

AD-A093 222

UTAH UNIV SALT LAKE CITY DEPT OF CHEMISTRY F/G 11/9
BRILLOUIN SCATTERING STUDIES OF THE EFFECT OF ORIENTATION ON ME--ETC(U)
DEC 80 D B CAVANAUGH, C H WANG N00014-79-C-0507

UNCLASSIFIED

TR-2

NL

For
2013-02-01

END
DATE
FILMED
2-2-84
DTIC

AD A093222

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LEVEL III

(12)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #2	2. GPOVT ACCESSION NO. AD-A093 222	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Brillouin Scattering Studies of the Effect of Orientation on Mechanically Deformed Poly(ethylene Terephthalate).		5. TYPE OF REPORT & PERIOD COVERED Technical Report.
6. AUTHOR(s) David B. Cavanaugh and C. H. Wang		7. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s) N00014-79C-0507 Serial RC-607		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS VNSF-DMR79-12457
10. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Utah Salt Lake City, Utah 84112		11. REPORT DATE Dec. 18, 1980
12. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quinby St., Arlington, Va. 22217		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 11 10 100 801		15. SECURITY CLASS. (of this report) unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited 14 11 11 11		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of abstract entered in Block 20, if different from Report) S D		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of Polymer Science		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Poly(ethylene terephthalate)film Internal Structure Brillouin Scattering Back Scattering Hypersonic Velocity Map Orientation Parameter		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Brillouin scattering is used as a tool for the study of the internal structure of oriented films of poly(ethylene terephthalate). Splitting in the longitudinal spectrum is observed as the film is stretched, indicating that the crystalline region is developed gradually from the amorphous region, and scattering from each region occurs independently. The hypersonic velocity data obtained from these two regions are used to draw directional maps of sound velocity propagating in different directions of the film. The results are discussed and correlated with		

DDC FILE COPY

DD FORM 1 JAN 73 1473

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

a recently proposed model. The orientational parameter in the amorphous phase is calculated from the hypersonic velocity data as a function of stretch ratio. The results are found in good agreement with the published values obtained by using a different technique.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

OFFICE OF NAVAL RESEARCH
Contract N00014 79C 0507
Serial RC-607

Technical Report No. 2

Brillouin Scattering Studies of the
Effect of Orientation on Mechanically
Deformed Poly(ethylene terephthalate)

by

David B. Cavanaugh and C. H. Wang

Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Prepared for Publication
in the
Journal of Polymer Science

December 18, 1980

DTIC
ELECTE
S DEC 29 1980 D
D

Reproduction in whole or in part is permitted for any purpose of the
United States Government.

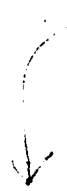
This document has been approved for public release; its distribution is
unlimited.

80 12 29 008

BRILLOUIN SCATTERING STUDIES OF THE EFFECT OF ORIENTATION ON
MECHANICALLY DEFORMED POLY(ETHYLENE TEREPHTHALATE)

David B. Cavanaugh and C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

ABSTRACT



Brillouin scattering is used as a tool for the study of the internal structure of oriented films of poly(ethylene terephthalate). Splitting in the longitudinal spectrum is observed as the film is stretched, indicating that the crystalline region is developed gradually from the amorphous region, and scattering from each region occurs independently. The hypersonic velocity data obtained from these two regions are used to draw directional maps of sound velocity propagating in different directions of the film. The results are discussed and correlated with a recently proposed model. The orientational parameter in the amorphous phase is calculated from the hypersonic velocity data as a function of stretch ratio. The results are found in good agreement with the published values obtained by using a different technique.



INTRODUCTION

Poly(ethylene terephthalate)(PET) is an important commercial polymer that has been extensively studied. Many polymers are known to contain crystalline and amorphous regions. In such polymers the distribution and weaving of the two regions determine the physical properties of the solid. Oriented polymer films have such a general utility that it is useful to understand deformation processes and superstructural details in these materials.

Although PET is crystalline when cooled slowly from the melt amorphous polymer can be formed by quenching the melt. Films and fibers of amorphous PET can be drawn into a highly oriented state. In this process structural changes occurring within the solid take place on two levels: molecular and supermolecular.

The molecular deformation in PET has been characterized using various techniques including X-ray diffraction,¹ infrared,² birefringence measurements,³ and ultrasonic measurements.⁴ The superstructure in some polymers including PET has dimensions comparable to a wavelength of visible light. Methods to study superstructural detail include small-angle light scattering (SALS)⁵ and optical microscopy,⁶ and considerable experimental data have been collected with these techniques. However, the detailed composition of the superstructure of the oriented PET is still uncertain.

Brillouin light scattering is a probe of the hypersonic acoustic phonons which propagate in a medium. Sonic velocity and acoustic attenuation information is obtained readily while the medium is maintained at thermo-

dynamic equilibrium. In the case when the refractive index is the same for the incident and scattered light, the hypersonic velocity in the medium is related to the Brillouin frequency shift by:

$$V_s = \frac{f_B \lambda_i}{2n \sin(\theta/2)} \quad (1)$$

where f_B is the measured frequency shift, λ_i is the vacuum light wavelength, n is the refractive index of the medium and θ is the scattering angle inside the medium.

Equation (1) is a good approximation for PET because the anisotropy in the refractive index is found to be small even for the stretched film; furthermore there is negligible dispersion for the incident and scattered light. Measurements of Brillouin scattering in media that exhibit strong elastic or surface scattering, which include polymer films,^{9,10} have been made possible with the multipass Fabry-Perot interferometer.⁷ In this paper, we report a Brillouin light scattering study of the effects of orientation in PET films.

EXPERIMENTAL

PET was purchased from the Aldrich Chemical Company as amorphous nuggets. Films were cast in a hydraulic press fitted with polished heated plates. The cast temperature was 270°C and 2 metric tons of pressure was applied for 10 minutes. The hot films were quenched in ice water. The strongly adhering aluminum foil jacket was dissolved in 1 M NaOH.⁸ Regions of the films having an unblemished surface and uniform thickness were selected for experimentation.

The films were uniaxially oriented in a water bath at 80°C using a manually operated film puller. The draw rate was about 100%/min. The final elongation was determined by measuring the separation of marks on the film before and after stretching. A stretch ratio of 4.66 was found to be just less than the break point at this temperature. The films were mounted in frames directly from the puller so that their tension was maintained. Annealing the PET films in heated baths tended to reduce the optical quality by making the samples slightly opaque; therefore, the films used in this experiment were unannealed.

The spectrometer used is a triple pass Fabry-Perot (FP) interferometer which provides high contrast resolution of the Brillouin doublets. The FP mirrors are scanned piezoelectrically. The free spectral range is 30 GHz. An argon ion laser tuned to 4880 Å and equipped with an etalon provides the incident radiation. The signal current from the photomultiplier tube is amplified with a picoammeter and the spectra are displayed on a chart recorder. To protect the PM tube from the intense Rayleigh light from the film surface, an attenuator is placed between the sample and collection optics. We use a photographic orange (02) filter mounted on a vertically swinging arm that allows it to be dropped into place as the Rayleigh line is approached. The beam is focused to a very small area on the film by a lens of 5 cm focal length.

The film thickness varies from 0.014 cm for the stretched film to 0.011 cm for the highest stretched one. Because of the small thickness, the interaction cross section with the laser beam is small. Furthermore, in the present

study the laser power was purposely made small to avoid overheating the film with the focused beam. As a result, scattering from the transverse phonons in PET is faint, and is not considered in the present paper.

The scattering geometries used are displayed in Fig. 1. The 90° geometry directs the surface reflections away from the collection optics. The 180° backscattering geometry was used to check the assignment of the Brillouin doublets.

In the angular dependence experiment, the angle of the film axis to the beam is measured with a calibrated rotation stage having its rotation axis in the scattering plane and at 45° to the laser beam. The film is held so that the center of rotation is in the scattering region.

The refractive index of the films was determined by finding the critical angle of total reflectance at the base of a prism with a layer of high index liquid between the prism base and the film. The index of the unoriented film is 1.588 at $4880 \text{ \AA}$. The film densities were determined by the flotation method using a tetrachloroethane-toluene mixture. The degree of crystallinity in the unoriented film is found to be less than 8%.

RESULTS AND DISCUSSION

Two sets of Brillouin doublets are found in the polarized spectrum of the amorphous film. One peak with higher intensity is present at 6.9 GHz and another peak with somewhat less intensity is found at 15.6 GHz. No peak is observed in the depolarized scattering spectrum in these films despite the fact that depolarized spectral peaks have been reported in polymer films.⁹ The 90° scattering geometry in Fig. 1a shows two incident light rays: The

first is from the incident beam as it makes the first pass through the film the second is the reflection from the back surface of the film. Thus for the 90° scattering there are two scattering vectors: $\underline{q}_1$, which lies in the plane of the film, and $\underline{q}_2$ which is tilted from the normal direction of the film. The scattering vectors involved in the 180° backscattering geometry are shown in Fig. 1b. When the film axis is at 45° to the incident beam, the same two scattering vectors are present but the sequence of the incident light rays are reversed. In agreement with this consideration, we found the frequencies of the two Brillouin peaks to be the same in both scattering configurations with the intensity of the peaks reversed. This result indicates that the sound dispersion is negligible in PET.

The spectra obtained in the 90° scattering geometry have an interesting feature. When the film bisects the scattering angle, it is easy to show that the sound velocity measured along the stretch axis ($\underline{q}_1$) is independent of the refractive index of the medium. In this case, the sound velocity is given by:

$$v_s = \frac{f_B \lambda_i}{\sqrt{2}} \quad (2)$$

While there is a large difference in Brillouin frequency for peaks associated with $\underline{q}_1$ and $\underline{q}_2$ (Fig. 2) the sound velocities are expected to be the same in the unoriented sample provided that there is no dispersion with wave vector. This result is confirmed as shown in Fig. 3. The result given in Eq. (2) is useful in studying samples having amorphous and crystalline regions that scatter light independently since we do not need to know the refractive index within each region to measure the sound velocity accurately.

Fig. 2 shows Brillouin spectra of oriented PET films where the scattering

vector q_{-1} (and thus the direction of sound propagation) is along the stretch axis of the films. One notes that as the film is stretched and undergoes orientation, a shoulder develops on the low frequency band and it splits into two components. Moreover, the bands also shift to higher frequencies with increasing orientation. The observed apparent decrease in the intensity of the two components with stretch ratio is due to the decrease in the thickness of the films.

The films have good optical quality and it is possible to rotate the films in the scattering plane and change the direction of the scattering vector in the film. Fig.3 is a set of sound velocity(SV) contours in the plane of the films. These are similar to those obtained for polymer films by other workers using ultrasonic techniques.¹¹ Brillouin scattering measures the sound velocity average approximately over a wavelength of light rather than over the bulk film dimensions, as in the case of ultrasonic measurements and thus reflects the microscopic properties of the polymer films. There are gaps in the SV contours at higher stretch ratios due to the fact that the bands either shifted to low frequencies and are covered by the Rayleigh scattering or the higher-frequency component becomes diffuse.

Another interesting result in the angular dependence experiment is a dramatic increase in the Brillouin scattering efficiency in the oriented films as the scattering vector approaches perpendicularity with the stretch direction. Since the Brillouin scattering cross section is proportional to the elasto-optical coefficients,¹² the large intensity increase due to chain orientation must correspond to the increase in the Pockel elasto-optical coefficients (p_{31} and p_{32}) perpendicular to the stretch direction.

Sound velocity data are useful to obtain information about chain orientation in polymer solids. Sound propagation is associated with the forces between neighbors in the structure which are stretched and compressed upon the passage of sound waves. In polymers both intermolecular forces between adjacent chains and intramolecular forces, which are the chemical bonds between monomer units are involved. Thus the sound velocity along the chain axis of the polymer is large compared with that propagating between adjacent chains where the intrachain interaction forces are soft. As a result, we expect a directional anisotropy in sound velocity in oriented polymer samples.

One should be cautious in assuming that the proposed mechanism for the propagation of sound waves in solids with an inhomogeneous structure is correct. We have assumed that the interaction forces between adjacent particles and the sound velocity in the medium are proportionally related. Crystals having a layered two dimensional crystal structure such as mica and graphite show a smaller elastic anisotropy in the layer planes and normal to them than would be expected when one considers the extreme difference of the intralayer and interlayer force constants. It can be shown that the anisotropy of the lattice spacing tends to compensate the anisotropy in the force constants.⁷ To extend this reasoning quantitatively to a general polymer solid, one is required to have detailed information about the average molecular spacing and conformation of polymer chains in the amorphous and crystalline regions and the forces that exist between them. For PET there is no evidence which suggests that there is anomalous spacing between chains in the crystalline and amorphous regions. Our intuitive model for the velocity of sound propagation in polymers may be reasonable on this basis.

Measurements of the sonic modulus in fiber and film samples have been used in combination with X-ray and birefringence measurements to obtain^{3,13} orientational parameters in solid polymers. This technique has been useful since it allows the determination of the orientation parameters in both the amorphous and crystalline regions of the solid. The assumptions involved in this approach are the independence of sound velocities in the crystalline and amorphous phases such that scattering from each region may be considered as a separate elastic continuum. Experimental evidence using long-wave length KHz sound waves have shown these to be valid. However, in polymers having superstructural crystalline and amorphous regions with a size smaller than or comparable with the wavelength of light, these assumptions should be used with caution. However, in the case that the sound velocities in both the crystalline and the amorphous regions can be measured independently it should be possible to extract information about the chain orientation parameter in each region.

As seen in Fig. 2, the band at low frequency develops a shoulder at a stretch ratio of 2.7. When the stretch ratio is increased to 3.6 and 4.7 the spectral shoulder separates into two bands. This result is an indication that two distinct superstructural regions in the polymer are developed. At the stretch ratio of 2.7, a considerable amount of crystallinity is developed in the films in the form of crystalline spherulites. This is reflected in the¹⁴ density changes and the infrared results.² The development of spherulites are easily seen in our samples under a polarizing microscope, an observation⁵ also reported by Misra and Stein. As the stretch ratio is increased, the sound velocity in both regions increases. This is shown in the plot in Fig. 3. As the film approaches the break point at $R_s = 4.7$, the strain is reflected

by an increase in sound velocity across the film (Fig. 3).

It is possible to obtain the anisotropy in formation regarding the propagation direction of sound velocities in the film plane by changing the direction of the scattering vector in the film. Fig. 4 shows the sound velocity maps drawn with this technique. The unoriented sample shows the expected sonic isotropy. At a stretch ratio of 2.7, the circle is distorted along the stretch direction (SD); the velocities away from the SD are the same as the unoriented velocities. At a ratio of 3.6 there are two regions. The oval which develops with its long axis in the SD is clearly defined. A second shape has also become evident in which the sound velocity increases slightly as the scattering angle approaches 45° to the SD. At a stretch ratio of 4.7 the oval in the stretch direction is highly elongated and slightly pointed. The second shape has been elongated in the SD. It should be pointed out that splitting in the high frequency peak corresponding to the back scattering vector q_2 is not observed in the highly oriented sample. Since q_2 lies at about 60° from the SD, it reflects mainly the scattering from the amorphous region, as the scattering from the crystalline region diminishes in intensity when the scattering vector is greater than 45° , as shown in Fig. 4.

Misra and Stein have proposed a model⁵ for the superstructure of PET which is oriented at 80°C . Their model is an extension of the model proposed by Statton and Dismore¹⁵ for oriented nylon 6-6 fibers which consist of extended chain crystallites. The model of Misra and Stein accounts also for the space filling amorphous and semicrystalline regions. For stretch ratios ranging from 1 to 1.8, their model predicts that rodlike shapes are formed within the amorphous matrix with the rods' long axis oriented in the direction normal to the stretch. The rods are non-crystalline. For stretch ratios of

2.7 to the break point, a fibrillar structure corresponding to the extended chain crystallites develops which is entwined with the crystalline spherulitic and amorphous regions. At the highest elongations the spherulitic ellipsoids are widened in the SD. They have estimated the crystalline ellipsoid size to be about 2-5 μm in diameter. These shapes are not volume filling, the matrix surrounding the ellipsoids is likely to be oriented amorphous or perhaps partially crystalline polymer. Since these regions are larger than a light wavelength ($\sim 0.5 \mu\text{m}$) we can justify independent scattering to occur from each region. Thus, it should be safe to assume that the regions with the highest sound velocity parallel to the SD are associated with the oriented amorphous region and the regions with the high sound velocity at 45° to the SD are with the deformed crystalline spherulites.

The effects of orientation on the crystalline and amorphous regions are seen from our data to be fundamentally different. For stretch ratios of 3.6 and 4.7, the direction of highest sound velocity in the crystalline regions is about 45° to the SD. The sound velocity in this region is expected to depend on the direction in which the crystal axes have a preferred alignment or where the aggregate crystallites have an anisotropic arrangement. To identify the effect as being due to an axial crystallite alignment we need to know the variation of sonic velocity along the crystal axes of a PET crystallite. To our knowledge, this data is not presently available. The effect might also be due to a variation in the crystalline "packing" with direction in this region. This would be consistent with Stein who proposes the rate of chain fold crystallization is greater perpendicular to the SD. The effect of orientation may be to tilt layers of chain folded crystallites from the SD perpendicular.

The propagation velocity of a sound wave in partially oriented polymer molecules is approximately related to the orientation function $\langle \cos^2\theta \rangle$ by:

$$\frac{1}{v^2} = \frac{1 - \langle \cos^2\theta \rangle}{v_{\perp}^2} + \frac{\langle \cos^2\theta \rangle}{v_{\parallel}^2} \quad (2)$$

where θ is the angle between the direction of sound propagation and the polymer chain axis. $v_{\perp}$ and $v_{\parallel}$ are the limiting velocities of a sound wave for a hypothetical sample in which the chain axes of all molecules are perpendicular and parallel to the direction of sound propagation respectively. Mosely¹⁸ has made the simplifying assumption that intramolecular forces along the chains are much larger than intermolecular forces between adjacent chains thus $v_{\parallel}$ may be set equal to infinity and, as a result Eq. (2) simplifies to:

$$\frac{1}{v^2} = \frac{1 - \langle \cos^2\theta \rangle}{v_{\perp}^2} = \frac{3}{2} \frac{(1 - \langle \cos^2\theta \rangle)}{v_u^2} \quad (3)$$

when v_u is sound velocity of the unoriented polymer. We have used $v_{\perp}^2 = \frac{2}{3} v_u^2$ to relate the unoriented and transverse velocities. Thus Herman's orientation function is related to sonic velocities as:

$$\frac{1}{2} [3 \langle \cos^2\theta \rangle - 1] = \alpha = 1 - \left(\frac{v_u}{v} \right)^2$$

With this basis and having identified the scattering from the amorphous region we have calculated α for the amorphous phase along the stretch axis (Fig. 1) using the Brillouin sound velocities. The results are shown in Fig. 5. Also shown are the values of α from Ref. 3 that were obtained with KHz sonic velocities, X-ray diffraction, and birefringence measurements. The two data sets are in reasonably good agreement. These workers suggest that the threshold for crystallite formation is $\alpha = .75$. Our data approaches this value at higher

draw ratios.

To our knowledge this is the first method which measures the amorphous orientation function directly and with a fair degree of precision, without requiring supplementary data. However, it should be noted that Brillouin measurements of the amorphous phase orientation is only possible in polymers having superstructural regions that are at least as large as the wavelength of light. In crystalline polymers having smaller superstructural details we have not observed this independent scattering.¹⁹

The above discussion has not taken into consideration the detailed symmetry change of the crystallites after the film is stretched. Neither has the effect of double refraction of the incident and scattered light beams on the longitudinal phonon corrected. However, since this paper is concerned mainly with the study of the effects of phase separation on the Brillouin scattering spectra and the quantitative effect of chain orientation on the change of the longitudinal phonon velocity in the amorphous region, the orientation of crystallites and double refraction will play only a minor role in affecting the result of this paper. This is especially true in the PET system as scattering from the crystallites is found to be independent of that from the amorphous region, due to the fact that dimension of the superstructure is greater than the wavelength of light in the highly oriented films. Without a doubt, the double refraction will affect the spectral intensity, but its effect on the phonon frequency is negligible, especially in the PET system for which the birefringence measured for PET with draw ratio equal to 4.5 is 0.21.²⁰ Scattering from the extraordinary ray will give the intensity below our detection level.

SUMMARY

Brillouin light scattering is used to study the internal structure of oriented films of poly(ethylene-terephthalate). Brillouin scattering was observed to occur independently from the crystalline and amorphous regions in the superstructure. Sound velocity data from these two regions are used to draw directional maps of the sound velocity in the films and are shown to give structural information for both regions. The results are discussed qualitatively and correlated with a recently proposed model. The Herman orientation parameter in the amorphous phase is calculated for a series of draw ratios using the hypersonic velocities. The results are in agreement with published values which were obtained by a different method.

Acknowledgement:

We acknowledge the Office of Naval Research and NSF Polymer Grant No. DMR 79-12457 for providing financial support of this research.

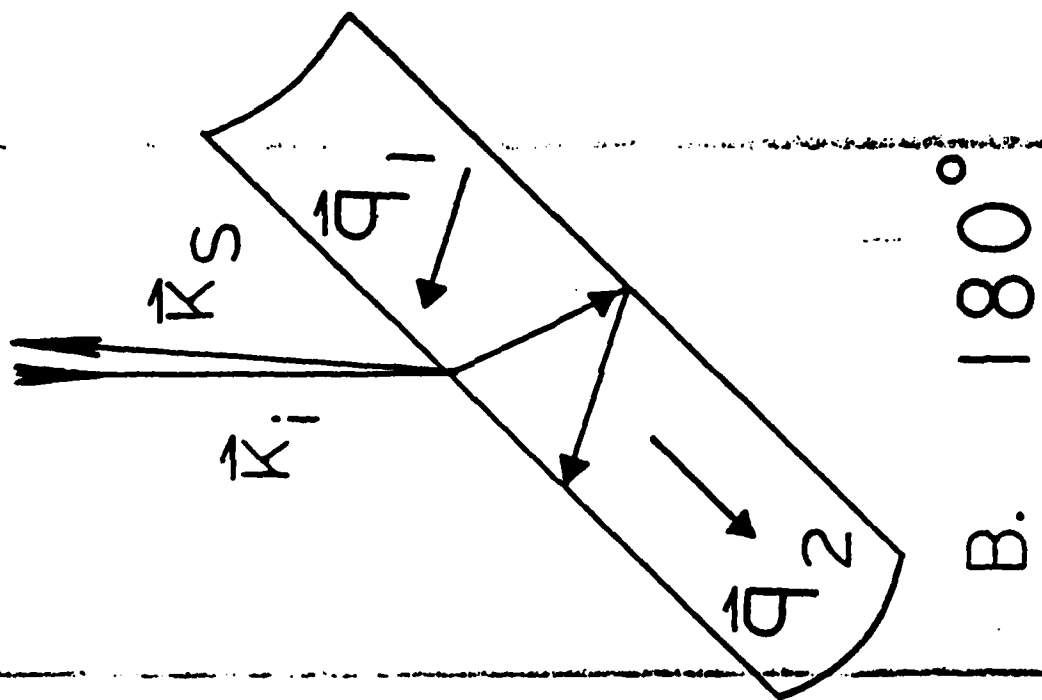
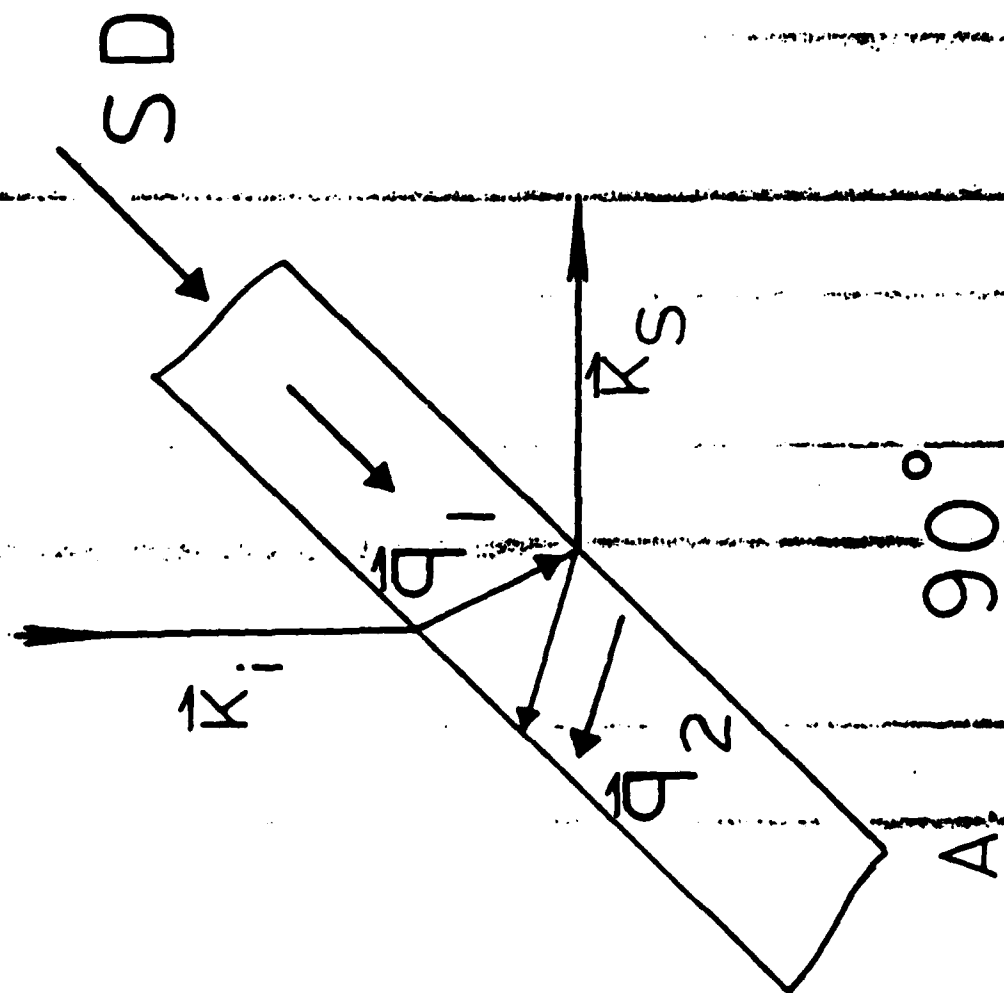
REFERENCES

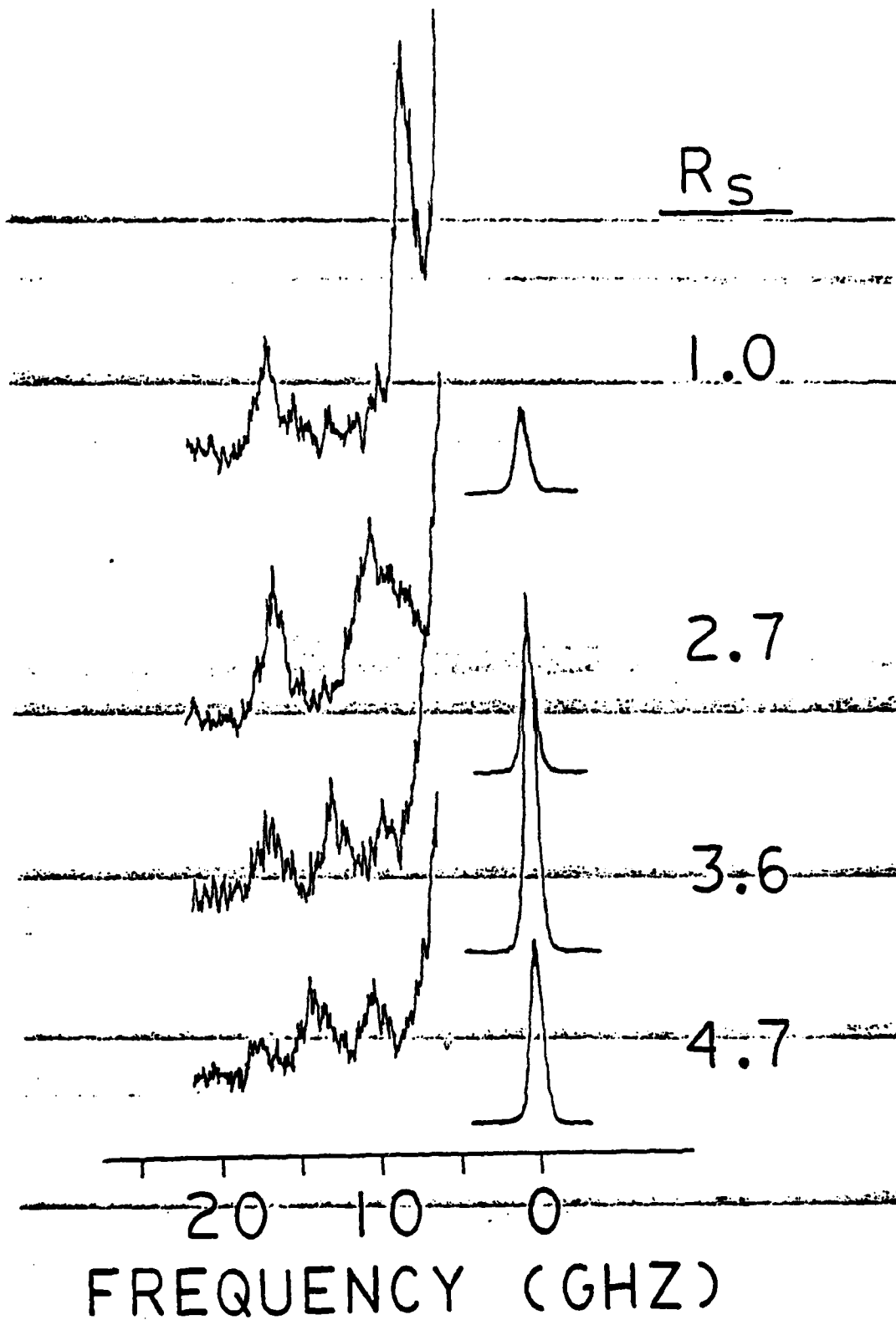
- 1) C. J. Heffelfinger and P. G. Schmidt; J. App. Poly. Sci. 9, 2661 (1965)
- 2) K. U. Mochlera and J. P. Bell, J. Poly. Sci. (Pol.Phys.) 11, 1779 (1973)
- 3) J. H. Dumbleton, J. Poly. Sci. A-2, 6, 795 (1968)
- 4) K. Matsumoto and Y. Yokota, Sen-I Gakkaishi, 34-3, 49 (1978)
- 5) J. J. Klement and P. H. Geil, J. Macromol. Sci., Rev. Macro Mol. Phys. 5, 505 (1971)
- 6) A Misra and R. S. Stein, J. Poly Sci. (Poly.Phys.) 17, 235 (1979)
- 7) A. Sandercock, Festkörperprobleme X V P. 183, 1975
- 8) J. P. Bell, J. Poly, Sci. A-2, 7, 1059 (1969)
- 9) G. D. Patterson, J. Poly. Sci. (Poly.Phys.) 14 143 (1976)
- 10) J. Kruger, and L. Peetz, Polymer 19, 1397 (1978)
- 11) K. Matsumoto and Y. Yokota, Sen - 1 Gakkaishi, 34-3, T-109 (1978)
- 12) W. Hayes and R. Loudon, "Scattering of Light by Crystals", Wiley Interscience Pub. 1978
- 13) R. J. Samuel, J. Polymer Sci. A, 3, 1741 (1965)
- 14) G. Farrow and I. M. Ward, Polymer 1, 330 (1960)
- 15) W. O. Statton, P. R. Dismore, J. Polymer. Sci. Part C 13 133 (1966)
- 16) A. Peterlin, "Structure and Properties of Polymer Films" Vol. 1 p. 253, R. W. Lenz and R. S. Stein Eds., Plenum Press 1973
- 17) R. J. Urick and W. S. Ament, J. Acoust. Soc. Am., 21, 115 (1959)
- 18) W. N. Mosely, Jr ., J. App. Polymer Sci. 3, 266 (1960)
- 19) C. H. Wang, D. B. Cavanaugh, Y. Hagashigaki (unpublished)
- 20) J. H. Dumbleton, J. Polymer Sci. (Part A-2), 6 , 795 (1968)

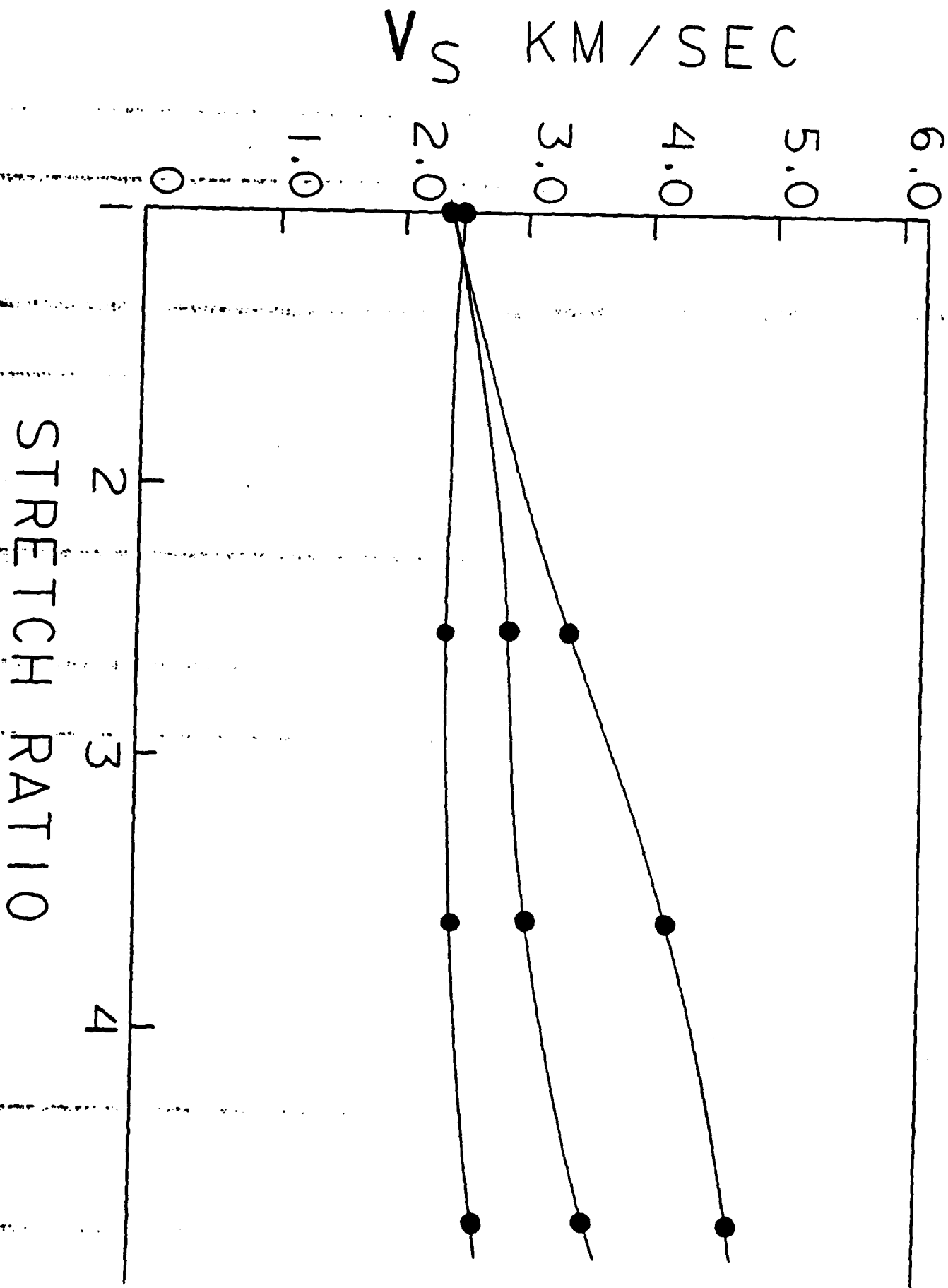
LIST OF FIGURES

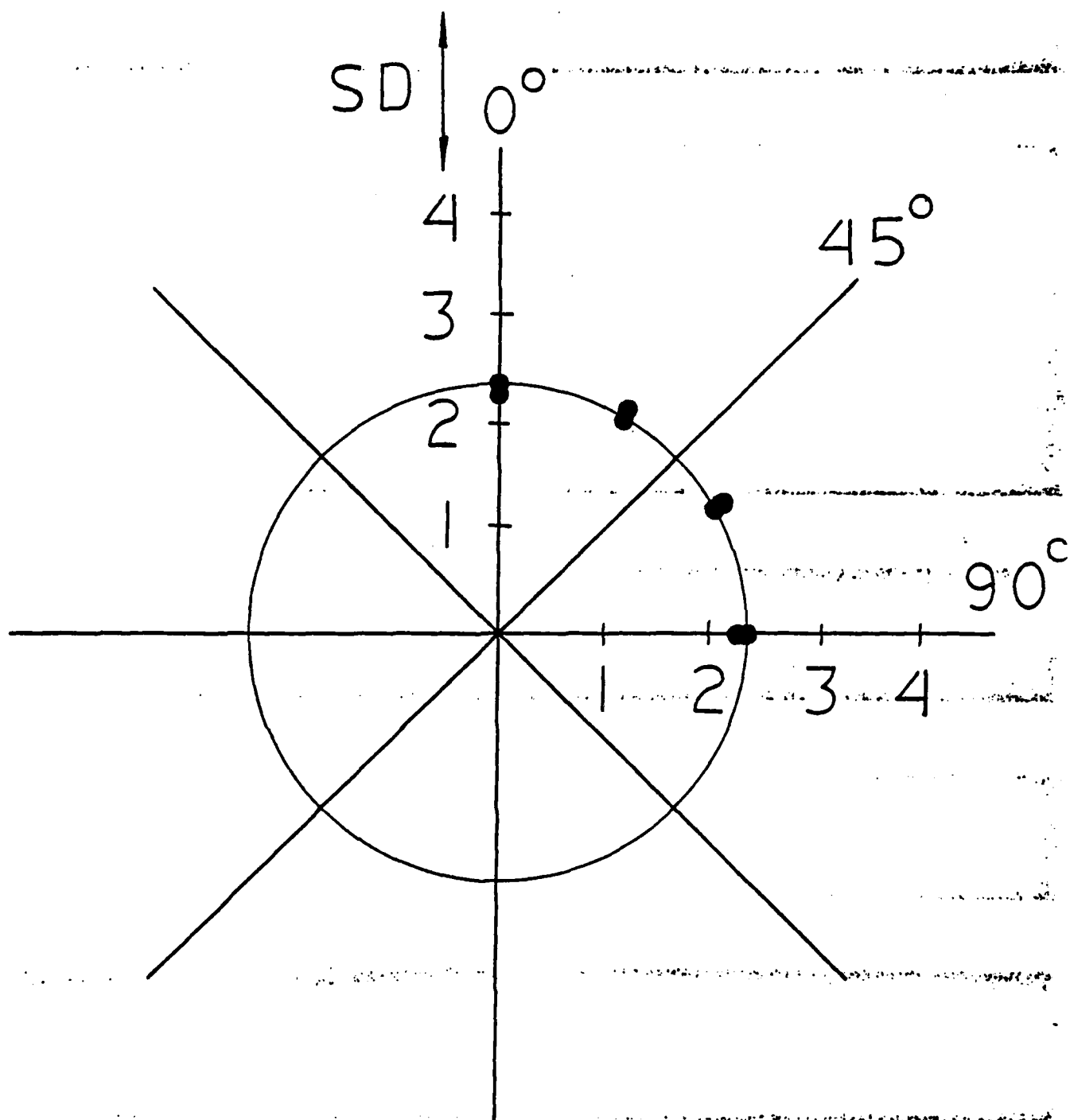
- Figure 1 A diagram of the two scattering geometries showing the scattering vectors in the films. The view is across the film thickness. The largest scattered intensity arises from the scattering vectors subscripted 1.
- Figure 2 Brillouin spectra as a function of stretch ratio; V V polarization and the 90° scattering geometry. The q , scattering vector is along the SD.
- Figure 3 The sound velocities along the stretch axis as a function of stretch ratio. Lower curve: sound velocity across the film thickness. Upper curves: sound velocities in the crystalline (middle) and amorphous (upper) superstructural regions.
- Figure 4 Sound velocity in the films plotted in polar coordinates showing the directionality of the sound velocity in each region. The isotropic shapes at low sound velocity in each map is from the scattering vector tilted from the film normal.
- Figure 5 Herman's orientation function parameter, α , for the amorphous phase plotted as a function of stretch ratio.

● our data Δ data of ref. 3.

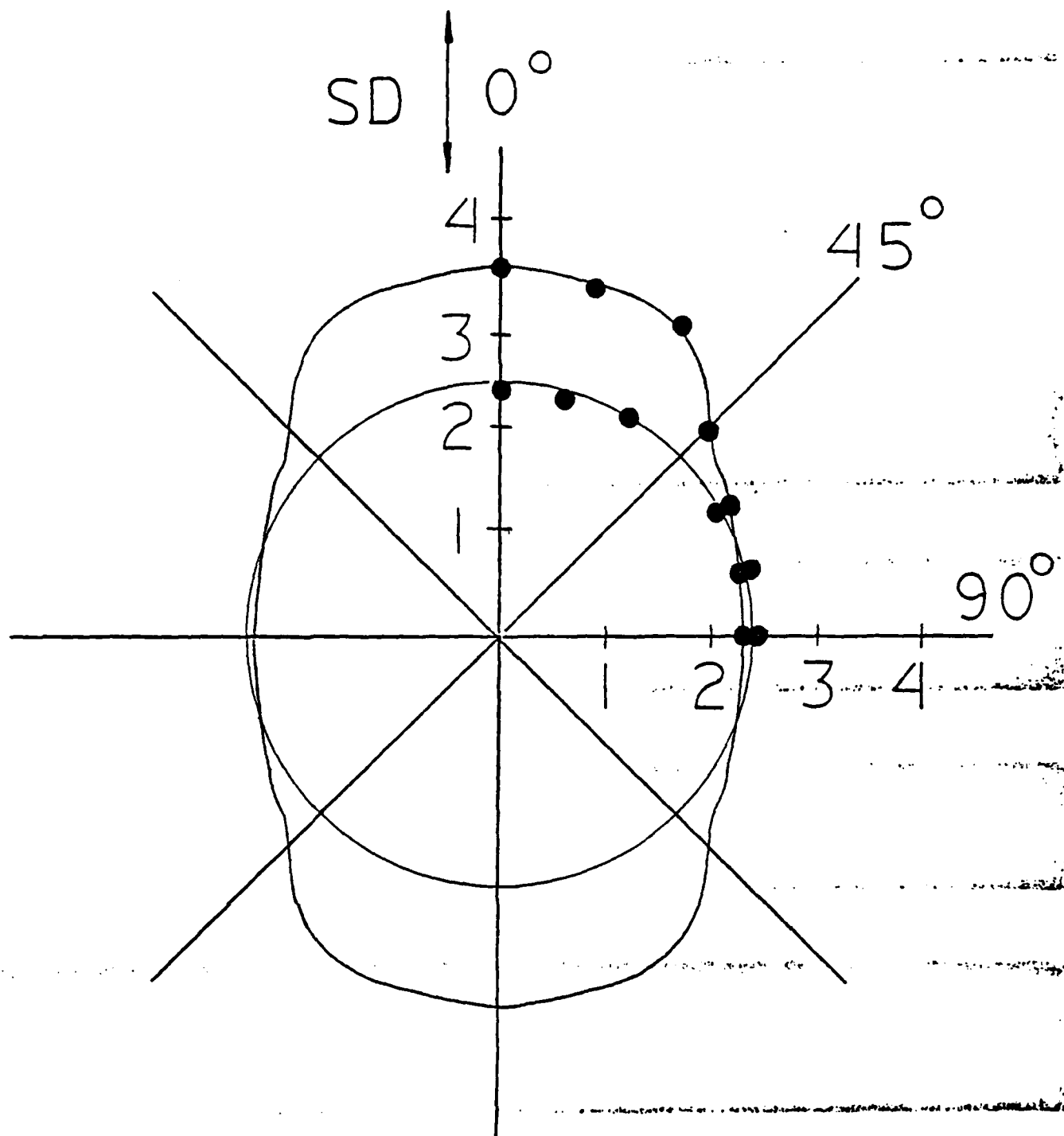




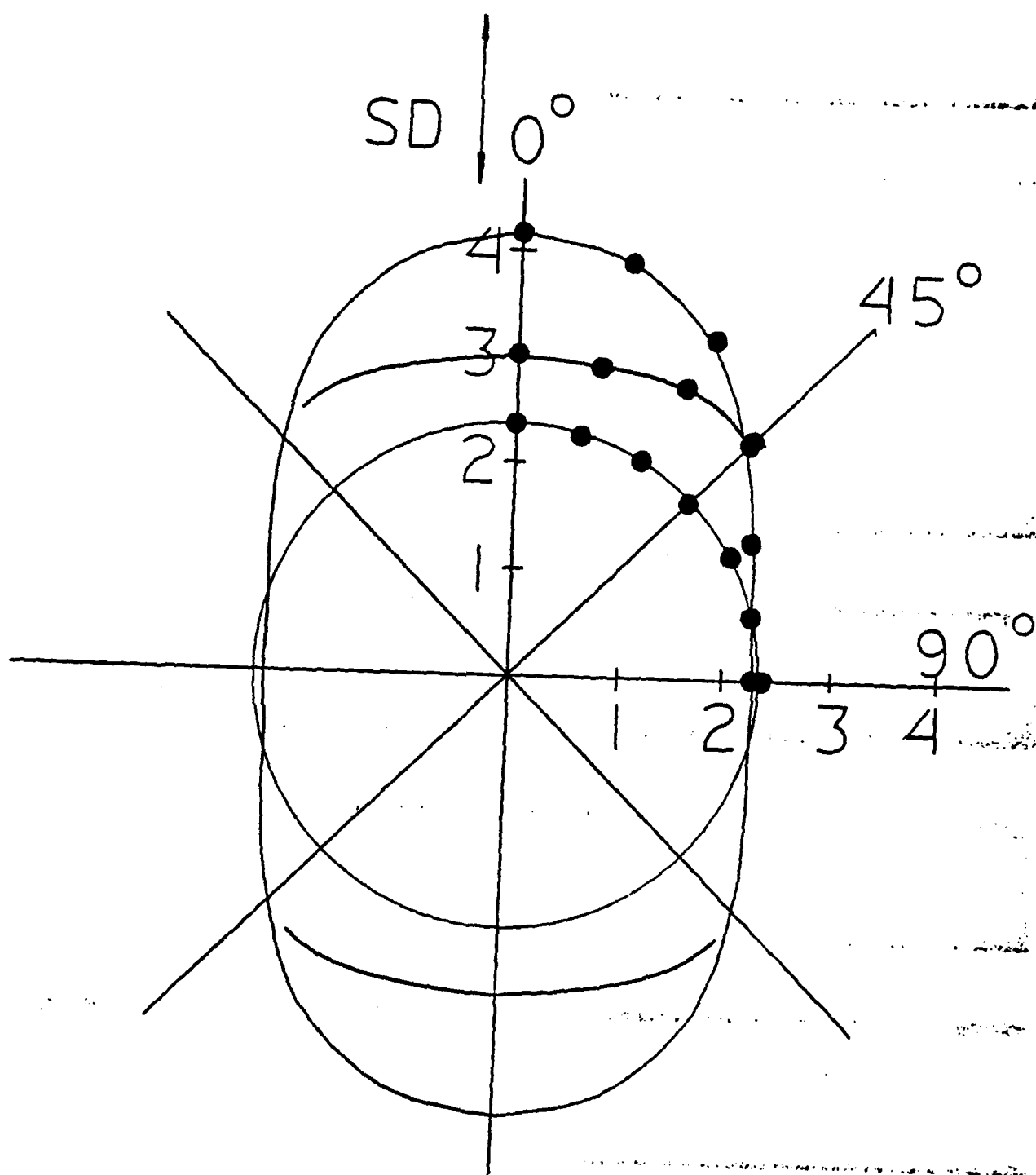




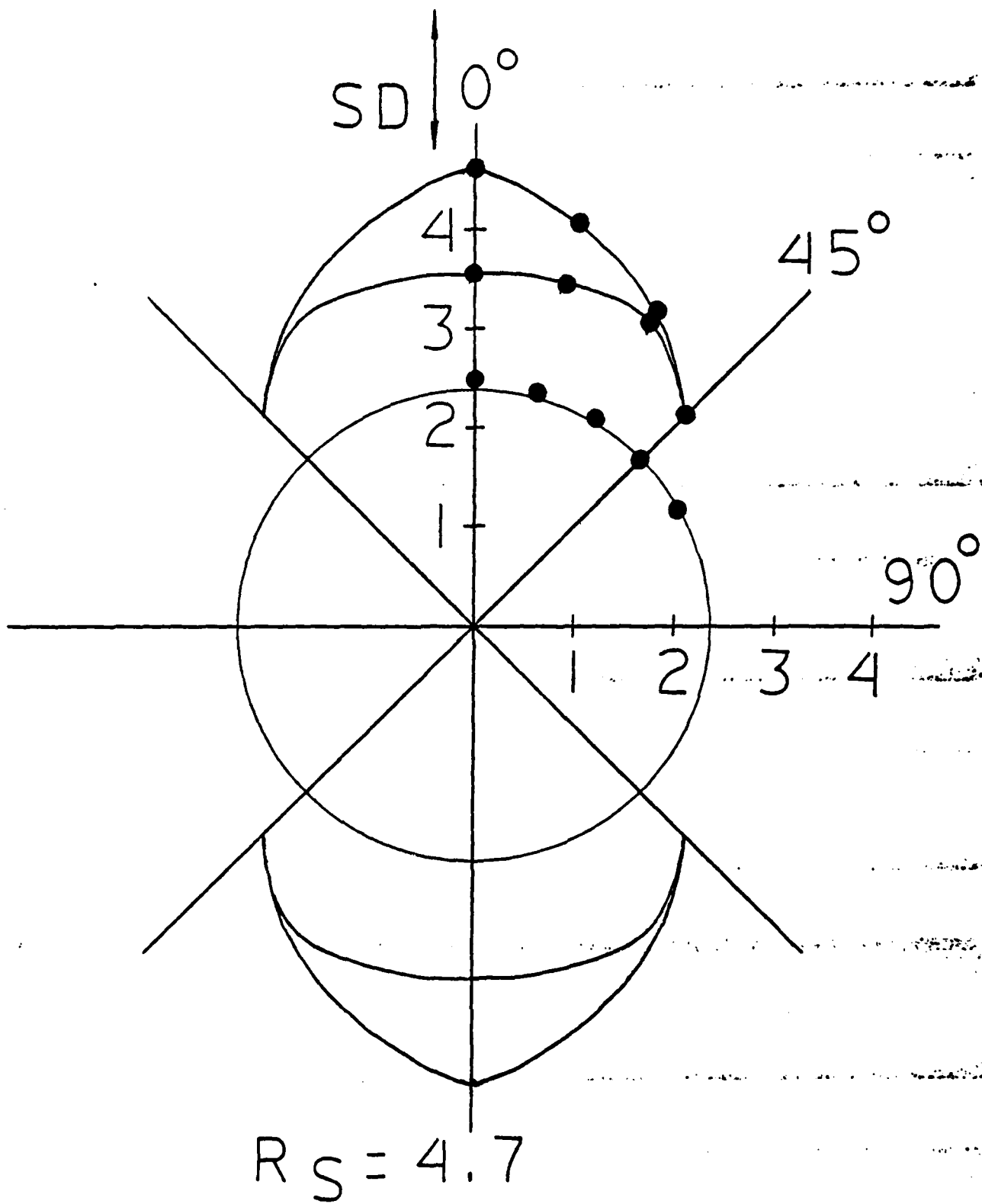
$$R_S = 1.0$$

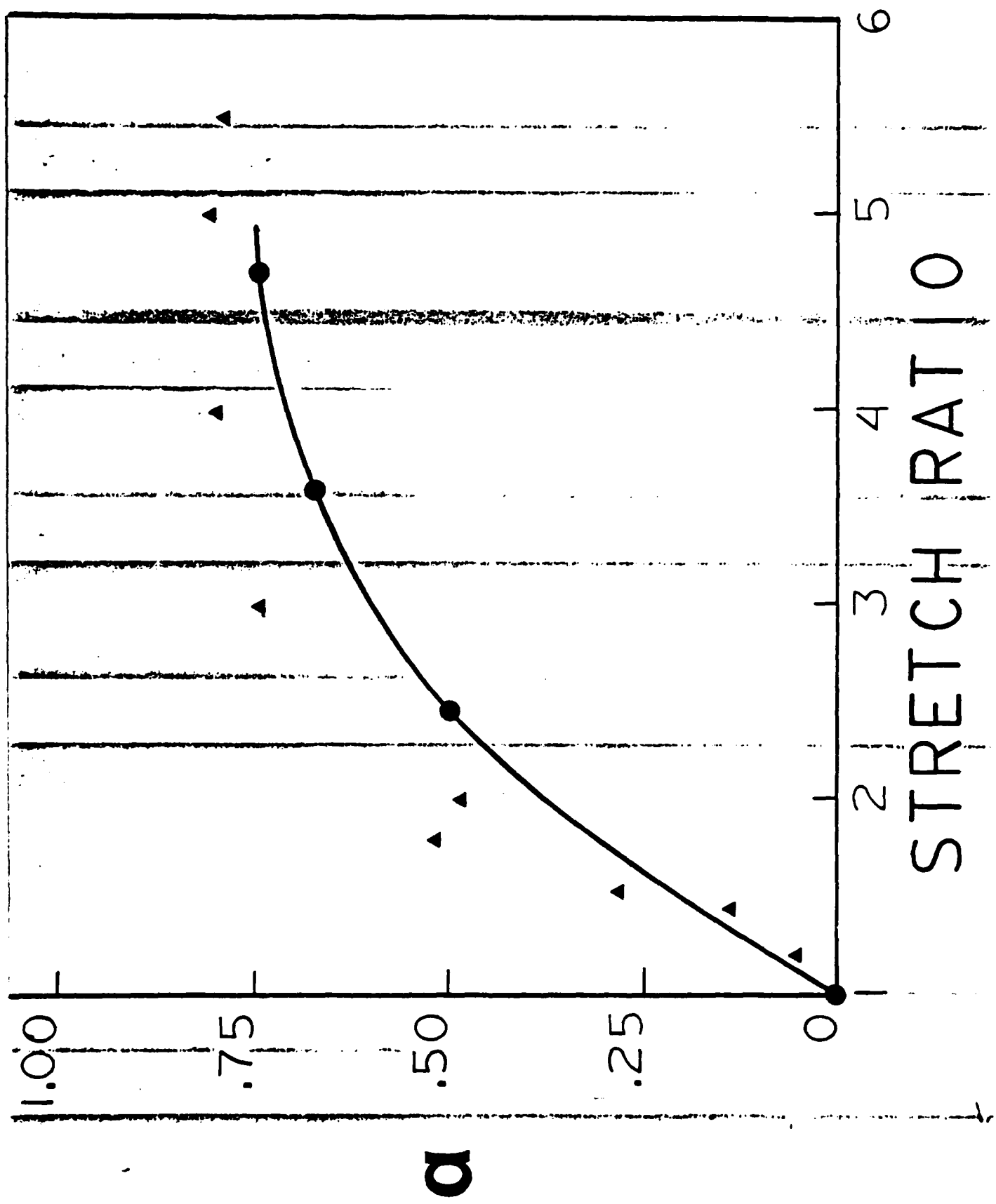


$$R_S = 2.7$$



$$R_S = 3.6$$





TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Stephen H. Carr Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Picatinny Arsenal Attn: A. M. Anzalone, Building 3401 SMUPA-FR-M-D Dover, New Jersey 07801	1
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U.S. Department of Commerce Washington, D.C. 20234	2	Dr. J. K. Gillham Department of Chemistry Princeton University Princeton, New Jersey 08540	1
Professor G. Whitesides Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Douglas Aircraft Co. Attn: Technical Library C1 290/36-84 AUTO-Sutton 3855 Lakewood Boulevard Long Beach, California 90846	1
Professor J. Wang Department of Chemistry University of Utah Salt Lake City, Utah 84112	1	Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. V. Stannett Department of Chemical Engineering North Carolina State University Raleigh, North Carolina 27607	1	Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
Dr. D. R. Uhlmann Department of Metallurgy and Material Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	NASA-Lewis Research Center Attn: Dr. T. T. Serofini, MS-49-1 21000 Brookpark Road Cleveland, Ohio 44135	1
Naval Surface Weapons Center Attn: Dr. J. M. Augl, Dr. B. Hartman White Oak Silver Spring, Maryland 20910	1	Dr. Charles H. Sherman Code TD 121 Naval Underwater Systems Center New London, Connecticut	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1	Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02192	1
Professor Hatsuo Ishida Department of Macromolecular Science Case-Western Reserve University Cleveland, Ohio 44106	1	Dr. Alan Gent Department of Physics University of Akron Akron, Ohio 44304	1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1	Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson AFB, Ohio 45433	1
Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	1	Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. M. Litt Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1	Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	1
Dr. R. S. Roe Department of of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1	Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	1
Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1	Dr. R. S. Porter Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002	1
Dr. Martin Kaufmann, Head Materials Research Branch, Code 4542 Naval Weapons Center China Lake, California 93555	1	Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	1
Professor S. Senturia Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. Kurt Baum Fluorochem Inc. 6233 North Irwindale Avenue Azusa, California 91702	1
		Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1