). With increasing lamellar thickness, caused by annealing, the crystalline absorptions of samples shift to the high temperature side in the same way as in the case of the isothermally crystallized samples. However, the absorption intensity of crystalline dispersion (E'')

of annealed samples decreases with increasing thickness contrary to the case of isothermally crystallized samples. Takayanagi (121) suggested that maximum crystalline dispersion temperature is primarily determined by the thickness of the crystal with almost perfect regularity; on the other hand, the absorption intensity $E''_{\max} (\alpha_c)$ is determined by the quantity of the crystal of the thickness L . If so, the quantity of such a perfect crystal with thickness L should be decreased by increased annealing temperature. However, Holland (47) found that the Moire pattern of the annealed single crystal of PE has considerable distortion indicating that the concentration of dislocations is increased by a factor of 1,000 compared with that of the original crystal. Thus, it is concluded that the decrease in the intensity of absorption curves is due to the increased number of defect regions in the crystal.

Transitions in the Bulk Crystallized Polymers. The morphology of the bulk crystallized polymer is considered to be composed of the spherulitic lamellae and amorphous region filling interlamellar space. Above the glass transition temperature the bulk crystallized samples resembles in some aspects the high impact plastics which are composed of rubber particles dispersed in a matrix of hard polymers. The high impact interpolymer resin shows the rubber absorption at the low temperature and plastic absorption at the high temperature of its dispersion curve. In the bulk crystallized polymer the primary absorption (α_a) and the crystalline absorption (α_c) can be observed in this dispersion curve as if the amorphous region and the crystalline region correspond to the rubber and to the plastic phase of the interpolymer respectively.

As mentioned before, in bulk crystallized PE structure, there are spherulites which are composed of stacked thin plate-like crystals (lamellae) which are very similar in their structure to the single crystals except an existence of tie molecules between neighboring lamellae in spherulite. Dynamic mechanical experiments on bulk crystallized samples revealed that these samples resemble the annealed single crystals in the shape of their dispersion curves. Compared to the dispersion curves isothermally crystallized single crystals, the lamellar phase of spherulites include a somewhat large defect region by which the intensity of the crystalline absorption is largely decreased. The same relation can be found in the absorption curves of poly--(oxymethylene) between the samples of single crystal mats and bulk crystallized film (122).

Detailed investigations of a absorption of HDPE revealed that there are two overlapping mechanisms in this transition (57). These transitions are called α_1 (α') and α_2 (α). Activation energies characterizing these dispersion mechanisms were evaluated to be ca.30 KCal./mol. and 50 KCal./mol. for α_1 and α_2 transitions respectively. (Kajiyama et al. (57) found 31 KCal./mol. and 46 KCal./mol. for the same transitions.) But, on the nature of these mechanisms opinions are divergent among the investigators. Expecially, the opinions are sharply divided as to whether the α_1 dispersion is related with the molecular motion in an amorphous phase or not. Some authors maintain that the α_1 dispersion is caused by the relaxation behavior of the mixture of crystallites and amorphous phase existing between them as "Grain Boundaries." In this case the amorphous phase plays an essential role for the nature

of the relaxations. In 1966, Hideshima (44) investigated the HDPE (Sholex 6009) with and without diluent treatment. They measured shear creep compliances with torsion creep instrument. It was found that only the α_2 dispersion was not affected by the presence of diluent. As for the other dispersions including α_1 dispersion the intensities were enhanced and the retardation times were reduced by the presence of the diluent. In consideration of the well-known fact that the diluent can only diffuse into the amorphous phase of crystalline polymers, the α_1 dispersion must evidently be related with an amorphous phase and is essentially different from the α_2 dispersion which can be explained satisfactorily as caused by the molecular motion in the crystalline phase.

Nature of α_1 Mechanism. This α_1 dispersion appears on the higher frequency side of the α relaxation. In 1961 Nakayasu et al. (81) separated this α_1 from a peak. The nature of α_1 mechanism is still subject to argument. Takayanagi (121) suggested that the α_1 mechanism be attributed to deformation processes occurring in the intramosaic block regions, activated by rotational or translational motion of chains. These molecular motions of chains in the intermosaic block regions seem to be easily induced by reduced potential barriers arising from molecular field distortion imposed by external force. This is supported by the result that the peak maximum (E'') of loss modulus increases with increasing magnitude $\bar{D}_{100}^2/L$ and η_2' (viscosity associated with the intermosaic regions).

Nature of α_2 Mechanism. There is almost total agreement among investigators (122, 120) that α_2 mechanism in HDPE arises from

motion in the crystalline regions. This is supported by the observed dependence of maximum relaxation time and the peak maximum of loss modulus (E'') with respect to the average crystallite size along the chain axis ($\bar{D}_{001}$).

Studies on Oriented and Annealed Samples. Takayanagi and co-workers (120) did an extensive study on annealed oriented PE, PP, PTHF, PEO and POM fibers. Orientation was given to fibers either by drawing or by rolling. SAXS pattern studies showed that after orientation heat treatment caused unification of microfibrils to huge fibrils. They used 100c/s. frequency in their studies of fibers. It was observed that the modulus (E'_0) along the fiber axis is higher than that of the perpendicular direction (E'_1) below the primary absorption temperature (α_a), they intersect at this temperature and above this temperature the modulus along the fiber axis (E'_0) becomes lower than the perpendicular one (E'_1). This phenomenon was observed for drawn annealed PP and PTHF fibers. The primary absorptions of HDPE and POM and their intersecting temperatures are not clear; but, they are considered to be location at around the temperatures of latent primary absorption (7). This relationship of E'_0 and E'_1 is considered to be general for oriented polymers with well established crystalline texture. The α_c crystalline dispersion temperatures are found to be 70-90° C for HDPE, 140° C for PP ($a_a = 0$ C), 150 C for POM (Figure 4 and 5).

The structural and mechanical model of Figure 4 and 5 is satisfactory to reproduce the viscoelastic properties of drawn and annealed polymers. However, there are some difficulties in interpretation with this model. The

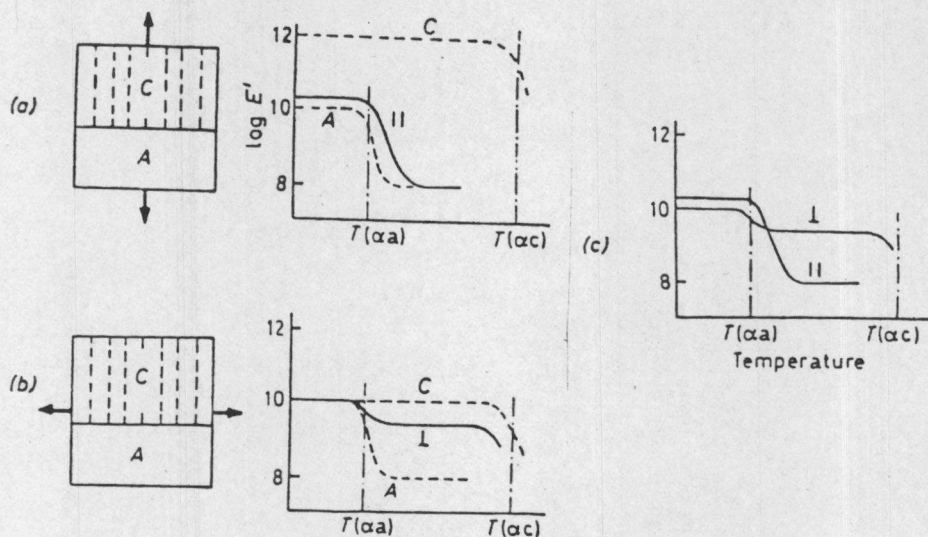


Figure 4. Schematic representation of dispersion curves of E' (solid lines) in parallel direction (a) perpendicular direction (b) to the draw direction; part (c) represents the difference between the dispersion curves of the parallel direction and perpendicular direction.

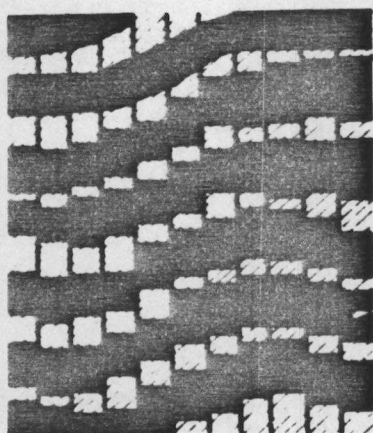


Figure 5. Structural model of hot-stretched linear polyethylene presented by Hoseman (50).

value of E' of the 0 direction does not fall as far above the α_a absorption temperature. Even in the 0 direction the crystalline dispersion clearly exists. These two factors cannot be interpreted by simple AC mechanical model shown in Figure 4. In order for the α_c to appear in the sample of the 0 direction, the C element must be connected in parallel with A element and then this AC parallel model is connected in series with the C element. Thus, the model shown in Figure 6 should be employed instead of the model shown in Figure 4. It was assumed that $E_c(II) = 10^{12}$ dynes/cm²., $E_z = 10^8$ dynes/cm² at $T > T_g$. Even for small parallelism ($1-\lambda = 0.01$) the contribution of this part to the modulus of whole system rapidly increases to give the value of modulus of the whole system $E = 10^{10}$ dynes/cm². This value is much higher than the value derived for the simple AC series model ($E = 10^8$ dynes/cm²).

$$E^* = \left(\frac{\phi}{\lambda E_a + (1-\lambda) E_c^*} + \frac{1-\phi}{E_c^*} \right)^{-1}$$

From above considerations, it is required that the A region of Hosemans microfibril must be more or less interrupted by the small C region along the 90 direction.

The model shown in Figure 7 successfully interprets the appearance of the crystalline absorption (α_c), and this model allows existence of the continuous C region along the 0 direction. Lack of registry of two neighboring A regions belonging to the neighboring ultrafibrils is expected to play the same role as the interruption of C regions across the continuity of the A region. However, the structure with discordance of the A regions does not give sharp a meridional spot in SAXS patterns

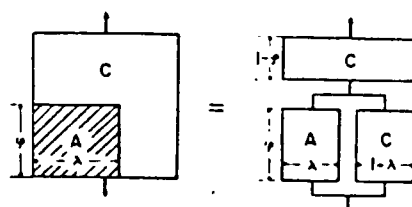


Figure 6. Mechanical model for interpreting the viscoelastic behaviors of crystalline polymer. Elements A and C correspond with the amorphous and the crystalline region respectively. The value of $\alpha\phi$ is equal to the volume fraction of amorphous region (120).

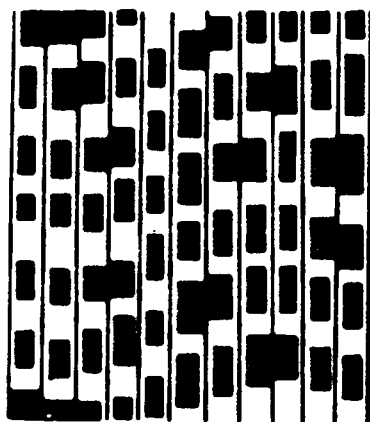


Figure 7. Structural model for drawn polymers suggested by Takayanagi (120).

as observed in drawn and annealed PE and PP. This structural model seems to satisfy both the results of structural measurements of the drawn and annealed polymers.

G. COLD DRAWN POLYETHYLENE AND POLYPROPYLENE

For these samples it was shown that the E' value along the 0 direction gives a higher value than the 90 direction over entire temperature range including the primary dispersion temperature (α_a). It was also observed that absorptions of PP so much broadened and overlapped that they cannot be separated by the fact that the crystalline absorption α_c shifts to a lower temperature and primary absorption (α_a) shifts to higher temperature in drawing the crystalline polymer at low temperature (123). SAXS studies of cold drawn PE revealed that the distribution of the diameter of microfibrils is broad and extends to the thin microfibril. The radial broadening of the meridional small angle reflection indicates the irregularity of the distance between the A and C regions within the fibril. The fact that the intensity distribution parallel to the equator along the meridional reflection is diffuse suggests irregularities in the arrangement of the A regions among ultrafibrils. The model shown in Figure 8 proposed for the structure of cold drawn PE and PP (50).

The α -relaxation studies of Kajiyama et al. (57) on HDPE revealed that the peak maximum of the α_1 mechanism (E''_{1max}) decreases with increasing temperature of measurement; on the other hand, that of α_2 mechanism (E''_{2max}) remains constant up to 70° C. This temperature was found to be optimum superdrawing temperature (85).

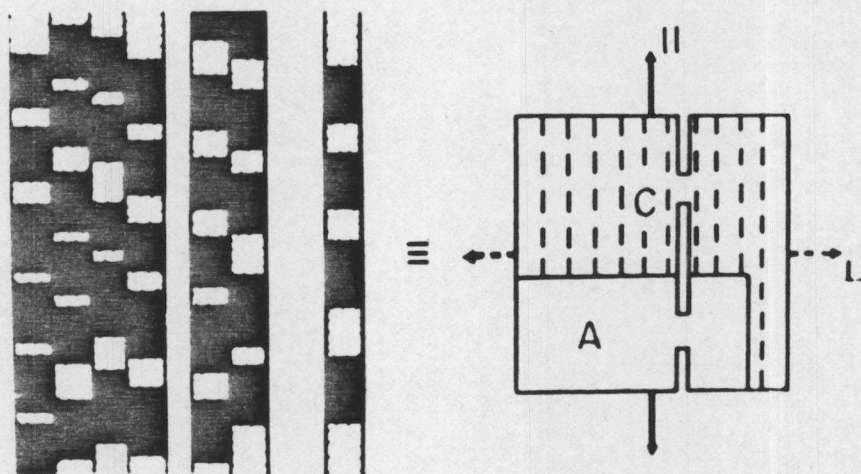


Figure 8. Structural model of cold drawn linear polyethylene presented by Hoseman (50) which is composed of split microfibrils with different diameters (b) mechanical model corresponding with the structural model in (a).

H. RELAXATIONS IN LOW DENSITY POLYETHYLENE (LDPE)

Low density polyethylene exhibits three characteristic relaxation peaks, namely α , β and γ . The first measurements of internal friction of dynamic modulus in LDPE were published in 1953 by Schmieder and Wolf (103) who studied the properties of the loss peaks as a function of chlorine content in chlorinated samples. At low chlorine concentrations the principal effect of chlorine atoms is to lower the density. The α peak ceases to exist in the samples with chlorine content of about 40 percent wt. and above. As no X-ray crystalline reflections are observed for these samples, Schmieder and Wolf concluded that the α relaxation is directly related to crystallinity of the sample. In 1954, Oakes and Robinson (83) studied the LDPE samples and concluded that β relaxation is due to side-chain activity because this relaxation is absent in HDPE. They found that activation energies corresponding to α and β relaxation were 40 KCal/mole and 30KCal/mole respectively. The effect of branching on the α and β peaks was studied by Kline et al.(66). The height of the β -relaxation peak increased with increasing branching, whereas the position of the α -relaxation shifted to lower temperatures with increasing branching. Neilsen (83) found that the peak position of the α -relaxation is related to the length of the crystallites. Therefore, in a material rapidly cooled from the melt, the α -relaxation temperature is lowered because the crystallites formed are smaller than those formed when the material is cooled slowly. The effect of cold drawing was studied by Hellwege et al. (42). They found that damping peak in tension had different values along the draw direction and along the transverse

direction. This "transverse anisotropy behavior of LDPE was modeled by Stachurski and Ward (111). The experiments done by Stachurski and Ward revealed that α -relaxation peak lays between 20-40° C depending on the sample preparation conditions. Since it is believed that the α -relaxation peak temperature is optimum for drawing of semi-crystalline polymers, the effect of temperature on mechanical properties of drawn LDPE is investigated in this research.

I. DYNAMIC MECHANICAL BEHAVIOR OF ULTRA-HIGH MODULUS LINEAR POLYETHYLENES

The theoretical upper limit of moduli for polymers are comparable to those of metals. Sakurada and co-workers found that (100) theoretical modulus of HDPE is 240 GPa. Weeks and Porter used solid state extrusion to produce high modulus polyethylene (134). The dynamic mechanical studies on their samples showed 70 GPa (E') modulus at room temperature at 110 cps. This modulus value decreased with increasing measurement temperature and remained above 10 GPa. up to 120° C. They attributed this retention of strength and dimensional stability at high temperatures to the presence of a thermally stable reinforcing component (extended chain crystals). They also found that E' increases with the increase of draw ratio at room temperature. They used a composite model which comprises extended chain crystals and sheaths consisting of other highly oriented crystals to relate the modulus to morphology of the solid state extruded specimens.

In 1975, Smith et al. (105) investigated highly drawn sheets of polyethylene by a specially designed apparatus at 20 Hz. Their samples

exhibited 80 GPa (E') at the draw ratio of 30. The intensity of α transition decreased with the increase of draw ratio. This could be attributed to reduction in the fraction of disordered regions. NMR broad line studies showed a decrease in the proportion of noncrystalline material in samples as the draw ratio increased. The modified series model showed consistency with the data they obtained over the temperature range from -160°C to -60°C .

J. DETERMINATION OF CRYSTALLITE SIZES FROM INTEGRAL BREADTH

If the crystallites making up the specimen are sufficiently small, the maxima of diffraction pattern are broadened by an amount inversely proportional to the crystallite size and measurement of additional broadening thus gives a means of estimating the size through Scherrer formula (102)(1).

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where L is apparent crystallite size λ is the wavelength and β (Breadth) is additional broadening in radians, and K is Scherrer constant which depends on the definition of "breadth" the crystallite shape and crystallite size distribution (Appendix A). One of the definitions of breadth is integral breadth concept which was first introduced by van Laue (71) (2);

$$\beta = \frac{\int I(2\theta) d(2\theta)}{I_{\max}} \quad (2)$$

Later, Stokes and Wilson (113) obtained the general equations for K Scherrer constants for simple crystallite shapes (Tetrahedron, Octahedron, Sphere etc.) for cubic system. As suggested by Langford et al. (69) h, k, l parameters may be replaced by direction cosines to use these general equations for other crystal systems such as orthorhombic.

K. A STATISTICAL APPROACH IN DETERMINATION OF CONTINUITY OF THE CRYSTALLINE PHASES

In 1978, Gibson et al. (39) proposed a statistical approach in determination of continuity of crystalline phases by the use of SAXS and WAXS techniques. Their theory is as follows:

Consider a chain within the crystalline phase and let p be the probability that this chain will traverse the disordered region to enter an adjacent crystallite. p therefore represents the area fraction of intercrystalline bridge material which traverses the disordered layer. The probability that a particular crystalline sequence will kink n blocks is then:

$$f_n = p^{n-1}(1-p) \quad (3)$$

since the sequence must traverse $n-1$ boundaries and fail to traverse one boundary. f_n also represents the number-fraction of crystalline sequences which link n crystallites.

The weight fraction of chains, F_n , which link n crystallites can be obtained by multiplying f_n by the sequence length and renormalizing. If the thickness of disordered region is xL then the length of a chain linking n crystallites is $(n-x)L$, and F_n is given by:

$$f_n = \frac{(n-x)Lf_n}{\sum_{n=1}^{\infty} (n-x)Lf_n} = \frac{(n-x)p^{n-1}(1-p)^2}{1-x(1-p)} \quad (4)$$

Since the integral breadth of the 002 reflection essentially measures a weight average chain length then:

$$\bar{D}_{002} = \sum_{n=1}^{\infty} (n-x)L \quad (5)$$

if we assume $X \ll 1$ (small disordered domains) then equations (4) and (5) simplify to:

$$F_n = np^{n-1}(1-p)^2 \quad (6)$$

and

$$\frac{\bar{D}_{002}}{L} = \frac{1+p}{1-p} \quad (7)$$

After rearrangement,

$$p = \frac{\bar{D}_{002} - L}{\bar{D}_{002} + L} \quad (8)$$

where $\bar{D}_{002}$ obtained from integral breadth of 002 planes by WAXS method

L = Long period obtained from SAXS method. This p value varies from zero for a sample with a perfect series arrangement of phases up to unity for a perfect crystals.

L. VARIATIONS IN THE UNIT CELL DIMENSIONS

POLYETHYLENE

The crystal structure of polyethylene has long been known to be essentially that of orthorhombic n-paraffins (11). The orthorhombic unit cell dimensions of a given polyethylene are not unique, but depend on the physical history of the samples. Eby and co-workers (22, 23, 24) extensively investigated the effect of crystallization conditions, annealing and deformation on the unit cell dimensions of solution crystallized and deformation on the unit cell dimensions of solution crystallized and melt-crystallized polyethylene and n-paraffins. They found that for undeformed solution grown crystals the changes in a, b dimensions of unit cell correlate with the reciprocal of crystal thickness but for deformed crystals the changes occur before the thickness increases (even below crystallization temperature). The dimensions were found to undergo the greatest change within the first 2 min. of annealing and change very little with time thereafter. They also observed similar effects when crystals, grown from the melt by slow cooling and quenching, are annealed at temperatures from 60-127° C. In these crystals, unit cell dimensions correlated well with the reciprocal of the long period and extrapolate to values of $7.372\text{\AA}$ and $4.933\text{\AA}$ for a and b respectively at infinite long period (23). The studies of the effect of temperature on unit cell dimensions (22) revealed that at low temperatures unit cell dimensions are independent of lamella thickness but at higher temperatures the basal area of the cell varies linearly with the reciprocal of the thickness. Swan (116) found an increase in the unit cell dimensions of polyethylene as the concentration

of chemical imperfections such as methyl branches increased possible origins of changes in unit cells. The origins of the changes in the unit cell dimensions are mainly due to effect of folds and, interior defects, crystal size and strain in the crystals.

Effect of Folds

Basset (3) showed that the specific interactions of folds cause a change of spacing of fold planes and therefore of other planes in solution grown crystals. Thus, it might be expected that changes in the structure of folds and fold surfaces would alter the interactions of the folds and change the unit cell dimensions. Various kinds of changes in the fold surfaces and their effect, on the unit cell dimensions are discussed in detail by Eby et al. (23). They speculated that all surfaces effects have smaller influence on the unit cell dimensions as the long period increased.

Effect of Interior Defects, Crystal Size and Strain

It was found by Huang (52) that point defects affect the unit cell dimensions. Thus point dislocation (Reneker defects) (98) and interior vacancies could contribute to the changes in the unit cell dimensions. It is possible to determine the crystal perfection by measurement of line broadening. Eby (23) qualitatively observed that the WAXS lines becomes sharper with increased crystallization temperature, annealing temperature and annealing time, indicating higher crystal perfection and size.

The variation of cell dimensions with n-paraffins has also found to be similar to that of melt crystallized polyethylene (128). Eby (24) studied n-paraffins and linear polyethylene and concluded that linear

dependence of unit cell dimension on reciprocal long period has a different slope for n-paraffins and melt crystallized polyethylene. Since the dependence on long period indicates a surface effect, these differences probably represent the differences between methyl interactions on the surface, fold interactions, different fold planes etc. They further concluded that some of the latter surface characteristics affect the thermal vibrations and thus influence the cell dimensions (9). According to Eby et al. (24), it is probable that steric effects such as fold packing also change the cell dimensions directly through lattice distortions. They further suggested that interaction of molecules at the surface of the crystal is not as important as the length of the molecular stems between the folds affecting the cell dimensions.

M. LINE PROFILE ANALYSIS

The X-ray wide angle peak profile observed in diffractometry is directly related to the emission profile of X-ray tube target. This emission profile is distorted by the instrument design, physical effects and the diffraction profile nature of the crystals which are making up the specimen. This distortion effect can be considered as taking intensity from one position and redistributing it within an angular range. Mathematically this process is called folding of functions. If the observed profile is represented by $h(x)$, it is the product of the folding of instrumental profile $g(x)$ and the sample profile $f(x)$ after correction for physical effects such as absorption. The following expression represents the folding operation,

$$h(x) = \int f(y) g(x-y) dy \quad (9)$$

where the range of integration extends over all values of y for which f and g are nonzero. The ranges for the emission profile and for the diffraction profile are, however, "infinite."

The shape and breadth of the pure profile f are determined both by the mean crystallite size or distribution of sizes, characterizing the specimen, and by the particular imperfection, prevailing in the crystalline lattice.

There are two steps to be taken in the analysis of line profiles:

1. Extracting the pure diffraction profile (f) from the profiles of suitable lines of the pattern (namely multiple orders of the same reflection).
2. Extracting size and strain parameters from this pure profile

Extraction of the Pure Line Profile

Since all of the profiles are affected by angular and other factors, they should be eliminated before actual separation of the pure profile.

Analysis, then, proceeds by an unfolding process which separates the pure diffraction profile (f) from the original observed line (h). The most important limitation in the process of line profile analysis is the use of finite limits in equation (9). If the limits are kept narrow, the results of this analysis becomes unreliable as will be covered in discussion section. However, in this unfolding procedure a standard profile (8) is required. This profile should carry only information due

to the instrumental broadening. Some of the characteristics required from standard sample are as follows:

1. The standard should have large crystal (like)s i.e., above 500-700Å°.
2. There should be no residual macro (or micro) strains in the sample (if present, strain drastically increases the breadth of the profile).
3. The standard should have a crystallite structure similar to the sample being investigated.
4. The standard and sample should have similar absorption characteristics.
5. The standard should have the same shape as the specimen.

In metals, simply by annealing the original sample, one obtains the standard sample. However in polymers, the annealing process still does not provide satisfactory characteristics to the polymer, mainly due to the semi-crystalline (crystalline-amorphous) morphology. To overcome this problem other alternative crystal structures were investigated by several researchers dating back to early 1960's. For example, Buchanan and Miller (10) used hexamethylene tetramine as standard for isotactic polystyrene line profile analysis. Katayama (59) used potassium iodide for line profile analysis of high density polyethylene, even though KI does not meet the fourth condition (absorption) mentioned above. However, they corrected the standard profile for absorption before using it for instrumental correction. In brief, the standard profile should not be broadened other than by instrumental effects.

Determination of Pure Diffraction Profile

The pure diffraction profile may be obtained by deconvoluting the observed broadened profile (h) with the structurally unbroadened standard profile.

There are two widely used methods which are available for deconvolution processes:

1. Stoke's Correction (114) Fourier transferring the two observed and standard profiles, dividing the transform of the observed profile by that of the standard, and transforming the ratio from reciprocal space to real space.
2. An iterative method based on the repeated convolution of observed and standard profiles (31, 32).

The fourier method is best adapted to well resolved profiles even in the broadened pattern (i.e., metals). The second iterative convolution method seems to be suitable for samples having very high broadening in their X-ray lines.

These relatively powerful methods were formerly of little practical value because of extensive and tedious computations involved, but today, because of the general accessibility of digital computers, they comprise essential tools for deducing numerical crystallite-size and lattice strain parameters with optimum absolute significance.

Fourier Analysis

One of the most elaborate techniques used over the last three decades is fourier analysis of line profiles. This techniques was first proposed by Warren and Averbach (130) and was applied mainly to metals

(especially cold worked) (130). The fourier analysis was not applied to polymers until the mid-1960's. This delay is due to the fact that line profiles of polymers are more complex than those found in most metals primarily due to the frequent overlap of adjacent peak profiles which creates difficulties in the calculation processes.

Application of fourier transform methods on metals started in the early 1950's. Warren and Averbach (130) studied cold-worked metals and found that root mean square ($\langle \epsilon^2 \rangle^{1/2}$) values averaged over lengths (na_3) decrease for increasing length (na_3) over the direction normal to the diffracting planes. This latter behavior indicated that strains are nonuniform in cold worked metals. They also indicated that if several orders of given plane are available, it is theoretically possible to obtain the distribution function of the strains directly from Fourier transformation. This technique is explained in detail in Appendix C. Some other applications of fourier techniques were done on supported metal catalysts by Pausescu et al. (86) and on cold worked thoriated tungsten by M. McKeehan and B. E. Warren (78). These latter authors also concluded that strains are slowly decreasing function of distance from an arbitrary origin (L) after a sharp increase at the origin. In 1961 Katayama (59) used the fourier technique to investigate the effect of annealing and deformation in HDPE. He separated the crystallite size and strain distortions of 110 and 220 peaks using Halls equation in Cauchy form. His results showed that crystallite size changes considerably with annealing but mean strain does not change considerably.

The first detailed study of the application of this method to polymers was made by Buchanan and Miller (10). They applied several other techniques to line profiles of isotactic polystyrene in addition to fourier analysis. Isotactic polystyrene has, as is in a typical polymer, overlapping X-ray line profiles, but its advantage to other polymers is its structure which allows several orders of the same diffraction peak to be observed. This latter characteristic is one of the main requirements of the fourier technique. They assumed the peak profiles were symmetric about their maxima, and then resolved the overlapping tails by trial and error. Their hexamethylene tetramine standard provided diffraction peaks close to these of isotactic polystyrene. This latter condition is also important in the fourier analysis. Since the standard peak should be broadened only by instrumental effects, and since the instrumental broadening increase, with the increase of diffraction angle (30) the peak to be used as standard for a particular polymer peak needs to be close to it (2-6°). Otherwise, the instrumental broadening will be overcompensated (higher angle) or undercompensated (lower angle).

N. THEORY OF FOURIER ANALYSIS

Extracting the Pure Diffraction Profile

As stated in a previous section (106, 114, 45) equation (9) represents the mathematical convolution relationship among $h(\epsilon)$, $g(\epsilon)$, $f(\epsilon)$. Let the fourier transforms of these be $H(\zeta)$, $G(\zeta)$, $F(\zeta)$ respectively. By application of Fouriers integral theorem it can be shown that,

$$F(\zeta) = \frac{H(\zeta)}{G(\zeta)} \quad (10)$$

and furthermore

$$f(\epsilon) = \frac{1}{\sqrt{2\pi}} \int F(\zeta) \exp(-2\pi i \epsilon \zeta) d\zeta \quad (11)$$

Variables ϵ and its auxillary ζ denote any appropriate angular scale on which the reflection may be portrayed such as 2θ

and .'. .

$$f(\epsilon) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \frac{H(\zeta)}{G(\zeta)} \exp(-2\pi i \epsilon \zeta) d\zeta \quad (12)$$

if we use the exponential form of Fourier integral, generality is preserved, and thus integrals becomes applicable to asymmetrical as well as symmetrical function.

Since, in practice, the line profiles are finite rather than infinite, the limits are changed from $\pm \infty$ to $\pm 1/2 \epsilon_m$ the minimum values of ϵ beyond which the intensity can be considered to have fallen to its background value.

The above (12) equation then becomes

$$f(\epsilon) = \frac{1}{\sqrt{2\pi}} \int \frac{H(\zeta)}{\epsilon_m G(\zeta)} \exp\left(\frac{-2\pi i \epsilon \zeta}{\epsilon_m}\right) A \zeta \quad (13)$$

The constant factors, $1/\sqrt{2\pi}$ and $1/\epsilon_m$, which affect only the height of the profile rather than its shape, can be neglected in practice.

This, then, gives,

$$f(\epsilon) = \frac{H(\zeta)}{G(\zeta)} \exp\left(\frac{-2\pi i \epsilon \zeta}{\epsilon_m}\right) \quad (14)$$

$$H(\zeta) = \sum_{\epsilon} h(\epsilon) \exp \left(\frac{2\pi i \epsilon \zeta}{\epsilon m} \right) \quad (15)$$

$$G(\zeta) = \sum_{\epsilon} g(\epsilon) \exp \left(\frac{2\pi i \epsilon \zeta}{\epsilon m} \right) \quad (16)$$

Since

$$e^{iz} = \cos z + i \sin z \quad (17)$$

Then the series obtained above can be expressed in real and imaginary terms,

$$G(\zeta) = \sum_{\epsilon} g(\epsilon) \cdot \cos \left(\frac{2\pi \epsilon \zeta}{\epsilon m} \right) + i \sum_{\epsilon} g(\epsilon) \sin \left(\frac{2\pi \epsilon \zeta}{\epsilon m} \right) \quad (18)$$

The first term on the right side is real (G_r) and second part is imaginary (G_i)

Then

$$G(\zeta) = G_r(\zeta) + i G_i(\zeta) \quad (19)$$

This above is the fourier transform representation of standard peak. For observed peak of the original sample can be expressed in the same form

$$H(\zeta) = H_r(\zeta) + i H_i(\zeta) \quad (20)$$

Then Stokes correction can be realized,

$$F(\zeta) = \frac{H(\zeta)}{G(\zeta)} = \frac{H_r + i H_i}{G_r + i G_i} \quad (21)$$

Then multiplying by the complex conjugate of denominator we obtain

$$F(\zeta) = \frac{(Hr+iHi) (Gr-iGi)}{Gr^2 + Gi^2} \quad (22)$$

$$Fr(\zeta) = \frac{HrGr+HiGi}{Gr^2+Gi^2} + i \frac{HiGr-HrGi}{Gr^2-Gi^2} \quad (23)$$

Then to obtain the desired pure diffraction profile the inverse Fourier transform of this above equation (23) is taken

$$f(\epsilon) = \sum_{\zeta} F(\zeta) \exp\left(\frac{-2\pi i \epsilon \zeta}{\epsilon m}\right) \quad (24)$$

$$f(\epsilon) = \sum_{\zeta} [Fr(\zeta) + i Fi(\zeta)] \left[\cos \frac{2\pi \epsilon \zeta}{\epsilon m} - i \sin \frac{2\pi \epsilon \zeta}{\epsilon m} \right] \quad (25)$$

$$\begin{aligned} f(\epsilon) &= \sum_{\zeta} Fr(\zeta) \cos \frac{2\pi \epsilon \zeta}{\epsilon m} = \sum_{\zeta} F_r(\zeta) \sin \frac{2\pi \epsilon \zeta}{\epsilon m} \\ &- i \left(\sum_{\zeta} F_r(\zeta) \sin \frac{2\pi \epsilon \zeta}{\epsilon m} + \sum_{\zeta} F_i(\zeta) \cos \frac{2\pi \epsilon \zeta}{\epsilon m} \right) \end{aligned} \quad (26)$$

But, $F(-\zeta)$ is complex conjugate of $F(\zeta)$ (See $F = \frac{H}{G}$) and therefore $Fr(-\zeta) = Fr(\zeta)$ and $Fi(-\zeta) = -Fi(\zeta)$ then imaginary terms in the above equation reduces to zero.

$$f(\epsilon) = \sum_{\zeta} Fr(\zeta) \cos \frac{2\pi \epsilon \zeta}{\epsilon m} + \sum_{\zeta} Fi(\zeta) \sin \frac{2\pi \epsilon \zeta}{\epsilon m} \quad (27)$$

it should be noted that for greater accuracy the ϵm should be kept very large (ϵm = increments in calculating the coefficients). Detailed discussion of data processing is given in experimental process section.

So far, the theoretical evaluation of instrumental broadening has been established and pure diffraction profile ($f(\epsilon)$) is obtained.

Extraction of Size and Strain Parameters

The pure profile obtained through Stoke's deconvolution process is also product of convolution of crystallite size profile and distortion profile. Mathematically these profiles are related by

$$A(L, s) = A_c(L) A_D(L, s) \quad (28)$$

in which L = distance from an arbitrary origin, $S(2\sin\theta/\phi)$. Here the c subscript represents the crystallite size profile on a D subscript the distortion profile. All A , A_c , A_D are in the form of Fourier cosine coefficients (137, 131, 132). According to Bertaut (5) we can assume each crystallite consists of an assemblage of columns parallel to L (the size along the direction perpendicular to the planes investigated) and each column is composed of a stack of unit cells sufficient in number to traverse the crystal from one surface to the other. If there are n_i columns composed of (i) cells and if $p(i) di$ expresses the number of column with length between i and $i + di$, $A_c(t)$ may be expressed as,

$$A_c(t) = \frac{1}{N} \int_{i=|t|+1}^{\infty} (i - |L|) p(i) di \quad (29)$$

In this equation N is the total number of unit cells

$$N = \sum_{i=1}^{\infty} i n_i$$

The derivative of $A_c(L)$ with respect to L at $L=0$

$$\frac{dA_c(L)}{dL} \Big|_{L=0} = -\frac{1}{\bar{N}} \int_{i=1}^{\infty} p(i) di = \frac{N_c}{\bar{N}} = \frac{1}{\bar{N}} \quad (30)$$

Here $\bar{N}$ is "Number average crystallite size" in the direction L .

It is necessary make assumptions to separate the crystalline-profile information and distortion information from the Stoke's corrected profile. Warren, Averbach, Bertaut solved this problem by assuming that strains in crystallites are small (5, 130, 133).

The distortion profile can be written as,

$$A_p(Ls) = \exp(-2\pi^2 s^2 L^2 \langle \epsilon_L^2 \rangle) \quad (31)$$

$$L_L = \epsilon_L \cdot L = L \frac{\Delta d}{d} \quad (32)$$

if we substitute this above equation (31) into equation (28) and take logarithm,

$$\log A(L,s) = \log A_c(L) - 2\pi^2 s^2 L^2 \langle \epsilon_L^2 \rangle \quad (33)$$

For orthogonal crystal systems this equation reduces to

$$\log A(L,s) = \log A_c(L) - 2\pi^2 L^2 \langle \epsilon_L^2 \rangle / d^2 \quad (34)$$

Plots of $\log A(L,s)$ vs. $1/d^2$ for any values of L reveal, $A_c(L)$ and $\langle \epsilon^2 \rangle$ respectively from ordinate intercepts and slopes at low angles. Finally

the values of $A_c(L)$ corresponding to a range of values of L are plotted as a function of L (Distance) and from the slope of this function at low L the "Number average crystallite size" $\bar{N}$ is obtained.

Iterative Repeated Convolution Method

In 1932, Burger and van Cittert (112) first used this method on the elimination of instrumental broadening from spectroscopic patterns. Due to the lack of computer at this time, they devised an optical integrator to perform iterative convolutions of (h) with (g) to yield pure profile f. The first application of this method to X-ray diffraction was done by Ergun (31, 32) in 1968. The concept, in this method, is to broaden the observed profile further by convoluting it with the instrumental plus emission profile, and then adding to it the differences between it and the doubly broadened profile. The result is a sharper profile which is a closer approximation to the pure diffraction profile alone.

O. CONCEPT AND THEORY OF PARACRYSTALLINITY

The classical concept of M. V. Laue (71) of a crystal starts from the assumption that each lattice cell, averaged over time, has the same shape. Thus, the long-range order is established in the crystals. On the other hand, the concept of liquids formulated

by Debye (26) states that no lattices exist and each point (atom, molecule) atom resp. molecule has the same priori statistical distance distribution relative to the other points resulting in a loss of long range order. However, in macromolecules, it is possible that each cell of the lattice does not contain the same number of atoms, since the constitution of the macromolecules or monomeric units from cell to cell may differ. For example, a molecule may twist or kink. Even for a constant constitution the configuration or conformation within each may be different. Consequently, different cells may have slightly different shapes as shown in Table 1. The concept of paracrystallinity treats lattices intermediate between those treated by the crystal and liquid theories.

The paracrystalline model may be thought of simply as the usual crystal structure which has been perturbed by two distinct kinds of statistics:

1. The displacement statistics which describe the displacement of the scattering points from their equilibrium lattice positions, and
2. The coordination of lattice statistics which describe the distortions of the actual lattice points. In the limit that the distribution functions describing these statistics approach unity, the paracrystal becomes the classical real crystal. On the other hand, as these

TABLE 1
BASIC PROPERTIES OF THE THEORIES

	Crystal (Laue)	Paracrystal	Liquid (Debye)
Long range order	Yes	No	No
Lattice	Yes	Yes	No
Distance distribution with variance	No	Yes	Yes
Spherically symmetric correlation function	No	No	Yes

functions become very broad, the diffraction maxima become broadened and change continuously from the shape Bragg peaks through the diffuse liquid-like scattering maxima to a continuous scattering characteristic of gas-like materials. Thus, the model of the paracrystal is capable of describing, at least statistically the nature of structures which can give rise to either the diffraction patterns of a highly crystalline material or the continuous scattering of highly disordered amorphous-like material.

It has been shown that the statistical amplitude of a paracrystal of reflection (h) is given by

$$|F_k(s)| = \exp \left(-2\pi^2 \sum_{i=1}^3 g_{ik} \frac{1}{a_k^2} s_i^2 \right) \quad (35)$$

where $s = \frac{2\sin\theta}{\lambda}$, $\bar{a}$ interplanar spacing of the first order g =paracrystallinity factor, and integral breadth of a peak superimposed on an amorphous background is given by

$$\delta\beta_k = \frac{1}{2|\bar{a}_k|} (1 - |f_k|) \quad (36)$$

and integral breadth is related to observed intensities by

$$\delta b(h) = \frac{\int I(s) ds}{I(0)} \cdot \bar{a} \quad (37)$$

here $\bar{a}$ is (d_{110}) in our calculations and $s = 0$ at peak maximum.

If we substitute 36 into 35, approximately for orthorhombic systems

$$\delta\beta_p = \frac{1}{2\bar{a}} [1 - \exp(-2\pi^2 g^2 h^2)] \quad (38)$$

where $h = 1, 2, 3$ for 110, 220, 330 respectively and $\delta\beta_p$ from the area under the peak excluding the amorphous background. However, the integral breadths calculated from experimental profiles ($hk0$) are affected by a shape factor and a paracrystallinity factor. Hoseman (51) and Kakudo, Kasai (58) suggested that it may be acceptable experimental procedure to take the root mean square of the breadths due to the two effects as an approximation to the measured breadth of the diffraction. Thus if the integral breadth of the broadening due to the small angle scattering accompanying the h 'th order diffraction is S_x , the breadth $\beta(h)$ of the h th order wide angle diffraction due to the two effects is

$$\beta(h) = [\beta_p^2(h) + \beta_s^2]^{1/2} \quad (39)$$

Assuming a rod shape, the integral breadth for small angle scattering function is determined by (58);

$$\beta_s = \frac{1}{t} = \frac{1}{Na} \quad (40)$$

where N = number of units along the observed direction and $\bar{a}$ is the average cell dimension and f = total crystal length.

Combination of equations 38 and 40 with Equation 39 gives

$$\beta(h) = \frac{1}{2\bar{a}} \left[\frac{4}{N^2} + (1 - \exp(-2\pi^2 g^2 h^2)) \right]^{1/2} \quad (41)$$

Then after squaring both sides of equation 41 and expanding the bracket containing the exponential term, and taking the first two terms of the expansion we obtain

$$\beta^2(h) = \frac{1}{a^2} \left(\frac{1}{N^2} + \pi^4 g^4 h^4 \right) \quad (42)$$

This equation establishes a linear relationship between the square of the integral breadth $\beta^2(h)$ of the diffraction and h^4 . However, Hoseman calculated that (48) this is not true for the case of drawn high density polyethylene and suggested that the crystallite size is not uniform in polyethylene. He assumed that the diffraction profile is Gaussian and applied a method for the solution of Gaussian functions having different breadths, as in the Jellinek-Fankuchen analysis for small angle scattering (55).

Hoseman assumed that each reflection of $hh0$ (110, 220, 330) is composed of two Gaussian functions

$$I_h(s) = I_{hi}(s) + I_{hq}(s) \quad (43)$$

$h = 0, 1, 2, 3$

$h = 0$ small angle scattering

This analysis will be developed further in the section on Experimental procedures.

CHAPTER III

CHARACTERIZATION OF POLYETHYLENE RESINS

In this research two polyethylenes were investigated. One was high density polyethylene (HDPE) TENITE 3340 supplied by Eastman Kodak Company in pellet form. The other was low density polyethylene (LDPE) DFD-4140. Some of the molecular characteristics of Tenite 3340 were determined by Chen (18). These are: 1.3 poise intrinsic viscosity and 49,000 viscosity average molecule weights. The properties of LDPE were obtained from the supplier company and some of which are 445,000 M_w , 36500 M_n , 2.39 (g/10min), melt index at 190° C, 44 psi. The summary of these characteristic data are presented in Table 2.

A. PREPARATION AND CHARACTERIZATION OF THE FILAMENTS

Initial Filament Formation

The high density polyethylene and LDPE filaments of diameter of 2-2.5mm were extruded at 180° C and 150° C respectively using the Barabender Screw extruder coupled with a take-up motor. To eliminate initial orientation in the filaments the spinline stress was kept minimum using a slow take-up speed. The filaments subsequently drawn at elevated temperatures in a hot-air chamber. The temperature variation in the air chamber was $\pm 3,4^\circ$ C.

B. DRAWING CONDITIONS AND PROCEDURES

Two methods of drawing were employed for HDPE, one being two stage drawing proposed by Clark and Scott (19) and the other being single stage

TABLE 2

PROPERTIES OF HDPE AND LDPE

Manufacturer and Commercial Code	Intrinsic Viscosity	Melt Index	M_n	M_n	M_v	M_z	Density	T_m
Eastman Tenite	1.3	2.6	-	-	49,000	-	0.95	-
DFD-4140	-	2.39	445,900	365,000	-	4,235,000	0.9173	98°C

drawing. For LDPE only two stage drawing process was used. The two stage method involves an initial rapid draw-rate until the natural draw ratio achieved (at which all necks propagated and disappeared) and a slow second stage which is believed to increase fraction of extended chain domains by unfolding the chains. The single stage drawing process incorporates only a fast draw rate stage throughout the drawing.

Drawing was carried out in a temperature controlled air chamber on Instron Table Model 1122 tensile tester. Special clamps were designed and inner surfaces were covered with leather paddings to prevent crushing of the samples during deformation

The drawing rates were 100 percent/min and 1 percent/min for first and second stages of two-stage drawing respectively. The second stage drawing was carried out immediately after the first stage to eliminate the secondary crystallization effects. The temperature was varied from 60°C to 110°C for HDPE and from 40-75° C for LDPE. The temperatures for first and second stages of the two step method were kept the same except for the samples drawn at 110° C. (natural draw stage was at 70 ° C). For single stage drawing the draw rate was 100 percent/min. The temperature range in which HDPE filaments drawn was 70-80°C. In the second stage of the two-step process the time the samples endured elevated temperatures varied from 45 min to 1.5 hours. Thus the two-step process incorporates combination of annealing and deformation. On the other hand, the one-stage drawing process took much shorter time (5-10 min) thus the effect of annealing on sample structure was greatly reduced.

C. MECHANICAL PROPERTIES

The mechanical properties of the superdrawn fibers were determined at ambient temperature by using an Instron Table Model 1122. An initial gauge length of 2cm of LDPE and HDPE fiber was used. Since superdrawn HDPE samples are weak in the lateral direction a special sandwich clamp system which consists of 1' x 1' axially grooved aluminum plate, fine emory paper and a leather pad, was used. All of the testing was done with a 1 percent/min extension rate. Testing was stopped for HDPE when the strain reached ~0.08 percent. Then modulus data for HDPE and modules, ultimate strength, elongation to break data for LDPE samples were obtained by averaging three tests on each filament. The crossectional area of each fiber was obtained from mass-density-volume relationship. Some of the modulus values were corrected to infinite gauge length using a plot of compliance versus reciprocal gauge length.

Density

The densities of undrawn, drawn and superdrawn HDPE were determined at 23° C with a density gradient column using a distilled water-isopropyl alcohol mixture. The construction of density gradient column was done by a method described by Tung et al. (126). Selected samples of lengths of 0.5-1 cm were left in the column for at least a day to seek their level of displacement

D. MELTING POINT MEASUREMENTS

The melting behavior of HDPE filaments, processed by two-stage and one-stage drawing methods, was investigated using a Perkin-Elmer DSC-1B.

The instrument was calibrated with indium samples ($T_m = 156^\circ \text{C}$). Each HDPE filament was cut into small pieces and placed into an aluminum sample pan. The mass of the samples was on the order of 4 mg. The specimen pan and an empty pan were heated at a constant rate of 10°C/min through the melting range while recording the differential heat flux in an atmosphere of purified nitrogen gas. The melting temperature T_m was determined from the temperature at the peak maximum.

E. CRYSTALLINITY MEASUREMENTS

The crystallinities of HDPE fibers measured by three methods, namely, density gradient column, differential scanning calorimetry and X-ray wide angle diffraction.

Density Method

The percent crystallinities of HDPE filaments were determined by assuming a two phase model (Amorphous-Crystalline) for the specimens. The relation between the measured density (ρ), 100 percent crystalline density (ρ_c) and amorphous density (ρ_{am}) and percent crystallinity is given by following expression,

$$\text{Percent C} = \frac{\rho_c (\rho - \rho_{am})}{(\rho_c - \rho_{am})} \times 100 \quad (35)$$

where $\rho_c = 0.997 \text{ gr/cm}^3$ determined from unit cell parameters and $\rho_{am} = 0.8591 \text{ gr/cm}^3$ obtained from the extrapolation of melt densities (139)

DSC Method

The crystallinities were obtained by the relation of heat of fusion of sample transition and heat of fusion of 100 percent crystalline sample

transition. The heat of fusion of sample is determined by following relation

$$A(\text{Cal/gr}) = \frac{\text{Area of Sample Transition Peak} \times \text{Range Setting} \times 60}{\text{Area of Rectangle} \times 1000 \times 2 \times W} \quad (45)$$

where W = weight of the sample in grams.

Area of Rectangle was 1.841 in^2 . All of the experiments were done with the range setting of 8.

Then crystallinity was obtained by

$$\text{Percent C} = \frac{A (\text{cal/gr})}{66 (\text{cal/gr})} \times 100 \quad (46)$$

where 66 cal/gr is heat of fusion of 100 percent crystalline polyethylene (54).

X-Ray WAXS Method

The theory applied to determination of crystallinity of PE was set forth by Matthews, Peiser, Richard (76). In this theory they assume that sufficiently large region of the reciprocal space is being examined so that the amorphous and crystalline intensities observed in this region, subject to angle dependent corrections, are directly proportional to the respective weight fractions of amorphous and crystalline material. This theory implies that the quantities to be compared for determination of an X-ray crystallinity are the square of the geometric structure factors multiplied by the appropriate multiplicity. That is

$$\frac{W_{am}}{W_{cr}} = \frac{|F_{am}|^2}{4|F_{(110)}|^2 + 2|F_{(200)}|^2} \quad (47)$$

where W_{am} and W_{cr} are the amorphous weight fractions. The structure factors are related to observed intensities by following relationship

$$I_{(110)} = 4(LP)(f_c^2) \exp(-2B \sin^2 \theta / \lambda^2) |F_{110}|^2$$

$$I_{(200)} = 2(LP)(f_c^2) \exp(-2B \sin^2 \theta / \lambda^2) |F_{200}|^2$$

and by the implication of the theory,

$$I(am) = LP(f_c^2) \exp(-2B \sin^2 \theta / \lambda^2) |F_{am}|^2$$

where LP = Lorentz polarization factor

f_c = Atomic structure factor for carbon

All the intensities of resolved peaks (110, 200, Amorphous) were corrected to find $|F|^2$ values. Then from the equation (47) the crystallinities were calculated.

F. SCANNING ELECTRON MICROSCOPY

These experiments were carried out on an AMR Model 900 high resolution electron microscope. The HDPE samples were coated with gold-palladium or silver in vacuum chamber to eliminate charging of the samples by electrons. The scanning electron microscope was operated at 6 KV and 40 mA. This low voltage operation was chosen particularly to

eliminate the destructive effects of electron beam on the samples.

Investigation by SEM is divided into three categories.

1. Surface studies of samples strained on the order of 0.08 percent.

The number average grade lengths were determined by following equation (48)

$$L_n = \frac{\sum_{l=1}^h n_l L_l}{\sum_{l=1}^h n_l} \quad (48)$$

2. Internal structure studies of samples of different draw ratios by peeling.

3. Studies on the effect of drawing on fiber at different temperatures.

G. EXPERIMENTAL PROCEDURES IN DYNAMIC MECHANICAL MEASUREMENTS

Measurements of dynamic viscoelasticity of HDPE samples were made by the direct reading dynamic viscoelastometer of Toyo Measuring Instrument Co., Ltd. Vibron DDV-II-C. Basically, this instrument applies a sinusoidal tensile strain to one end of a sample and measures the stress output at the other end. The available frequencies on the instrument are 3.5, 11.0, 35.0 and 110 Hz. Two transducers are used to read directly the dynamic force and phase angle (δ) between stress and strain. The experimental procedures used were those discussed in the instruction manual of the instrument.

The experiments were done at 110 Hz at room temperature and the initial sample gauge length was 4cm. The effect of temperature on some

selected samples were investigated over a 20-130° C range. The temperature increased with a heating rate of 2°C/min. The complex moduli were obtained by following equation:

$$|E^*| = 2.0 \frac{1}{D.F-K} \times \frac{L}{A} \times 10^{-1} \quad (\text{GPa}) \quad (49)$$

where

$|E^*|$ = the ratio of maximum stress amplitude to maximum strain amplitude.

D.F. = Dynamic Force (dynes/cm²)

K = Dynamic force corresponding to zero gauge length (determined from D.F. vs. gauge length plot) (dynes/cm²)

L = Sample gauge length in centimeters

A = Sample crosssection area determined by a microscope (cm²)

The storage moduli (E') and loss moduli (E'') were obtained from following relations.

$$E' = |E^*| \cos (\delta) \quad (50)$$

$$E'' = |E^*| \sin (\delta) \quad (51)$$

H. QUANTITATIVE SMALL ANGLE X-RAY DIFFRACTION, AND QUALITATIVE WIDE ANGLE DIFFRACTION

Small angle X-ray patterns were obtained on selected LDPE and HDPE samples of varying draw ratios using a Statten-Warhus camera mounted on Philips-Norelco X-ray generator. The generator was operated at 40KV and 20mA. During experiment, the camera was evacuated by a vacuum pump to

eliminate the air scatter from the patterns. Exposure time for HDPE filaments stacked in a parallel manner was 48 hours. The long periods, if any, of the samples were calculated by the Bragg's Law. The sample to film distance was 32 cm. The meridional microdensitometer traces of some selected patterns were obtained.

Wide angle patterns of LDPE and HDPE samples were taken using the same equipment described above. The exposure time was about 3-4 hours depending on the sample thickness.

I. INTEGRAL BREADTH PROCEDURE

The wide angle X-ray diffraction data were obtained and processed as explained in Section I. Then the integral breadths of these resolved peaks were calculated using equation (2). The integral breadths were corrected for instrumental broadening by following equation:

$$\beta = \beta_0 - B_{\text{inst.}} \quad (52)$$

which assumes cauchy type peaks

where

$$\beta_0 = \text{Observed}$$

$$B_{\text{inst.}} = \text{Instrumental peak.}$$

The peaks of hexamethylene tetramine were used as instrumental peak. Then the particle sizes for 110, 220, 200 and 310 planes were determined using the Scherer equation and Scherer K constants which are given in Appendix A.

The 002 reflections of the samples were obtained by X-ray transmission technique and corrections were made as explained above. In this case LiF peaks used for instrumental peak.

J. EXPERIMENTAL PROCEDURE OF UNIT CELL DETERMINATION

In these experiments polyethylene fibers of different draw ratio processed at 70° C and 80° C were investigated. Fibers were coated with a thin layer of spectroscopically pure Na Cl powder (325 mesh). X-ray powder diagrams were obtained with a (114.6) mm diameter Scherer powder camera and Nickel filtered CuK_α (1.54178Å) radiation. The film was placed asymmetrically in the camera. The shrinkage of film due to processing was determined from NaCl lines using front and back reflections. The hko reflections were used to calculate the a,b dimensions from plots of $\cos^2\theta$ versus a, or b by least square linear regression procedure.

K. EXPERIMENTAL PROCEDURE OF FOURIER ANALYSIS

As stated in previous literature survey section, a standard crystalline sample is needed for elimination of the instrumental broadening effect from the polyethylene diffraction profiles. It was found that hexamethylene tetramine (HMTM) satisfies the conditions which are required from a standard sample for PE. It has comparable linear absorption coefficient to PE and can be crystallized with large perfect crystals.

Sample Preparation

Crystalline HMTM was recrystallized by a sublimation process with a careful temperature control to eliminate strains in the crystals. Recrystallized HMTM was then ground and sieved to achieve 100 mesh particles. The sieved sample powder was then compacted to 0.3mm and 0.5mm

discs at 80° C. These discs subsequently were reshaped to achieve a geometry similar to polyethylene samples. Then these samples were glued on epoxy sample holders. The High Density polyethylene fibers were prepared by drawing in the air chamber at 70° and 80° C. Draw rate for natural and super drawn stages were 100 percent/min and 1 percent/min respectively. Selected samples with varying draw ratios were, then, cut into 2cm in lengths, and glued on the sample holder (epoxy cylinder) in a parallel manner.

Diffraction Data Acquisition

The diffraction patterns of HDPE and HMTM were obtained with a Norelco X-ray generator and Philips diffractometer which is equipped with a graphite monochromator, (1°) receiving slit (1°) divergence slit and step scanning motor. The line focus side of the copper target tube was used as a source of radiation. The signals coming from solid state scintillation counter processed by preamplifier and an ORTEC pulse height analyzer. The generator was operated at 40KV and 20 mA. Scanning step was 0.02°2 θ /step and counting time per step was varied for each particular sample to insure that at least 3,000 counts were obtained. (The count time was varied between 20-100 sec/count.) The data were automatically punched on the paper tape of a teletype. It was observed that the X-ray intensity is affected by background radiation and changes in the cooling water temperature. To eliminate this inconsistency in the system the following method was used.

Amorphous polystyrene (Dow Styron 6742) was melted at 180° C and compacted into discs. Then these discs were annealed at 95°-100° C for 2 hours to eliminate built-in stresses in the samples. These samples were

then glued on the epoxy sample holder. Before and after each experiment this PS standard was placed on the diffractometer and counting was recorded for 60 second 10 to 15 times at $2\theta^\circ=100^\circ$. Then mean of these counts provided that particular day's relative intensity. One of these mean counts was chosen as a basis and the others were normalized according to this basis. Then the correction factors were obtained according to following equation (53)

$$CF_i = \text{Corr. Fac.} = \frac{I_0}{I_i} \quad (53)$$

I_0 = Basis (60 sec. count)

I_i = One particular experiment's average. PS count intensity

The intensity sensed by counter does not solely come from the sample and tube emission. It also contains background radiation and radiation from the epoxy (Amorphous) sample holder and electronic noise produced by the devices on the system. To eliminate this excess background from the data a sample holder was placed on the diffractometer without the samples. Diffraction data were taken 0.02° 2θ /step for the same angular region as the data taken for the sample. This obtained background processed as explained in the following section.

Data Processing

The data, punched on paper tape, read to the PDP-10 computer through a teletype. Several programs were written and some of the programs written previously by Benaim (4) were used for various correction purposes.

Each intensity spectrum point was multiplied by its normalized correction factor. Then the noise background, which is corrected for day to day changes, was subtracted from the data. Hexamethylene tetramine data were eliminated from the unwanted peaks except 110 and 222 peaks which are chosen as standard for 110 and 200, and 220, 400 peaks of polyethylene respectively. No overlap of peak tails in HMTM diffraction data was observed which simplifies the further background corrections. On the other hand the polyethylene diffraction data show overlap of peak tails (Figures 9 and 10). This phenomenon has been the major drawback in the application of fourier analysis to PE and other crystalline polymers.

The background for HMTM diffraction profiles was assumed to be linear between the two locations where the peak tails emerge from the background. However for PE profiles a certain degree of judgment was necessary. It was found that linear subtracting of 30-60 percent of the original background gave quite satisfactory results in separation process and fourier analysis.

Separation Process

Over the last two decades, researchers have tried to resolve these overlapping peak tails through several mathematical treatments. They assumed the peaks are symmetric about their maximum then resolved the tails (10).

In 1976 Benaim (4) used Pearson VII curve fitting to resolve peaks of polyester and to calculate orientation factors. This curve fitting method was chosen due to the fact that it is more versatile for the curve fitting process.

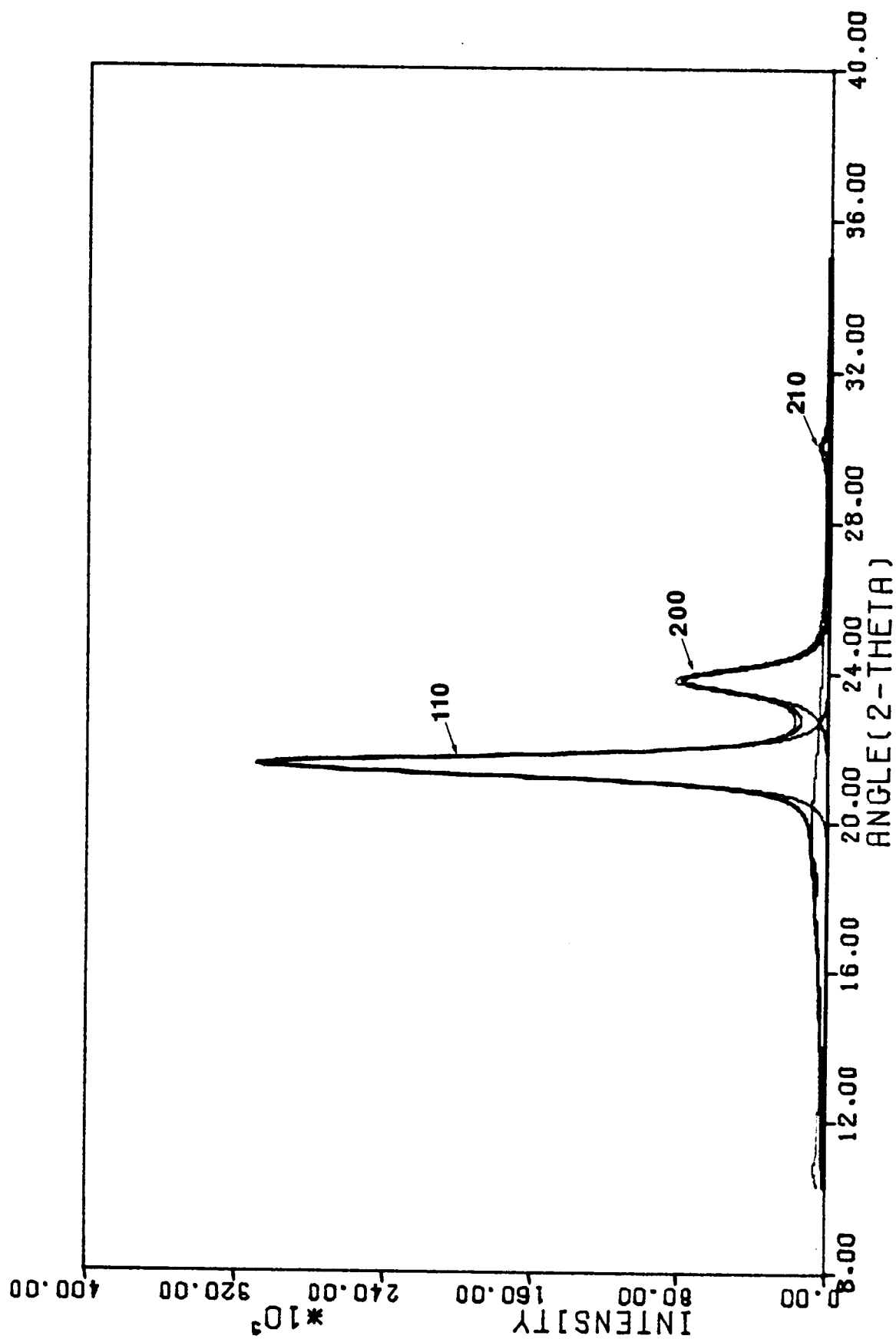


Figure 9. WAXS X-ray diffraction profile which is separated into the Pearson VII peaks (low angle).

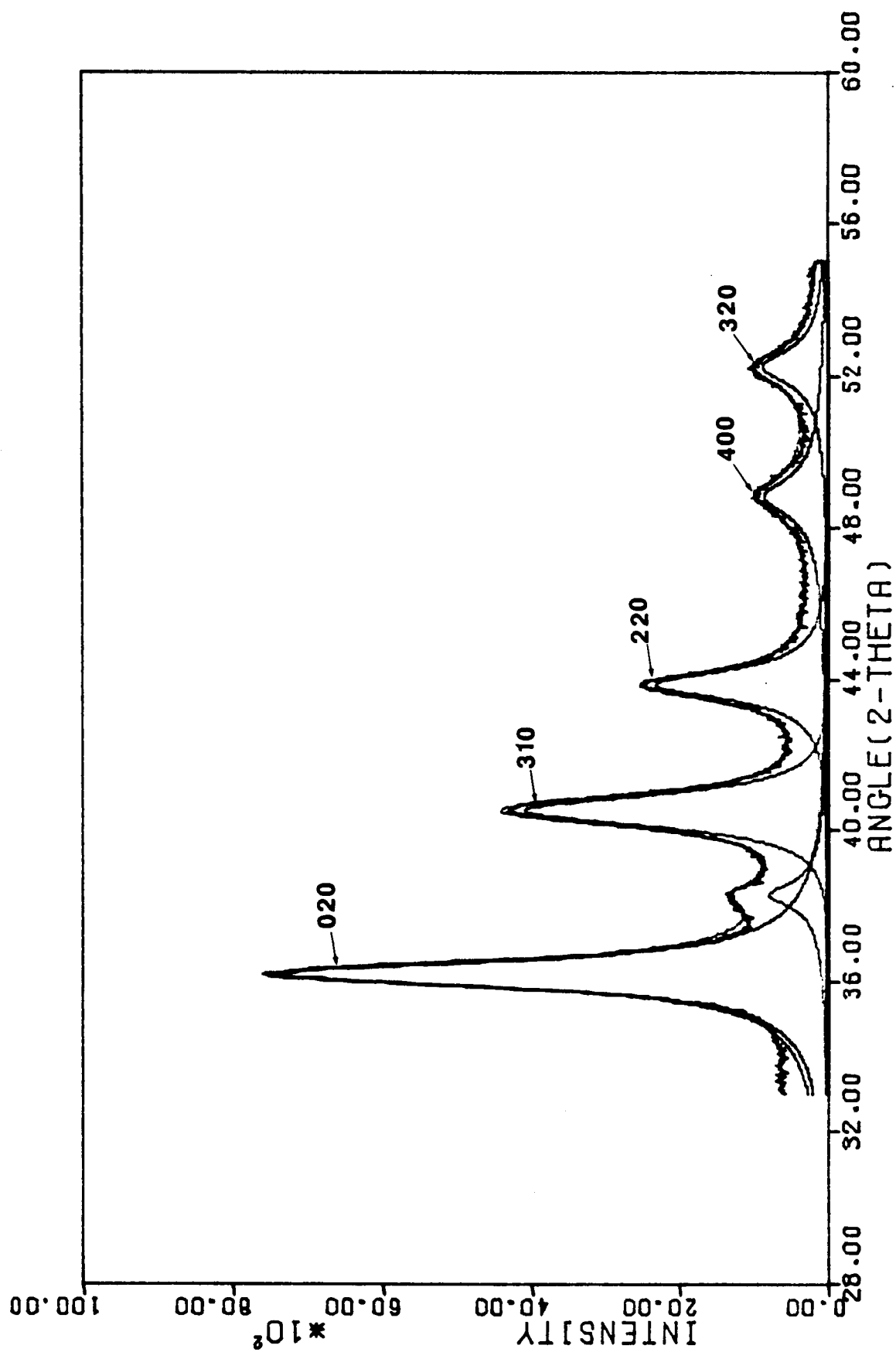


Figure 10. WAXS X-ray diffraction profile which is separated into the Pearson VII peaks (high angle).

Examples which were resolved through this curve fitting method are shown in Figure 9 and Figure 10. This curve fitting was achieved through a computer program which uses an iteration process.

Angular and Other Corrections

Hexamethylene tetramine. The HMTM profiles which are corrected for background and day to day change, still do not represent the diffraction profile needed for Fourier analysis. They are distorted by following factor.

1. Structural Factor
2. Lorentz-Polarization factor (L.P.)
3. Multiplicity Factor
4. Absorption factor
5. Temperature factor

Structure factor was calculated through

$$F(hkl) = \sum_{n=1}^N f_n \exp [2\pi i(hx_n + ky_n + lz_n)]$$

L.P. factor

$$L.P. = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \quad (54)$$

Temperature factor

$$T.P. = \exp (-0.0125 \cdot \Sigma h^2) \quad (55)$$

where

$$h^2 = h^2 + k^2 + l^2$$

This temperature factor was the result of work done by Brill et al. (8) on the structural analysis of hexamethylene tetramine.

These factors are presented in Appendix B. The factors mentioned above were multiplied for each data point in the diffraction spectrum. Then these combined factors were normalized by dividing them with the combined factor corresponding to the peak position of the profile. Then intensities were divided by their corresponding normalization factors

Polyethylene Profile Correction

Some procedures as above was applied to the PE profiles. The temperature factor was taken as

$$\text{R.F.} = \exp \left(-10 \frac{\sin^2 \theta}{\lambda} \right) \quad (56)$$

This temperature factor was determined by Bunn (11). All the crystallographic data pertaining PE is given in Appendix B.

Profile Analysis

Figure 11 shows the flow chart of the program. The standard data first run and cosine and sine coefficients are determined. Then first order reflection is read. The 2θ scale is converted to "s" units. The intensities are adjusted accordingly by Lagrange interpolation of order of 4. Then the peaks are made symmetrical about their center of gravity then Stokes correction applied and then fourier size and cosine coefficients are calculated. Then the second order profile data is read and same procedure is applied. Then the W-A method is applied and results are printed.

L. EXPERIMENTAL PROCEDURES FOR GUINIER-WARREN-HOSEMAN ANALYSIS

In these experiments only the samples of different draw ratios drawn at 70°C and 80°C in the air chamber were investigated. The

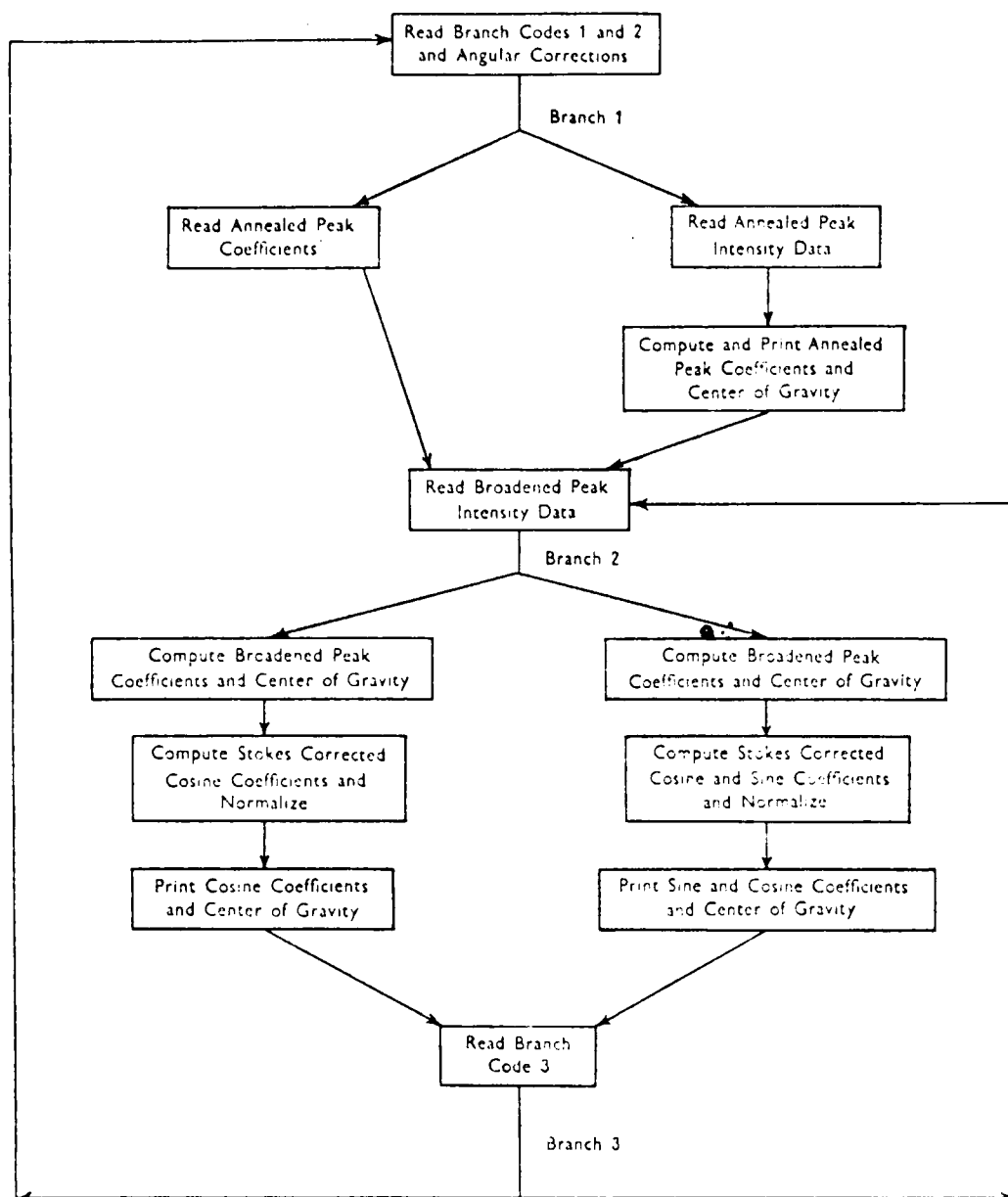


Figure 11. Flow chart of Fourier Analysis program.

diffraction data acquisition and corrections were done as explained in the previous fourier analysis section. Since the paracrystalline model states that only the intensities above the amorphous background should be included in the analysis instead of curve fitting to the profiles as was done for fourier analysis, the background for the peaks was assumed to be linear between the positions where the tails emerge to the background or overlap. These profiles were processed by a computer program which is presented in Appendix E. The computer program process first divided the peak selected (110 or 220) into two parts from its maximum. Then the logarithm of intensities on the higher angle side of the profile was taken and the 2θ scale was changed to an s-scale ($\frac{2\sin\theta}{\lambda}$). The s-value corresponding to peak maximum (s_h) was subtracted from the rest of the s-values, making the s-value of the peak position zero. Having obtained a plot of $\log I$ vs $|s-s_h|$, the component, I_1 , was found by drawing a tangent to the lower end of this curve. Due to the small fluctuations of the intensity data, the determination of this latter tangent was done by fitting a second order curve to the major portion of the tail.

$$\log I = a_0 + a_1 |s-s_h| + a_2 (s-s_h)^2 \quad (57)$$

Then the slope was obtained from the derivative of this equation (1) by

$$\frac{d\log I}{d|s-s_h|} = a_1 + 2(s-s_h)^2 \quad (58)$$

introducing the last ($s-s_h$) value to (equation 58). Naturally a_0 of equation (57) is the intercept of the tangent at $(s-s_h) = 0$. A second component I_2 was obtained by drawing a tangent to the lower end of the

curve derived by subtraction of the diffraction intensity of the first tangent, i.e., of the component I_1 , from the original diffraction intensity curve. This latter subtraction was obviously done in linear scale rather than in logarithmic scale. This latter process is illustrated in Figures 12, 13; breadths of the I_1 and I_2 components were obtained according to equation (59)

$$\delta\beta = \frac{d_{110}}{\lambda} \cdot \frac{\int I(\theta) \cos\theta d\theta}{I_{\max}} \quad (59)$$

which is an alternate way of expressing the equation (50)

From equation (55) one obtains the relation for component I_1 ,

$$\delta\beta_1^2(h)_{\text{exp}} = \frac{1}{N_1^2} + (\pi g_1 h)^4 \quad (60)$$

and for component I_2 ,

$$\frac{1}{\delta\beta_2^2(h)_{\text{exp}}} = \frac{1}{\delta\beta_2^2(n)_{\text{exp}}} + \frac{1}{\frac{1}{N_2^2} + (\pi g_2 h)^4} \quad (61)$$

Thus,

$$\delta\beta_2'^2(h)_{\text{exp}} = \frac{1}{\frac{1}{\delta\beta_2^2(h)_{\text{exp}}} - \frac{1}{\delta\beta_1^2(h)_{\text{exp}}}} = \frac{1}{N_2^2} + (\pi g_2 h)^2 \quad (62)$$

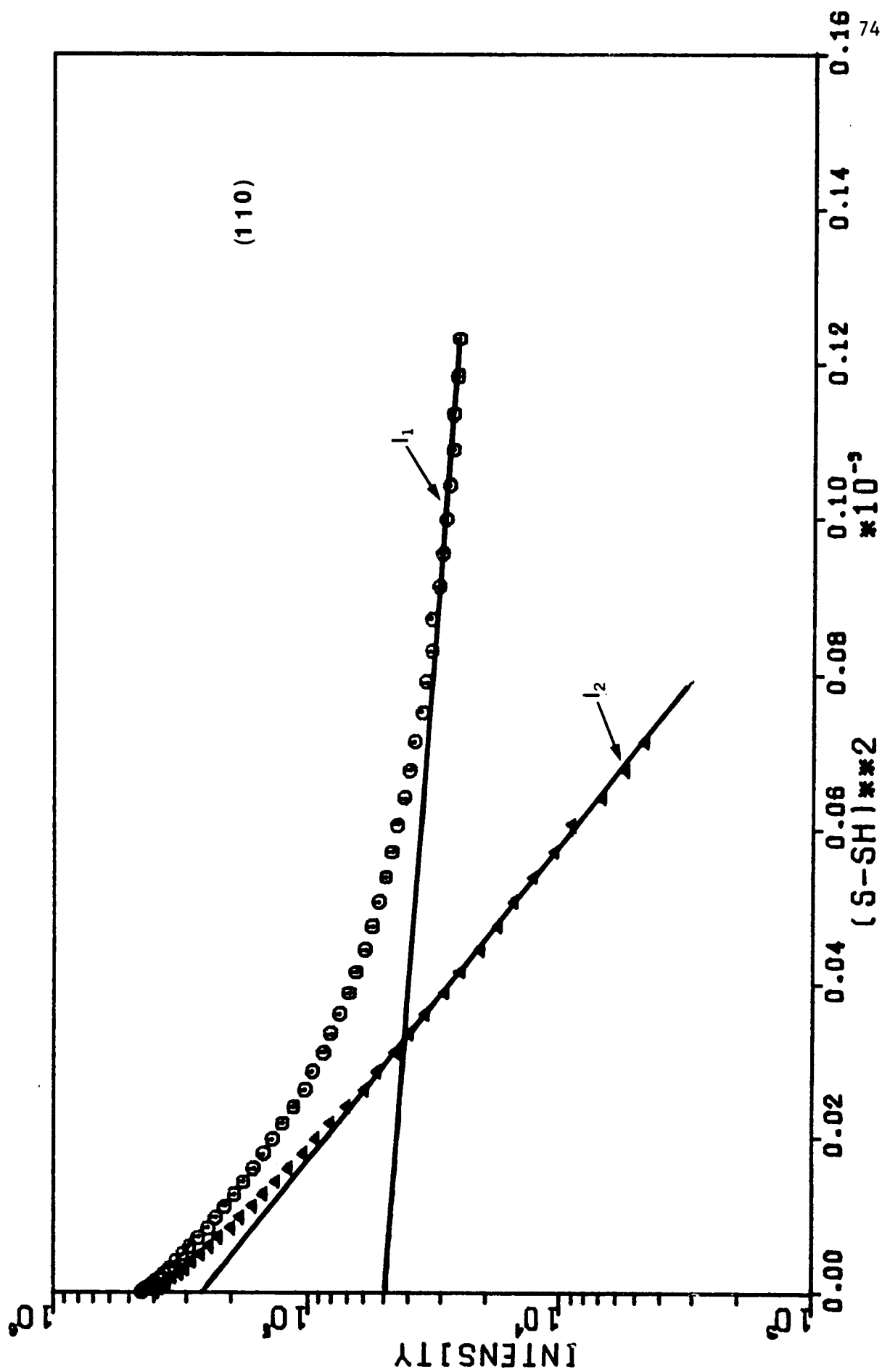


Figure 12. Guinier plot of 110 reflection peak showing the I_1 and I_2 components.

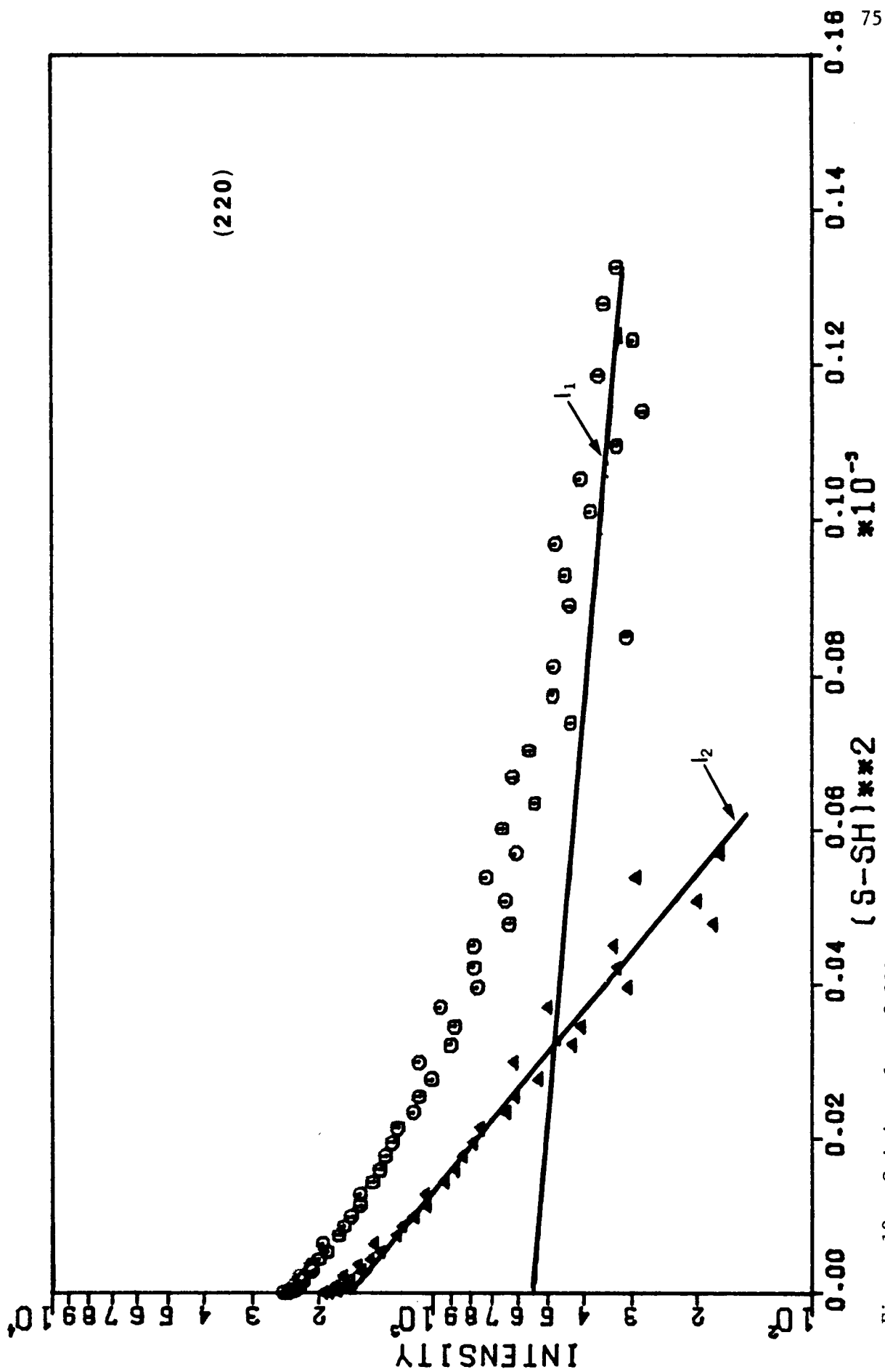


Figure 13. Guinier plot of 220 reflection peak showing the I_1 and I_2 components.

From plots of $\delta\beta_1^2(h)_{\text{exp}}$ vs. h^4 and $\delta\beta_2^2(h)_{\text{exp}}$ vs. h^4 are obtained N_1, N_2, g_1, g_2 .

where

N_1 = Average number of planes parallel to 110 planes in component I_1

N_2 = Average number of planes parallel to 110 planes in component I_2

and

g_1 = paracrystallinity parameter for component I_1

g_2 = paracrystallinity parameter for component I_2

The illustration of this process is given in Figure 14 from which one can determine $\frac{1}{N_1}$ from the intercept and g_1 from the slope. The average

"number column lengths" for each component was calculated by

$$L = N_i d_{110} \quad (A^\circ). \quad (63)$$

The paracrystallinity parameter (g) is defined by

$$g = \frac{\sqrt{L_1^2 g_2^2 - L_i d_{110}^2 g_1^2}}{d_{110}} \quad (64)$$

which is related to the boundary neighboring chain molecules, belonging to different ultrafibrils.

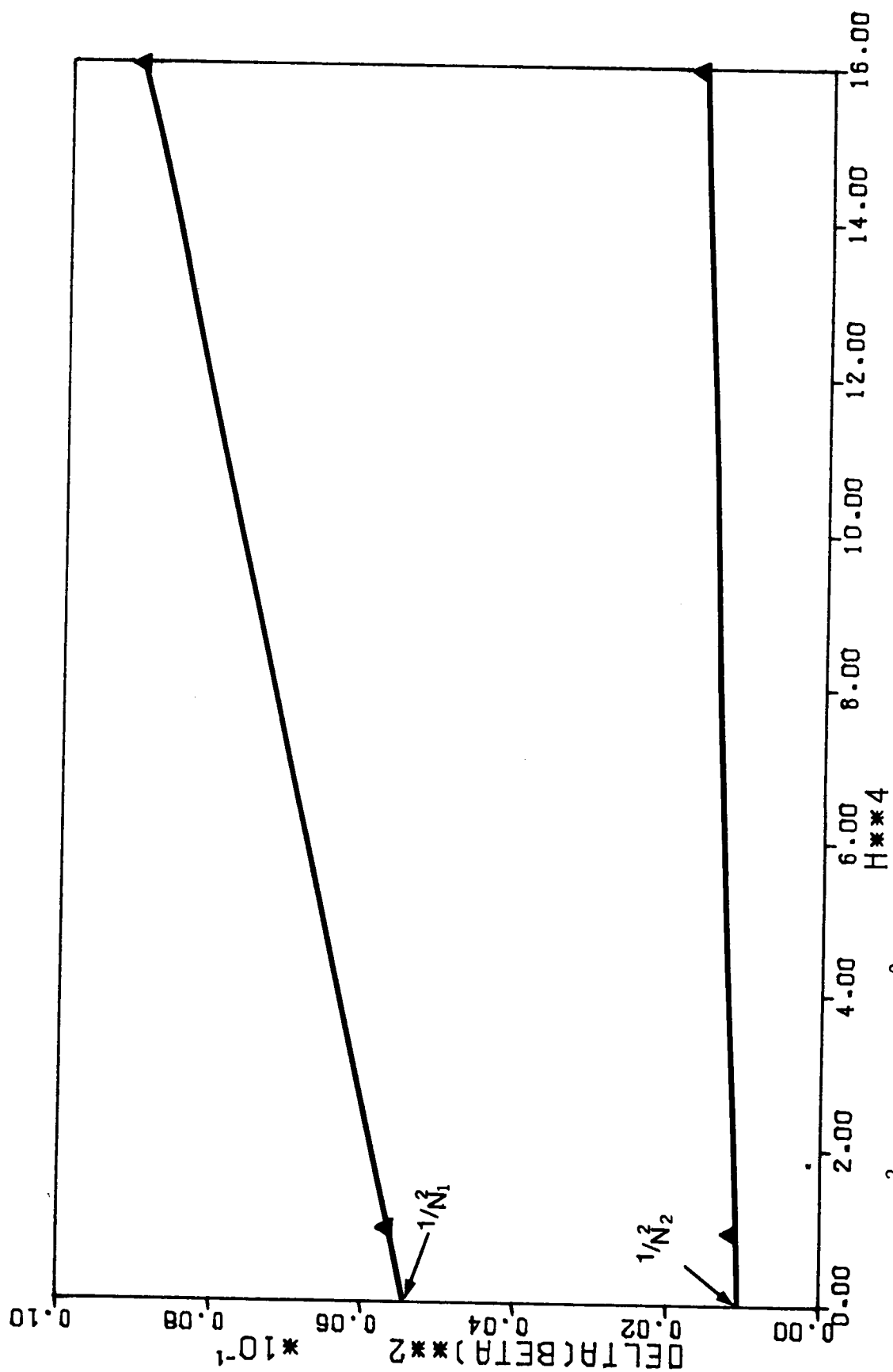


Figure 14. $\delta\beta^2(h)_{\text{exp}}$ versus $h^2(H)$.

CHAPTER V

MACROPROPERTIES

A. MECHANICAL PROPERTIES OF LOW DENSITY POLYETHYLENE

The main objective of drawing of Low Density Polyethylene (LDPE) at different temperatures was to investigate whether the optimum drawing temperature corresponds to that of α -relaxation a fact that was found to be correct for High Density Polyethylene (85, 117). As reported by Stachurski and Ward (111) the peak temperature of α relaxation is very sensitive to the preparation conditions. If the samples are quenched as they are extruded, the α relaxation peak shifts towards a lower temperature. Thus, depending on the preparation conditions the α transition peak shifts from 40° C downward.

In our experiments, a draw rate of 1 percent/min and draw temperature of 40, 60 and 75° C were utilized in extensional deformation of LDPE. As implied in Figure 15, the maximum draw ratio of the samples were found to be sensitive to the drawing temperature. The Figure 15 clearly indicates that the magnitude of modulus values of drawn samples decreases with increasing process temperature. The highest modulus values are found for the samples drawn at 40° C. It seems that the relation between the α transition and optimum draw temperature also holds. The modulus of the samples drawn at 75° C does not change with the draw ratio. Thus, it appears that as the process temperature increases the effect of drawing on the orientation of the chains decrease. This may be the result of chain slippage due to the higher chain mobility at higher temperatures.

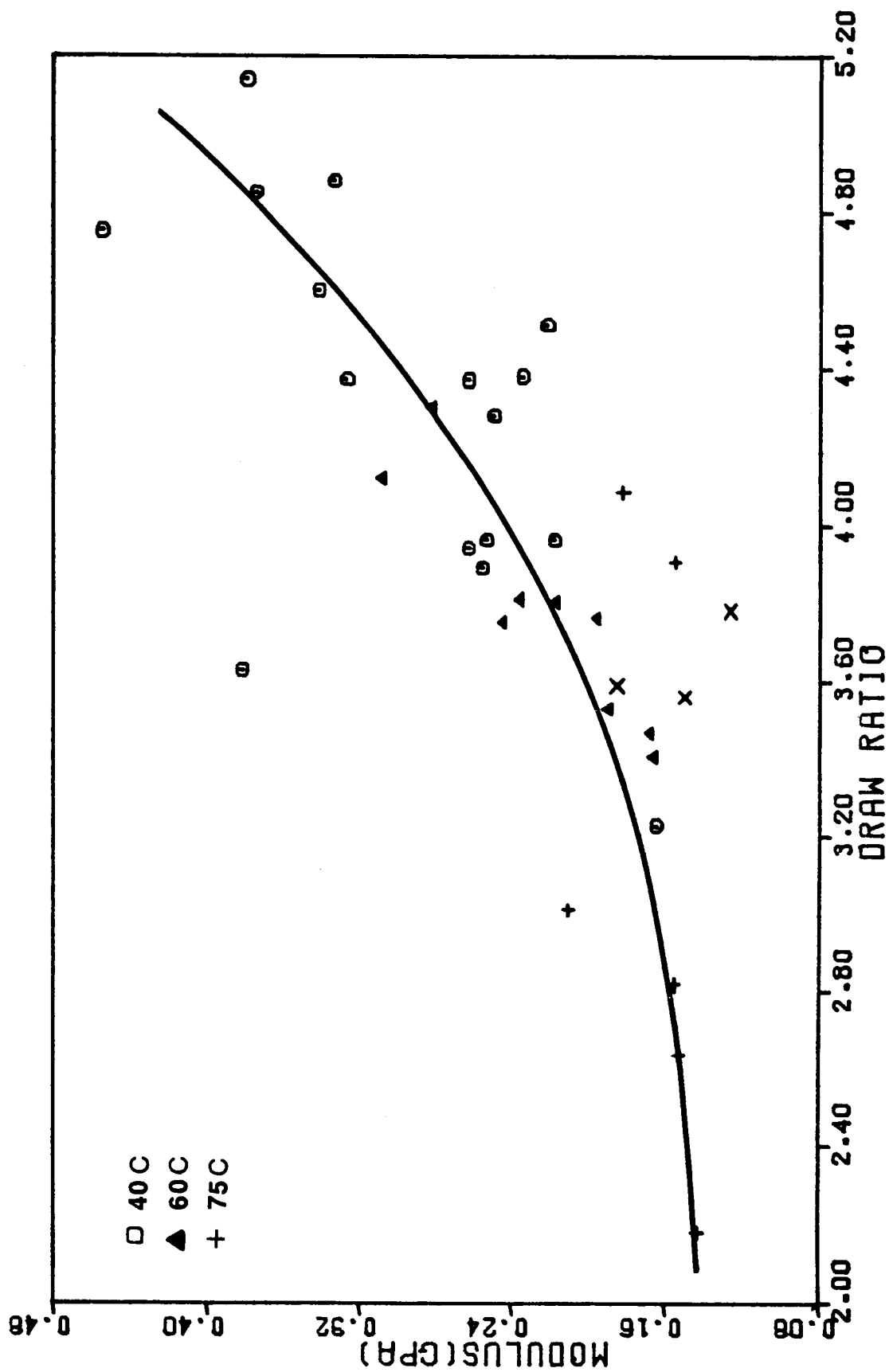


Figure 15. Tensile modulus versus draw ratio for LDPE samples drawn at 40, 60, 75°C.

In Figure 16 it can also be observed that the highest tensile strength was obtained for the samples drawn at 40° C. Even though there is an increase in tensile strength with draw ratio, it seems the relation of tensile strength with draw ratio is not well-defined. As expected, the elongation to break is the lowest at the highest draw ratios as shown in Figure 17. The decrease of the elongation to break with draw ratio indicates that as the draw ratio increases the fraction of domains available for drawing decreases

B. MODULUS OF HIGH DENSITY POLYETHYLENE

Since an extensive study of mechanical properties of superdrawn high density polyethylene was done previously by Omotoso (85) in this section of the thesis only those aspects required additional clarification were studied. As shown in Figure 18 the modulus values linearly increase with the draw ratio for samples drawn at 79° C and 80° C. At 90° C process temperature, this latter linearity holds for low draw ratios but at high draw ratios, the increase of modulus with draw ratio is lessened; at 110° C process temperature, the modulus-draw ratio curve attains a negative slope (Figure 19). It should be noted that the attempts to draw the samples from their undrawn states at 110° C were unsuccessful due to the "taffy pull" effect which is the result of the slippage of load bearing elements in the structure at that temperature. Thus, only for high temperature study the samples were natural-drawn at 70° C and the superdrawing was proceeded at 110° C.

A summary of the conclusions on the structure-property relationship drawn at several temperatures is as follows:

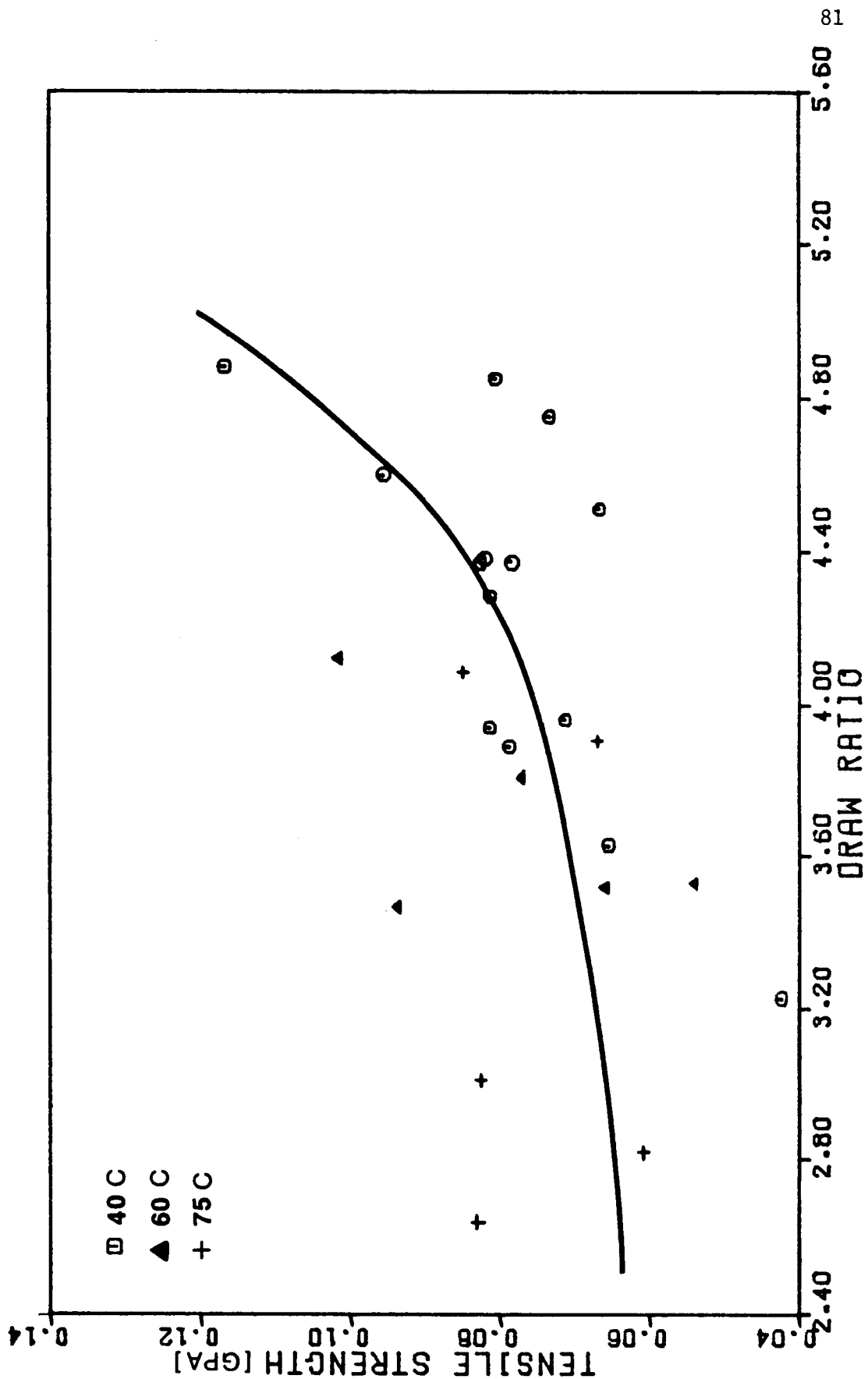


Figure 16. Tensile strength versus draw ratio for LDPE samples drawn at 40, 60, 75°C.

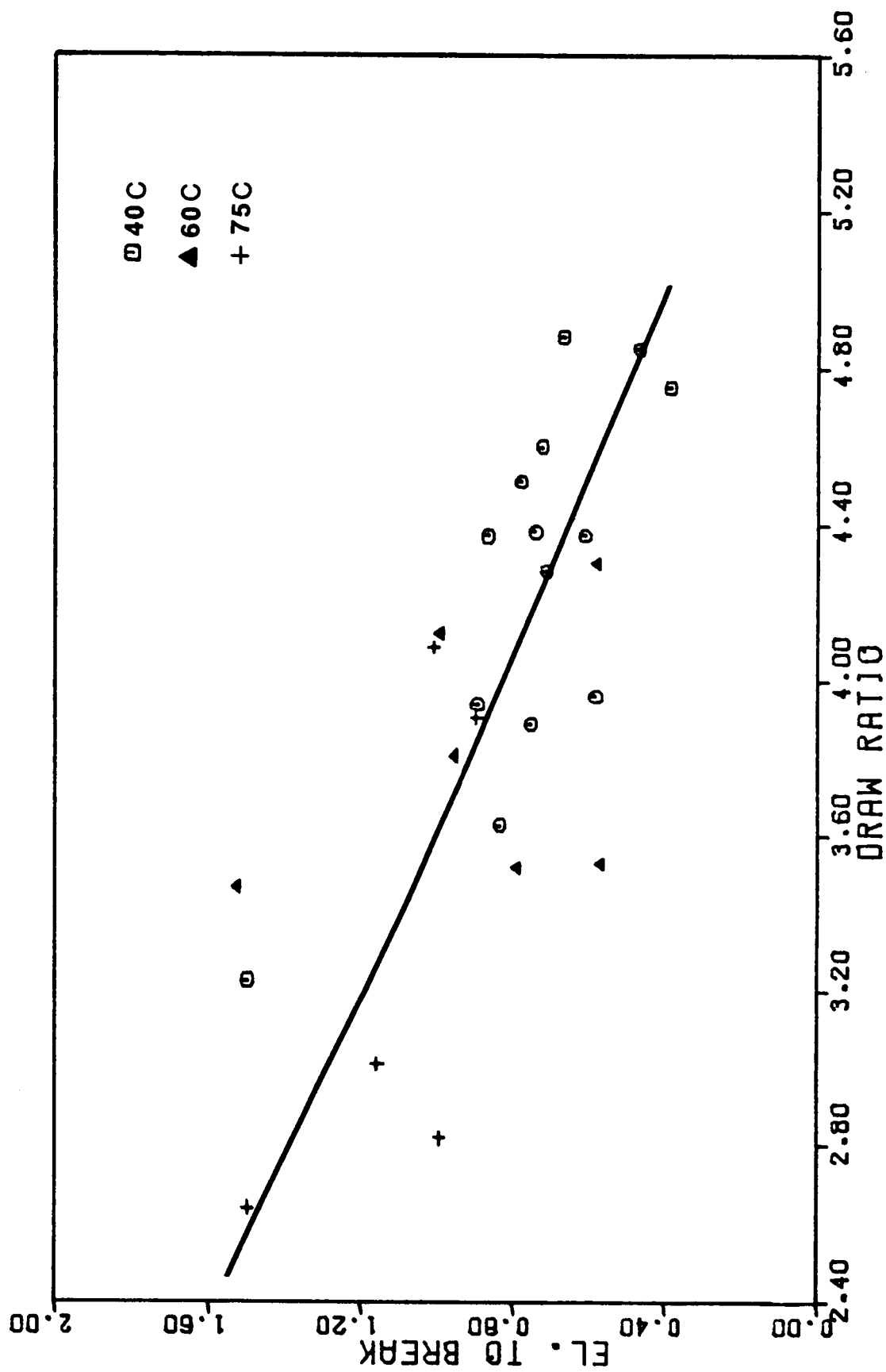


Figure 17. Elongation to break versus draw ratio for LDPE samples drawn at 40, 60, 75°C.

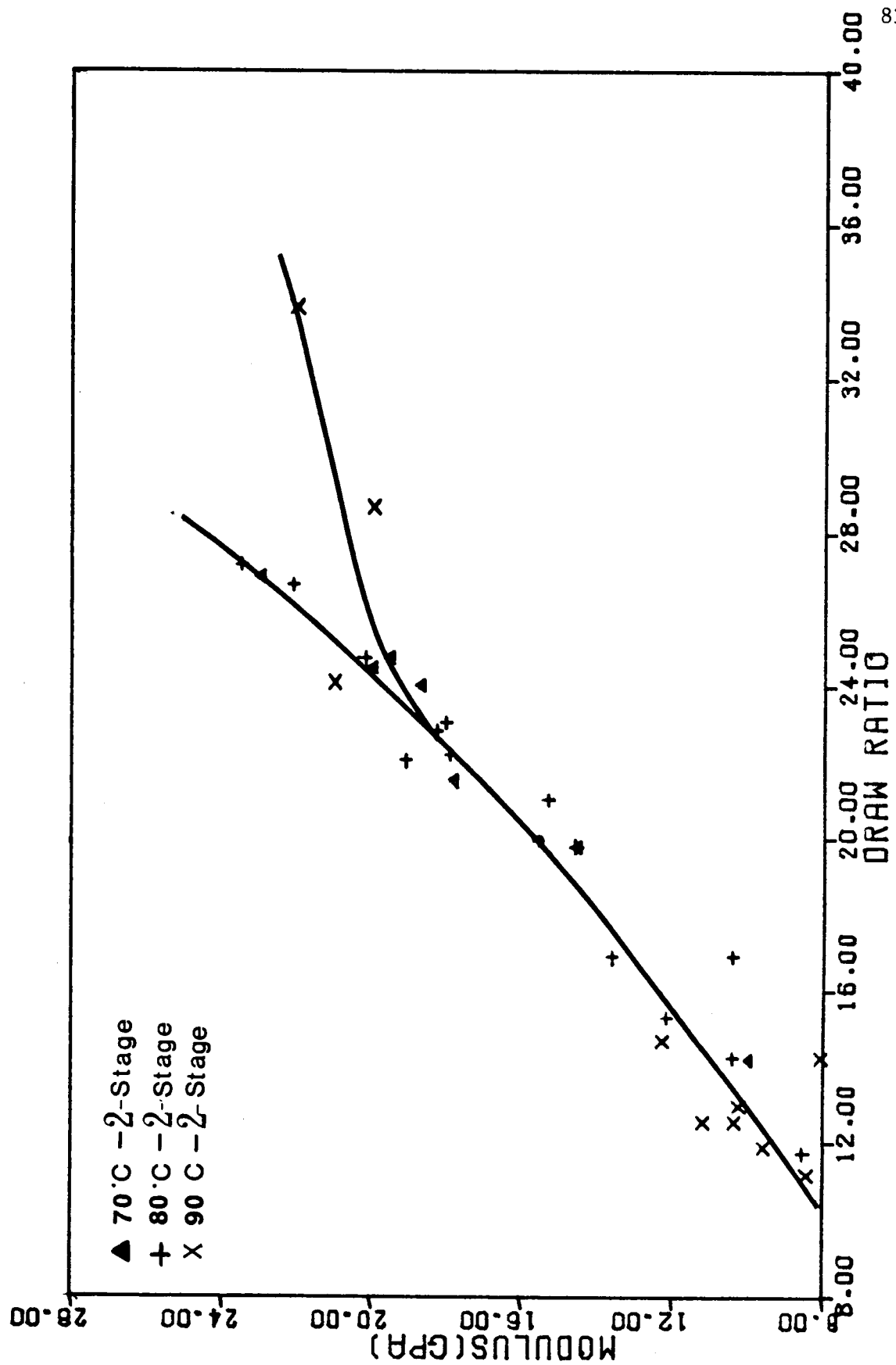


Figure 18. Tensile modulus versus draw ratio for HDPE samples drawn at 70, 80, 90°C.

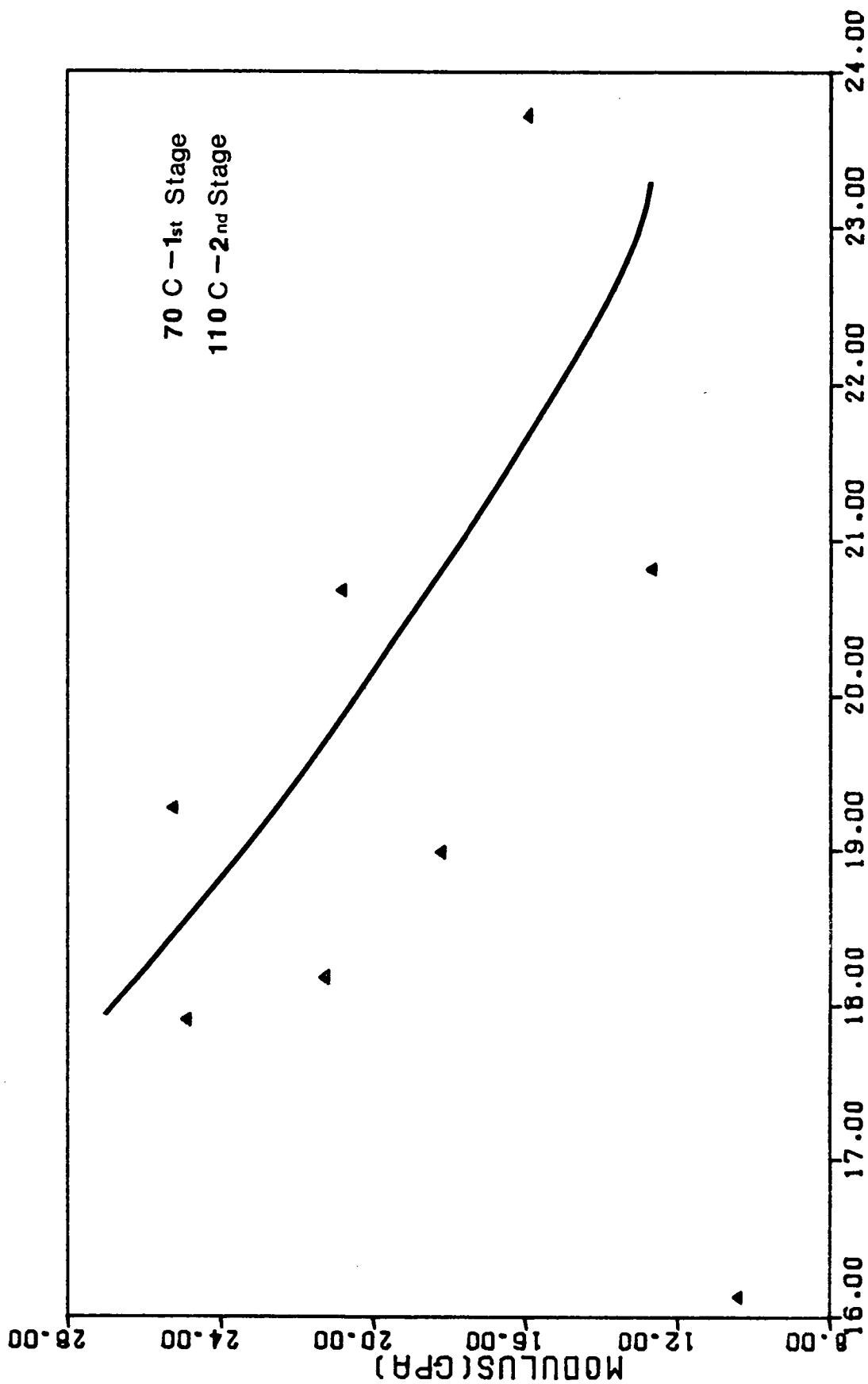


Figure 19. Tensile modulus versus draw ratio for HDPE samples drawn at 110°C.

1. At low temperatures (70, 80° C) which are in the range of optimum process temperature (α -transition) the highest moduli are achieved which are the consequence of orienting effects of interfibrillar and intrafibrillar friction which results from the forces exerted on the ends of the sample.

2. As the process temperature increases, the drawing mechanism changes and the "friction" between and within the fibrils is lessened due to higher mobility of the segments in the structure at higher temperatures; thus the orienting effects of external forces are lessened.

3. Above a critical temperature, another mechanism comes into play, namely refolding of extended chains. The orienting effects of external forces at this critical temperature are considerably decreased, but, microfibril and/or chain slippage increase (decrease of friction), and chain refolding prevails resulting in a decrease in modulus values.

The comparison of moduli values of samples drawn by one stage and two stage methods is presented in Figure 20. This comparison was done primarily to investigate the effect of draw rate on the final moduli.

The two stage method, as previously mentioned, utilizes low draw rates in the second stage (1 percent/min) whereas the one-stage method utilizes 100 percent/min initial strain rate throughout the drawing process. The moduli of the samples drawn by both methods follows a linear increase with draw ratio up to the draw ratio of 24. After this draw ratio the modulus of samples drawn by the one stage method showed a somewhat lower increase than those of the two stage method. If we compare the two drawing processes, it could be found that the

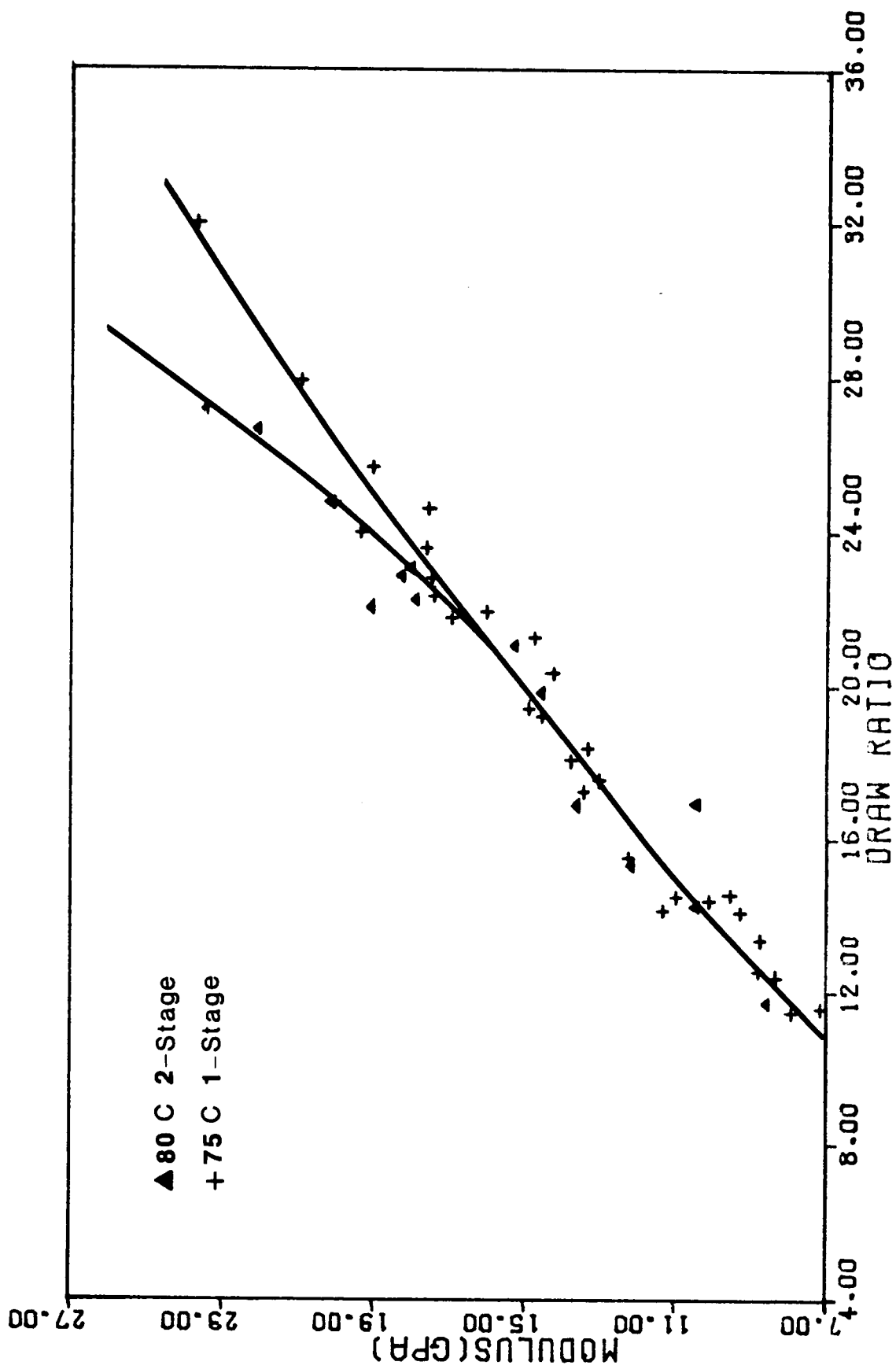


Figure 20. Tensile modulus versus draw ratio for HDPE samples drawn by one-stage and two-stage methods.

rates up to the natural draw are identical since the 100 percent/min is the rate used by the first stage of the two stage process and throughout the one-stage process. Further drawing of samples of different draw rates may be the source of the divergence of the linear relation observed in Figure 20.

The compliance as shown in Figure 21 increases linearly with reciprocal gauge length. Thus indicating end effects in the measurement of modulus. This results indicates that actual moduli of these highly oriented samples may be as much as twice their values measured by short gauge length.

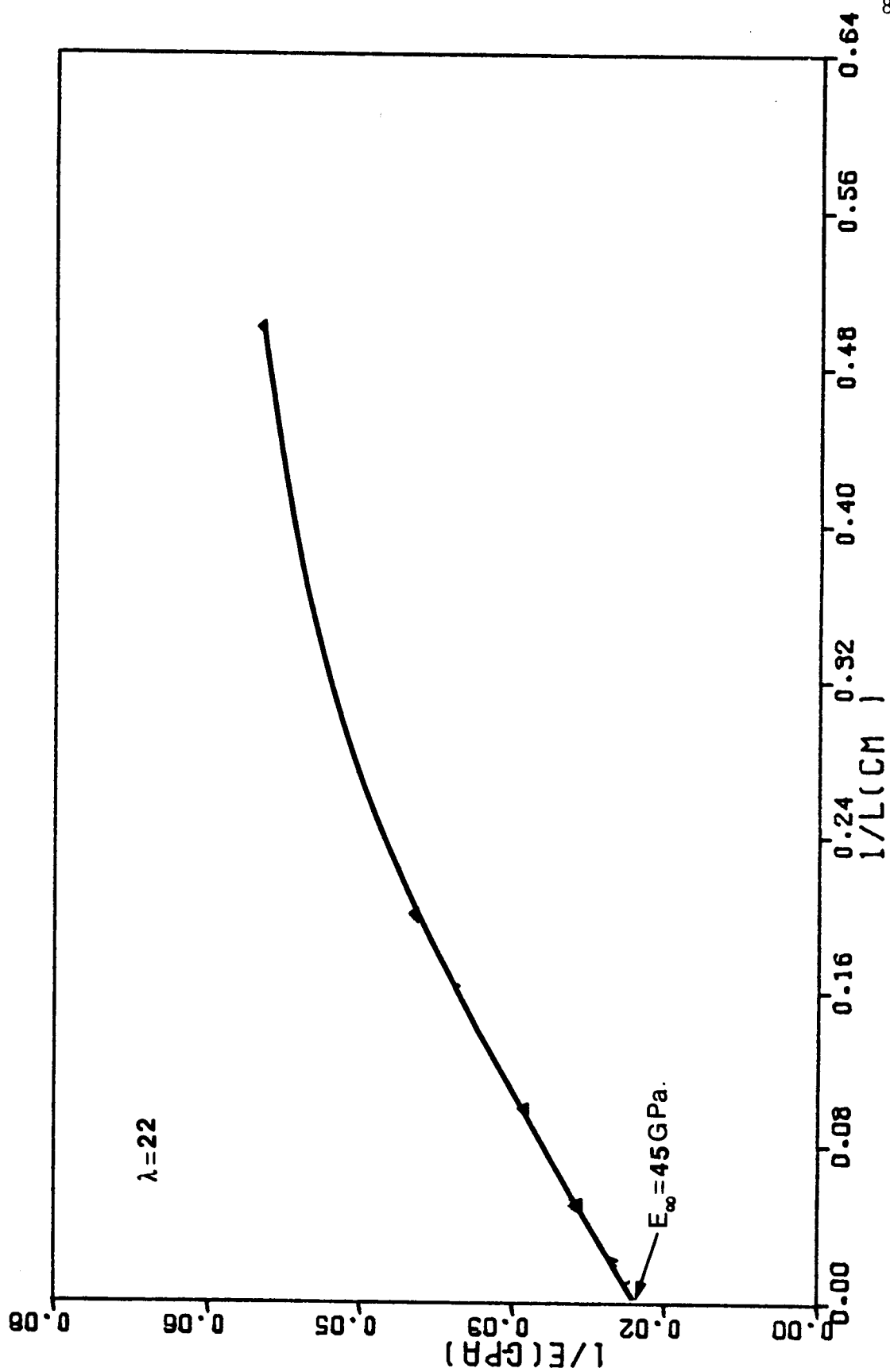


Figure 21. Compliance versus reciprocal gauge length for an HDPE sample.

C. DENSITY

The densities determined from Density Gradient Column shows a substantial increase with an increase of draw ratio for HDPE samples drawn by the two-stage method at 60°, 70° and 80° C (Figure 22). In 1976, Omotoso (85) found that the density of HDPE samples decreased with the increase of draw ratio at higher draw rates and attributed this behavior to void formation in the samples. The above behavior indicates that draw rate at the second stage of drawing may play a significant role in the void formation in the structure of the final product.

D. MEASUREMENTS OF MELTING POINTS OF HDPE SAMPLES

The melting points of undrawn and superdrawn samples, processed by one-stage and two-stage drawing methods, were determined by using the differential scanning calorimeter at a heating rate of 10° C/min. All the samples examined gave single endothermic peaks. No peak separation was observed. The Figure 23 shows an increase of the peak melting temperatures as the draw ratio increases for sample drawn by both techniques. A comparison of melting peaks of natural drawn and superdrawn samples indicate a sharpening of peaks as the draw ratio increases (Figure 24). Clements et al. (20) also observed similar trend for their ultradrawn HDPE samples. Peterlin and Meinel (88) studied drawing effects on HDPE and indicated the increase of T_m with draw ratio. Ward et al. (20) also found that in addition to draw ratio, the molecular weight also affects the position of the melting temperature. Hellmuth et al. and T. Arakawa and B. Wunderlich (43, 140) found that the increase of melting is associated

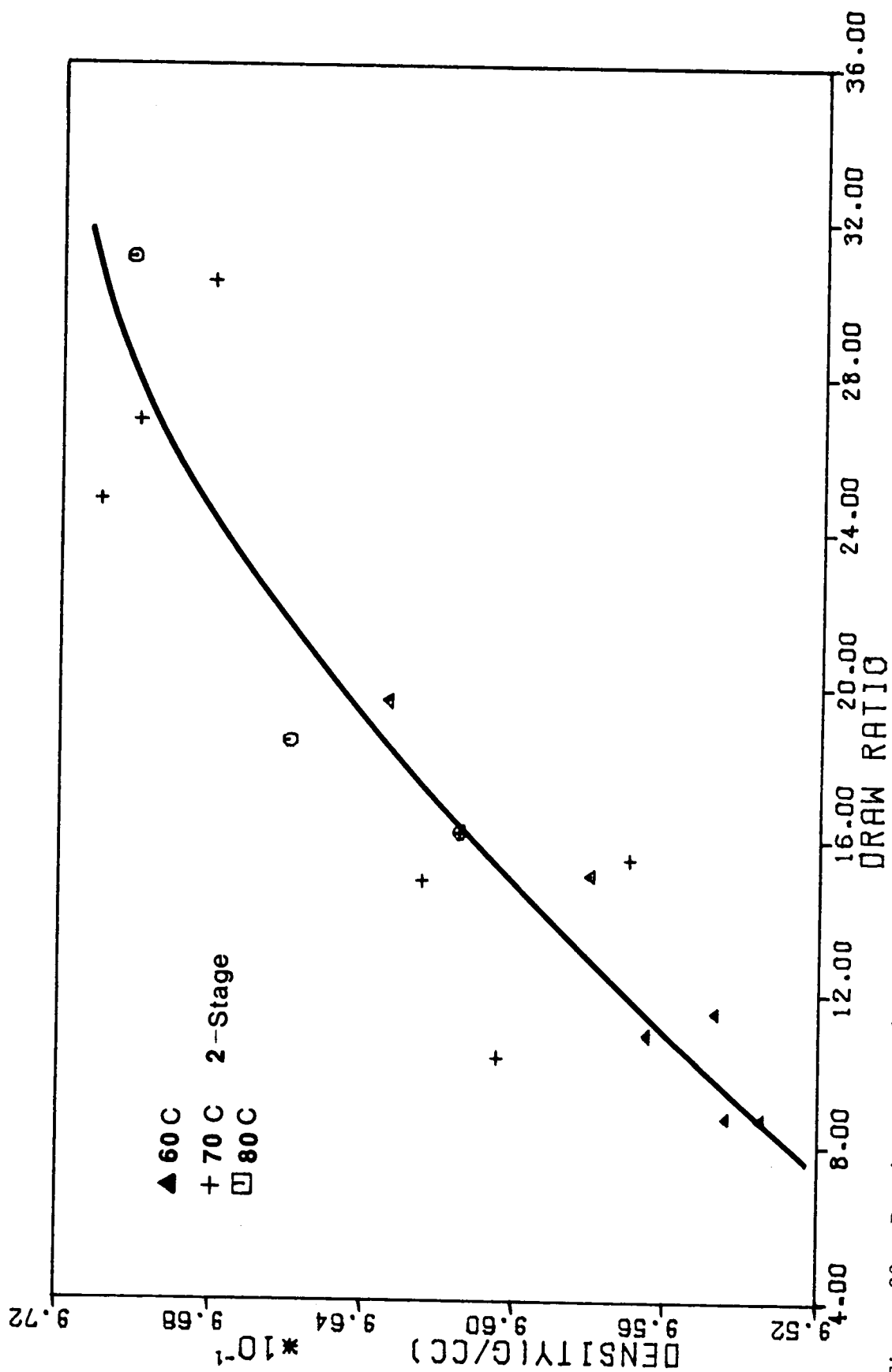


Figure 22. Density versus draw ratio for HDPE samples drawn at 60, 70, 80°C.

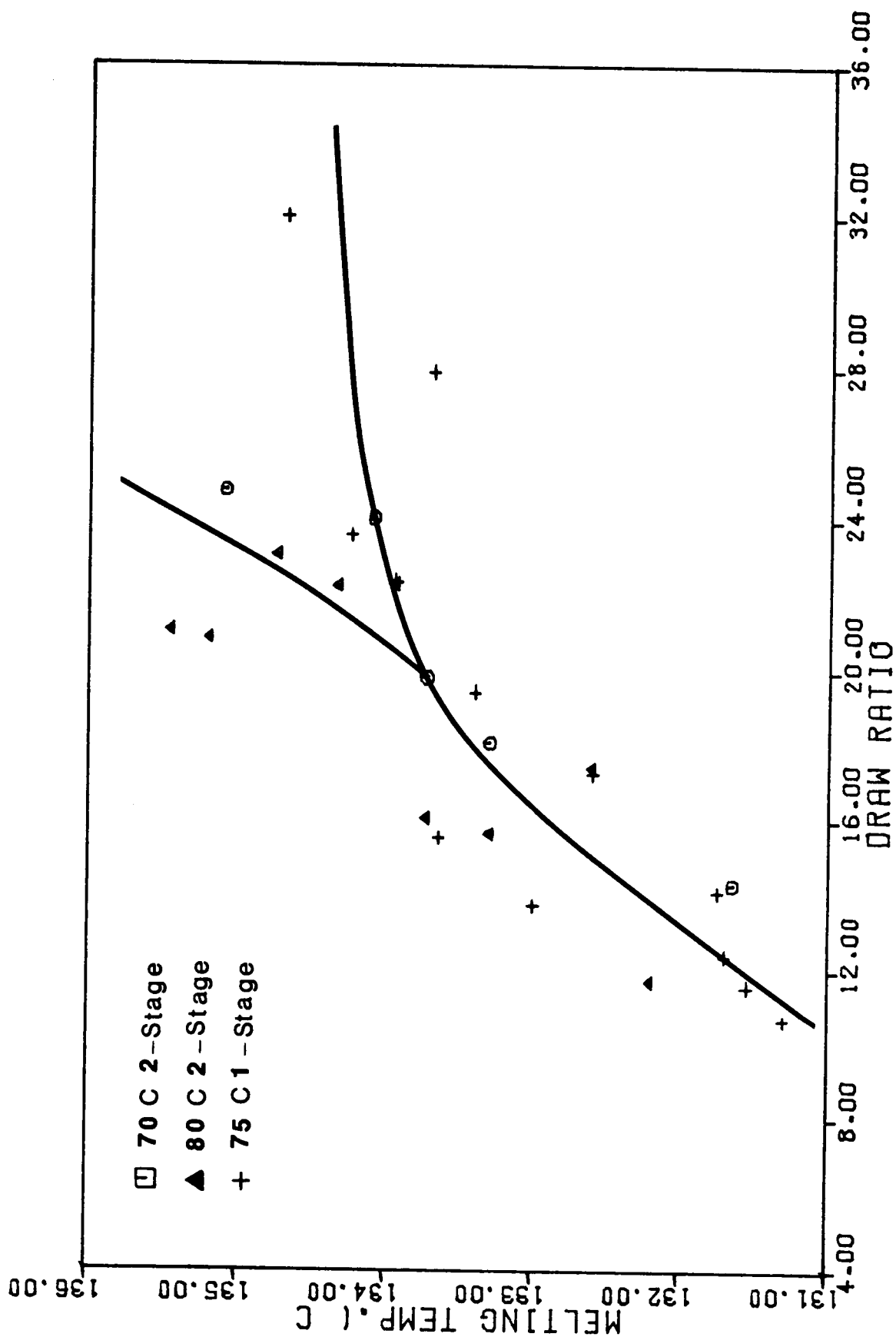


Figure 23. Melting temperature versus draw ratio for HDPE samples drawn by one-stage and two-stage methods.

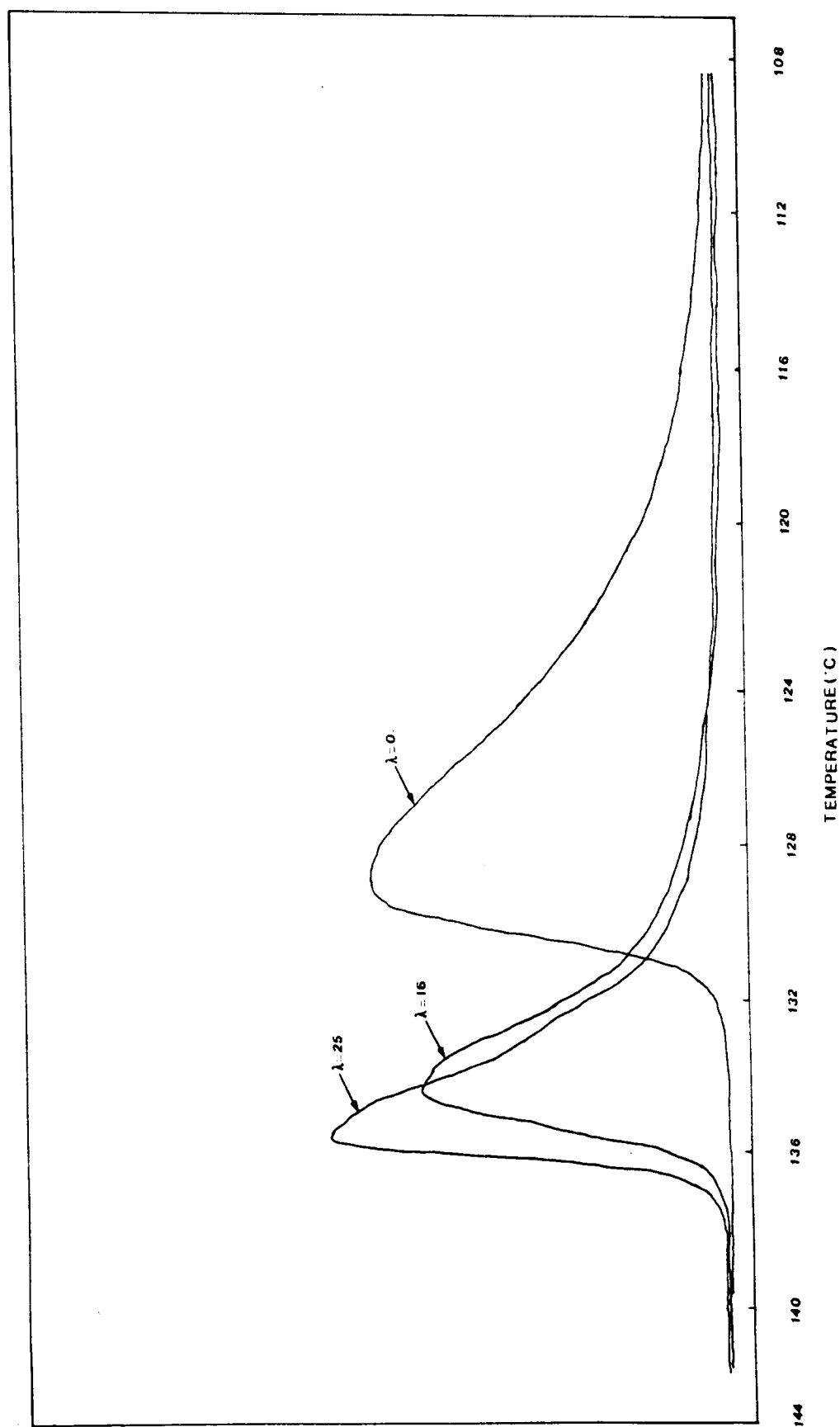


Figure 24. Melting peaks of natural drawn and superdrawn samples.

with the crystallite size in pressure crystallized HDPE. Lauritzen and Hoffman (72) associated the increase of melting temperature with the increase of long period in HDPE.

Thus we may conclude that slow drawing produces larger crystallites while faster drawing (one step method) inhibits the increase of crystallite sizes above the draw ratio of 22. A remelting of the samples showed lower melting temperatures indicating that the structure of the samples is changed after the initial melting.

E. MEASUREMENT OF CRYSTALLINITY

Three different methods, Density, Differential Scanning Calorimetry and X-ray diffraction, were used to obtain the crystallinities of undrawn the natural drawn and superdrawn HDPE samples. The crystallinities determined from all three methods showed an increase with the increase of draw ratio for samples drawn by the one-stage and two-stage processes at temperatures from 60° C to 80° C (Figures 25, 26, 27). Meinel et al. attributed this behavior to the increasing number of tie molecules with draw ratio and increasing perfection of crystals. Depending on the method used, the magnitude of crystallinities was varied for the same draw ratio. The highest crystallinities were obtained from X-ray analysis (Figure 26) and lowest were obtained from Differential Scanning Colorimeter measurements (Figure 25).

The DSC measurements showed that the crystallinities of samples drawn by one-stage and by two-stage methods are the same for low draw ratios, but above 22X the crystallinities of samples drawn by one-stage

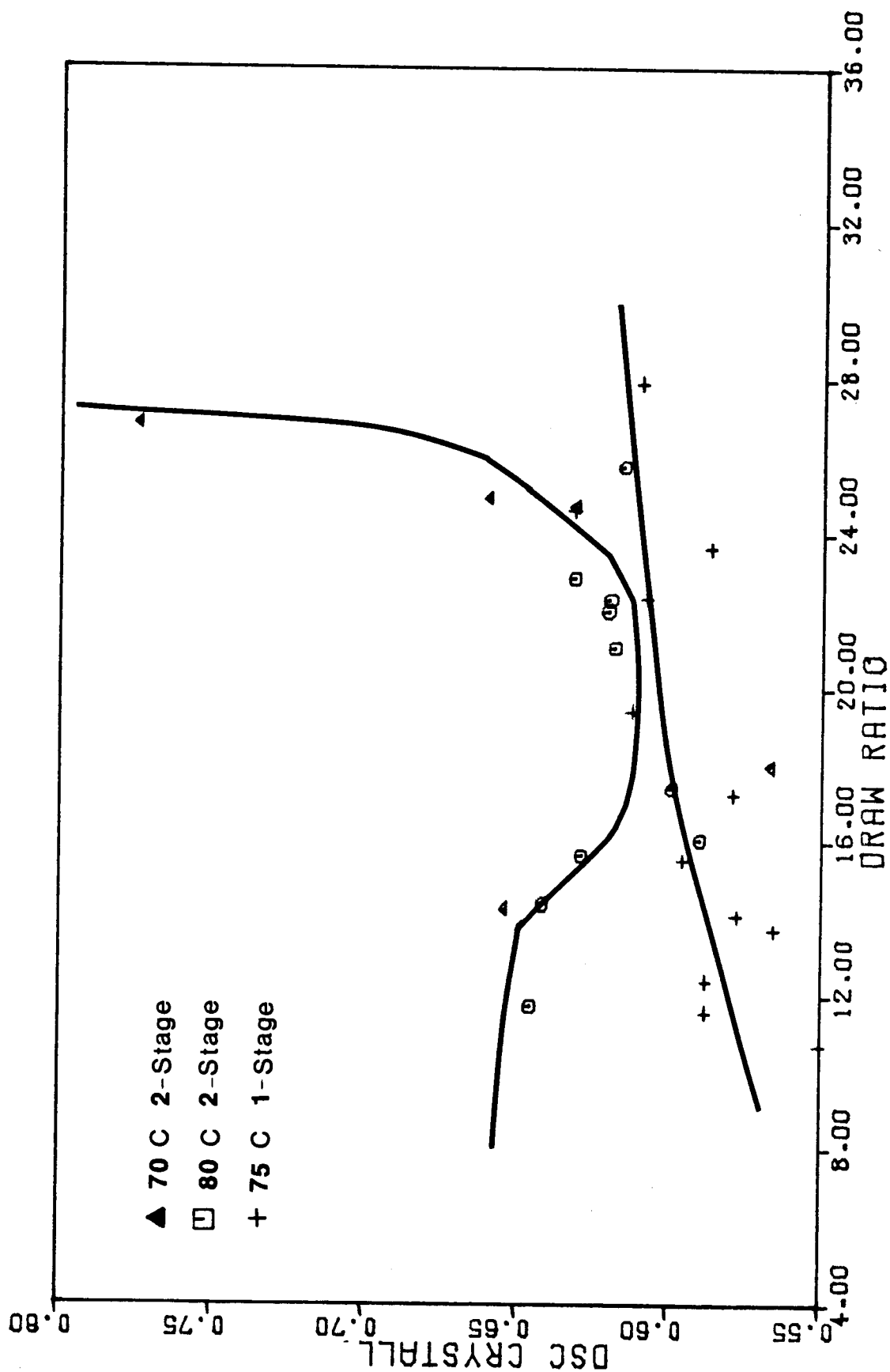


Figure 25. Crystallinity versus draw ratio for HDPE samples drawn by one-stage and two-stage methods (DSC).

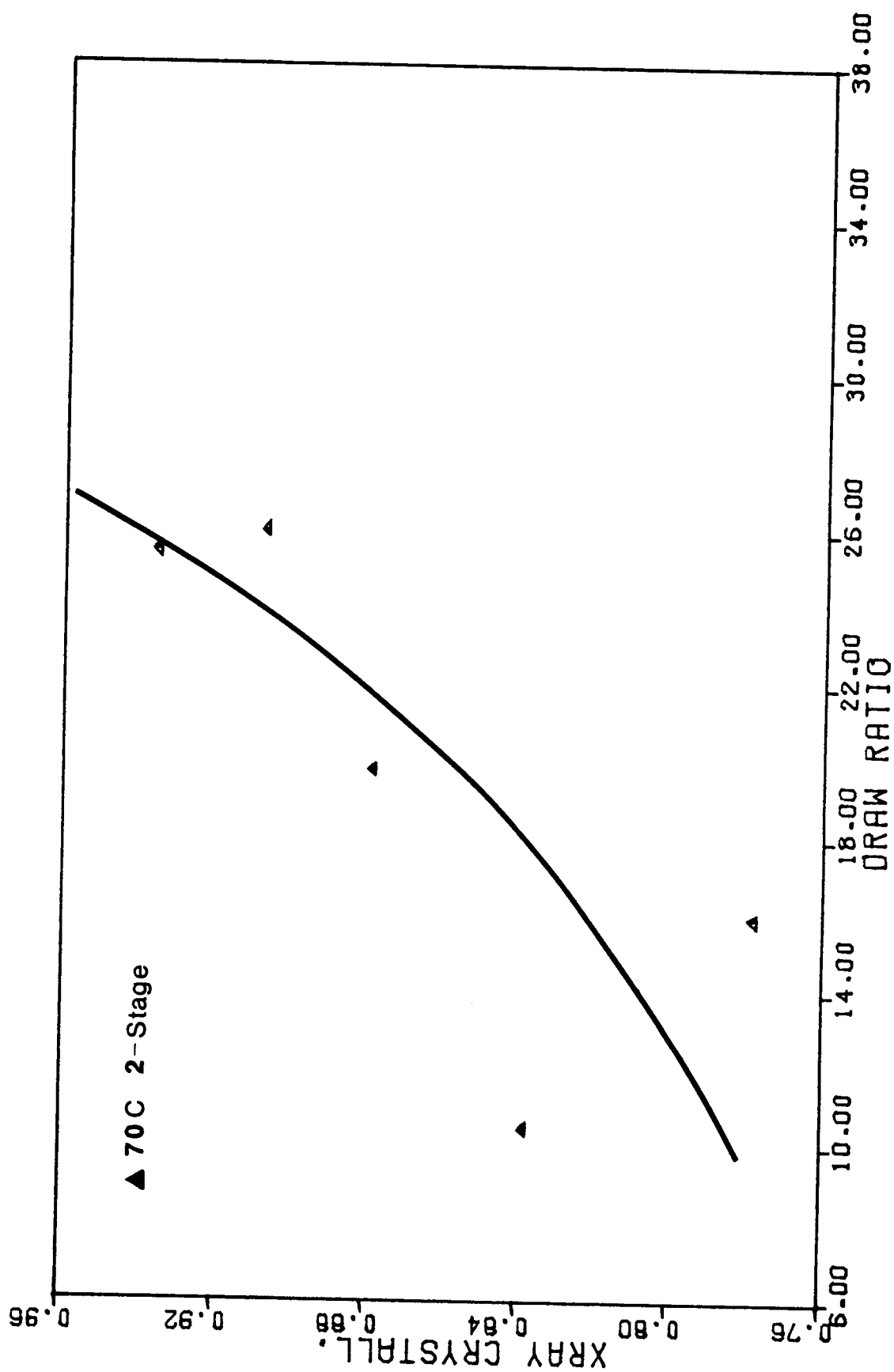


Figure 26. X-ray crystallinity versus draw ratio for HDPE samples drawn by two-stage methods.

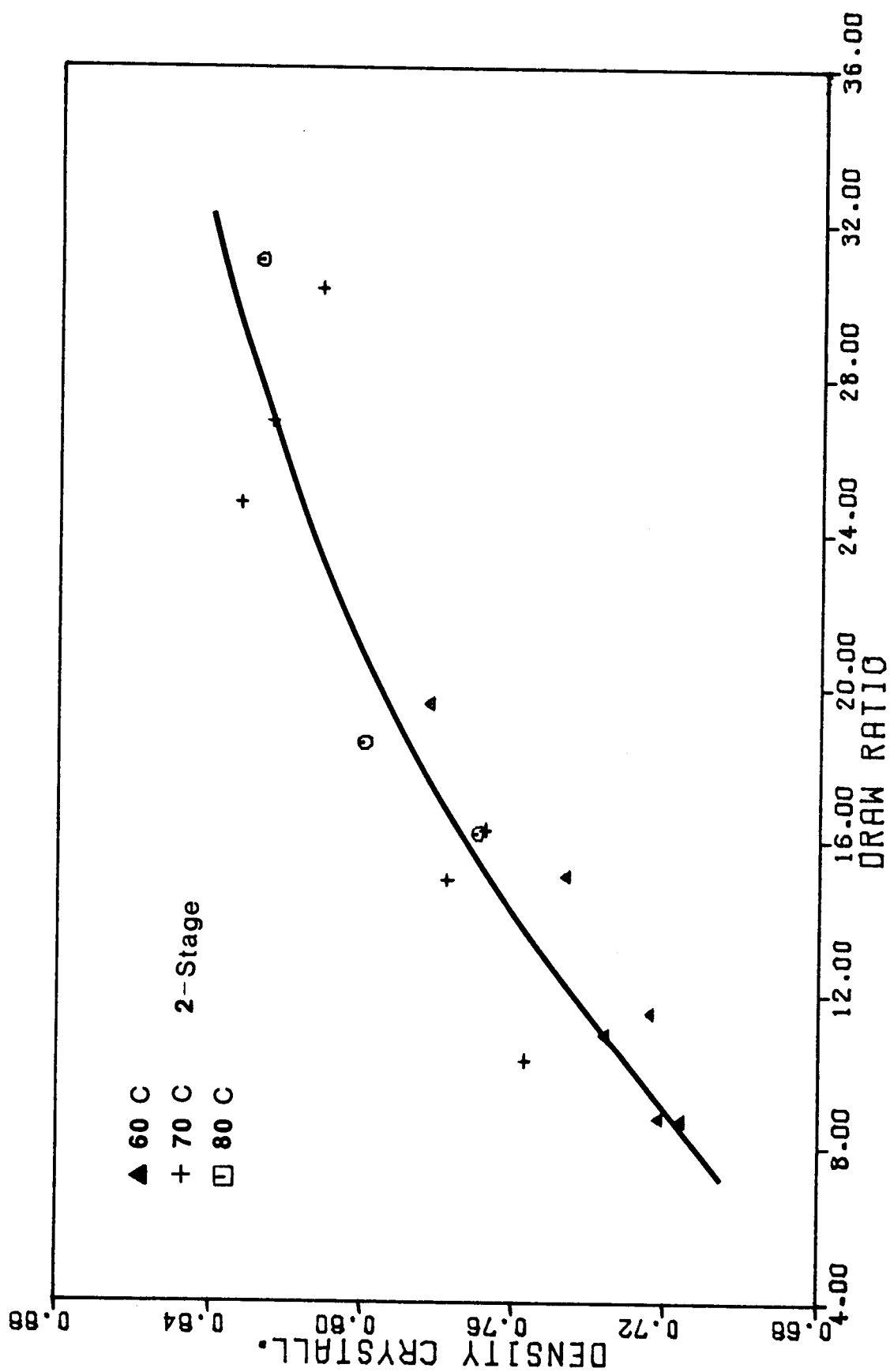


Figure 27. Density column crystallinity versus draw ratio drawn by two-stage method.

method becomes less than those of the samples drawn by two stage method for the same draw ratios (Figure 25). This implies that the one-stage method, which comprises faster draw rate, introduces imperfections to the samples.

F. CHARACTERIZATION BY SCANNING ELECTRON MICROSCOPE

The SEM micrographs of selected samples were taken to observe the morphological change, as small as 1 μm . In these observations three objectives were pursued which are: the determination of the effects of drawing on the surface structure, and on internal structure; quantitative statistical observations of change of crack sizes of samples which were strained up to 0.8 percent and the observations on the failure of samples at high temperatures.

The electron micrographs of the surfaces of the natural drawn and superdrawn samples are shown in Figure 28. The surface of the natural drawn sample shows distinct smooth and fibrillar regions. These morphological difference on the surface structure may be due to the inhomogeneous deformation of the sample during processing.

Figure 28b shows a typical fibrillar surface structure which was observed on the surfaces of the most of the superdrawn samples drawn at a 1 percent/min second stage extensional rate and 70° C or 80° C. It was observed that the extent of formation of the fibrillar striations is much higher on the surfaces of super drawn samples. This latter behavior is the consequence of drawing which causes slippage of strong fibrillar domains. While the strong fibrillar domains slip by each other



Figure 28. SEM micrographs showing the surface structure of (a) natural drawn, (b) superdrawn samples.

the less ordered interphase which comprises the chain segment, connecting the adjacent fibrils deforms and becomes oriented. It is believed that the valleys observed between the microfibrils are the result of this nonuniform microdeformation.

The Figure 29 shows the SEM peel structure micrographs of the natural drawn and superdrawn samples. The superdrawn sample surface shows much higher fibrillations than that of natural drawn sample. It could be observed that the at high draw ratios drawing process much thinner fibrils. A closer picture of the peel surface (Figure 30) shows cracks extending in perpendicular direction to fiber axis which may be originated from disordered domains.

The effect of lateral deformation of the superdrawn sample can be observed in Figure 31. A higher magnification inside surface of the bent sample clearly shows kink bands (Figure 31) which are due to compressive force imposed on the anisotropic sample with no recoverability. This type of structure on the surfaces of bent high strength samples were also observed by Omotoso, Taylor and Clark (19, 85, 124).

Structural and Statistical Observations on Extensionally Strained Samples

The surface structure of natural drawn and superdrawn samples which were strained on the order of 0.8 percent at room temperature, shows cracks running perpendicular to testing direction (Figure 32). These cracks probably were formed due to stress concentrations on the sites which are composed of disordered regions. A closer look at one of these cracks shows (Figure 33) a foam-like structure resembling the craze structure which is observed on amorphous polymers. The lengths of the

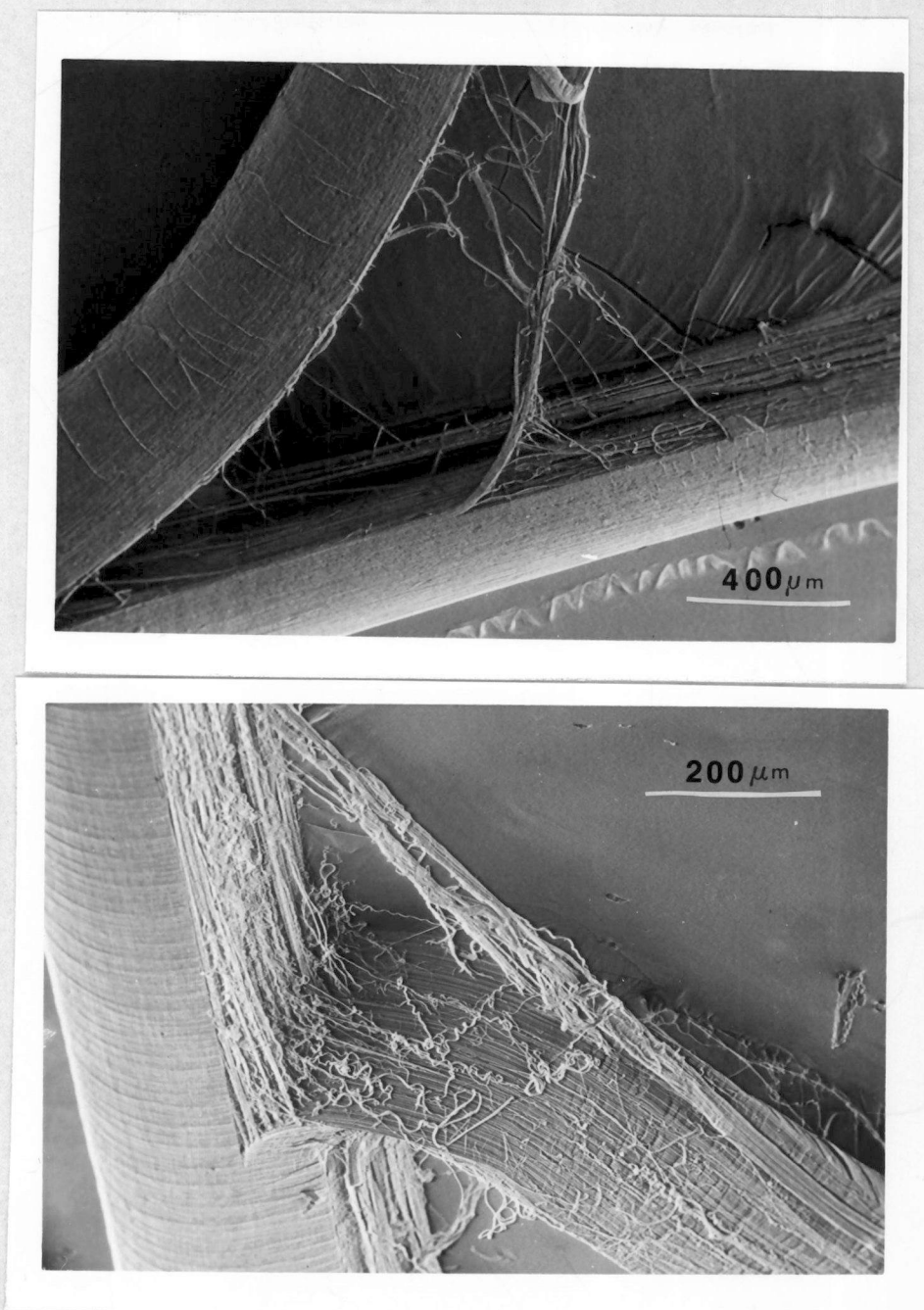


Figure 29. SEM micrographs showing the fibrillation inside the peel structure of (a) natural drawn, and (b) superdrawn samples.

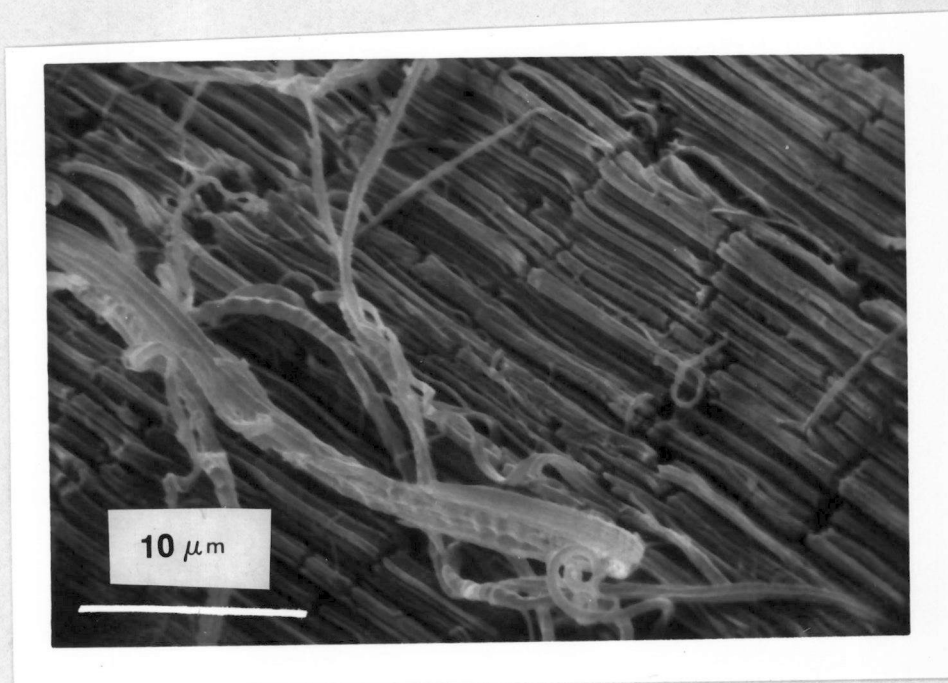


Figure 30. SEM micrograph of inside peel surface of superdrawn sample showing the cracks perpendicular to fiber direction.

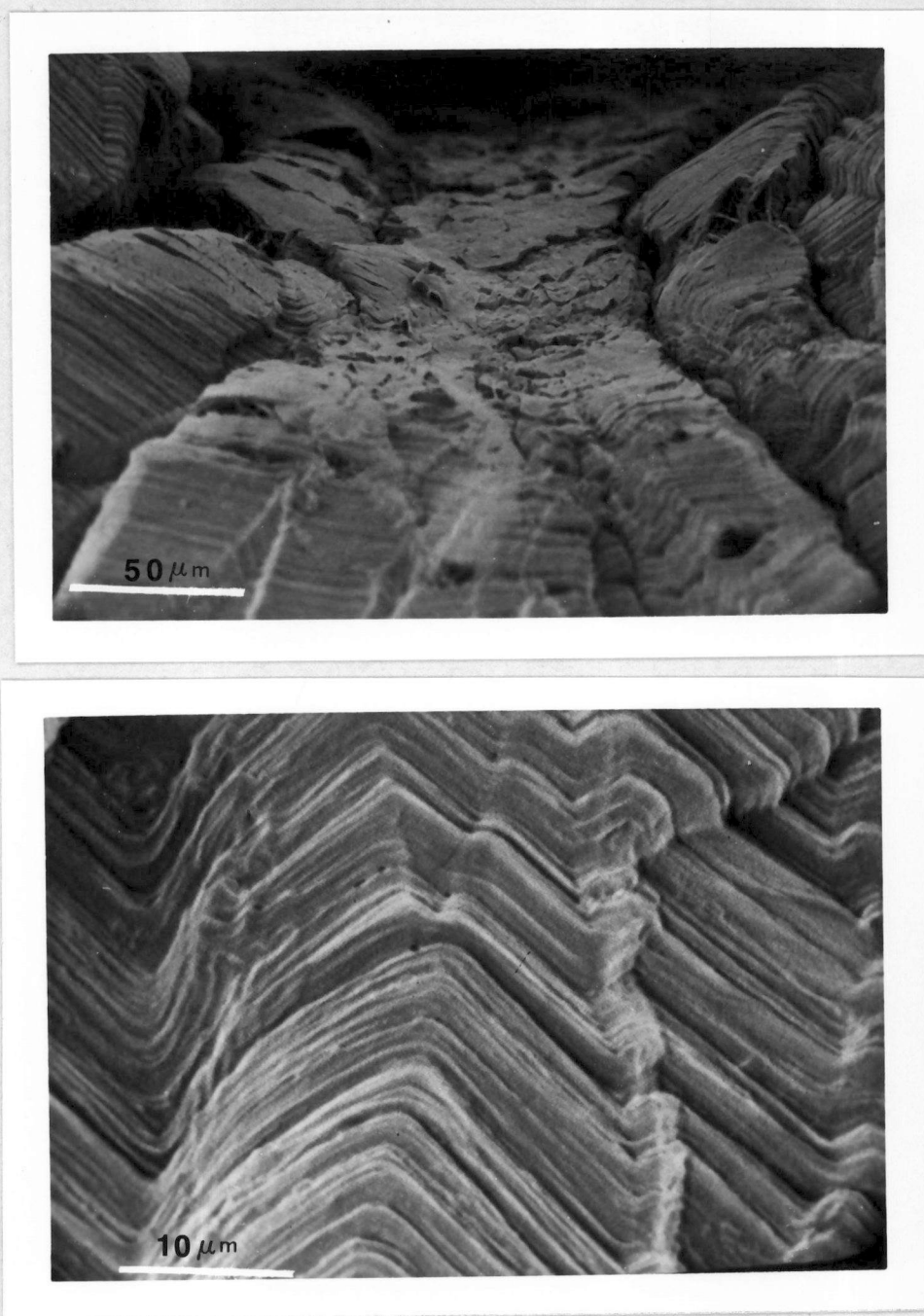


Figure 31. SEM micrographs showing (a) the inside surface of bent superdrawn sample and (b) the kink bands.

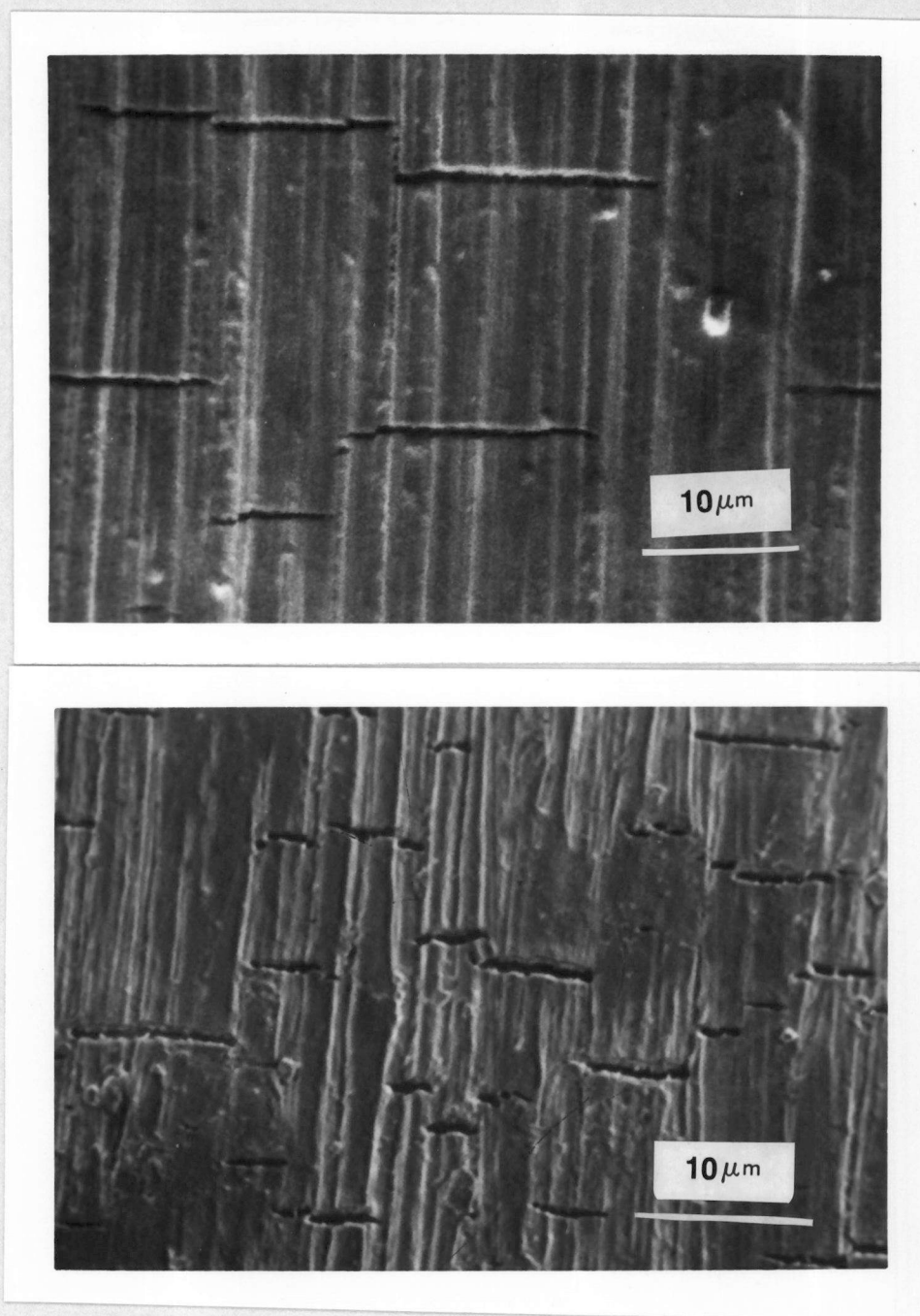


Figure 32. SEM micrographs of extensionally strained (a) natural drawn and (b) superdrawn samples showing the cracks in a direction normal to the fiber axis.

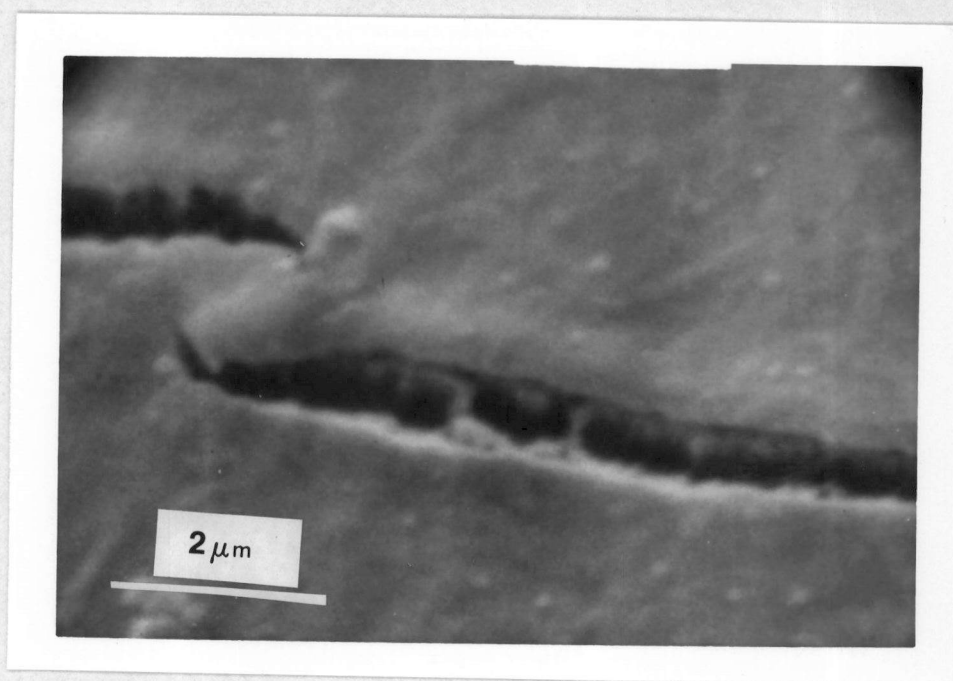


Figure 33. SEM micrograph of a crack on the surface of drawn polyethylene showing the fibrils crossing the crack.

cracks on the surfaces of the superdrawn samples were found to be much shorter than those found on the surfaces of the natural drawn samples. The change in the number-average crack length with draw ratio is shown in Figure 34. The decrease of number average crack length indicates an increase of fraction of stronger phase which inhibits the propagation of the cracks further. It could be speculated that these stronger regions may be related to extended chain domains. No apparent difference in the distribution of crack lengths observed on the samples prepared by one-stage and two-stage processes. It should be noted that very little or no cracks observed on the strained samples drawn above 90° C.

The samples failed to draw at 110° C from original undrawn samples. The surface studies on these samples (Figure 35) indicates presence of loose structure which may be due to chain slippage at this high temperature ("taffy pull").

G. VISCOELASTIC PROPERTIES

The experiments undertaken in this investigation can be divided into two categories: one was to determine the viscoelastic properties of HDPE samples at room temperature (22°C) and the other was to determine the effect of temperature change on these properties.

The results of experiments done on samples processed by the two-stage drawing method shows a decrease in $\tan \delta$ as the draw ratio increases at room temperature (Figure 36). This indicates that as the draw ratio increases, the elasticity of samples increases. This result is in accordance with the microfibrillar model of Peterlin (77,90). In Figure 37 the increase of elastic storage modulus with draw ratio at room temperature

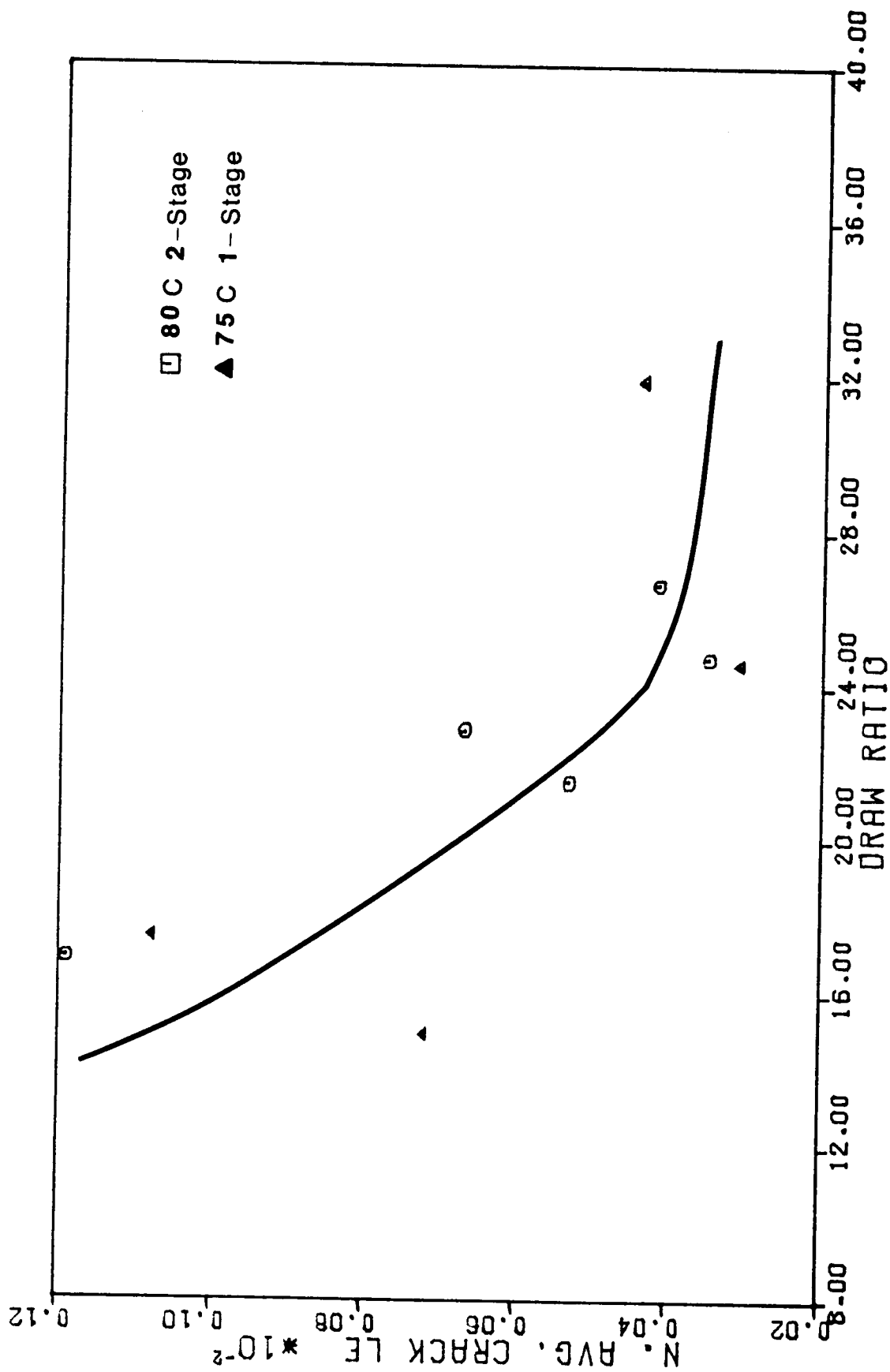


Figure 34. Effect of draw ratio on the number average crack length of strained samples drawn at 70, 75, 80°C by one-stage and two-stage methods.

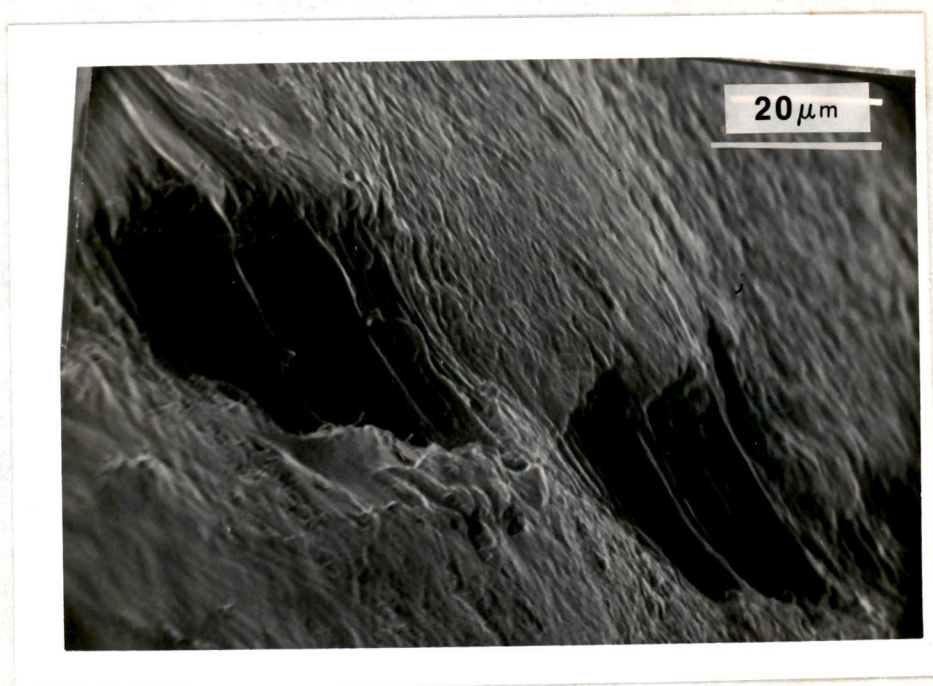


Figure 35. The SEM surface micrograph of samples which failed to draw at 110°C showing loose fibrillar structure on the neck region.

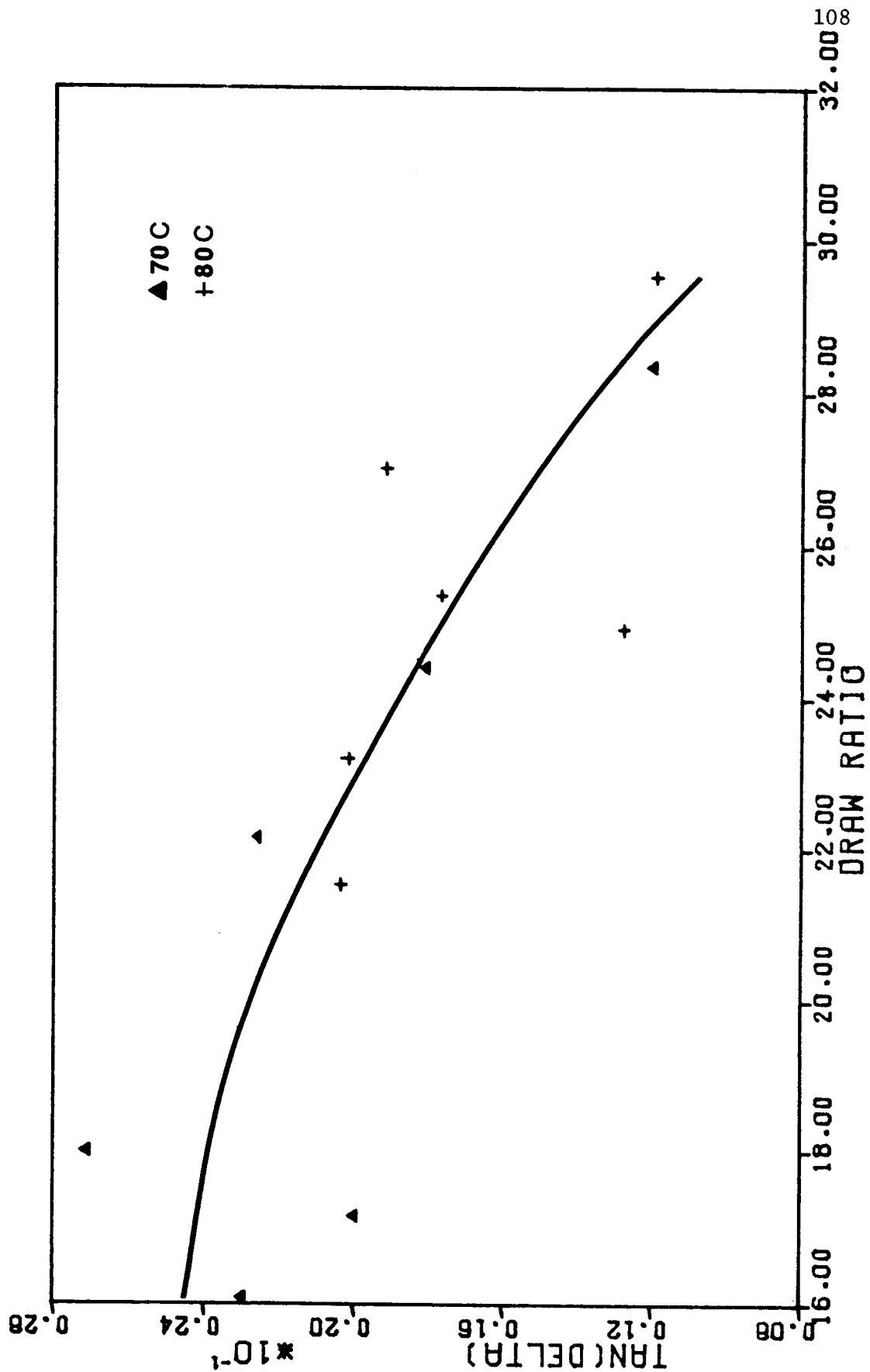


Figure 36. Effect of draw ratio on room temperature $\tan \delta$ (delta) of samples drawn at 70°C and 80°C by two-stage method.

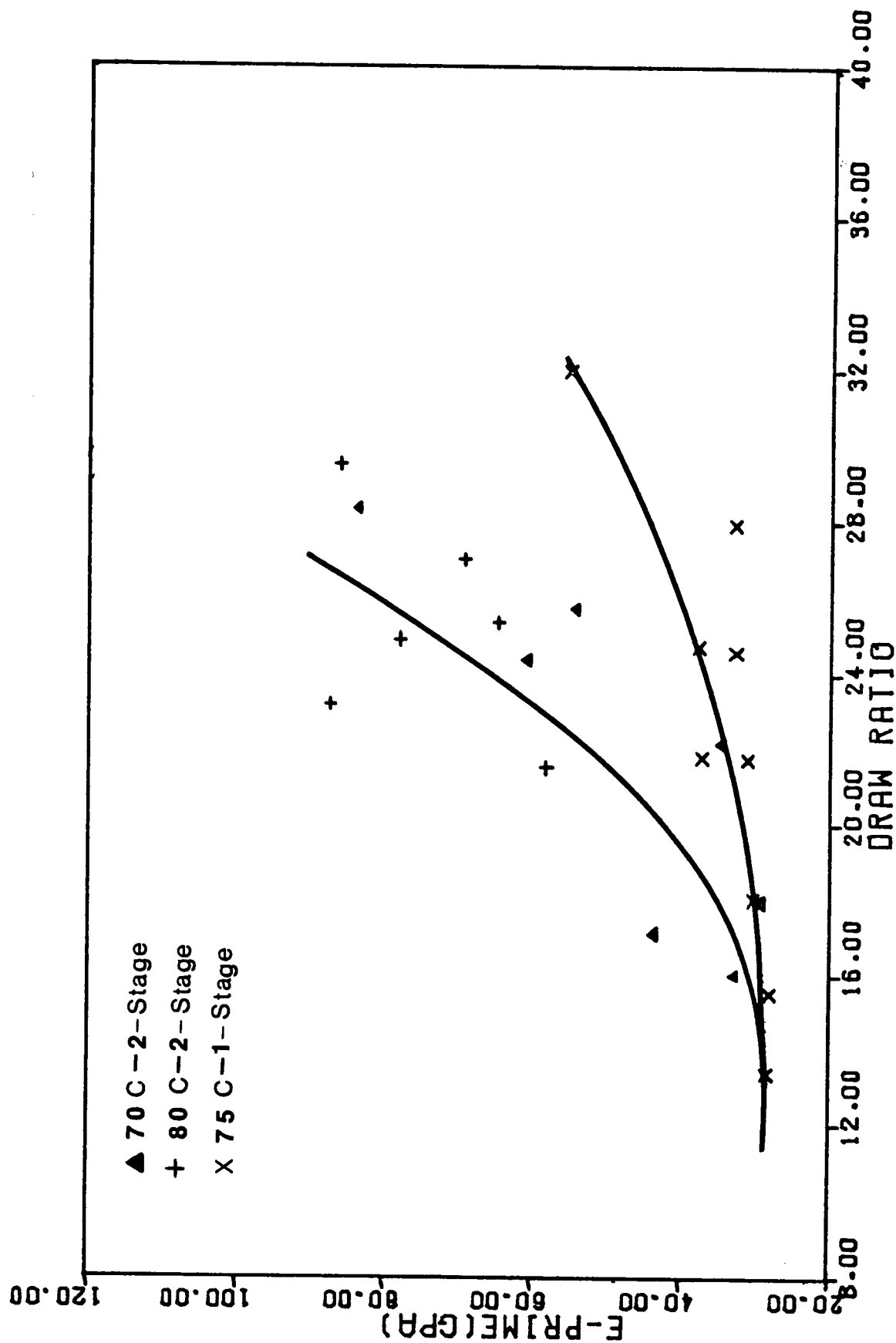


Figure 37. Effect of draw ratio on room temperature storage modulus (E') (E' -prime) of samples drawn by one-stage and two-stage methods.

may be correlated with the increase of orientation as suggested by Takayanagi (117). This latter room temperature behavior of drawn samples is extended over 80-130° C temperature range as shown in Figures 38 and 39. It can be observed from Figures 38 and 39 the superdrawn sample ($\lambda=26$) shows remarkably low $\tan \delta$ and high E' around 125° C. This is a clear indication that superdrawn samples are highly stable even at 10° C below their melting temperatures. On the other hand, natural drawn samples ($\lambda = 14, 16$) show very high $\tan \delta$ values and low E' around 125° C. These Figures 38 and 39 are typical of crystalline samples of different crystallite size and orientation. The resolution of α_1 and α_2 transition peaks was not observed in the samples investigated in the 20-140° C range. However, the peak maximum temperature was found to increase with the increase of draw ratio as shown in Figure 40. The same behavior was observed by Gibson on their ultradrawn polymer (39). Takayanagi (118) also observed this behavior and concluded that drawing at high temperature results in a more perfect crystals than those in undrawn samples (117). This increase of perfection of the crystal may be attributed to the annealing effect accompanying the drawing process at elevated temperatures.

In Figure 41 absorption peaks (E'') of natural drawn and superdrawn filaments are shown. In 1960, Takayanagi (119) presented a hypothesis that the mechanism of this (α_c) absorption is directly related to the crystalline region. Takayanagi et al. found that as the size of crystallites increases the α_c peak shifts toward a higher temperature region and the intensity increases. Their results showed that the position of the absorption peak is determined by the state of aggregation of chains. Takayanagi's studies on drawn samples showed an increase

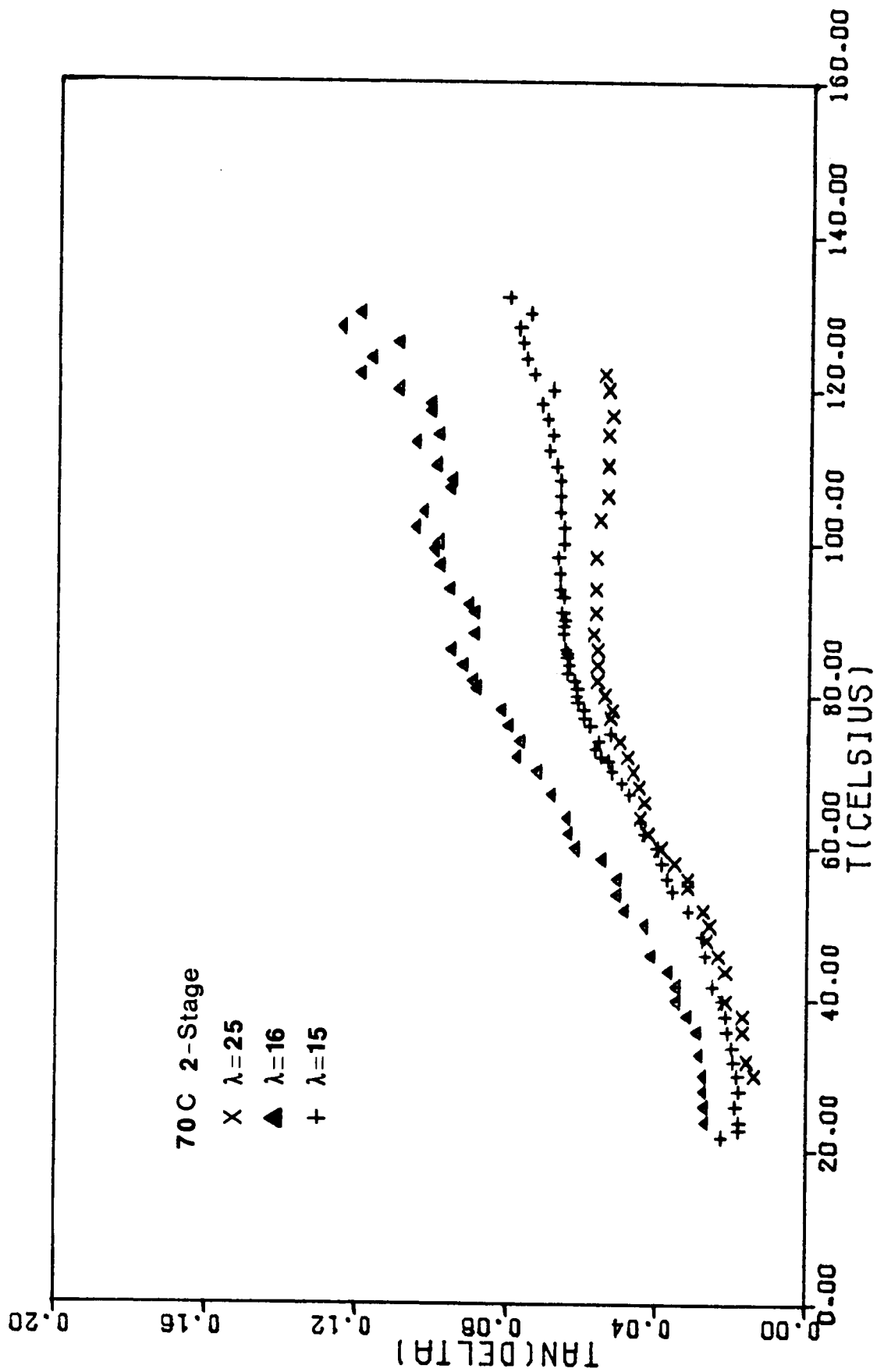


Figure 38. Effect of temperature on the $\tan (\delta)$ values of natural drawn and superdrawn samples drawn by two-stage method.

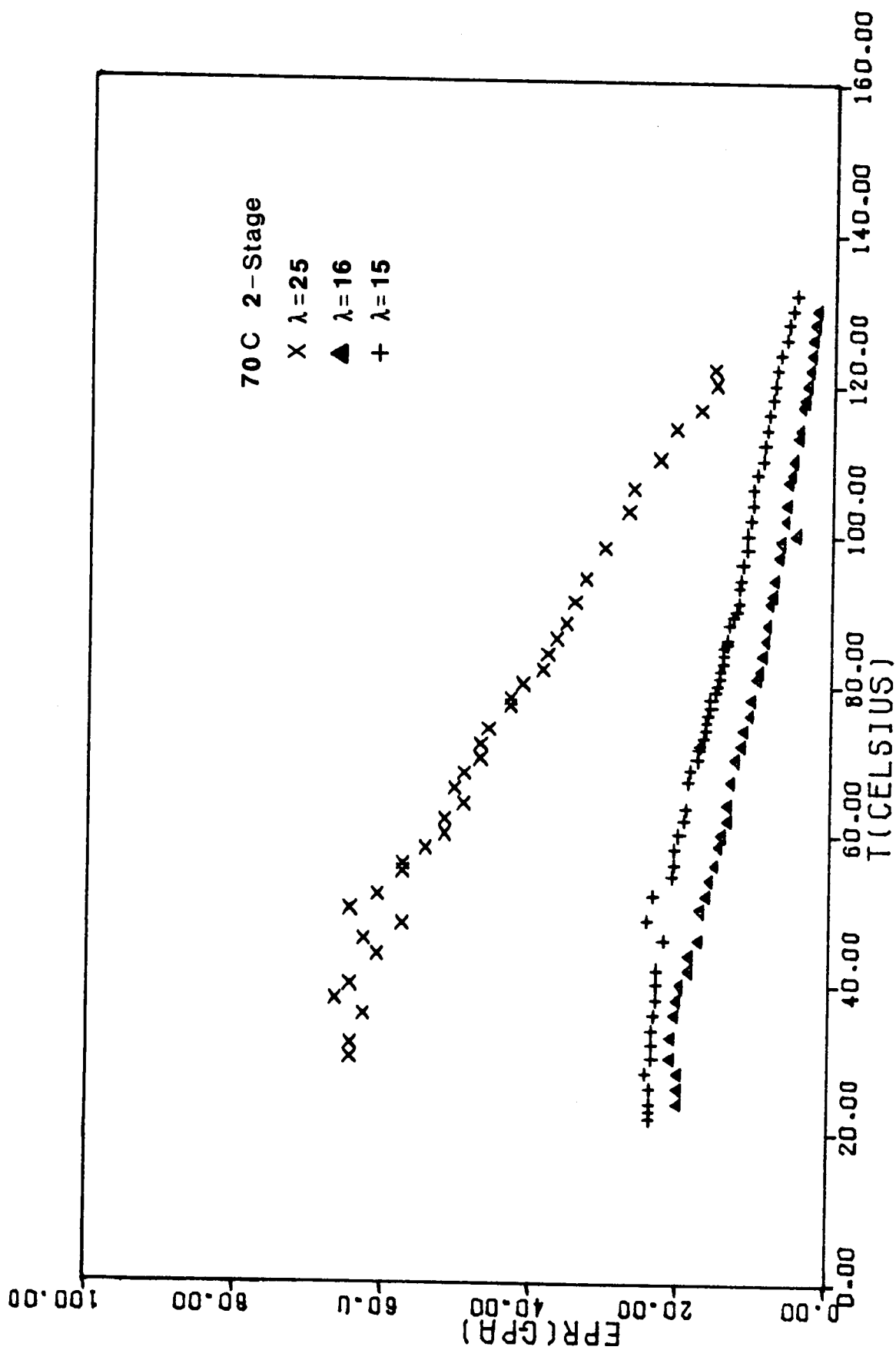


Figure 39. Effect of temperature on the storage modulus (E') (prime) of natural drawn and superdrawn samples drawn by two-stage method.

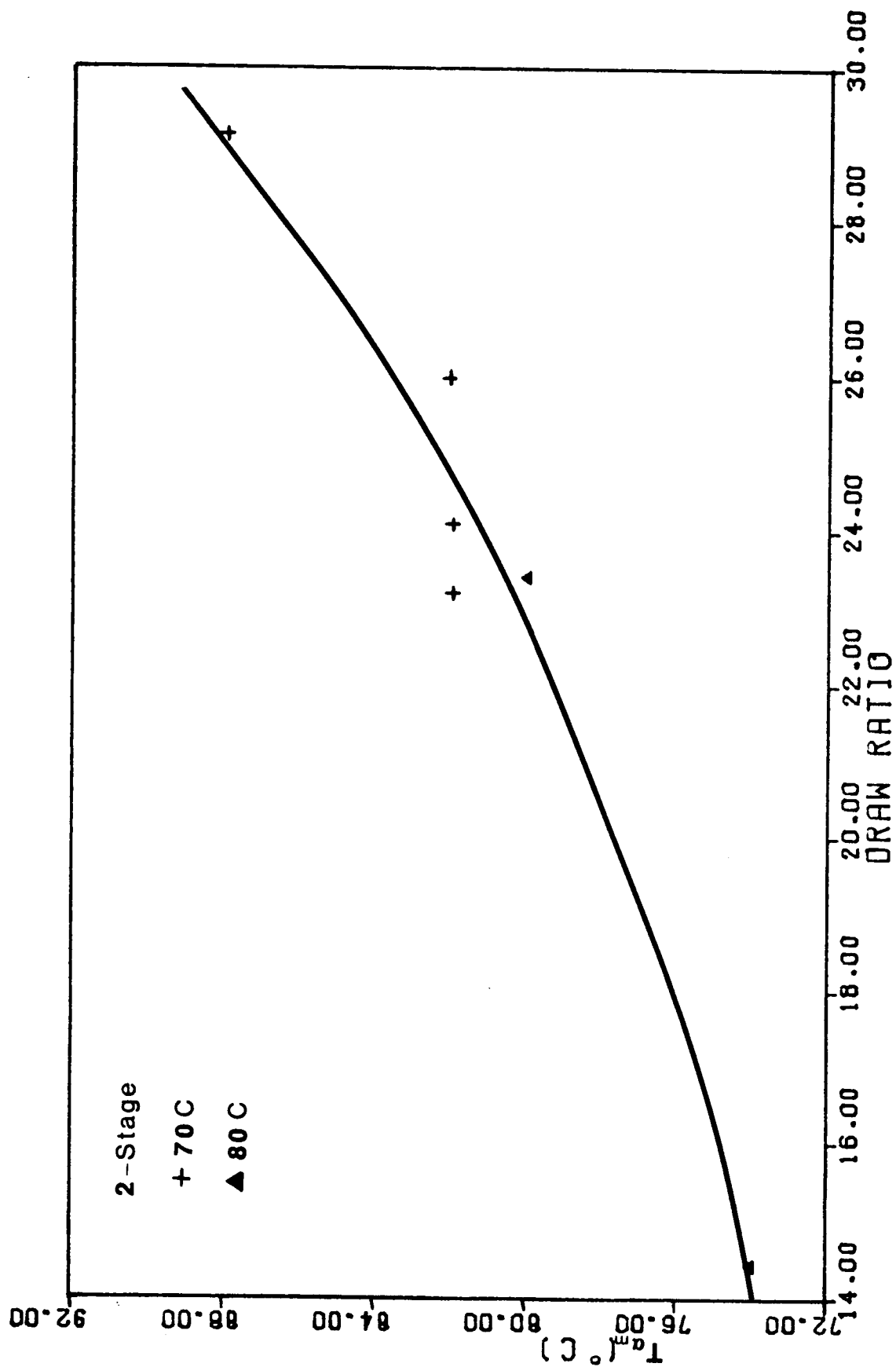


Figure 40. Effect of draw ratio on the α_c transition peak maximum of samples drawn by two-stage method at 70°C and 80°C.

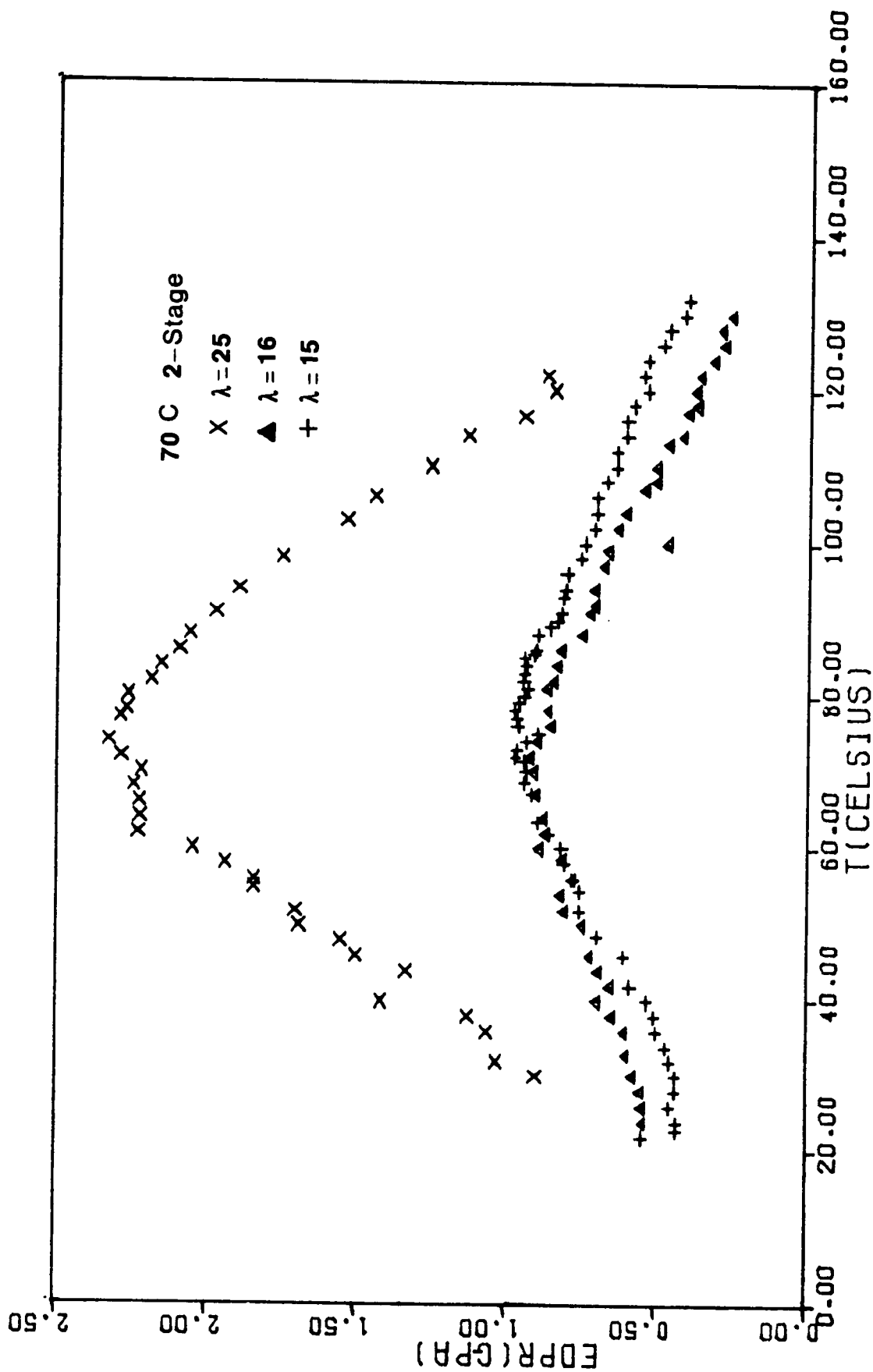


Figure 41. Effect of temperature on the loss modulus (E'') of samples drawn by two-stage method at 70°C.

of broadening of the absorption peaks with deformation. It is clearly observed that the absorption peak of superdrawn polyethylene is broader and more intense than those of the natural drawn samples. This behavior was interpreted by Takayanagi as follows: As the orientation and crystallinity increases greater restraints are added to the molecular chains of noncrystalline regions. The reason why the absorption shapes become broad is increased restraint on the molecular chains with increasing draw ratio. The relaxation mechanism thus, requires a much longer time or higher temperature. He concluded that the location of the absorption peak temperature represents the state of aggregation of molecular chains. If the degree of crystallinity increases along with increasing orientation, the intensity of absorption increases. Figure 41 clearly shows the increase of the absorption peak and a shift ($\sim 5^{\circ}$ C higher) of absorption temperature as the draw ratio increases, and Figure 42 also shows increase of E'' as the draw ratio increases at room temperature. The SAXS and WAXS studies revealed, as will be explained in Chapter VI, a large increase of crystal size along the fiber axis; Guinier and Fourier analyses indicated an increase in perfection of crystals as the draw ratio increases. Thus, these X-ray methods are in agreement with what is observed in Rheovibron data.

The differences in the effects of two stage and one stage drawing methods for polyethylene are shown in Figure 37, 43, and 44. The Figure 34 indicates that the one stage drawing results in a lower E' modulus than that of the two-stage process at high draw ratios. As mentioned earlier SAXS patterns of samples drawn by the one stage process show a very high intensity equatorial streaks which indicates the presence

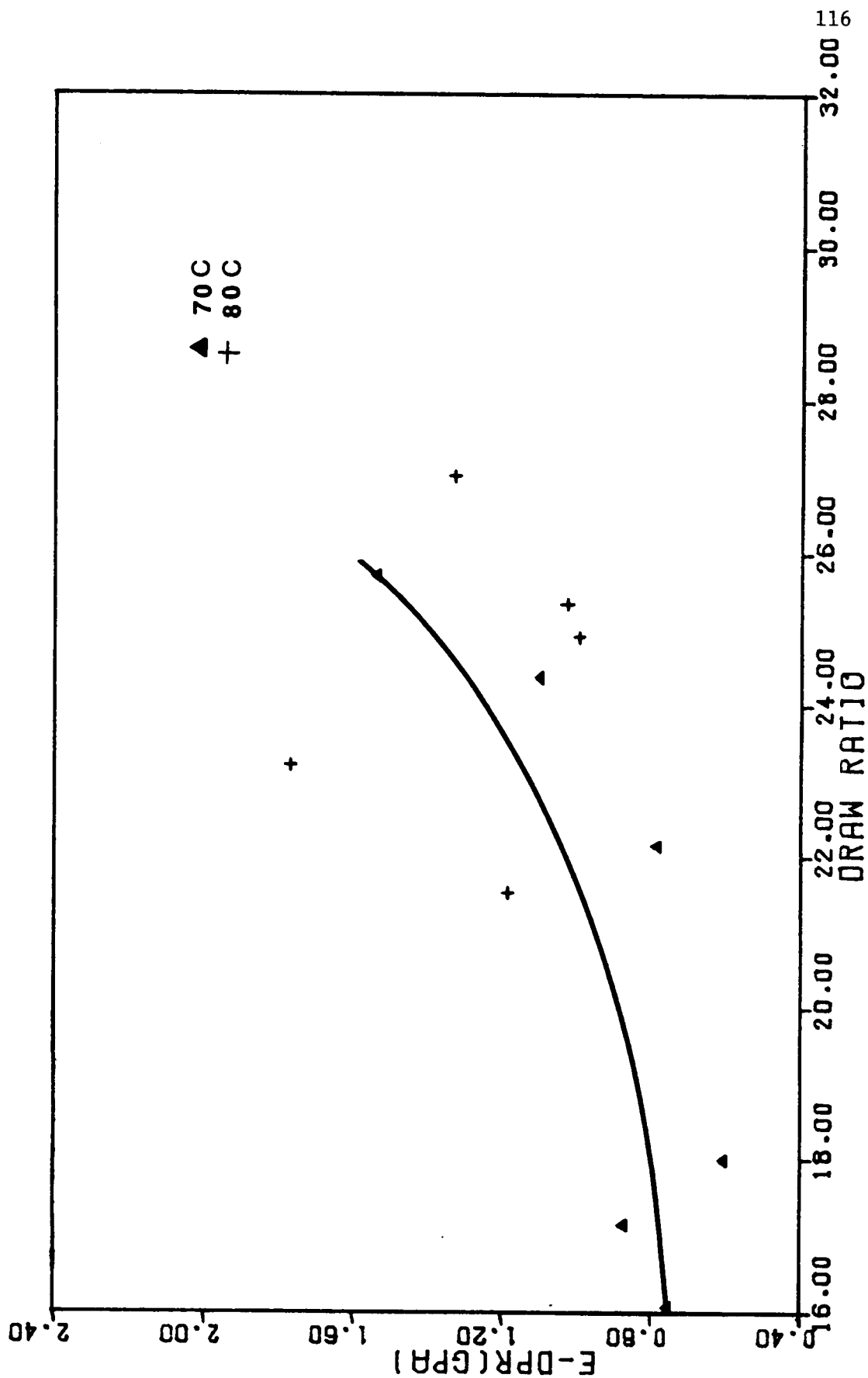


Figure 42. Effect of draw ratio on the room temperature loss modulus (E'') of samples drawn by two-stage method at 70°C and 80°C.

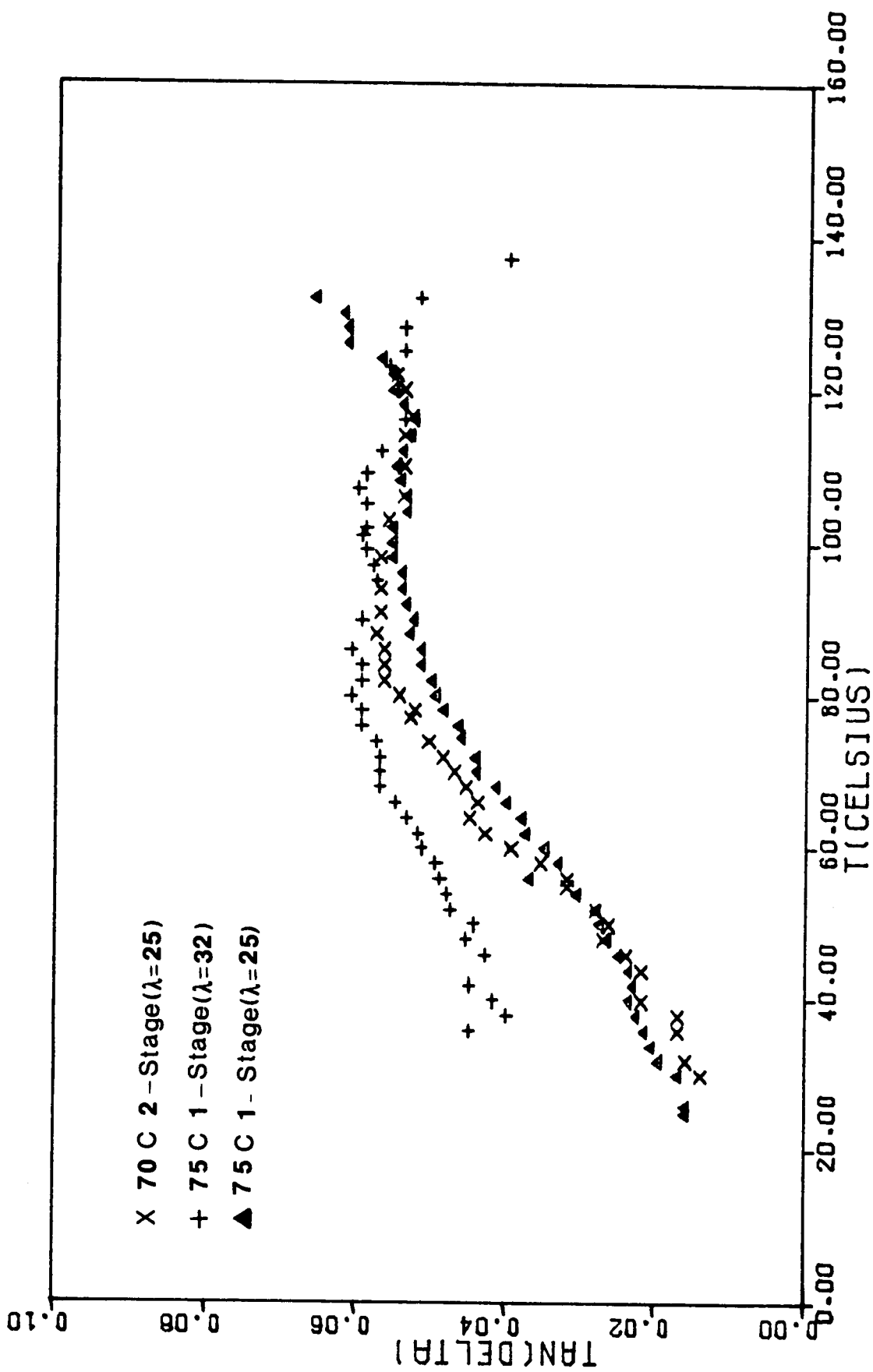


Figure 43. Effect of temperature on the $\tan(\delta)$ (delta) values of superdrawn samples drawn by two-stage and one-stage methods.

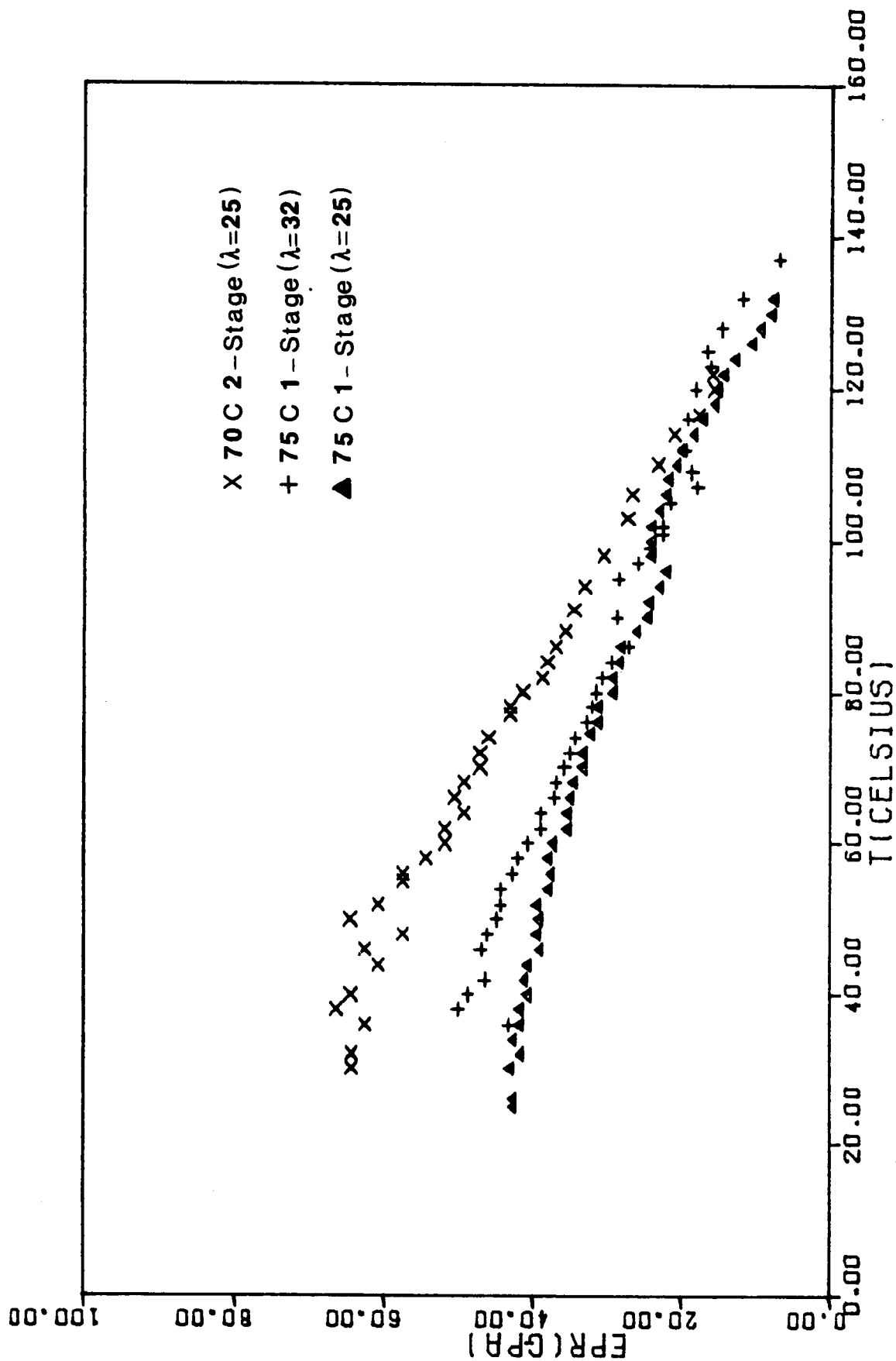


Figure 44. Effect of temperature on the storage modulus (E') (prime) of the superdrawn samples drawn by two-stage and one-stage methods.

of large elongated voids parallel to the axis of the filaments. Thus these results can be interpreted as an increase of void content in the fibers drawn by the one stage method. Even though the samples drawn by the one-stage have higher draw ratios. Figure 43 shows the $\tan\delta$ values are higher than those of sample drawn by two stage. Figure 44 also shows that the storage modulus of samples drawn by one stage method are lower than those observed for superdrawn sample drawn by two stage method even though the draw ratio of latter is less than those of former. In Figure 45 the absorption peak of samples drawn by one stage is much broader than that of the two stage drawn sample. The peak position is $\sim 30^\circ$ C less. Since the position of the absorption peak has been attributed to the aggregation of chains in the sample, we may conclude that the one-stage method results in less ordered structure in the drawn filaments. The similar absorption intensities of the samples drawn by both methods is probably due to the similar orientation of the chains in both samples.

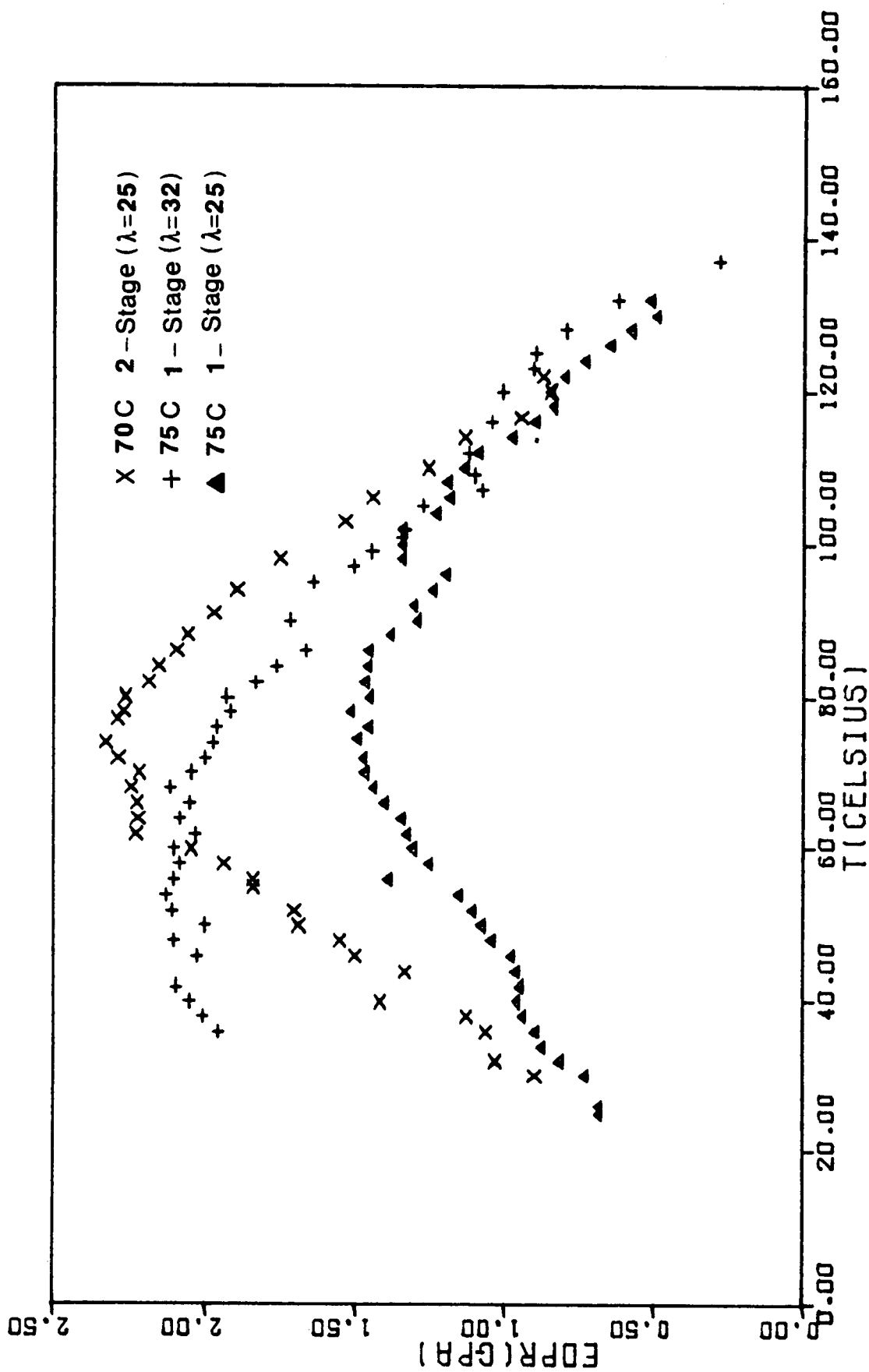


Figure 45. Effect of temperature on the loss modulus (E'' , EDPR) of the superdrawn samples drawn by a two-stage and one-stage method.

CHAPTER VI

CHARACTERIZATION BY X-RAY DIFFRACTION

A. WIDE ANGLE X-RAY DIFFRACTION (WAXS)

Low Density Polyethylene

The wide angle X-ray patterns of selected undrawn, natural drawn ($\lambda=2$) and superdrawn ($\lambda=4.5$) filaments of low density polyethylene are shown in Figure 46.

The WAXS pattern of undrawn samples shows concentric rings corresponding to (110) and (200) planes. This indicates that the undrawn filament which was formed by extrusion with low elongational stress on spinline does not have any preferred orientation. As the deformation progressed these ring patterns split into arcs (Figure 47 b, c). Qualitatively it could be observed that the differences in orientation between natural drawn and superdrawn samples is small. This is probably due to the inherent structure of LDPE which comprises chain entanglements, and branches inhibiting samples to achieve higher orientations.

High Density Polyethylene

The undrawn, natural drawn ($\lambda=15$) and superdrawn ($\lambda=26$) sample patterns are similar to those of LDPE (Figure 47). However, the HDPE do not contain as much chain branching and entanglements as the LDPE. The drawing process provided much higher orientation on the samples resulting in small and intense arcs. The superdrawn samples shows even smaller arcs implying a higher level of orientation.

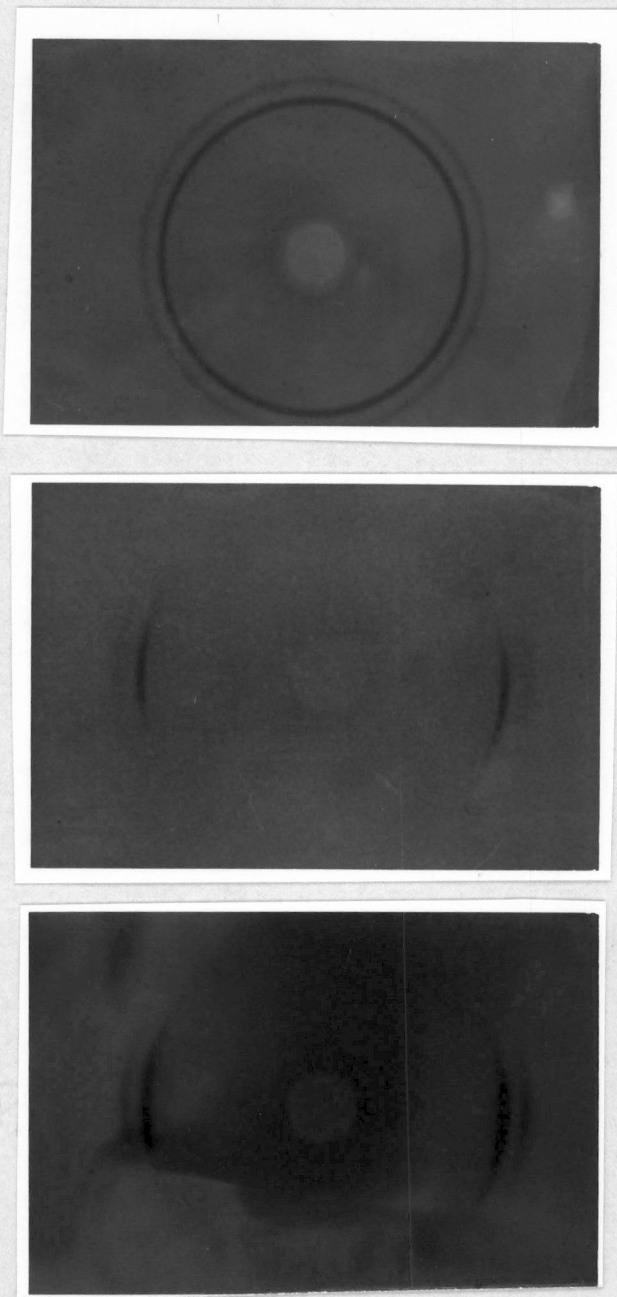


Figure 46. WAXS patterns of selected (a) undrawn, (b) natural drawn, (c) superdrawn LDPE samples.

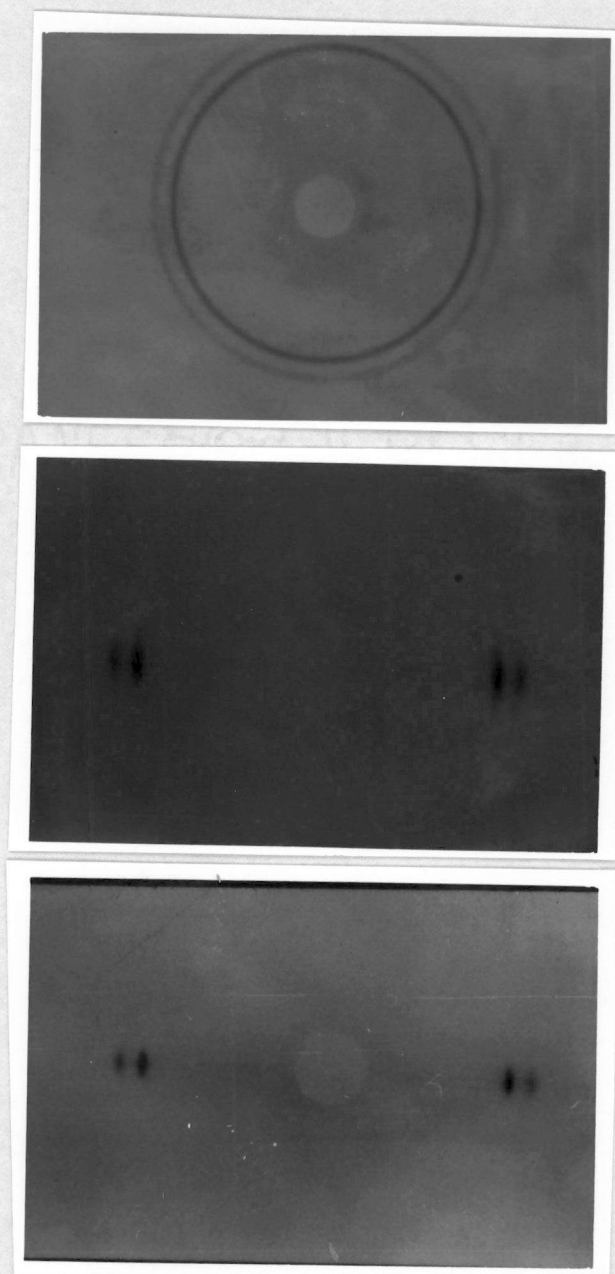


Figure 47. WAXS patterns of selected (a) undrawn, (b) natural drawn, (c) superdrawn HDPE samples.

B. SMALL ANGLE X-RAY DIFFRACTION (SAXS)

Low Density Polyethylene

Figure 48 contains SAXS patterns of LDPE filaments including selected undrawn and superdrawn filaments ($\lambda=4.8$). The pattern for undrawn LDPE filament shows a diffuse halo which indicates that the filament is unoriented. The superdrawn sample SAXS pattern shows discrete two point scattering along the meridian corresponding to a long period of $125\text{\AA}$. This two point pattern indicates presence of orientation in the structure of the sample (draw ratio of 4.8). No equatorial scattering was observed in the SAXS patterns of drawn LDPE filaments.

High Density Polyethylene

In this section the results of qualitative as well as quantitative observation of SAXS patterns of samples drawn by one-stage and two-stage drawing techniques are discussed.

Qualitatively, the SAXS patterns show the usual transition from diffuse halo to two point diagram as the deformation increases (Figure 49). The microdensitometer meridional traces of SAXS patterns are shown in Figure 50. The latter traces indicate sharpening of the half peak and shift of peak position as the deformation increases which is the result of increase of long periods of samples.

Quantitative studies of the SAXS patterns of natural drawn and superdrawn filaments shows an increase in the long period as the deformation increases as shown in Figure 51. The long periods of $166\text{\AA}$ and $193\text{\AA}$ were determined for the samples of draw ratio of 14 and 27 respectively. This

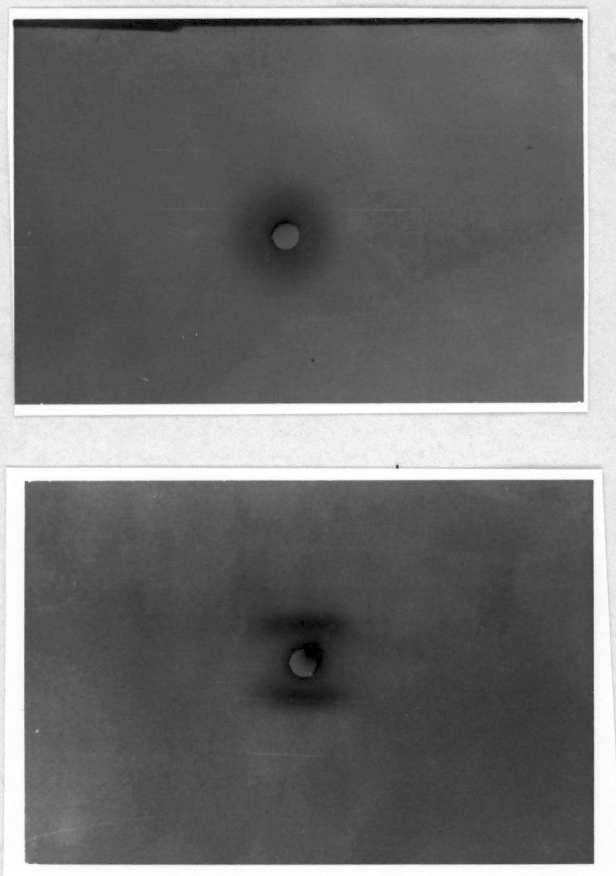


Figure 48. SAXS patterns of selected (a) undrawn, (b) superdrawn LDPE samples.

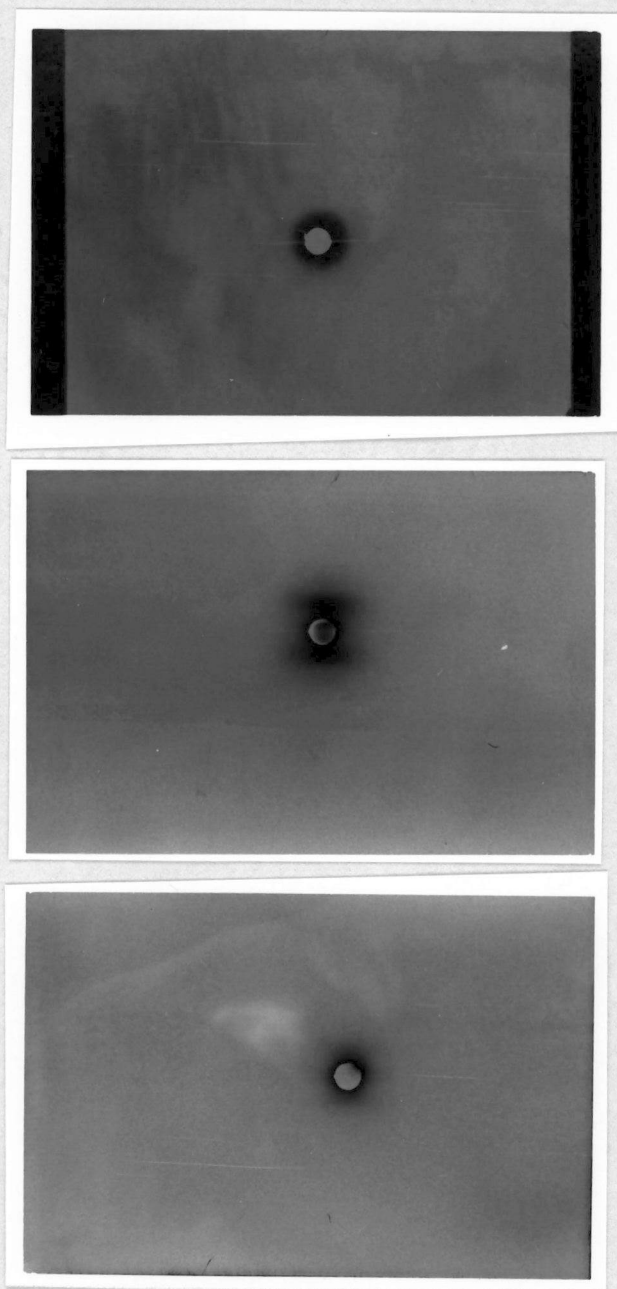


Figure 49. SAXS patterns of selected (a) undrawn, (b) natural drawn and (c) superdrawn HDPE samples drawn by two-stage method.

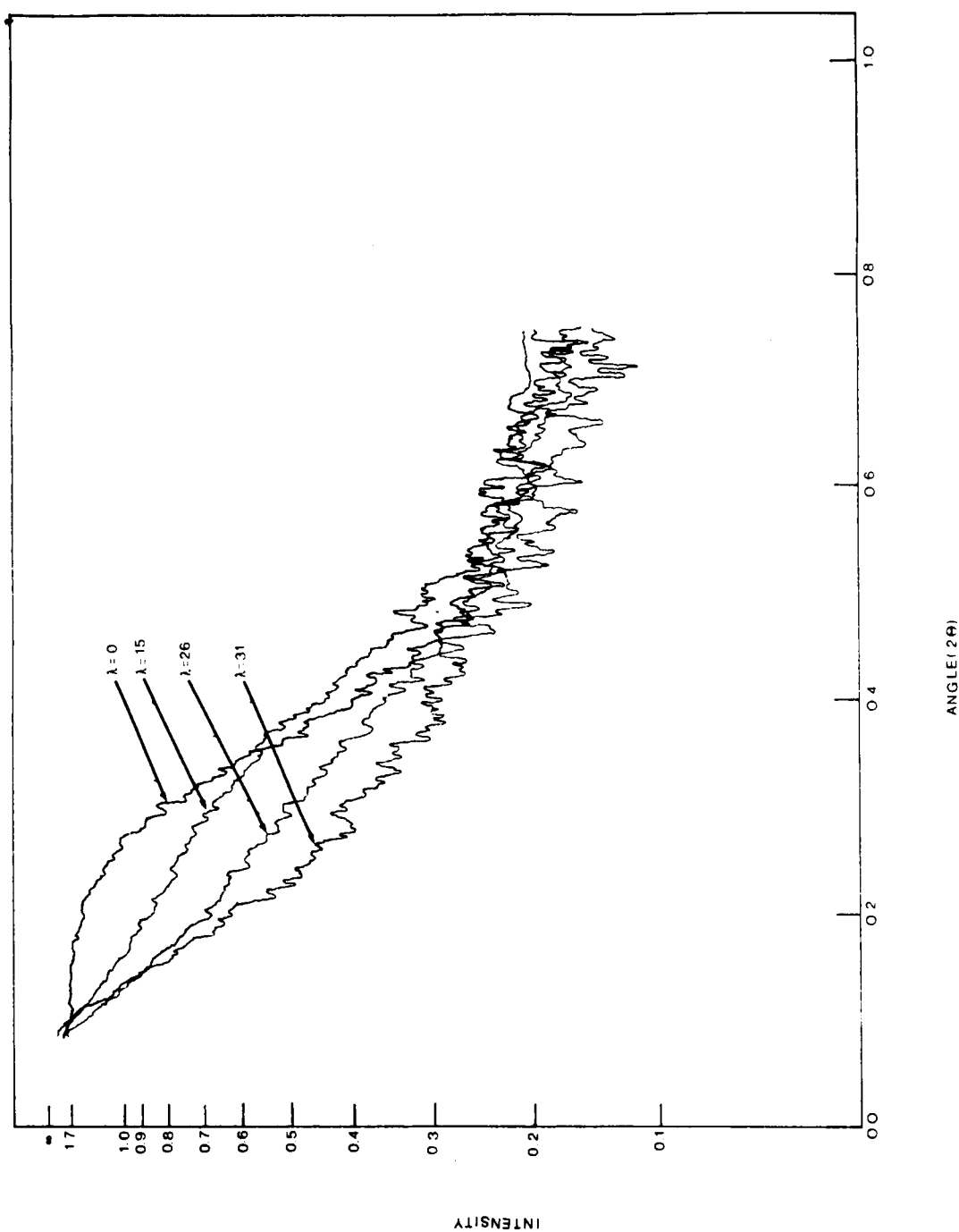


Figure 50. Microdensitometer meridional traces of SAX patterns of samples of different draw ratio drawn at 70°C .

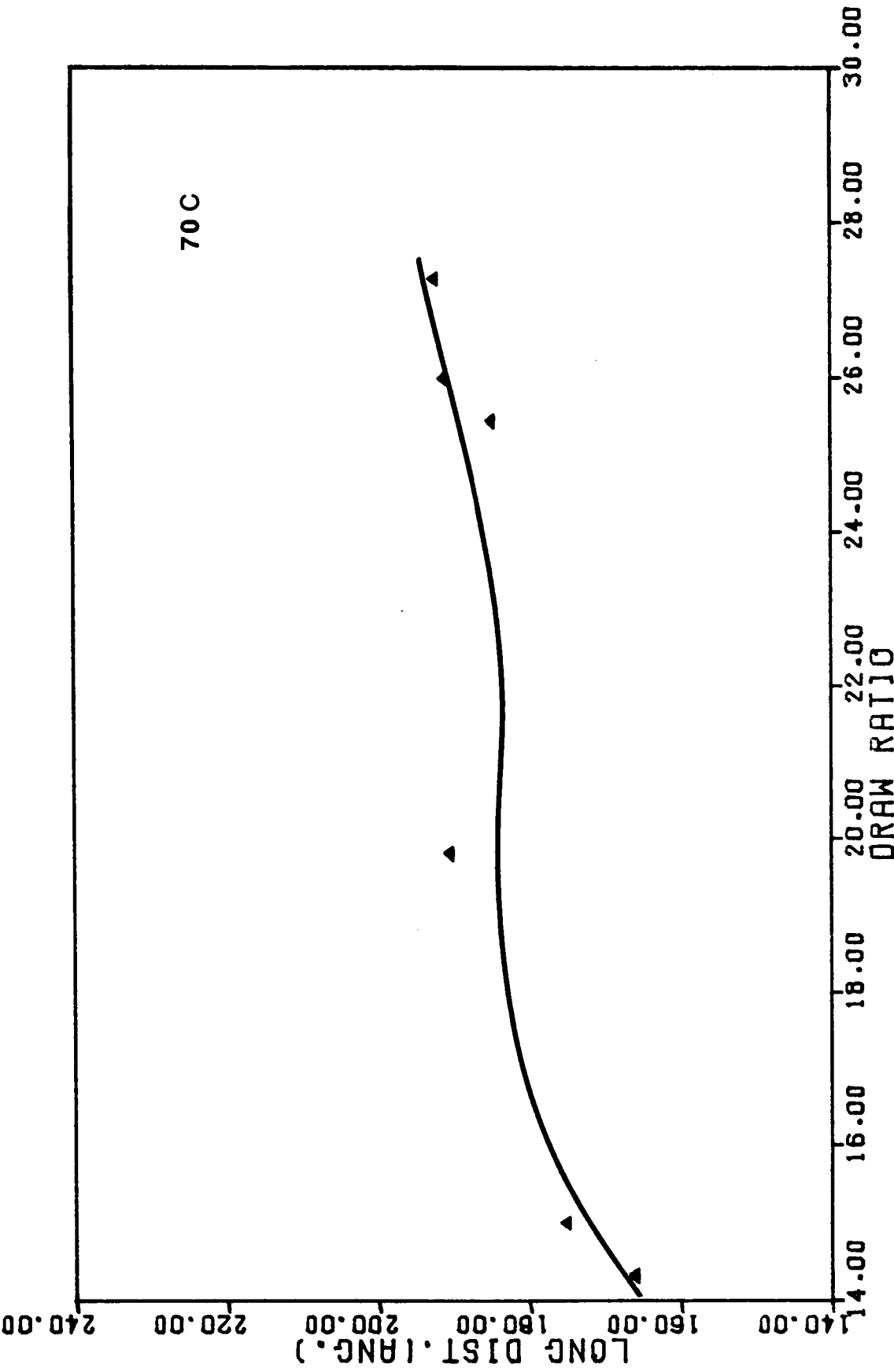


Figure 51. Effect of draw ratio on the long distance of HDPE samples drawn at 70°C.

increase of long period is probably due to the annealing of the samples as they are drawn at elevated temperature (70°C)

Comparison of SAXS Patterns of Samples Drawn by One Stage and Two Stage Methods

Very weak equatorial reflections are observed in the SAXS patterns of samples drawn by the two-stage method (Figure 49). On the other hand, the samples drawn by the one-stage method show very intense equatorial scattering resulting from presence of longitudinal voids in the sample structure (Figure 52).

Since the one-stage process incorporates high draw rates than two stage process, we may conclude that second stage draw rate is an important factor in determining the final structure of the HDPE samples.

C. PARTICLE SIZES FROM INTEGRAL BREADTH CALCULATIONS

The main objective of these experiments was to determine the changes in the shape of an "average crystallite" from the two-stage drawing process. For this purpose, the 110, 220, 310 and 220 lines from X-ray reflection patterns and the (002) line from X-ray transmission patterns were investigated. The weight average particle sizes along the directions perpendicular to these latter planes were determined using the Scherrer equation. Figure 53, 54, 55, and 56 show that the weight average particle size increases with the increase of draw ratio in directions perpendicular to the fiber axis. The highest increase of size was observed along the direction normal to (110) planes (Figure 53)(45A°) and the lowest increase was observed along the direction normal to (310) planes (Figure 56).

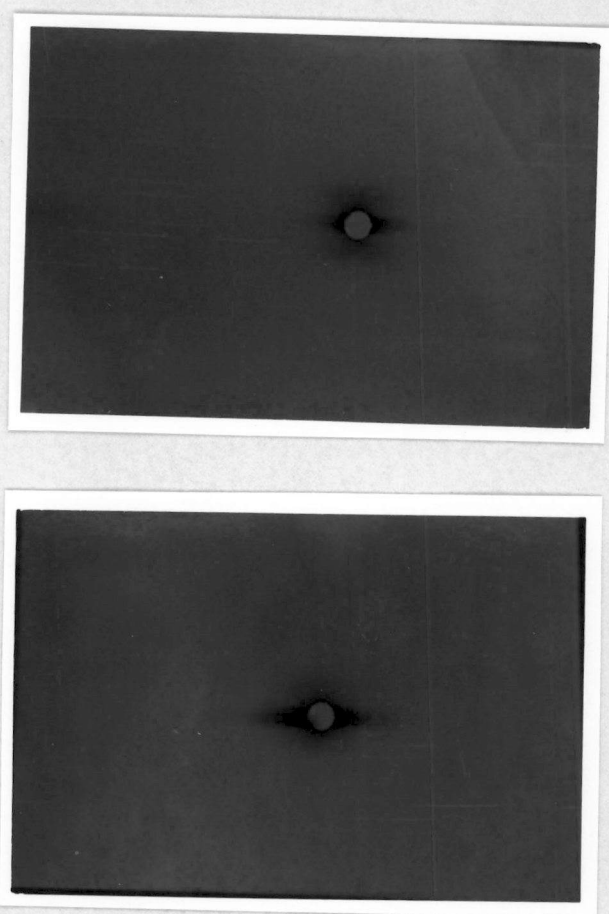


Figure 52. SAXS patterns of selected (a) natural drawn and (b) super-drawn samples drawn by one-stage method at 75°C.

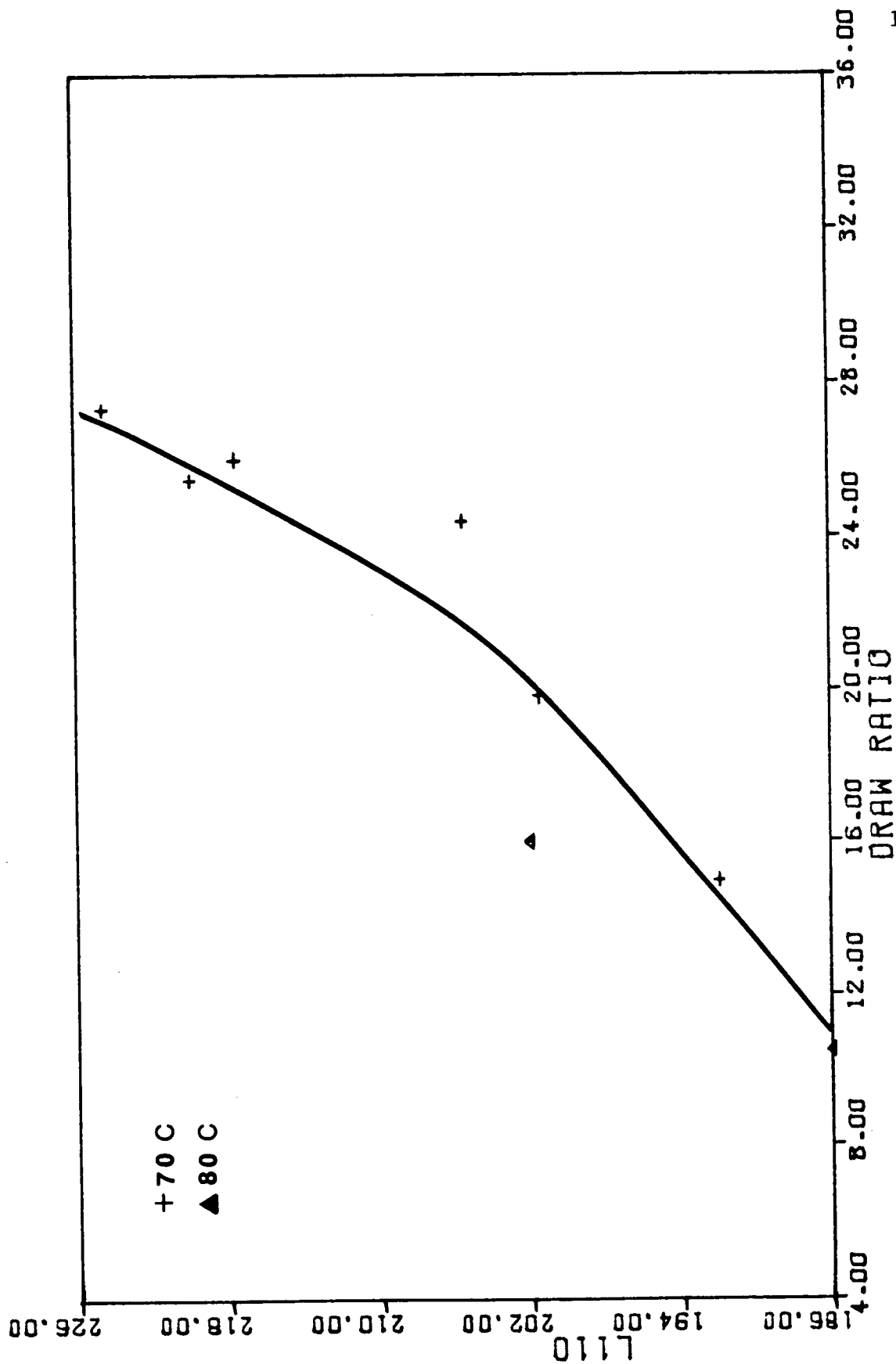


Figure 53. The effect of draw ratio on weight average size $L(110)$ in the direction normal to (110) planes of HDPE samples drawn by two-stage method at 70°C and 80°C.

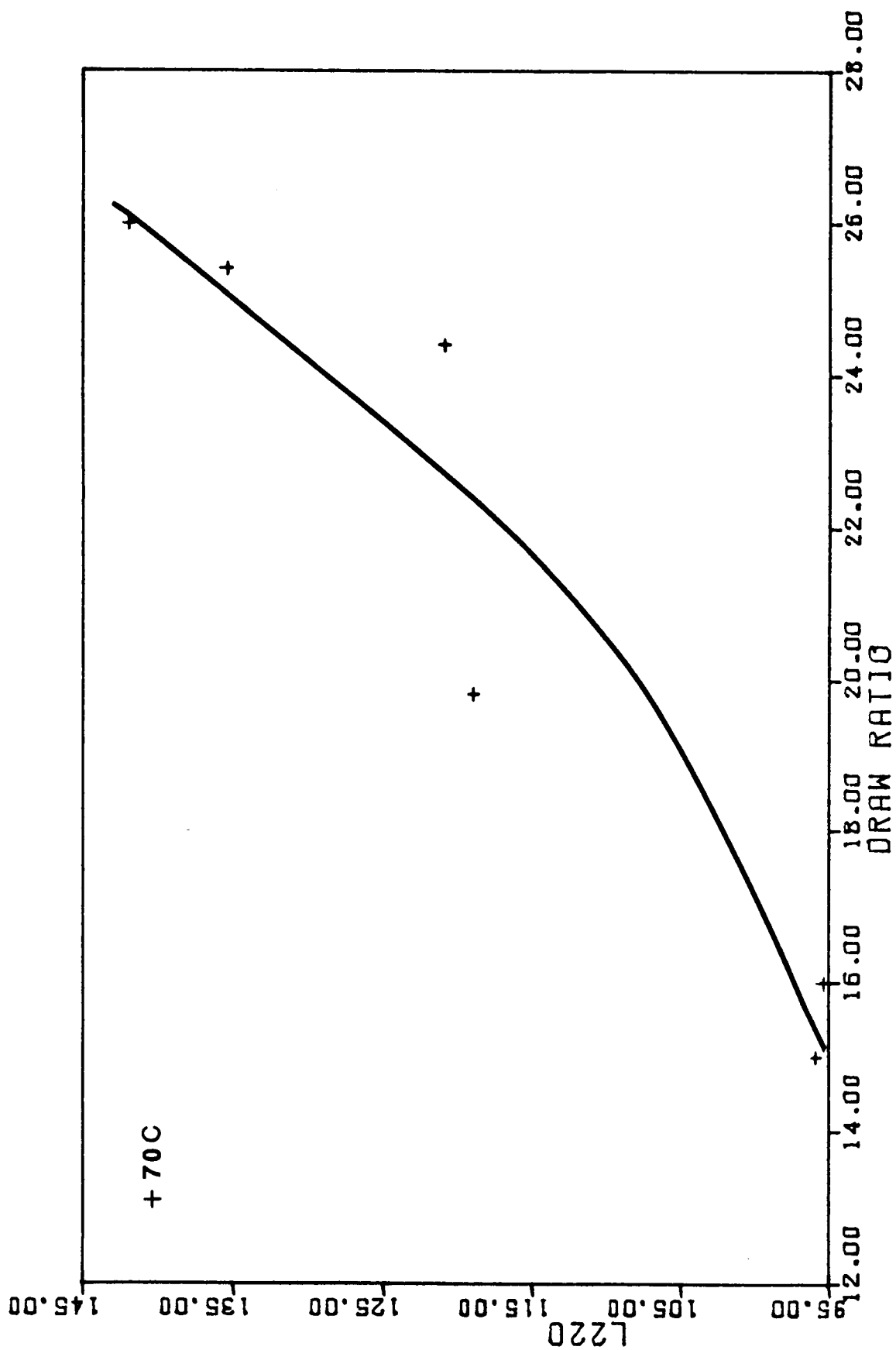


Figure 54. The effect of draw ratio on weight average size $L(220)$ in the direction normal to (220) planes of HDPE samples drawn by two-stage method at 70°C and 80°C.

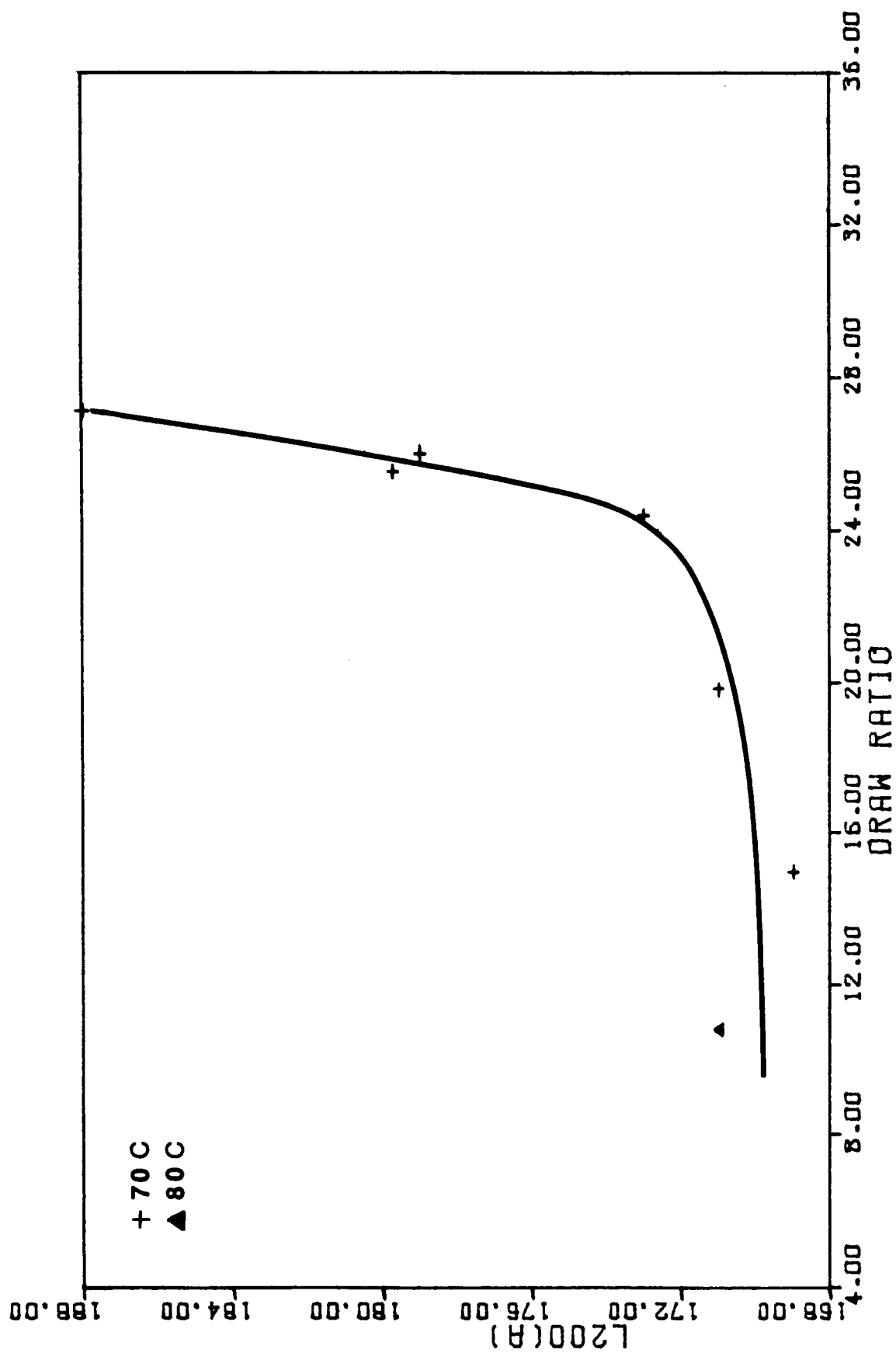


Figure 55. Effect of draw ratio on weight average size in the direction normal to the (200) planes of HDPE samples drawn by two-stage method at 70°C and 80°C.

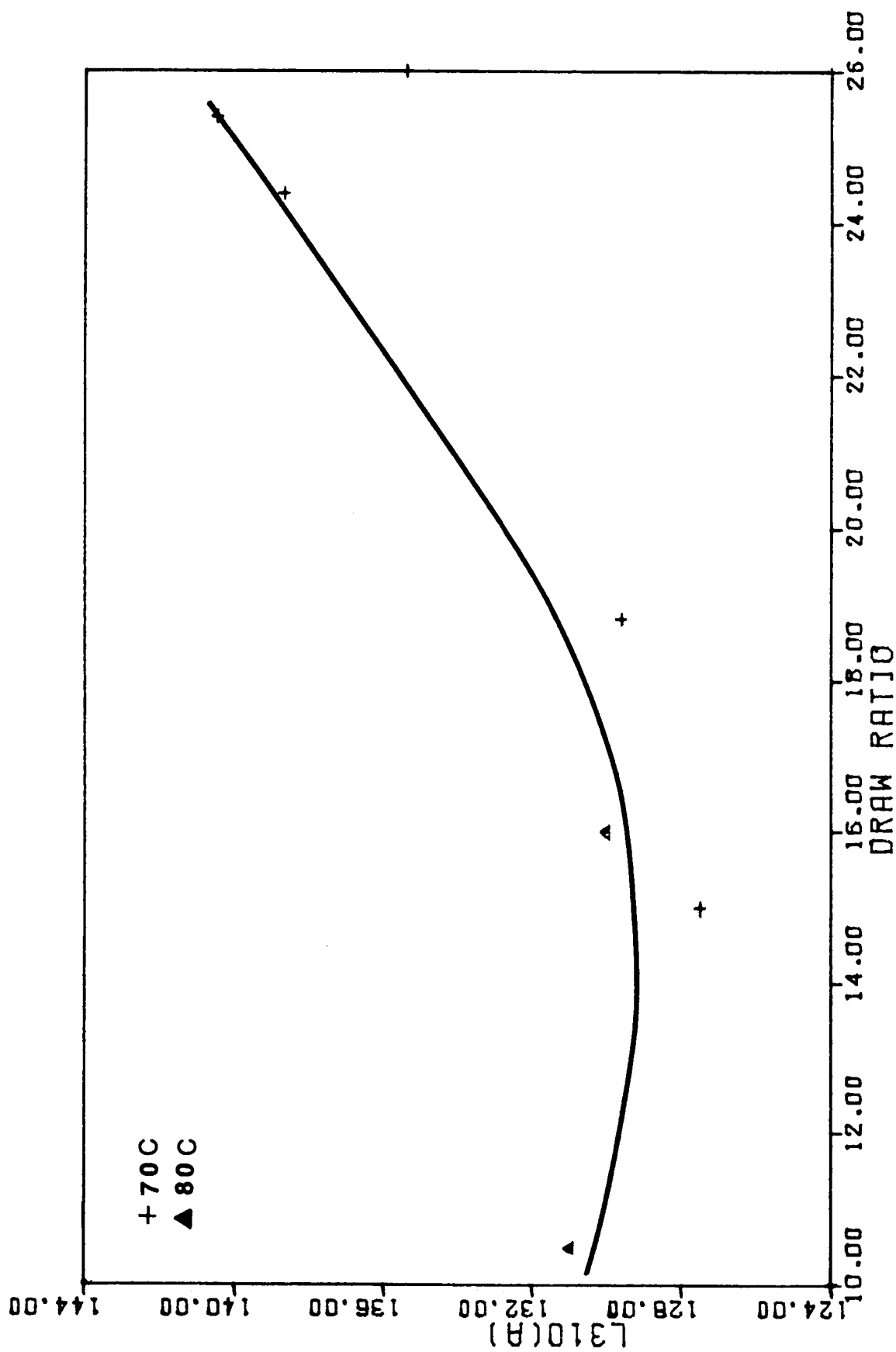


Figure 56. Effect of draw ratio on weight average size in the direction normal to L(310) planes of HDPE samples drawn by two-stage method at 70°C and 80°C.

Analyses of (002) lines revealed a striking increase of weight average particle size along the fiber axis (deformation direction with the draw ratio (Figure 57)). The particle size of the natural drawn (15x) was found to be 75°A and long period from SAXS data (157). The difference between these two values (18A°) could be interpreted as the average size of amorphous regions along the fiber axis.

As shown in Figure 57 the particle size (L) along fiber axis increased linearly in logarithmic scale with the increase of draw ratio. These values are much higher than their respective long periods as determined by small angle X-ray diffraction. This indicates that while some folded regions deform and create extended chain regions, others do not unfold by this process. This leads to the conclusion that the samples drawn above 15x draw ratio exhibit three regions, namely folded chain, extended chain and amorphous regions.

The change of crosssection of an average particle with deformation is shown in Figure 58 which clearly indicates an increase in the lateral crystalline area. All the changes observed above indicate that the structure of the samples approaches the extended chain model (17, 19). Gibson, Davies and Ward (39) also observed similar changes in drawn HDPE sheets. The solid state extrusion technique also produces samples with 10 percent extended chain domains as determined by Crystal and Southern (21).

D. DETERMINATION OF CONTINUITY FACTOR

The probability that a chain traverse the disordered region to enter adjacent crystallite (p) can be calculated from long periods and

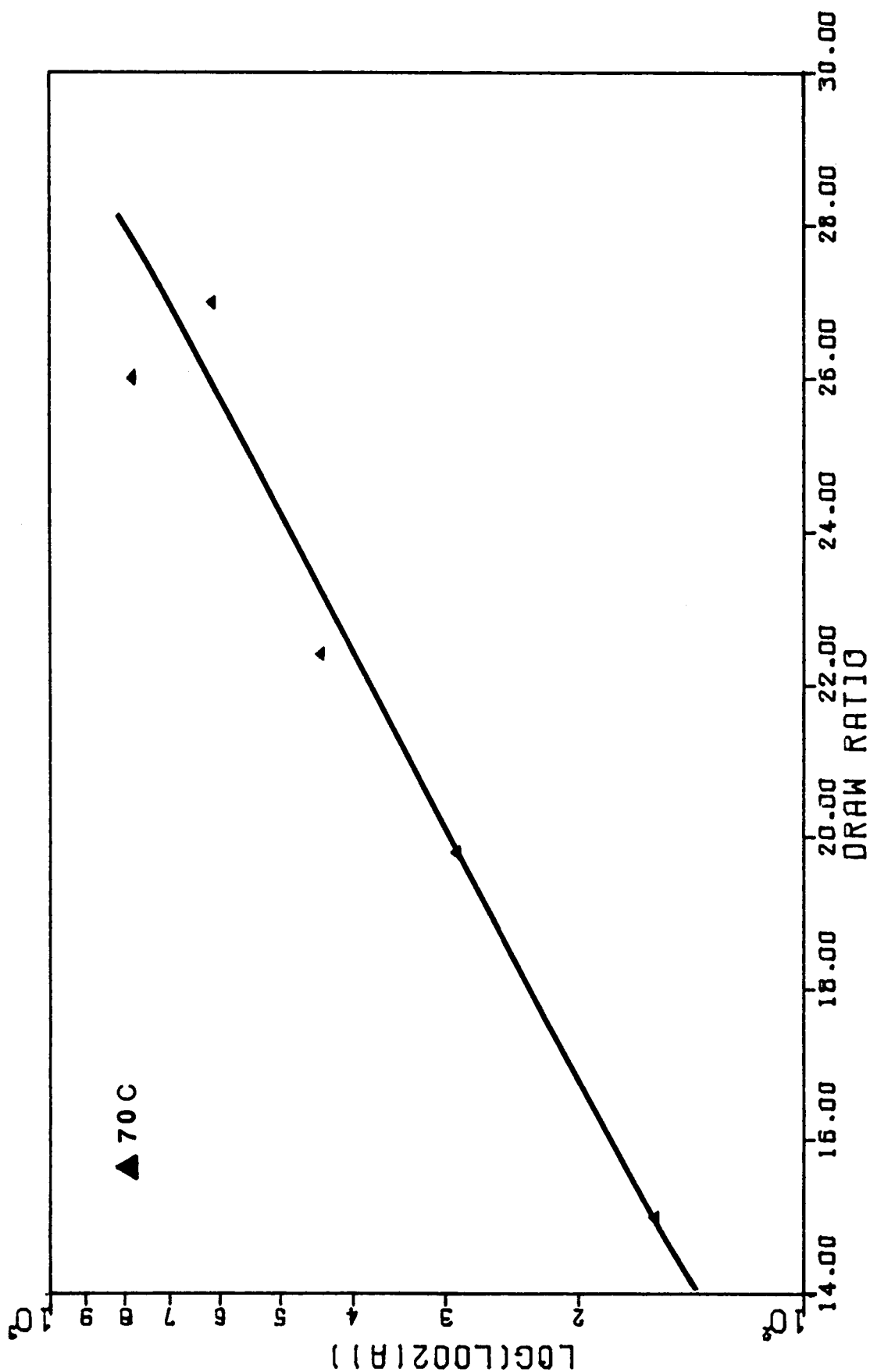


Figure 57. Effect of draw ratio on weight average size in the fiber direction [001] of HPDE samples drawn by two-stage method at 70°C.

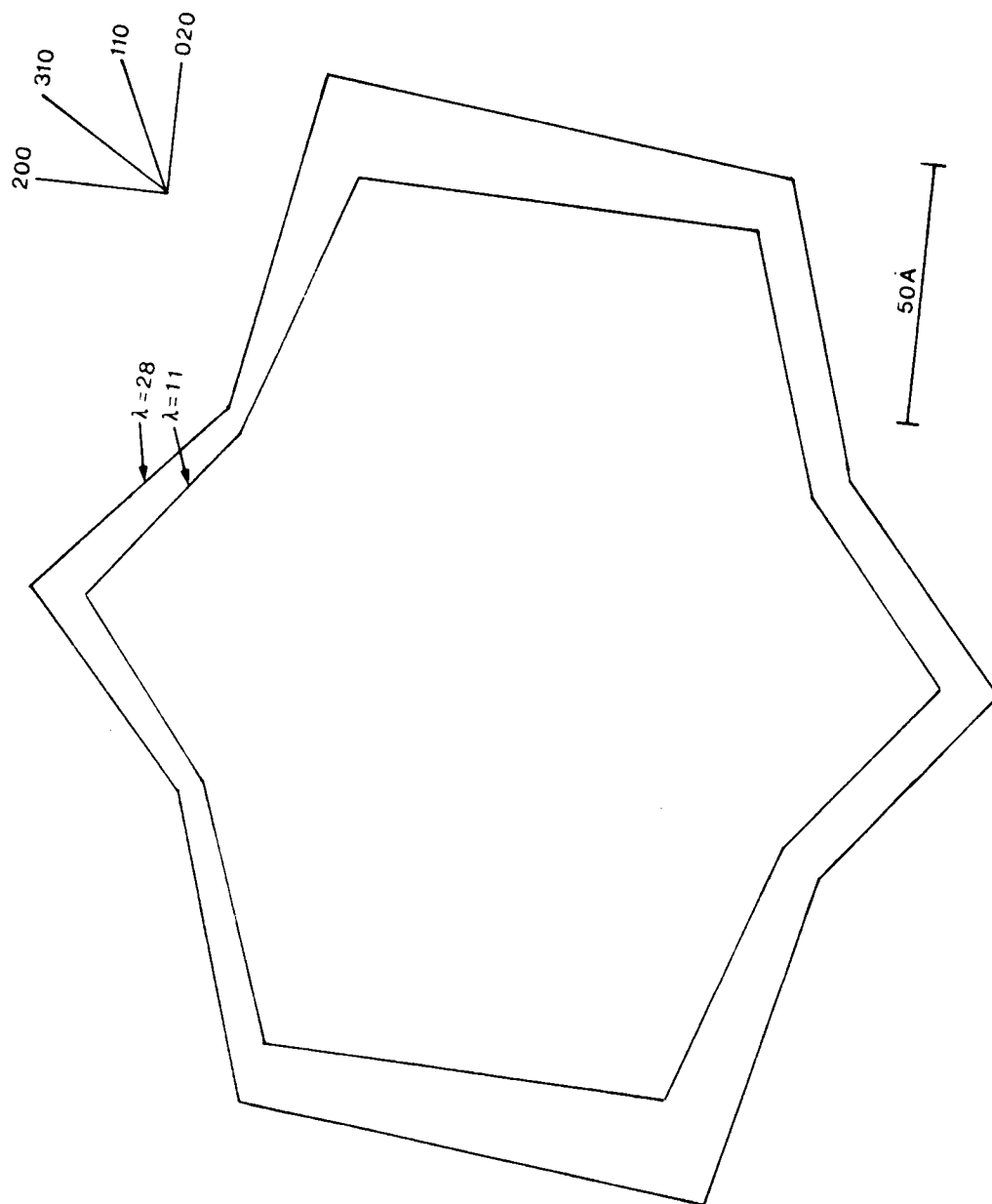


Figure 58. Effect of deformation on approximate shape of the crosssection of average crystal in HDPE fibers.

particle size along the fiber axis which are determined from SAXS and WAXS analyses. In Figure 59 the data from Gibson et al who used one-stage drawing method, as well as the data determined from our experiments are presented. The p parameter determined from our experiments shows a steady increase with the increase of draw ratio, reaching the value of 0.6 at the draw ratio of 26. The data from Gibson et al. (39) shows a convex increase and achieve a p value of 0.4 at the draw ratio of 30. These results indicate that both the one-stage and two-stage methods provide increasing fractions of extended chain domains in the sample structure as indicated by the increase of p . However, the two stage method provides higher p values at lower draw ratio.

E. CHANGES IN UNIT CELL DIMENSIONS

The changes of a , b unit cell dimensions of polyethylene of varying draw ratios are presented in Figures 60, 61. It was found that the a , b dimensions decrease almost linearly with the increase of draw ratio. Since long periods of polyethylene increase with draw ratio (Figure 51, page 128) the decrease in a , b are roughly related to the inverse of the long periods which was also observed by Eby (23). However, Eby found that the unit cell dimensions of melt crystallized polyethylene extrapolate to $7.322\text{\AA}$ and $4.933\text{\AA}$ for a and b respectively for infinite long period. At high draw ratios the a and b values were found to approach these values which qualitatively indicate the presence of large long periods (extended chain domains) in the highly drawn samples. The fact is confirmed by the result of WAXS transmission data which shows much higher dimensions in fiber direction than does the long period (Figure 57).

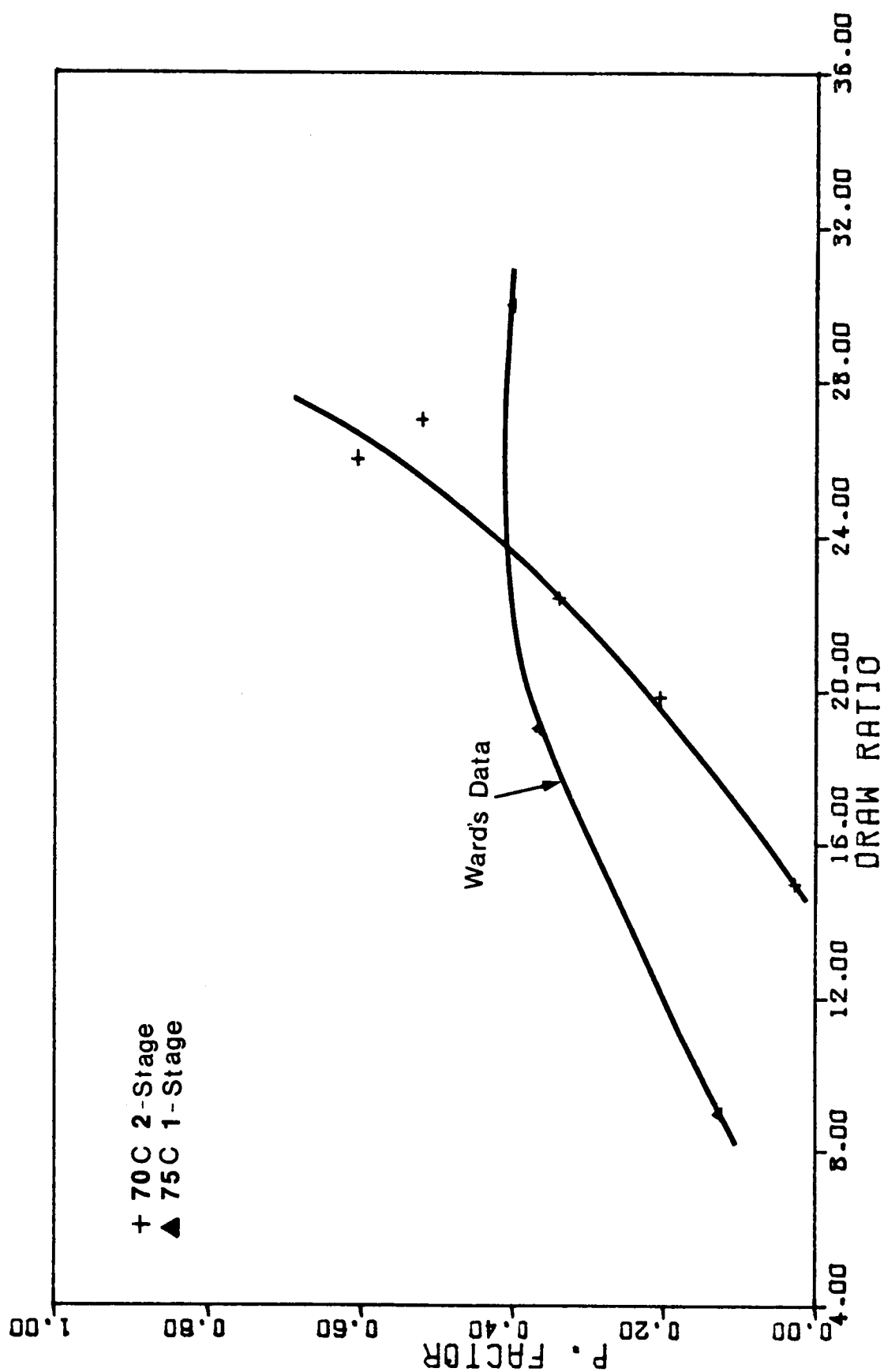


Figure 59. Effect of draw ratio on the probability that chain traverse the disordered region to enter adjacent crystallite along the fiber axis of HDPE samples.

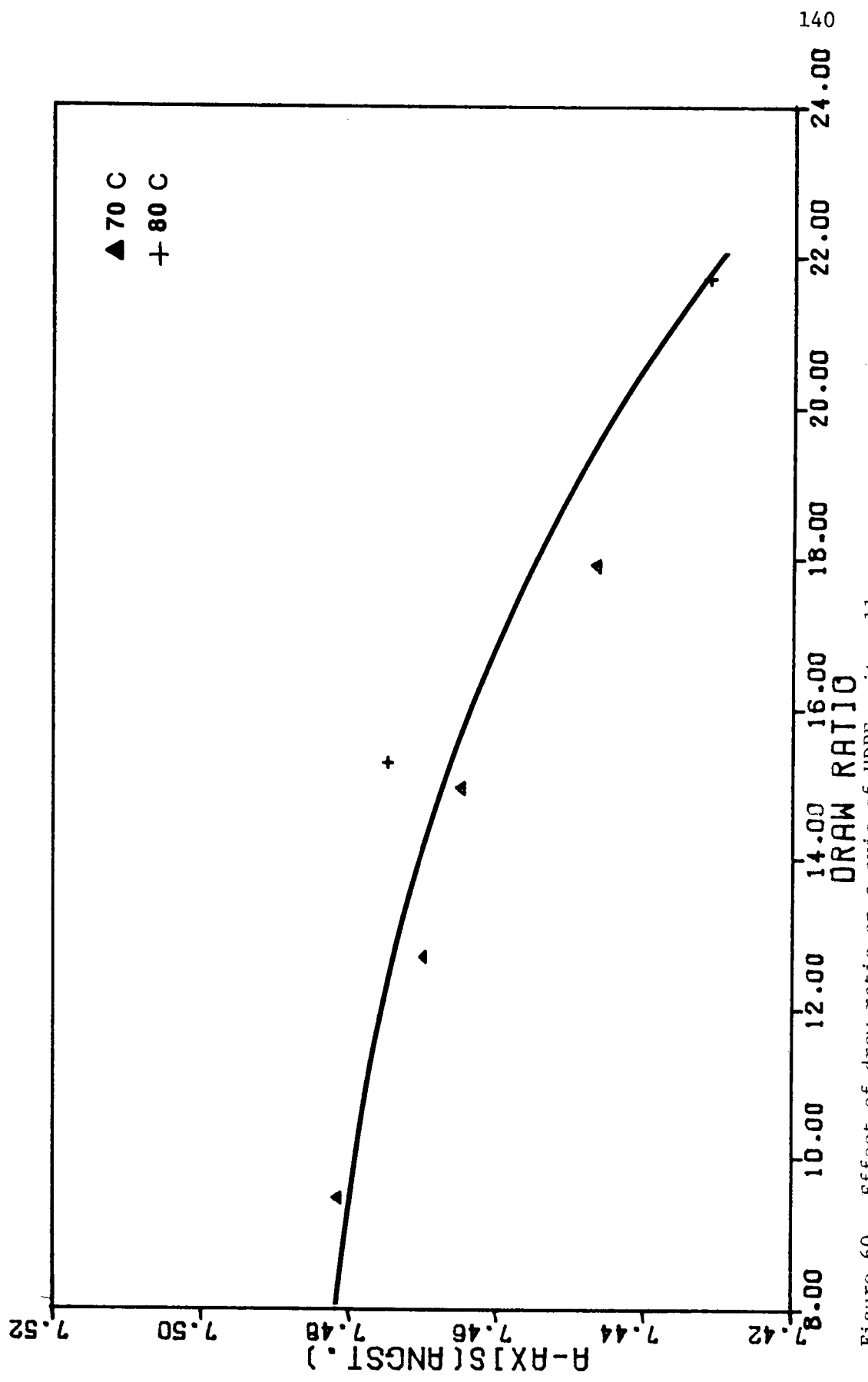


Figure 60. Effect of draw ratio on a-axis of HDPE unit cell.

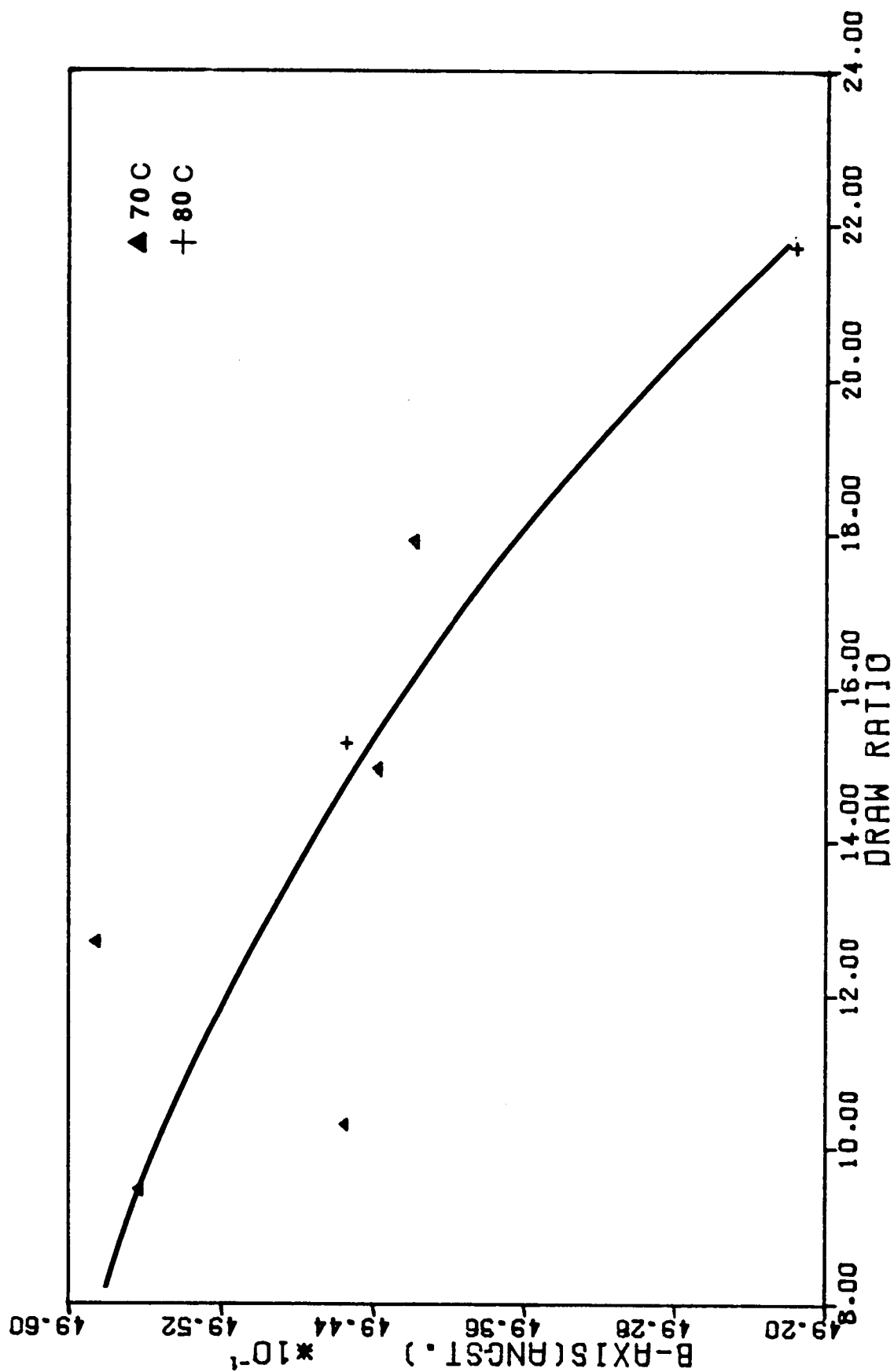


Figure 61. Effect of draw ratio on b-axis of HDPE unit cell.

This fact was also observed by Gibson et al. (39) for their highly oriented polyethylene sheets. Thus, this is an indication that the drawing process produces extended chain domains but fails to unfold some regions in the structure, consequently, these folded regions give rise to a two point pattern in small angle X-ray diffraction diagrams.

The decrease of a,b unit cell dimensions is further supported by line broadening analysis as will be discussed later. The root mean square strains decrease for a particular distance with the increase of draw ratio along a direction normal to (110) planes, indicating an increase of packing efficiency of crystals laterally (normal to fiber axis).

F. RESULTS AND DISCUSSIONS OF FOURIER ANALYSIS

The results obtained by Warren-Averbach Fourier transform method are shown in Figures 62-67. The extrapolation procedure for different (L) are shown in Figure 62 for a particular sample drawn at 70° with the draw ratio of (26). As Buchanan and Miller (10) indicated, the extrapolation procedure gives better results if the number of orders from one reflection increases. In the case of polyethylene 110 and 220 and 200, 400 reflection were recorded with reliable accuracy. The inability to obtain higher order reflections is primarily due to the crystalline imperfections (paracrystallinity) which is common among the polymers. In fourier analyses, five polyethylene samples having different draw ratios but the same process temperature (70° C) were investigated. In Figure 63 and 64 it can be observed that almost all samples showed the "hook" effect. This hook effect is the result of truncation of profile tails.

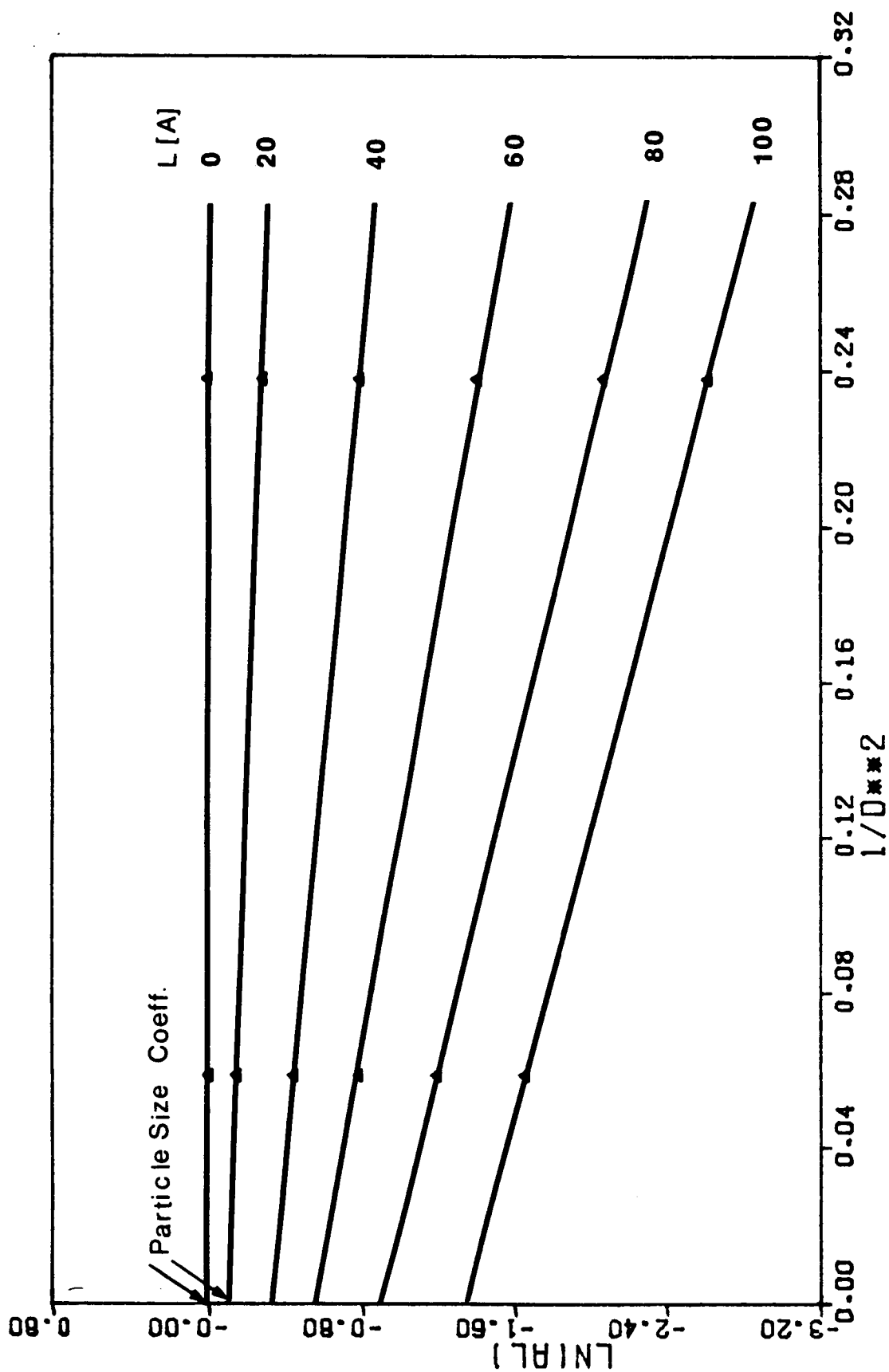


Figure 62. Extrapolation procedure in determination of particle size coefficients. The slopes of the curves are related to strain coefficients.

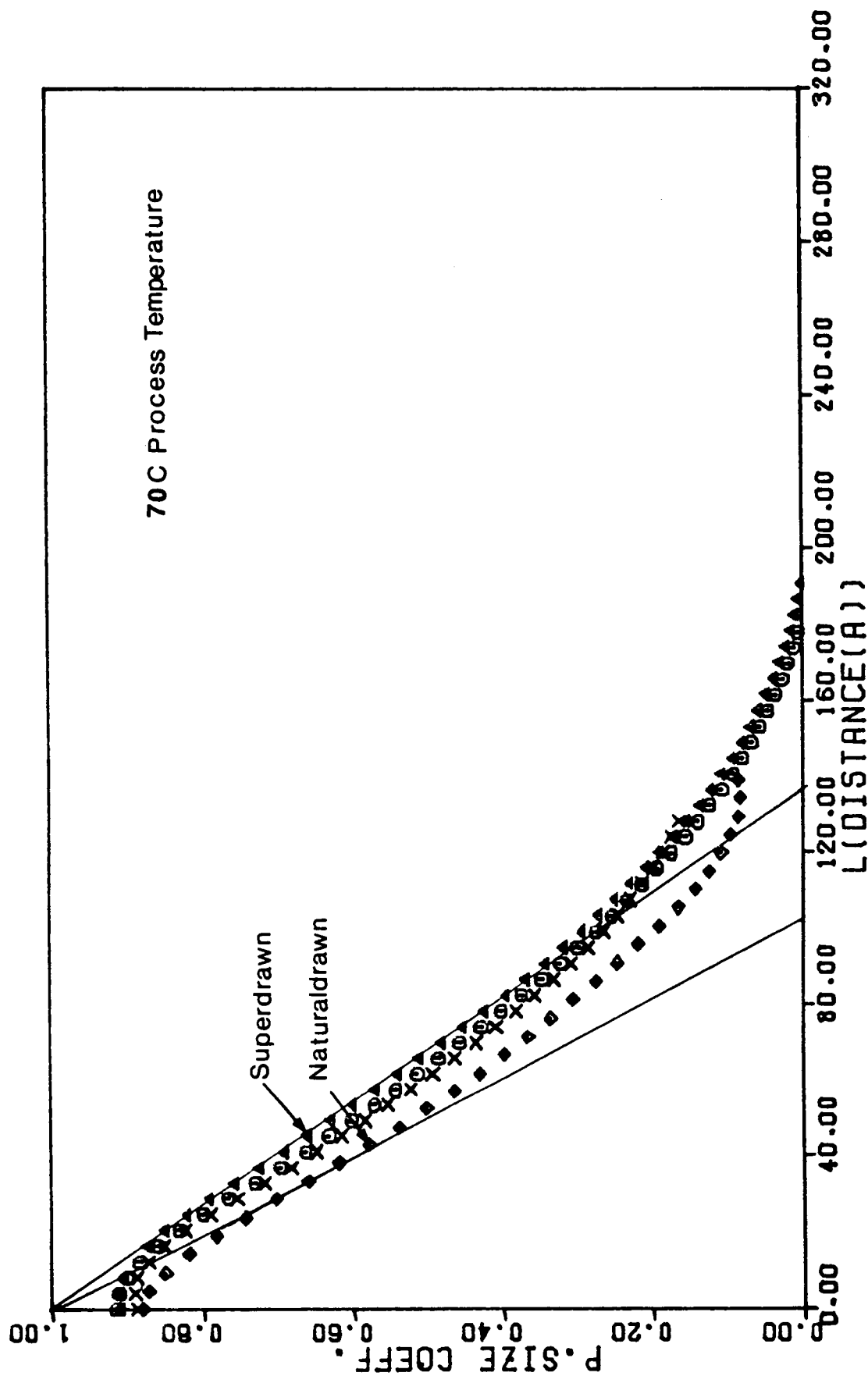


Figure 63. Particle size coefficients versus distance (length)(Å) along the direction normal to (110) plane for samples with varying draw ratios.

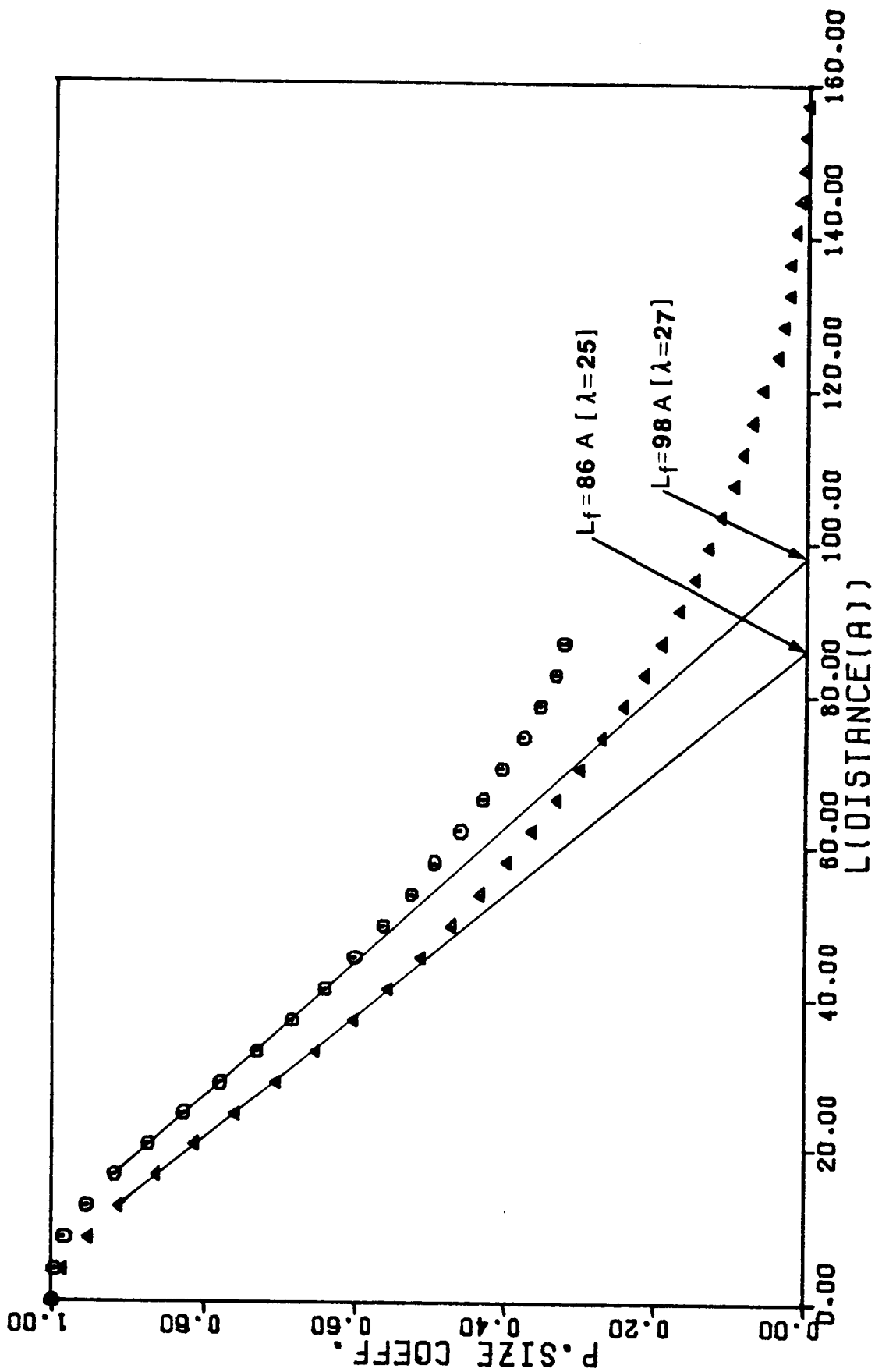


Figure 64. Particle size coefficients versus distance (Å) along the [100] direction for superdrawn samples.

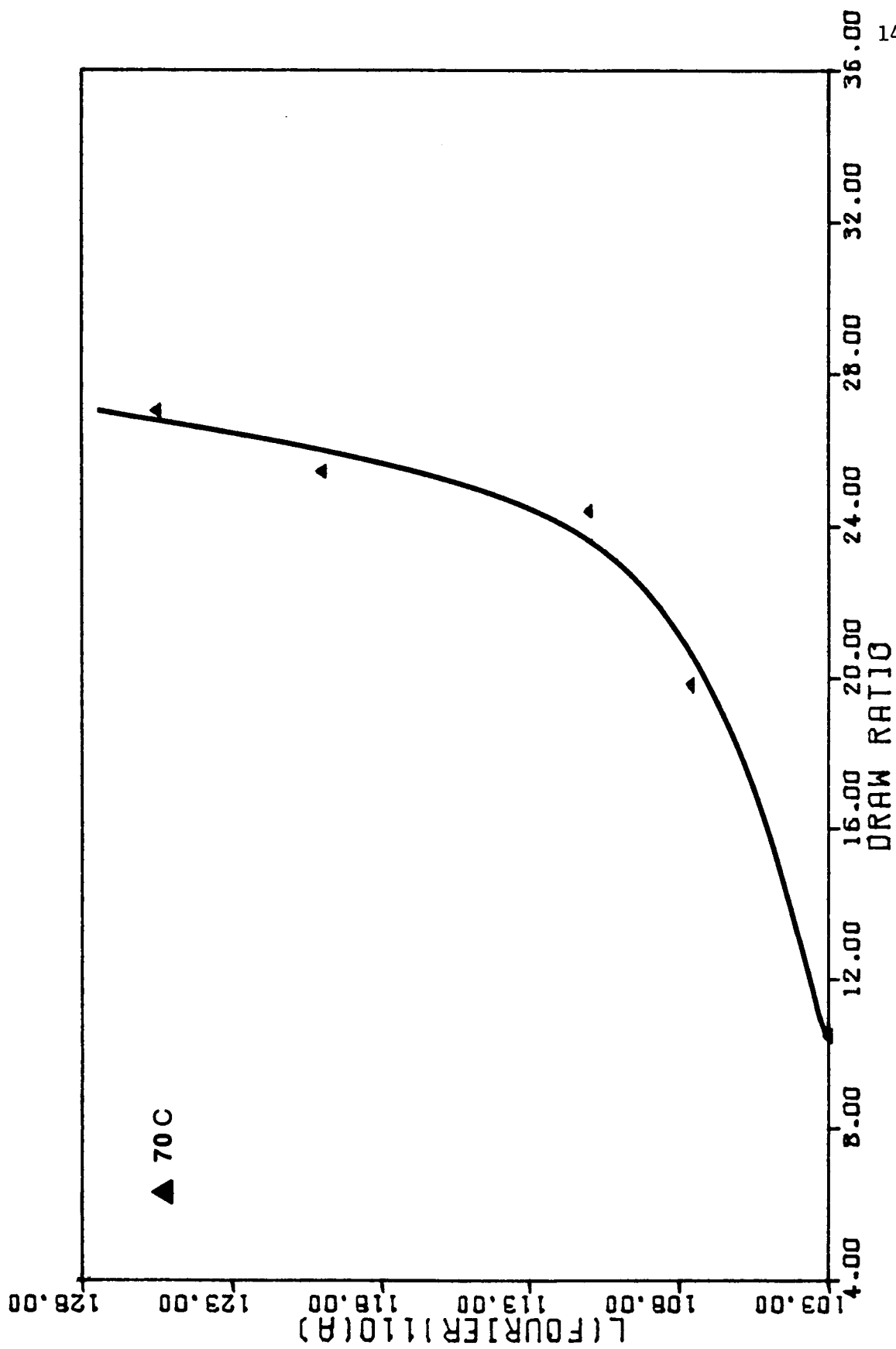


Figure 65. Effect of draw ratio on number average crystal length $L(110)$. (Results of Figure 60.)

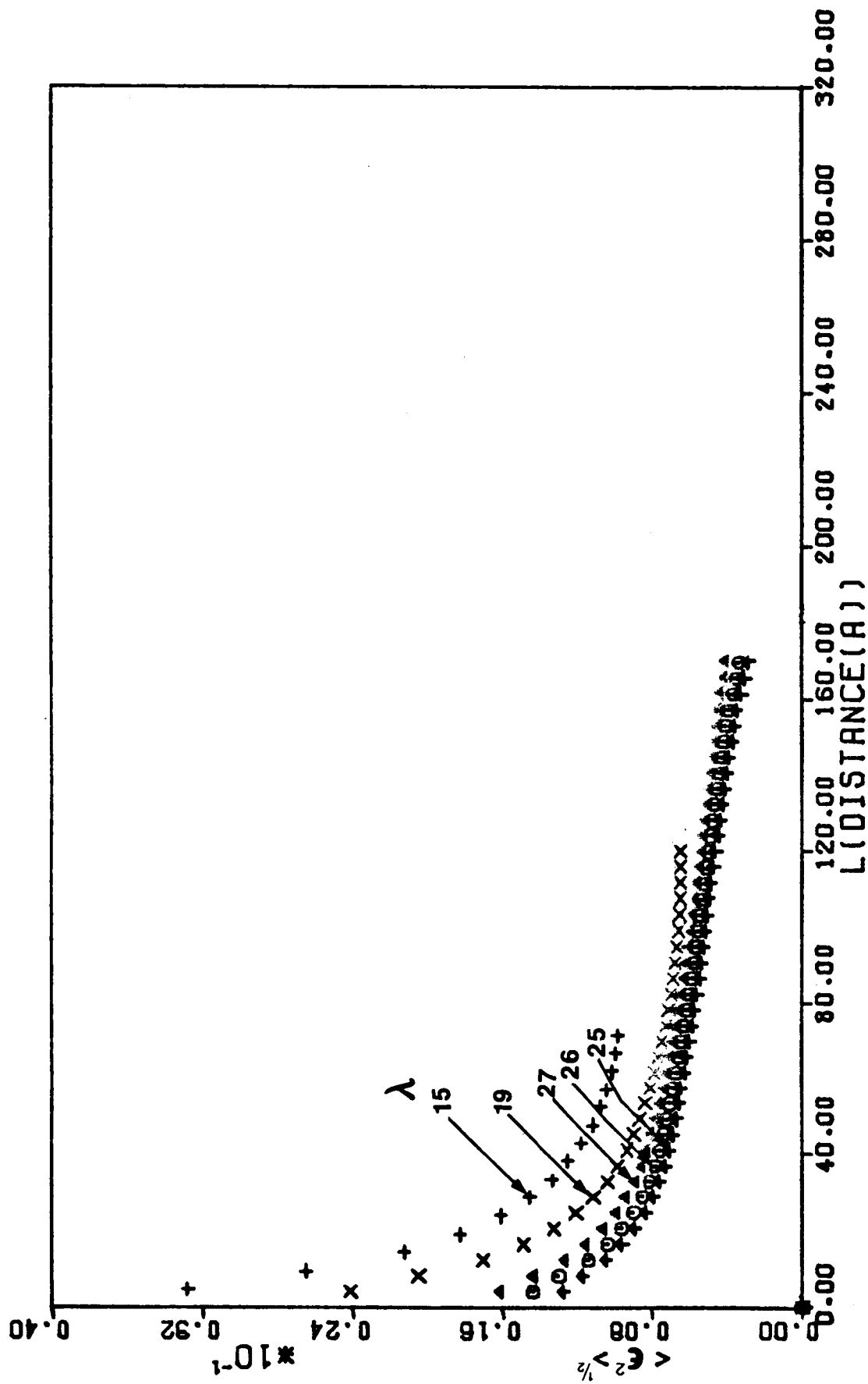


Figure 66. The change of root mean square strain ($\text{SQRT}\langle E^2 \rangle$) with distance along the direction normal to (110) plane.

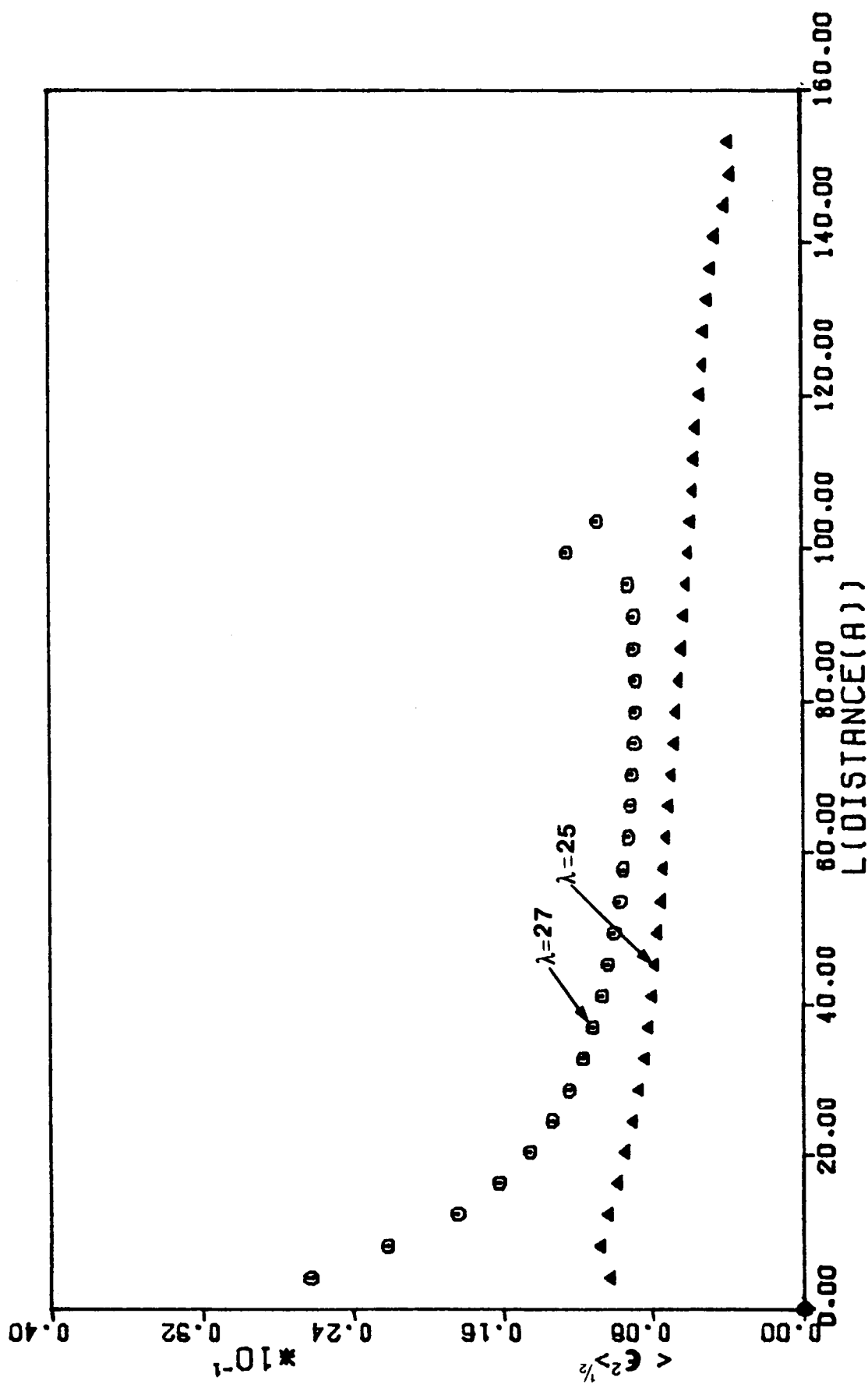


Figure 67. The change of root mean square strain ($\sqrt{\langle E^2 \rangle}$) with distance [100] direction.

In the calculation procedure all the cosine coefficients are normalized by the first coefficient (A_0). This first coefficient is directly proportional to the area under the peak, and since the theoretical integration limits $(-\infty, +\infty)$ are impracticable, the truncation of these limits to practical limits naturally will result in the first cosine coefficient being slightly less than the next few coefficients (A_1, A_2, A_3, A_4). On the other hand, the rest of the fourier coefficients depends very little upon the long tails: consequently, they are almost unaffected by the truncation. A correction of the "hook effect" is obtained by recognizing that the experimental A_0 value is too uncertain to be used. Instead, the linear portion of the (particle size coefficient vs. L) plot was extrapolated to $L = 0$ and all values renormalized to make the new intercept unity.

The results of these extrapolations which gives number average size along the direction normal to (110) planes versus draw ratio are shown in Figure 64 and 65). The Figure 65 indicates that the microfibrils get larger along direction normal to (110 as the draw ratio increases. This result is in total agreement with the model proposed by Peterlin (90, 95, 112). This model states that as the drawing increases, the microfibrils coalesce. The same observations were made along (100) direction as shown in Figure 66 and 67 which contain the variation of $\langle \epsilon^2 \rangle^{1/2}$ along the direction normal to (110) planes and along [100] direction.

Warren (132) suggested that the decrease in $\langle \epsilon^2 \rangle^{1/2}$ with increasing L can be due to the inhomogeneity in strains and also to the fact that with increasing L there is no longer a contribution from the smaller domains where the strains are probably larger. The results in G-W-H analyses

confirms this fact in the next section. Figure 66 also indicates that as the draw ratio increases the $\langle \epsilon^2 \rangle^{1/2}$ values for particular L get smaller. This fact indicates a more efficient lateral packing of chains. This result is also in agreement with Figures 60 and 61 which show a decrease of a and b parameters of the unit cell as the draw ratio increases. Even though Figure 67 indicates an increase in root mean square strain with draw ratio, the magnitude of these values is still small compared with the root mean square strains observed in the direction normal to (110) planes (Figure 66).

G. RESULTS AND DISCUSSION OF GUINIER-WARREN PLOTS

The main objective of the analysis of Guinier-Warren plots by Hosemann's (48) technique (G-W-H method) was to determine the changes of crystallite size of microfibrils and of cluster of microfibrils. In addition, the changes of paracrystallinity parameters of microfibrils and clusters were correlated with the draw ratio of the fibers. Since all of the highly drawn polyethylene fibers exhibit extremely high orientation factors, the parameters that control the mechanical properties seem to be the sizes of microfibrils and their perfection. The study of crystallite sizes and paracrystallinity parameters should give insight into the macrobehavior of drawn fibers.

Hoseman and Wilke (48) applied paracrystalline theory to polyethylene fiber of a draw ratio of 60X. The observed two distinct crystallite sizes: $83\text{\AA}$ (l_L) and $174\text{\AA}$ (l_2). They interpreted these values as the diameters of a single microfibril and a cluster of four microfibrils. The paracrystallinity factors were 3.2 percent and 2.2 percent for g_1 and g_2 respectively. The g value corresponding to the

boundary existing between different microfibrils (not between microfibrils within the clusters) was 42 percent. They explained these findings with the help of a model proposed by Hess and Keisig (45). This Hess and Kiesig model is shown in Figure 68. They concluded that the $83\text{\AA}$ particles build on paracrystalline lattice with a g value of 3.2 percent; some of these microfibrils exist isolated from the other chains by splits (Figure 68); some others build up thicker fibrils, consisting of four microfibrils each. The boundary between the latter microfibrils (disordered regions within the clusters) is much less disturbed than that of "isolated" microfibrils (interfibrillar disordered domains). They attributed this behavior to the presence of I_2 component at the (000) reflections (equatorial reflections from SAXS diagram). They further suggested that the lattice planes of the single four microfibrils in clusters are so well adjusted that they scatter more or less coherently; a fact which was attributed to the presence of I_2 components in $hh0$ reflections (Figure 38, page 111).

According to their paracrystallinity factors (g_1 , g_2 , g) the highest order (the lowest paracrystallinity factor) is present in the cluster regions and the lowest is present in the interfibrillar domains.

The results of Guinier-Warren-Hoseman analyses are presented in Figures 69, 70, 71, 72, 73, and 74.

According to Figure 69 the I_1 component length does not change with the draw ratio. This I_1 component represents the microfibrils which are the basic backbones of the fiber structure. The size of the clusters (I_2 component) which consist of microfibrils separated by extended disordered chain domains, increases with the increase of draw

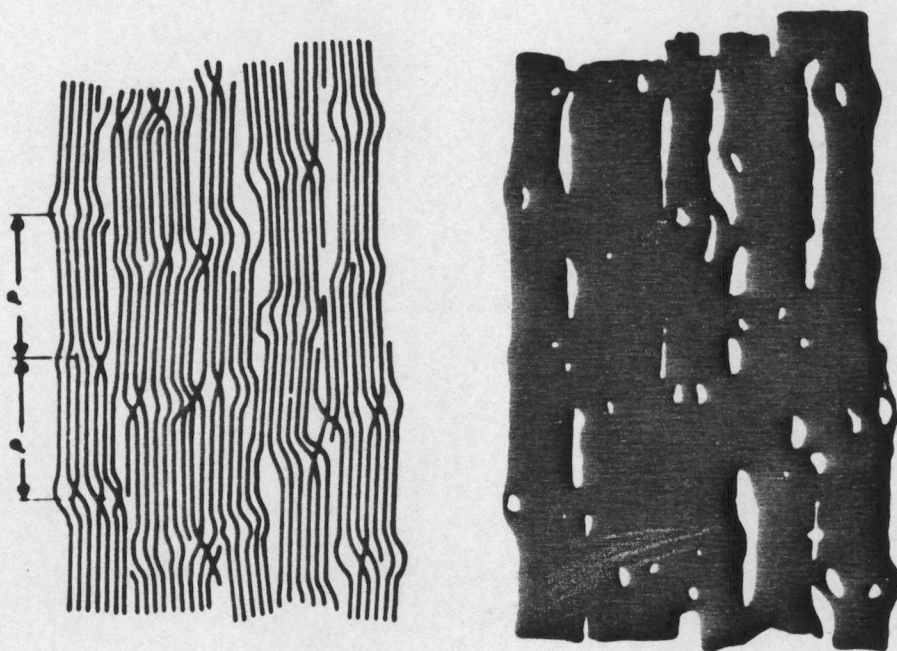
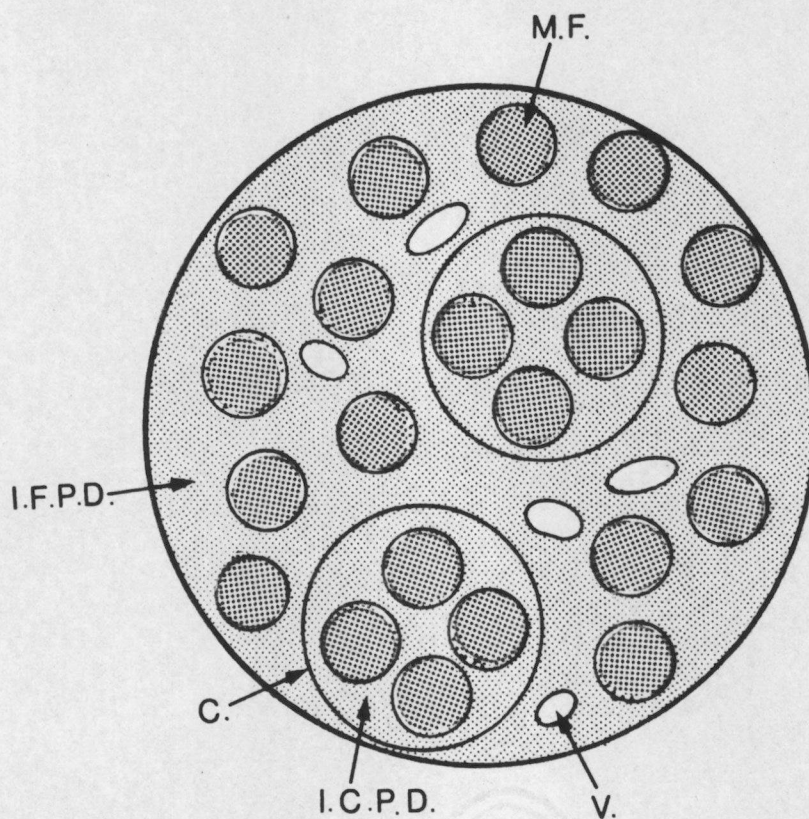


Figure 68. (a) Hess-Kiesig model for drawn semicrystalline polymers and (b) simple cross-section of the sample.



M.F. _ Microfibril

I.F.P.D _ Interfibrillar Paracrystalline Domain

C. _ Cluster

I.C.P.D. _ Intraclusteral Paracrystalline Domain

V. _ Void

Figure 68 (continued)

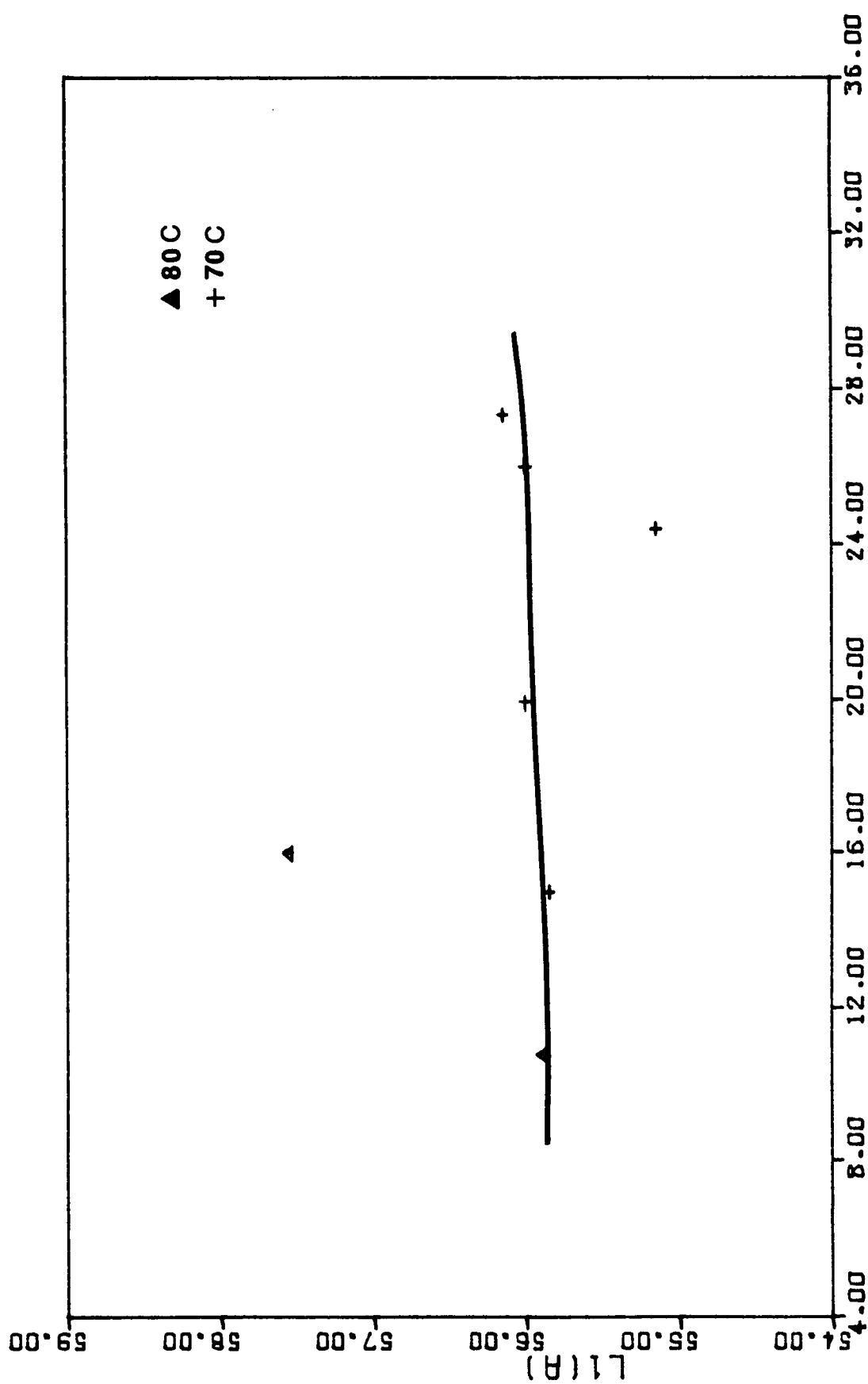


Figure 69. Number average microfibril size $(L_1)(A)$ with draw ratio.

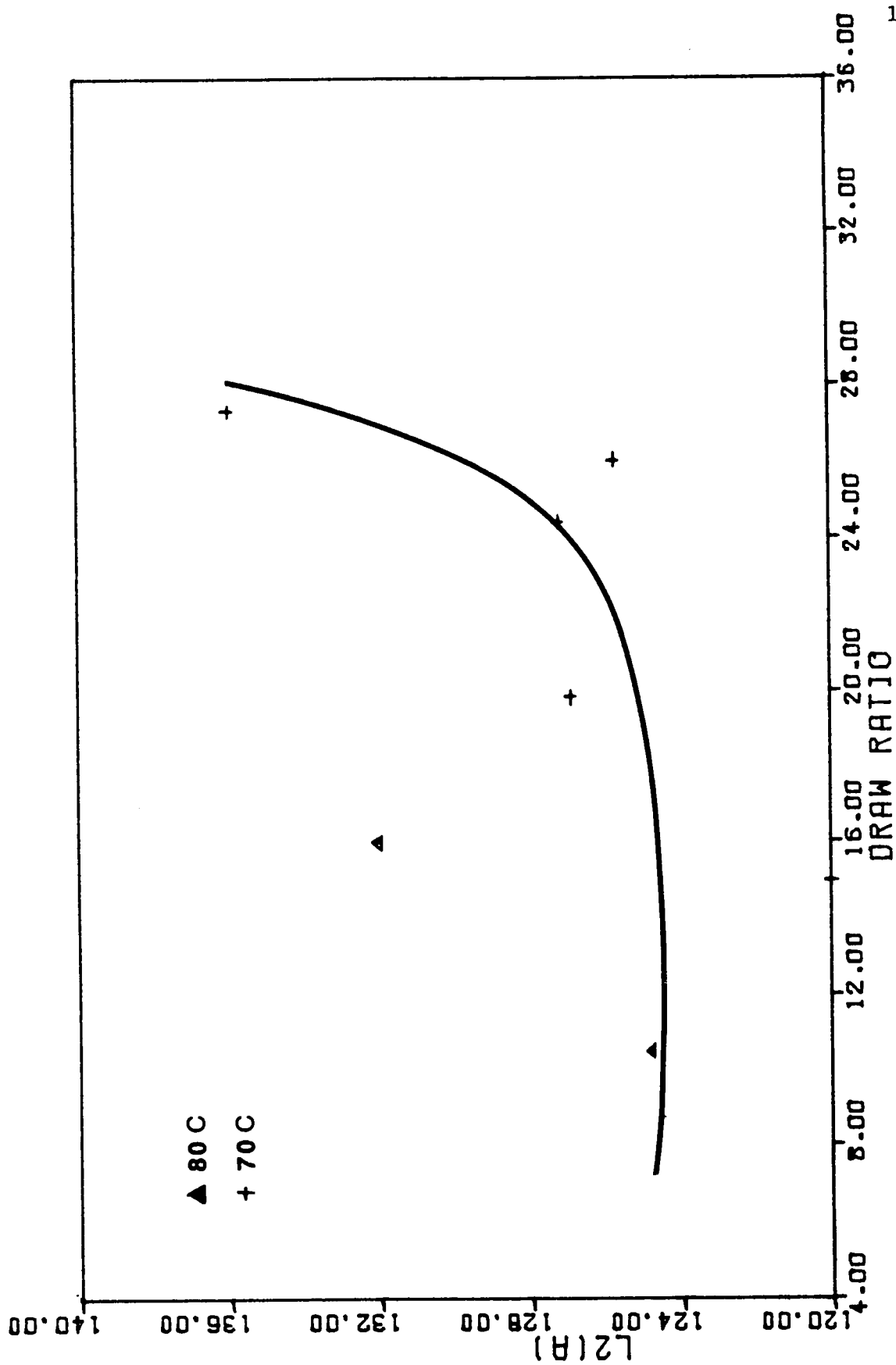


Figure 70. Number average cluster size change $(L_2)(\text{\AA})$ with draw ratio.

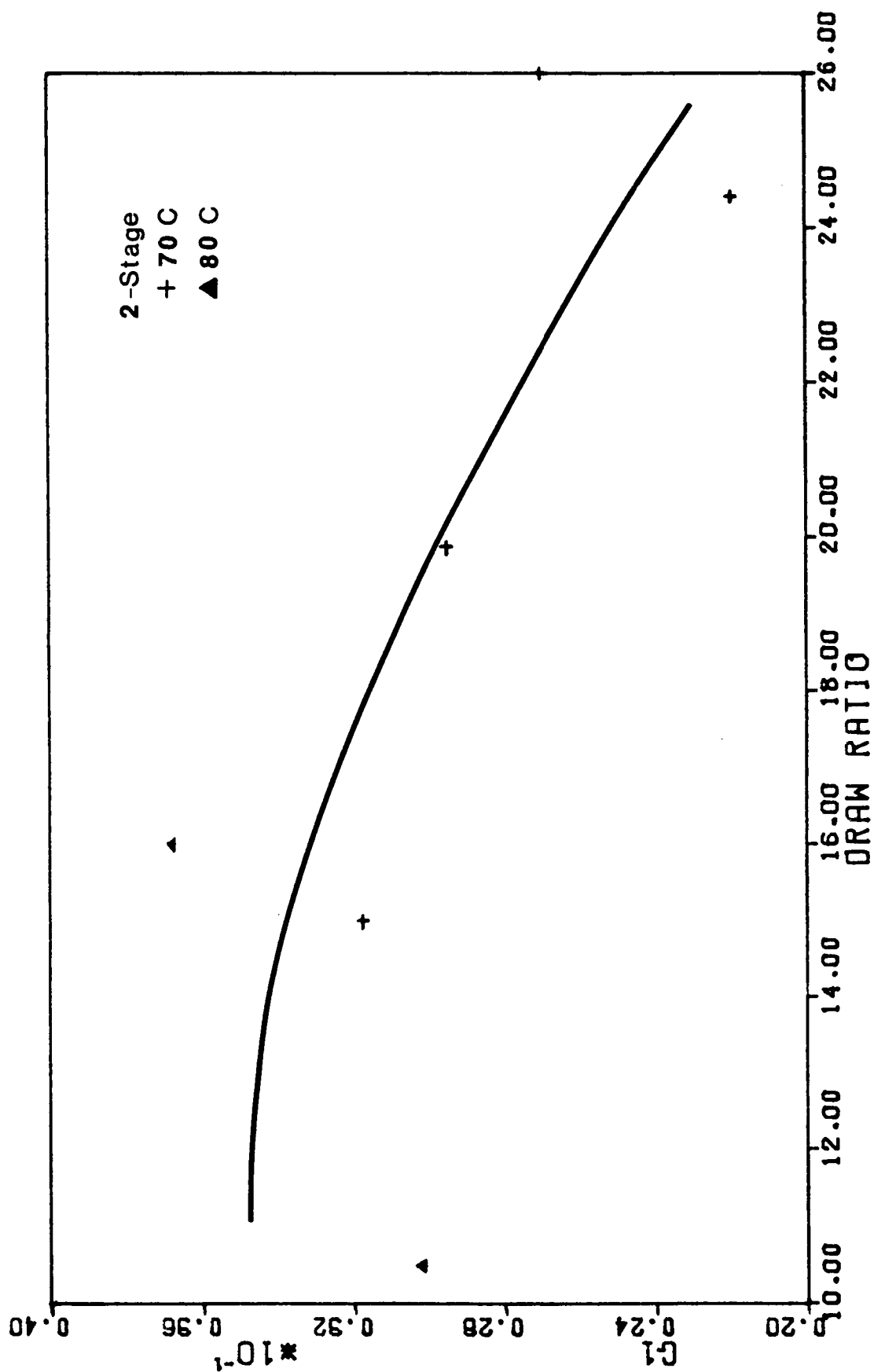


Figure 71. Microfibril paracrystallinity parameter (g_l) change with draw ratio.

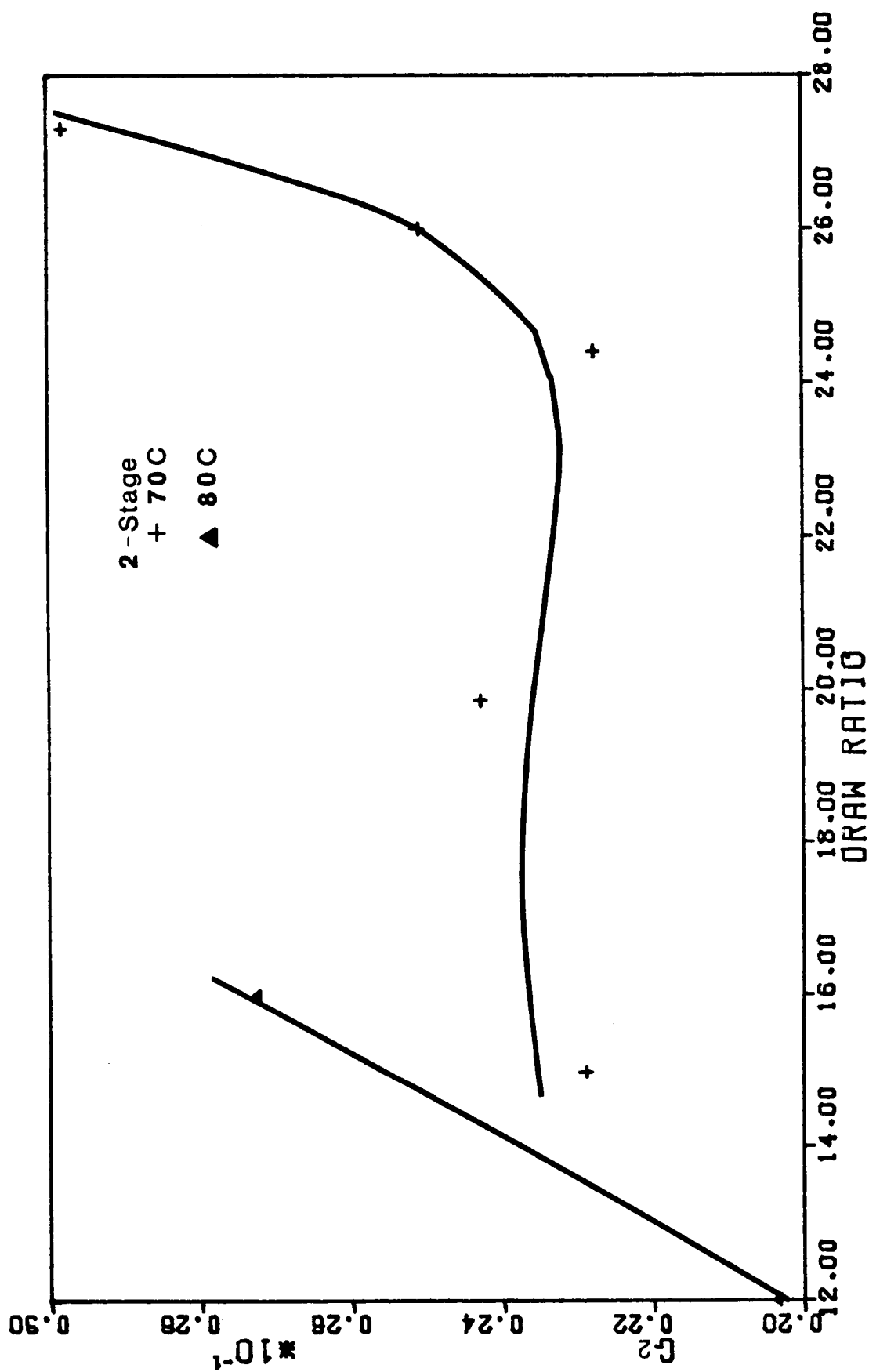


Figure 72. Cluster paracrystallinity parameter (g_2) change with draw ratio.

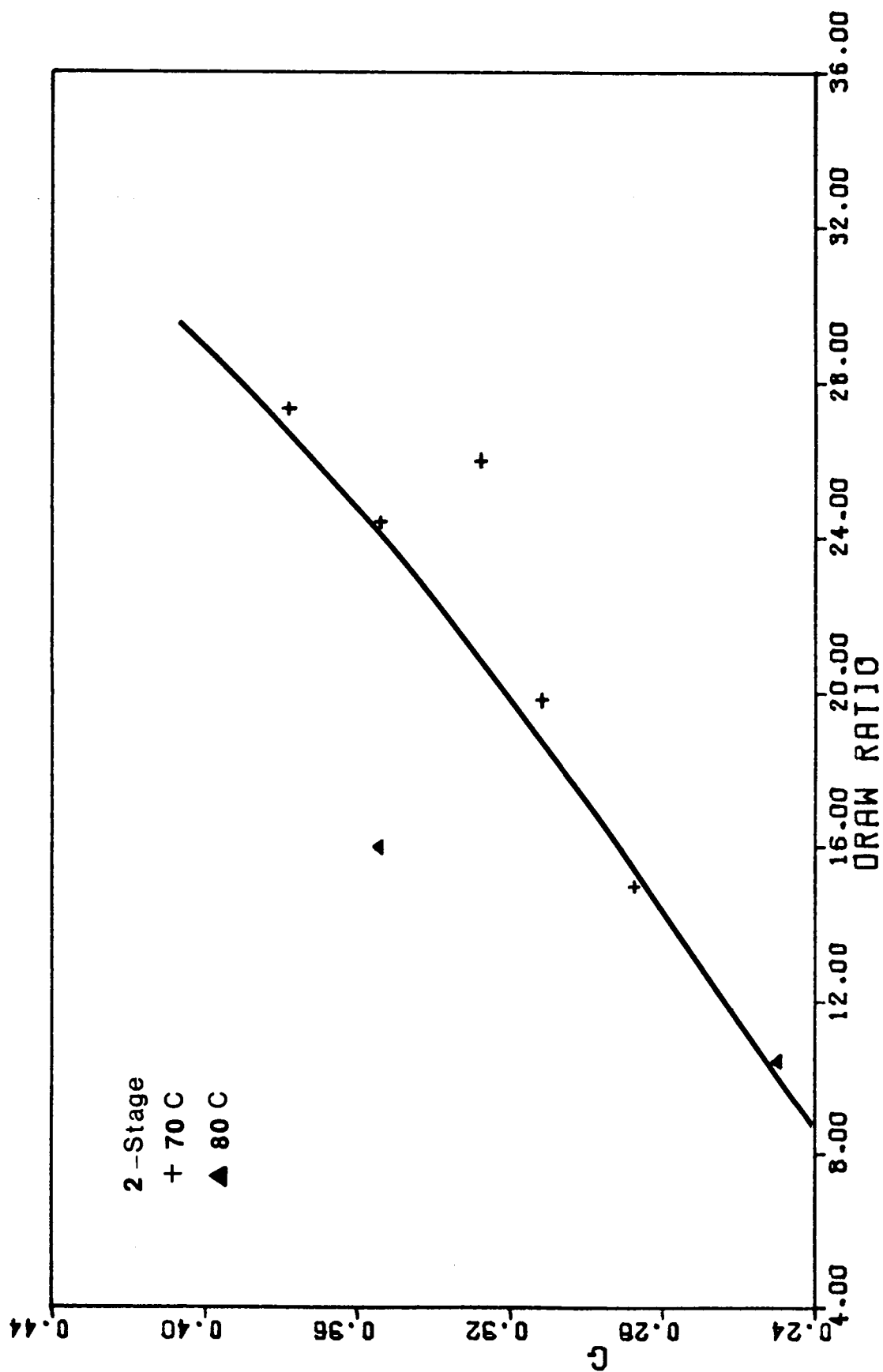


Figure 73. Interfibrillar (and/or) interclusteral paracrystallinity parameter (g) changes with draw ratio.

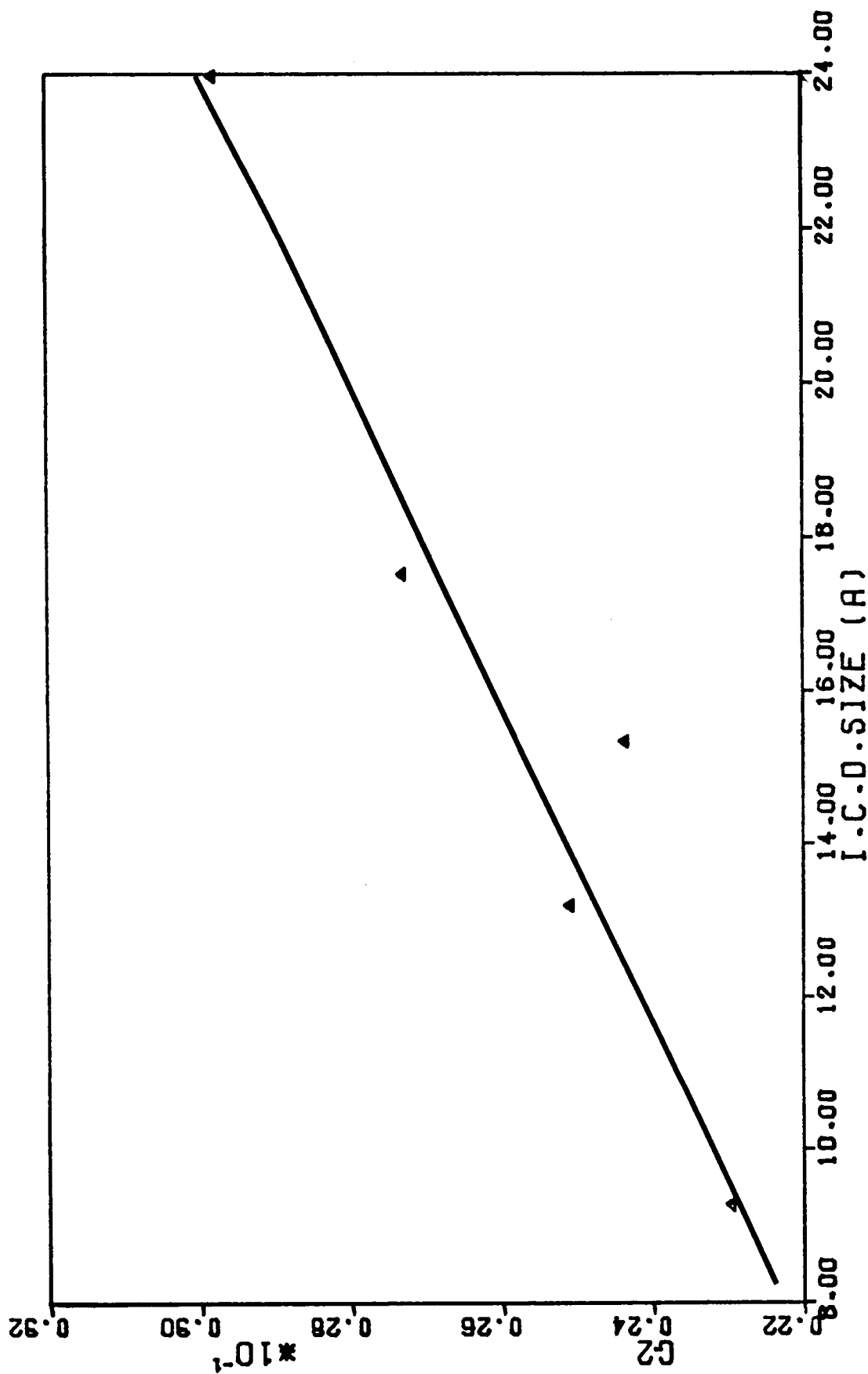


Figure 74. The change of (g_2) paracrystallinity parameter with paracrystallinity domain size within the clusters (I.C.P.D. size) (Å).

ratio (Figure 70). The paracrystallinity factor for microfibrils, however, was found to decrease with the increase of draw ratio (Figure 71). The paracrystallinity factors for clusters (g_2) were found to increase with the increase of draw ratio (Figure 72). The g paracrystallinity factor which is related to interfibrillar regions also shows an increase with draw ratio in Figure 73.

These above findings indicate that as the draw ratio increases, interfibrillar disordered domains within the clusters become extended and form paracrystallites, a fact supported by the increase of crystallinity. A simple model which represents these changes is shown in Figure 68b.

The increase of perfection of microfibrils as the draw ratio increases may be attributed to two factors.

1. As the draw ratio increases the chains unfold in the microfibrils and intrafibrillar disordered domains become more highly oriented. These oriented domains may become paracrystalline if not totally crystalline. As also indicated by Figures 60 and 61 the unit cell a , b parameters get smaller as the draw ratio increases; the packing efficiency of the chains becomes higher in the directions perpendicular to the chain axes. Thus, successive interplanar spacing fluctuations become less.

2. Since the superdrawing is slow process, the time that the sample is exposed to the hot environment increases for higher draw ratios. Thus, this annealing effect also contributes to the increase of packing efficiency.

Since the packing efficiency increases and the disorder parameter decreases in microfibrils as the draw ratio increases, the major source of the decrease of order (increase of g_2 paracrystallinity parameter) (Figure 72) in clusters is intermicrofibrillar domains within the clusters.

Since the disorder parameter is averaged over the length along the direction normal to (110) planes, and since the microfibril sizes do not change with draw ratio, the less ordered paracrystalline intermicrofibrillar domains within the clusters contribute to the (g_2) paracrystallinity parameter in increasing fraction as their size increases, consequently, causing the increase in (g_2) paracrystallinity parameter. It should also be noted that the magnitude of highest (g_2) factor is not higher than that of (g_1) factor.

The linear relation between g_2 and paracrystalline domain size within the cluster as shown in Figure 74 further indicates that the increase of g_2 is solely due to increase of sizes of paracrystalline domains.

In Figure 73 the paracrystallinity factor (g) which is related to interfibrillar (and/or interclusteral) boundary shows an increase with the draw ratio. The source of this increase is probably due to the following factor: Since the wide angle X-ray diffraction peaks are not too sensitive to the diffraction from amorphous domains they do not contribute to the shape or intensity of crystalline peaks which are used in this technique, however, as the draw ratio increases the amorphous domains are stretched and may become paracrystalline, if not totally crystalline. Thus these regions begin to contribute to the crystalline diffraction

peaks (in other words, the WAXS peaks) begin to see these relatively ordered regions). This concept is also supported by the increase of crystallinity.

Since the paracrystallinity factors are averaged over the directions perpendicular to the diffracting planes, as the fraction of paracrystalline regions between the microfibrils increases, the g factor also increases. It should be emphasized that the regions which become paracrystalline are formerly disordered (amorphous) regions. However, one should recognize that this G-W-H method is not sensitive to small distortions. At this point the root mean square strain which is determined by fourier analysis comes into play. This fourier analysis is sensitive to the low disorders. The rms strain as shown in Figure 66 decreases with the increase of draw ratio indicating an increase in overall packing efficiency. This latter behavior also supports the concepts presented above. Furthermore, since both techniques give "number average" crystal size, the similar sizes should be expected. This similarity can be observed clearly by comparing Figure 70, page 155, and Figure 65, page 146, which indicate that the sizes obtained by both method ($L(\text{fourier})$ and L_2) are in the same range. Thus we may conclude that the Fourier techniques and the G-W-H technique are complementary to each other rather than contradictory.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This chapter contains the major conclusions based on the experimental research carried out.

Low Density Polyethylene

The scouting experiments performed on LDPE showed that it is very difficult to draw LDPE to high draw ratios indicating the presence of high concentrations of entanglements in the structure. The optimum temperature of draw is found to be $\sim 40^{\circ}\text{C}$ which is in the peak range of the α -relaxation results from the relaxations in the crystalline regions in the sample. The draw ratio of LDPE samples was found to be sensitive to the process temperature.

High Density Polyethylene

Conclusions on changes of HDPE sample moduli with draw ratio and temperature are divided into three characteristic temperature regions;

A. At low temperatures (70°C , 80°C) which are in the range of the optimum process temperature (α -transition) the highest moduli are obtained. This is the consequence of orienting effects of interfibrillar and intrafibrillar "friction" which results from the forces exerted on the ends of the samples.

B. As the process temperature increases ($\sim 90^{\circ}\text{C}$), the friction between and within the fibrils is lessened causing a decrease in the orienting effects of the external forces causing a slope change in modulus versus draw ratio curve.

C. At very high temperatures (110°C), the mobility of chains is so high that refolding can occur even during the drawing process, thereby decreasing the modulus as a result of fewer load bearing elements in a given crosssection.

The increase in density, crystallinity and melting temperature with draw ratio for samples drawn by the two stage method at 70°C and 80°C , is also the consequence of chain orientation which causes tighter packing of the chains. This latter effect also causes the sharpening of the 110 and 200 WAXS reflections.

Comparison of the One Stage and Two Stage Method

A comparison of moduli of samples drawn by the one stage and two stage methods showed that at low draw ratios, no apparent differences exist, but at high draw ratios (above 25X) samples drawn by the one-stage method showed a somewhat lower modulus than the respective samples drawn by the two-stage method. This result is believed to be the consequence of void formation in the samples drawn by the one stage method which utilizes a much higher draw rate than the two-stage method. This void formation gives rise to the intense equatorial streak in the small angle patterns. In agreement with the above conclusions, the samples drawn by the one-stage method showed lower melting temperatures and crystallinities than those drawn by the two-stage method above the draw ratio of 22X.

Conclusions from SEM Micrographs

The statistical studies on the crack length in samples, strained at room temperature showed that the number average crack length decreases

with the increase of draw ratio indicating an increase in the fraction of extended chain structure which inhibits crack propagation.

Viscoelastic Properties of HDPE Samples Drawn by the Two-Stage Method

The room temperature studies showed a decrease in $\tan\delta$ and an increase in storage modulus (E') indicating an increase of elasticity in the structure drawn polyethylene. The increase of room temperature loss modulus with draw ratio indicates higher orientation of the chains as suggested by Takayanagi (117). The studies on the effect of temperature on viscoelastic properties revealed that the superdrawn samples have greater dynamic-mechanical stability than natural drawn samples at elevated temperatures. The increase of peak temperature of the α -transition with draw ratio further implied the increase of crystal perfection (119). Thus, we may conclude that the two-stage drawing process results in higher chain packing efficiency, higher orientation and higher crystallinity in the structure of HDPE.

Comparison of Viscoelastic Properties of Sample Drawn by The Two-Stage and One Stage Methods

In room temperature studies, the interesting demarkation at the draw ratio of 22 which was found in the measurements of young modulus also is evident in the viscoelastic properties. Above this draw ratio single stage samples showed lower storage modulus than their counterparts drawn by the two-stage method. These and the observations high temperature studies indicated that even though the two-stage and one-stage processes provide similar orientations in the samples, the crystal perfection is

greatly reduced for the sample drawn by the one-stage method.

Conclusions of Quantitative WAXS and SAXS Studies of HDPE Samples Drawn by the Two Stage Method

In general, three domains are observed in drawn samples--namely amorphous, folded chain and extended chain domains. As the draw ratio increases, the folded chain and amorphous chain domains deform under the "frictions" and transform into the extended chain domain. The highest increase in weight average crystal size with draw ratio was observed along the fiber direction. The crystal sizes were observed to increase in the radial direction in the fiber structure. Even though an increase of long periods of the samples with draw ratio was observed, this behavior may be due to the increased annealing effects of the hot medium as the sample residence time increases at higher draw ratios. The probability that a chain traverses the disordered regions to enter adjacent crystallites (along the fiber axis which is a good measure of extended chain fraction in the samples) also increased with draw ratio. As the extended chain fractions and long periods increased, the a, b unit cell parameters decreased, which is the result of decrease of steric hindrances on the unit cell dimensions within the crystallites.

Conclusions of Fourier Analysis

The Fourier analysis of multiple orders of 110 and 200 reflections showed an increase in the number average crystallite size in the directions normal to these planes. The increase of chain packing efficiency is also reflected in the decrease of the root mean square strains in the directions

normal to the 110 and 200 planes.

The Conclusions of G-W-H Analysis

This analysis revealed that there are two distinct types of crystallites in the drawn polyethylenes namely, isolated microfibrils, and clusters which are comprised of four microfibrils each. In addition, two types of disordered domains are observed, one of which is between the microfibrils within the clusters, the other between isolated microfibrils and clusters. As the draw ratio (and annealing effects) increases the microfibril size does not change but the perfection of crystals within the microfibrils increases. On the other hand, the cluster size increases with draw ratio but the overall perfection of the cluster decreases. This is the result of an increased fraction of paracrystallites domains within the clusters originating from amorphous domains. The interfibrillar (isolated) and/or interclusteral perfection is also reduced due to the latter effects. However, the magnitude of disorder within the cluster is much lower than that of disorder between interfibrillar and/or interclusteral domains.

Since the Fourier analysis is sensitive to low disorder and the G-W-H analysis is not, the results obtained by both methods are complementary.

Recommendations

1. The Fourier analysis and G-W-H method should be applied to polypropylene, nylon and polyethylene terephthalate, to investigate the inherent differences in the drawing behavior of these polymers.

2. The curve-crystal focalizer system which provides relatively undistorted transmission data should be used in data acquisition for line profile analysis.

3. The deconvolution technique which has recently been proposed by Ergun (31, 32) should be used with the Warren-Averbach analysis.

4. These powerful Fourier and G-W-H techniques should be applied to samples deformed by bi-axial orientation.

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APPENDICES

APPENDIX A

DETERMINATION OF SCHERRER CONSTANTS FOR ORTHORHOMBIC SYSTEM

As suggested by Langford and Wilson (69), the direction cosines of planes can be used for Scherrer shape constant orthorhombic systems in general equations.

$$\begin{array}{ll} h \geq k + 1 & h \leq k + 1 \\ \text{Tetrahedron } K_{\beta} = (2h/3^{1/3})N^{1/2} & K_{\beta} = (H/3^{1/3})W^{1/2} \end{array}$$

where

$$H = h + k + l$$

$$W = h^2 + k^2 + l^2$$

Then for orthorhombic planes the K Scherrer constant is given in Table 3 .
The h,k,l taken as directions cosines and they are rearranged as h>,k>,l.
They are not interpreted as conventional h,k,l parameters.

TABLE 3
SCHERRER CONSTANTS FOR ORTHORHOMBIC SYSTEMS

Plane	K_{β}
110	1.154463
200	1.386722
210	1.10922
670	1.3867225
120	1.3157174
310	1.240682
220	1.154463
400	1.386722
320	0.981009

APPENDIX B

Crystallographic Data for PE

<u>Structure Factors</u>	<u>Multiplicity</u>
$ F_{110} = f_c (3.99)$	4
$ F_{200} = f_c (3.99)$	2
$ F_{310} = f_c (3.9755)$	4
$ F_{220} = f_c (3.9754)$	4
$ F_{400} = f_c (3.9754)$	2
$ F_{002} = f_c (4)$	2

where

$$|F_{hho}| = F * F^* = (A^2 + B^2)^{1/2}$$

where A and B real and imaginary parameters respectively.

Lorentz Polarization Factors

For reflection,

$$L.P. = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}$$

For transmission

$$L.P. = \frac{1 + \cos^2 2\theta}{2 \sin^2 \theta \cdot \cos \theta \cdot t}$$

where $t = 0.815\beta_{1/2}$ radians

Temperature factor

$$\text{T.F.} = \exp\left(-10 \frac{\sin^2 \theta}{\lambda^2}\right)$$

APPENDIX C

OTHER METHODS RELATED TO LINE PROFILE ANALYSIS

As mentioned in the literature survey section of the line profile analysis, a conventional fourier transform method is generally used to separate the pure diffraction profile from original profile. Recently Kidron and DeAngelis (62) proposed a better method which comprises Least Square Analysis (L.S.A.) to calculate fourier coefficients of line profiles. The advantage of L.S.A. over fourier analysis is that the input data $y = f(x)$ does not have to be continuous (evenly spaced) in the independent variable (x). In fourier analysis, in order to calculate the coefficients, one has to take data points for x going from $-\infty$ to $+\infty$. In practice one has to terminate the input data $y = f(x)$ for some finite x . This introduces, in many cases, what is called "termination effects." Such effects are taken care of in L.S.A. by multiplying the data by a "pseudo temperature factor" of the form $\exp(-\alpha^2 x^2)$ and adjusting the fourier transform by the use of error function. One can directly calculate fourier coefficients of $K\alpha$ component from the total $K\alpha$ doublet intensities. The only disadvantage of this method is that it requires much longer computer time than conventional fourier analysis.

Separation of the Particle Size and Microstrain Components

in the Fourier Coefficients of a Single

Diffraction Profile

Separation of crystallite size and strain components from a single diffraction peak has been studied by Mitra et al., Pines et al., and Smith

(79, 92, 107). It was argued by Gangulee (34) that the principal deficiency in these approximate methods for analyzing single diffraction profile is the fact that each assumes the average microstrain to be independent of the averaging distance, which is an unrealistic assumption. Gangulee (34) further suggested that the particle size and the microstrain component in the fourier coefficient of a single diffraction profile can be separated if the functional form of the dependence of average microstrain on the averaging distance is known. They showed that if the fraction and form is approximated as $\langle \epsilon^2 \rangle = c/n$ where c is constant, acceptable separation of the two components can be obtained. Gangulee compared his findings with those obtained with the multiple order Warren-Averbach method and found reasonable agreement between them.

Relation Between Fourier Column Distribution with True Size Distribution

It is known that for mixtures of crystallites of uniform shape but differing size the fourier analyses of a number of profiles can lead to information on the nature of the distribution of sizes. Smith (108) related the fourier column distribution $g(n)$ to the true size distribution $G(A)$ by assuming simple shapes for crystallites (i.e., Cube, sphere, tetragon).

Strain Distribution Function Determination

It was pointed out by McKeehan and Warren (78) that one could determine the strain distribution function directly from experiment. The component of strain along the column direction averaged over the

distance L along the column is called ϵ_L , where

$$\epsilon_L = \frac{a_3^2 n}{a_3 n}$$

Introduce a normalized strain distribution function such that

$$\int_{-\infty}^{\infty} p(\epsilon_L) d\epsilon_L = 1$$

McKeehan and Warren showed that fourier size coefficients are small or negligible if one uses the center of gravity of profile as the origin of the fourier interval.

Therefore

$$A_D(L) = \langle \cos(2\pi L \epsilon_L s_b) \rangle$$

The average can be expressed in terms of the distribution function

$$A'(S_b) = \int_{-\infty}^{\infty} p(\epsilon_L) (\cos(2\pi L \epsilon_L s_b)) d\epsilon_L$$

where

$$s_b = \frac{2 \sin \theta_b}{\lambda} = \frac{1}{L}$$

For a given value of L_g the strain distribution function $P(E_L)$ can be obtained from the above equation by a fourier transform.

For cubic systems

$$P(E_L) = \frac{2L}{a} \int_0^{\infty} A(\frac{L}{d}) \cos(2\pi E_L h_0/a) dh_0$$

For orthogonal systems

$$s_b = \frac{1}{L}$$

$$P(E_L) = 2L \int_0^{\infty} A(\frac{L}{d}) \cos(2\pi E_L \frac{1}{d}) d(\frac{1}{d}).$$

APPENDIX D

SOME OF THE PROBLEMS ENCOUNTERED DURING APPLICATION OF FOURIER ANALYSIS AND THEIR ELIMINATION

1. Background problem and correction proposed by DeAngelis
2. Errors coming from W-A assumption
3. Correction of spurious oscillations in crystallite size distribution

1. Errors in determining $D(hkl)$ and strains arise from two distinct sources:

- A. Inaccurately measured peak profiles, in particular neglecting long tails, and
- B. Method of separation of particle size and strain broadening.

In the first category, the choice of background level in the cases of large broadening and overlapping neighboring peaks will lead to considerable errors in the values of fourier coefficients, in particular in the value of $A(0)$ which is proportional to the area under the broad (observed) peak. Wilkens and Hartman (137) found that the strains may appear unreasonable at small L when too high a background level of second order peaks is chosen. This high sensitivity of root mean square strains prevents one from placing too much reliance upon the magnitudes of these strains at small L . The high background selection also results as a maximum at low levels (Figure 75).

In the fourier studies of polyethylene same phenomena was observed. If the background of (i.e., 220) is taken high the strain coefficients oscillate and appear unreasonable (Figure 76) but particle size coefficient

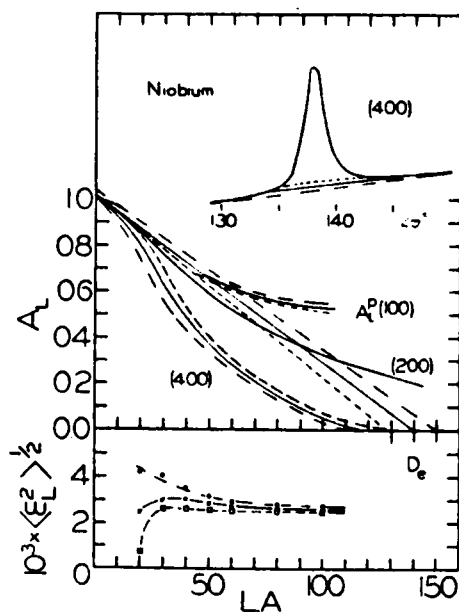


Figure 75. Background effect on cold worked niobium filings.

versus plot (Figure 77) seems reasonable. This phenomenon helps one, roughly, to correct for background. However, Wilkens and Hartman concluded that presence or absence of hook effect is no indication of the accuracy of either fourier coefficients or the calculated particle size and strains.

A method to correct the background effect was suggested by DeAngelis et al. (25), which assumes that background is linear and proceeds on independent analysis of the problem (25).

2. The Warren-Averbach analysis of the separation of particle size and strain involves a cosine and a logarithmic power series expansion. Delhez et al. (27) showed that the neglect of higher order terms in the logarithmic series expansion introduces larger errors at small values of the strain than the cosine series while at larger values the dominance is less pronounced. Thus, they suggested the use of cosine series expansion rather than logarithmic expansion.

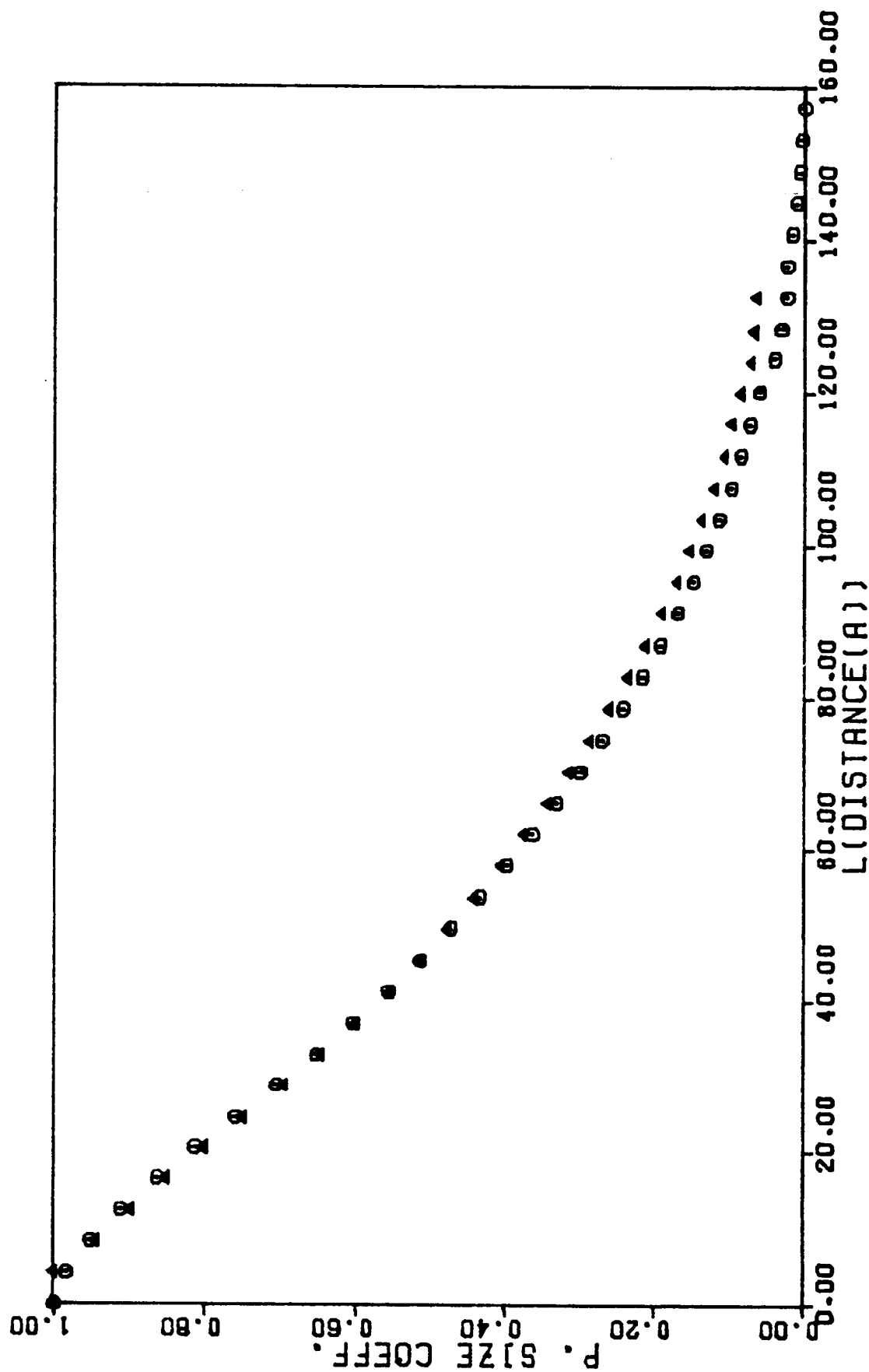


Figure 76. Particle size versus distance for a sample with and without a high background.

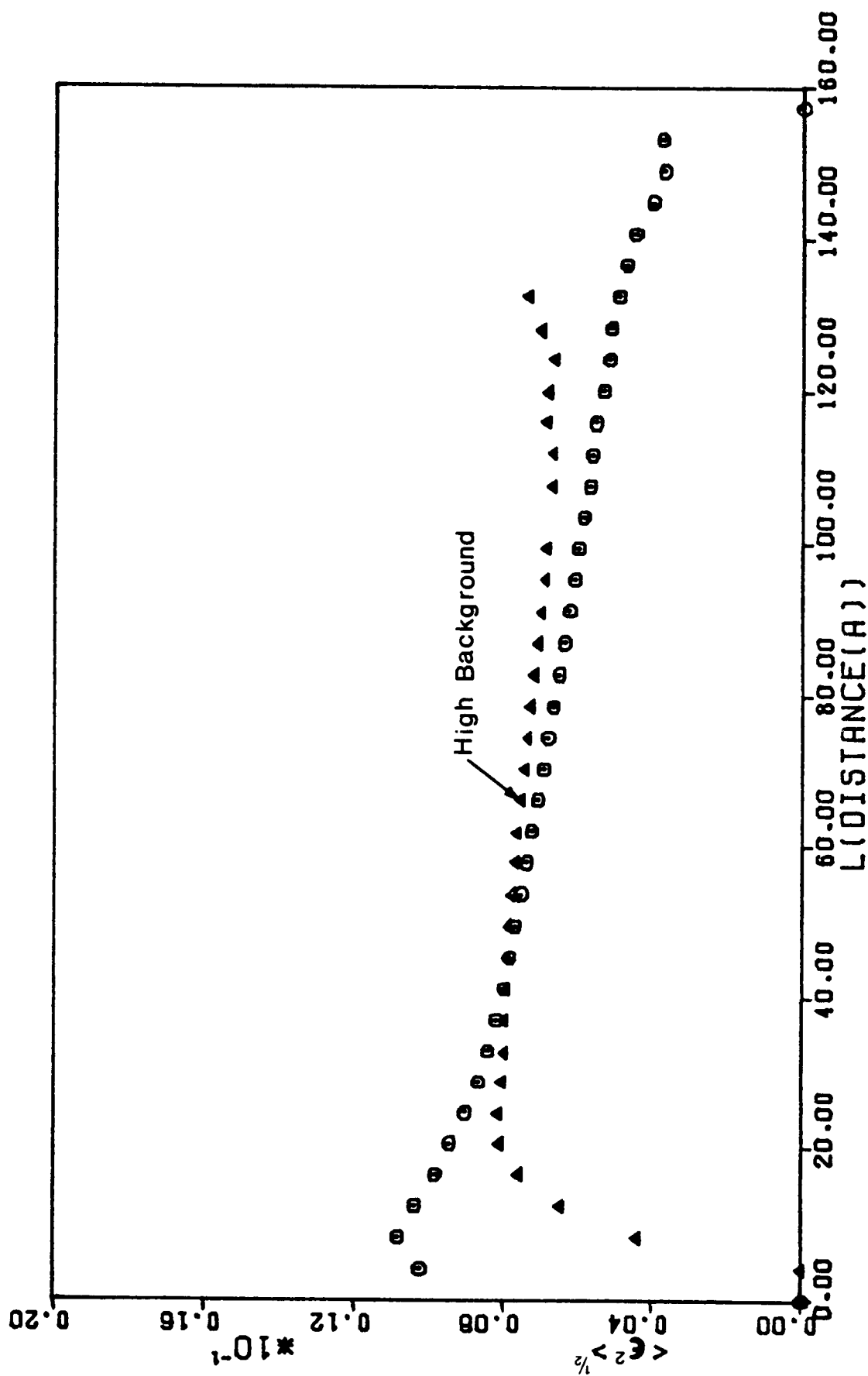


Figure 77. Root mean square strain versus distance for a sample with and without a high background.

3. Another problem in fourier analysis of line profiles is that the crystallite size distribution in finely divided materials are frequently complicated by spurious oscillations. LeBail et al. (73) used least squares smoothing procedure to eliminate this problem.

APPENDIX E

```

00100      DIMENSION DER(999),RADY(999),SVAL(999),AINT(999)
00200      DIMENSION SL(999)
00300      DIMENSION BLOGI(999),SQVAL(999)
00400      DIMENSION SVEL(2000),EINT(2000)
00500      DIMENSION YI(999),SUB1(999),AYI(999),AYI2(999)
00600      DIMENSION DER2(999),RADY2(999),AYI1(999)
00700      DIMENSION AYI2(999),YI2(999)
00800      WAVE=1.5+178
00900      READ(30,1)HEAD,DAY
01000      1  FORMAT(A5,T16,G15.7)
01100      CALL SKIP(DAY)
01200      READ(30,1)DATA,VAL
01300      IVAL=VAL
01400      DO 5 I=1,IVAL
01500      READ(30,88)DER(I),AINT(I)
01600      5  CONTINUE
01700      DO 15 I=1,IVAL
01800      RADY(I)=DER(I)*3.14156/360.
01900      SVAL(I)=2.*SIN(RADY(I))/1.5+178
02000      15  CONTINUE
02100      PEAK=AINT(1)
02200      DO 25 I=2,IVAL
02300      DIFF=AINT(I)-PEAK
02400      IF(DIFF)25,25,-0
02500      40  PEAK=AINT(I)
02600      M=I
02700      25  CONTINUE
02800      TYPE *,AINT(M)
02900      K=0
03000      DO 55 I=M,IVAL
03100      K=K+1
03200      SVEL(K)=SVAL(I)-SVAL(M)
03300      EINT(K)=AINT(I)
03400      SQVAL(K)=SVEL(K)**2
03500      DER2(I)=DER(I)
03600      KK=K
03700      55  CONTINUE
03800      DO 114 I=1,KK
03900      BLOGI(I)=ALOG10(EINT(I))
04000      114  CONTINUE
04100      DO 116 I=1,KK
04200      WRITE(24,88)SQVAL(I),BLOGI(I)
04300      WRITE(23,88)SQVAL(I),EINT(I)
04400      116  CONTINUE
04500      Z=1.
04600      LL=KK
04700      CALL TRANS(KK,SQVAL,BLOGI,Z,SLO,PA)
04800      TYPE *,SLO,PA
04900      WRITE(6,111)
05000      C  READ(5,*)SLO
05100      WRITE(6,112)
05200      C  READ(5,*)PA
05300      111  FORMAT(2X,'TYPE THE SLOPE OF I1')
05400      112  FORMAT(2X,'TYPE THE INTERCEPT OF I1')
05500      88  FORMAT(2015.7)
*
```

```

05600 C-----FIND ALL DISCRETE VALUES FOR I1
05700 DO 100 I=1,LL
05800 YI(I)=SLO*SQVAL(I)+BA
05900 100 CONTINUE
06000 DO 200 I=1,LL
06100 SUP1(I)=BLOGI(I)-YI(I)
06200 200 CONTINUE
06300 I=2.
06400 MM=LL
06500 CALL TRANS(LL,SQVAL,SUP1,Z,SLO1,PA1)
06600 TYPE *,SLO1,PA1
06700 WRITE(6,111)
06800 C READ(5,*)SLO1
06900 WRITE(6,112)
07000 C READ(5,*)PA1
07100 C=====FIND DISCRETE VALUES FOR I2
07200 DO 300 I=1,MM
07300 YI2(I)=SLO1*SQVAL(I)+PA1
07400 300 CONTINUE
07500 C=====CONVERT ALL I1 AND I2 INTENSITIES BACK TO NORMAL
07600 DO 350 I=1,MM
07700 AYI(MM+I-1)=EXP(YI(I)*2.302585093)
07800 AYI2(MM+I-1)=EXP(YI2(I)*2.302585093)
07900 350 CONTINUE
08000 C=====MAKE SYMMETRIC PEAKS ABOUT THEIR MAXIMUM
08100 DO 400 I=1,MM-1
08200 LV=MM-I
08300 AYI(LV)=AYI(MM+I)
08400 IF(AYI(LV).LT.0.)AYI(LV)=0.
08500 AYI2(LV)=AYI2(MM+I)
08600 IF(AYI2(LV).LT.0.)AYI2(LV)=0.
08700 IF(AYI(MM+I).LT.0.)AYI(MM+I)=0.
08800 IF(AYI2(MM+I).LT.0.)AYI2(MM+I)=0.
08900 400 CONTINUE
09000 C=====FIND X VALUES IN DEGREES FOR ALL POINTS
09100 DO 450 I=1,MM-1
09200 DER2(MM-I)=DER2(MM-I+1)-0.02
09300 450 CONTINUE
09400 C=====FIND RADIAN'S OF ALL X VALUES IN(THETA)
09500 IJ=2.*MM
09600 DO 500 I=1,IJ
09700 RADY2(I)=DER2(I)*3.14159265/360.
09800 500 CONTINUE
09900 C=====FIND INTENSITY*COS(THETA)
10000 DO 525 I=1,IJ
10100 AYI1(I)=AYI(I)*COS(RADY(I))
10200 AYI2(I)=AYI2(I)*COS(RADY(I))
10300 525 CONTINUE
10400 CALL AREA(IJ,RADY2,AYI1,RADY2(1),RADY2(IJ),A)
10500 CALL AREA(IJ,RADY2,AYI2,RADY2(1),RADY2(IJ),B)
10600 BRET1=(2.*A)/(WAVE*AYI(MM))
10700 BRET2=(2.*B)/(WAVE*AYI2(MM))
10800 AKK=MM
10900 U=0.0000000
11000 WRITE(26,1)HEAD,U

```

```

11100      WRITE(26,1)DATA,AKK
11200      SQBRE1=BRET1**2
11300      SQBRE2=BRET2**2
11400      WRITE(5,*)SQBRE1,BRET1
11500      WRITE(5,*)SQBRE2,BRET2
11600      DO 550 I=1,NM
11700      WRITE(26,88)SQVAL(I),BLOGI(I)
11800      550 CONTINUE
11900      WRITE(27,1)DATA,AKK
12000      DO 600 I=1,IJ
12100      WRITE(27,88)DER2(I),AYI(I)
12200      600 CONTINUE
12300      WRITE(28,1)DATA,AKK
12400      DO 650 I=1,IJ
12500      WRITE(28,88)DER2(I),AYI2(I)
12600      650 CONTINUE
12700      WRITE(29,1)DATA,AKK
12800      DO 700 I=1,NM
12900      WRITE(29,88)SQVAL(I),SUB1(I)
13000      700 CONTINUE
13100      STOP
13200      END
13300      SUBROUTINE SLOPE (IVAL,XX,YY)
13400      DIMENSION XX(999),YY(999),SL(999),B(999)
13500      LL=IVAL-1
13600      DO 10 I=1,LL
13700      SL(I)=(YY(I+1)-YY(I))/(XX(I+1)-XX(I))
13800      B(I)=YY(I)-SL(I)*XX(I)
13900      10 CONTINUE
14000      TYPE *,(SL(IVAL-I),B(IVAL-I),I=1,5)
14100      TYPE *,(SL(I),B(I),I=1,5)
14200      END
14300      SUBROUTINE SKIP(DAY)
14400      I=IFIX(DAY)
14500      IF(I.EQ.0)RETURN
14600      DO 10 N=1,I
14700      READ(30,20)
14800      10 CONTINUE
14900      RETURN
15000      20 FORMAT(' ')
15100      END
15200      SUBROUTINE APEA(N,X,Y,X1,X2,A)
15300      DIMENSION X(N),Y(N)
15400      DO 5 J=1,N
15500      IF(X(J).LE.X1) NS=J
15600      IF(X(J).LE.X2) NL=J
15700      5 N2=NL-NS+1
15800      IF(MOD(N2,2).EQ.0) N2=N2-1
15900      A=0.
16000      M=N2-3
16100      H=(X(NS+M2-1)-X(NS))/(M2)
16200      DO 10 J=2,M,2
16300      Y1=-.*Y(J+NS-1)+2.*Y(J+NS)
16400      10 A=A+Y1
16500      A=(A+Y(NS)+.*Y(NS+M2-2)+Y(NS+M2-1))*H/3.
16600      6 WRITE(5,*) N2,X(NS),X(NS+M2-1),A
16700      6 TYPE *,A
16800      RETURN
16900      END

```

Linear and second order curve fitting subroutines are not presented.

VITA

Mukerrem Cakmak was born in Istanbul, Turkey, on November 2, 1953.

He attended Ataturk elementary school in Mus and was graduated from Private Isik High School in June 1971. The following September he entered The Technical University of Istanbul, and in October 1975 he received a Bachelor of Science degree in Chemical Engineering. While at the Technical University of Istanbul, he did summer practices at the PET-KIM petrochemical compound factory and Cayirova glass factory.

Having won the first place on the nationwide scholarship examination, he was sent to the United States to attend the University of Tennessee. He received the Master of Science degree with a major in Polymer Engineering in June 1979.

The author is a member of the Society of Plastics Engineers.