



## Calhoun: The NPS Institutional Archive

---

Theses and Dissertations

Thesis Collection

---

1966

Effects of polymer chain orientation upon the thermal conductivity of polymethyl methacrylate at liquid nitrogen temperatures.

Galstan, Gerald Needham.

---

<http://hdl.handle.net/10945/9493>



Calhoun is a project of the Dudley Knox Library at NPS, furthering the precepts and goals of open government and government transparency. All information contained herein has been approved for release by the NPS Public Affairs Officer.

**Dudley Knox Library / Naval Postgraduate School  
411 Dyer Road / 1 University Circle  
Monterey, California USA 93943**

<http://www.nps.edu/library>

NPS ARCHIVE  
1966  
GALSTAN, G.

EFFECTS OF POLYMER CHAIN ORIENTATION  
UPON THE THERMAL CONDUCTIVITY OF  
POLYMETHYL METHACRYLATE AT LIQUID  
NITROGEN TEMPERATURES

GERALD NEEDHAM GALSTAN

DUDLEY KNOX LIBRARY  
NAVAL POSTGRADUATE SCHOOL  
MONTEREY CA 93943-5101

LIBRARY  
NAVAL POSTGRADUATE SCHOOL  
MONTEREY, CALIF. 93940

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







EFFECTS OF POLYMER CHAIN ORIENTATION UPON  
THE THERMAL CONDUCTIVITY OF POLYMETHYL  
METHACRYLATE AT LIQUID NITROGEN TEMPERATURES

by

Gerald Needham Galstan  
Lieutenant, United States Navy  
B.S., University of Illinois, 1957

Submitted in partial fulfillment  
for the degree of

MASTER OF SCIENCE IN PHYSICS

from the

UNITED STATES NAVAL POSTGRADUATE SCHOOL  
May 1966



966  
Galstan, G.

thesis  
G1408  
c. 1

### ABSTRACT

Measurements of the thermal conductivity of commercial samples of polymethyl methacrylate (Plexiglas) with random and partially oriented polymer chains were made at liquid nitrogen temperatures to provide empirical guidelines into relationships of heat transfer mechanisms of amorphous polymers. Cast samples were formed to have degrees of stretch of one, two, three and four times original length. These samples were found to have thermal conductivities of 1.67, 1.91, 2.05 and  $2.10 \pm .04$  mwatt/cm-°K respectively. An extruded sample was determined to have an effective degree of stretch of two. Comparison was made with an empirical model based on component thermal conductivities obtained by partitioning with respect to vibrational modes into longitudinal and one- and three-dimensional transverse components.

## TABLE OF CONTENTS

Section	Page
1. Introduction	9
2. Experimental Matters	20
3. Results and Conclusions	31
4. Acknowledgments	34
5. Bibliography	35



## LIST OF TABLES

Table	Page
1. Measured and Calculated Thermal Conductivities	31



## LIST OF ILLUSTRATIONS

Figure	Page
1. Model for the effects of orientation	16
2. Equivalent ellipsoidal distribution	19
3. Stretch parameter versus stretch degree	19
4. The sample holder	28
5. Sample number one	29
6. Final sample design	29
7. Stretching blank and assembly design	30
8. Orientation effect on thermal conductivity	33



## 1. Introduction

The change of the thermal conductivity of the high polymer polymethyl methacrylate (PMMA) caused by polymer chain orientation will be studied in this thesis. The desired result of this study is to obtain insight into the mechanisms of heat transport in polymers. For the purposes of this study a model will be introduced which will take into account the effect of chain orientation upon thermal conductivity.

It has long been known that in the equilibrium state a polymer molecule will assume a long, randomly oriented chain [1]. Above the glass temperature Brownian motion will cause this chain to writhe, squirm and change its configuration continuously under the action of thermal motion. Below the glass temperature the molecule is locked in position. It is this property which allows orientation of the polymer by the application of stress while the polymer is heated above the glass temperature and then cooling below the glass temperature while still under stress.

Heat transfer through a solid is mainly through elastic vibrations of the atoms. Each atom has a fixed equilibrium position. Displacement from this equilibrium position may be resolved into normal modes of vibration of the solid as a whole. Each normal mode may be conveniently represented locally as a standing wave, which in turn may be analyzed into travelling waves of opposite directions, if only instantaneous displacements are considered. These travelling waves may be referred to as phonons, the quanta of the vibrational field [18].

Structural imperfections result in interactions between phonons. The heat transfer current is determined by the distribution of the phonons, which obey Bose-Einstein statistics. This phonon distribution is obtained as a solution of a Boltzmann equation. Klemens



has obtained an approximate solution of this equation for the case of a disordered solid and an expression for the thermal conductivity, by considering the following scattering mechanisms:

1. Three-phonon processes in which energy  $\hbar\omega$  and momentum  $\hbar k$  are conserved.
2. Elastic scattering of a phonon by a structure defect or boundary. The energy is unaltered, but the momentum is changed.
3. Inelastic scattering.
4. Higher order phonon interactions. [11]

Process 1. arises from anharmonicities of the interatomic forces. This perturbation results in a transition in which one phonon is destroyed and two created, or vice-versa. Processes 2. and 3. arise from defects in the structure, boundaries, microcrystalline structure, etc. At low temperatures, the effects of process 4. may be disregarded.

The mean free path for a phonon of wave vector  $q$  may be represented as  $\lambda = A/aq^2$  where  $A/a$  is constant, having dimensions of inverse length and relates to the correlation length of properties within the amorphous material. For wavelengths of the order of, or less than the correlation length, a constant mean free path would be expected. Waves with wavelengths much greater than the correlation length average over the disorder, and have a longer mean free path. For long wavelengths the mean free path is proportional to the square of the wavelength, and a linear dependence of the thermal conductivity with temperature is obtained. The constant  $A/a$  will vary between modes and materials.

In three-phonon processes not all the phonons can have the same polarization, if momentum and energy are to be conserved simultaneously. Longitudinal waves, those having the greatest phase velocity, behave differently than transverse waves in the

three-phonon interaction. All processes should be considered as tending to restore equilibrium, including those in which momentum is conserved. A longitudinal mode of vibration tends to return to its equilibrium value mainly by means of interactions with transverse waves of about the same frequency and by processes not involving the conservation of momentum. Low frequency transverse modes return to equilibrium by interactions with modes of frequency  $kT/h$ . This difference in behavior results in a considerably larger relaxation length for longitudinal waves than transverse waves.

For an amorphous substance which lacks long range symmetry and periodicity, the transverse modes can be scattered much more easily than the longitudinal modes. The conversion, therefore, of longitudinal modes to transverse modes which are subsequently scattered, must be considered. This conversion can be characterized by phenomenological processes utilizing  $T_0$ , a parameter with dimensions of temperature, which depends primarily on the coupling between longitudinal and transverse vibrations, and  $A$ , a constant related to the mean free path for wavelengths small compared to the correlation length. Klemens writes this mean free path as  $Aa$  for longitudinal modes, and  $Ba$  for transverse modes. Here  $A$  and  $B$  are pure numbers and  $a$  is taken to be the typical distance between vibrating units. Considering both processes, the expression for thermal conductivity contributed by longitudinal vibrations is:

$$\chi_L = \frac{k^2}{3\pi h} \frac{A}{a} T \left(\frac{T_0}{T}\right)^3 \int_0^\infty \frac{e^x}{(e^x - 1)^2} \frac{x^2}{x^2 + \left(\frac{T_0}{T}\right)^3} dx$$

where  $k$  is Boltzmann's constant,  $h$  is Planck's constant, and  $T$  is absolute temperature. [11]

The high frequency transverse vibration contribution was taken by Klemens to be:

$$\chi_T = \frac{1}{3} S_T c B a$$

where  $S_T$  is the transverse sound velocity, and  $c$  is the specific heat per unit volume. The contribution of transverse modes proportional to  $T$  at low temperature is small and can be considered to be contained in  $\chi_L$ . [13] The total thermal conductivity is then the sum:

$$\chi = \chi_L + \chi_T .$$

According to Klemens theory the thermal conductivity at liquid helium temperature is due solely to phonons of the longitudinal mode of vibration. In this temperature range, the predominant scattering mechanisms for these longitudinal phonons are processes not conserving the wave vectors of the phonons, or structure scattering. The mean free path of the phonon is inversely proportional to the square of the wave vector for structure scattering resulting in the thermal conductivity being proportional to temperature. [2] At higher temperatures, the longitudinal-transverse phonon interaction becomes important, resulting in the thermal conductivity increasing less rapidly than temperature.

In 1949, Kittel deduced from measurements that the phonon mean free path in various glasses does increase with decreasing temperature at sufficiently low temperatures. [10] He suggested that this would be expected to occur for temperatures such that the dominant phonons correspond to wavelengths greater than the size of the unit cell in the glass. For such phonons, the scattering by the disorder in structures decreases with increasing wavelength, in keeping with the above.

A slight modification of Klemen's theory can be made which will better account for the temperature dependence of the thermal conductivity in polymers. The heat capacity of polymers can be accounted for by a model due to Tarasov which assumes that the vibration spectrum can be broken into two parts: first, a three-dimensional part for frequencies from zero to a frequency characterized

by an equivalent temperature  $\theta_3$ , and second, a one-dimensional part for frequencies lying between  $\theta_3$  and a second characteristic temperature  $\theta_1$ . [15] The vibration spectrum in the first region is taken to be that of a three-dimensional continuum (Debye) model while that in the second is of a one-dimensional continuum. The specific heat can thus be separated into a part due to the three-dimensional vibrations,  $C_3$ , and a part due to one-dimensional vibrations,  $C_1$ . The modifications of Klemens' theory which is made here is the association of separate constant mean free paths with the one-dimensional and three-dimensional vibrations. Physically this implies that a difference in scale of the elastic environment might be expected along the chains as compared to that existing between the chains of the polymer. The high frequency transverse vibrational contribution is therefore divided into two parts, a part due to the three-dimensional vibrations,

$$\chi_3 = \frac{1}{3} S_{T3} c_3 B a \quad ,$$

and a part due to one-dimensional vibrations,

$$\chi_1 = \alpha S_1 c_1 \lambda$$

where  $\alpha$  is a pure number reflecting the orientation of the polymer chains,  $s_1$  is the velocity of one-dimensional vibrations which can be found from  $\theta_1$ , and  $\lambda$  is a constant mean free path.

This simple modification of Klemens' theory leads to much better agreement with experiment. Unfortunately, the application of the modified theory is made uncertain by difficulties encountered in the separation of the acoustic contributions to the heat capacity from other contributions, and from uncertainties in separating the acoustic heat capacity into one- and three-dimensional parts. A slight modification of the Tarasov model for the calculation of heat capacities can be made by giving separate velocities to

transverse and longitudinal vibrations. [13] This modification can be used to better predict the temperature dependence of the thermal conductivity.

Reese fit this modified theory of Klemens' with a heat capacity partition obtained with a ratio of 2.5 for longitudinal to transverse sound velocities to the thermal conductivity of PMMA using the following parameters:  $A/a = 2.24 \times 10^9 \text{ cm}^{-1}$ ,  $T_0 = 7.0 \text{ }^\circ\text{K}$ ,

$$S_{T3} B a = 5.0 \times 10^{-3} \text{ cm/sec} \quad \text{and} \quad \lambda = 7.3 \text{ \AA}.$$

Estimating  $a$  from the density to approximate the distance between polymer chains to be  $7.5 \text{ \AA}$  and evaluating  $S_{T3}$  from  $\theta_3$ ,  $A$  was found to be 168 and  $B$  slightly less than 1.<sup>1</sup> [13] These results imply that transverse three-dimensional modes are highly damped since  $B$  is small.

At higher temperatures the mean free path associated with three-dimensional vibrations is of the order of  $a$ , in agreement with the ideas proposed by Eiermann in analysis of the thermal conductivity of polymers employing a model in which the polymer is replaced by a network of elementary thermal resistances. [6]  $\chi_1$  is analogous to the thermal resistance presented by each covalent bond and  $\chi_3$  to thermal resistance of secondary bonds in the explanation of Eiermann of the behavior of the thermal conductivity through the glass temperature. [5] In this analysis, Eiermann constructed a general model for the thermal conductivity of amorphous substances. The thermal resistance of a macroscopic amorphous specimen was considered as consisting of a network of elementary thermal resistances with the atoms as the

<sup>1</sup> See W. Reese, "On the low temperature excess heat capacity in glassy polymers," J. Appl. Phys., (To be published). If account is taken of the excess specific heat found in amorphous polymers at low temperatures, a value of approximately one would be obtained for  $B$ .

points of junction. The elementary thermal resistances were dependent on the binding force. Therefore a primary valence is equivalent to a small thermal resistance and a van der Waals bond to a large one. On this basis the thermal conductivity of amorphous high polymers is mainly determined by the behavior of the van der Waals bonds. [6, 7] In the work previously referred to, Reese found the ratio of thermal conductivities due to one-dimensional vibrations to that of three-dimensional vibrations to be approximately ten to one at room temperature as estimated by Eiermann from his model. [13]

When amorphous polymers are oriented by stretching at temperatures higher than the glass temperature, there is an increase of thermal conductivity in the direction of stretch and a decrease perpendicular to it. [3, 8] Eiermann noted an increase in the thermal conductivity of approximately 18% between unstretched PMMA samples and those stretched 375%. [4] He explains this effect by noting that in the stretched polymer the chain molecules are oriented in the direction of stretch, so that in the network of bonds the primary valences with small thermal resistance are chiefly arranged in the direction of stretch and the van der Waals bonds with large thermal resistance are mainly perpendicular to it. [5] Therefore the transport of energy takes place more easily along the main valences than along the secondary valences and van der Waals bindings. [4] The following facts were listed in favor of this assumption: 1. Inorganic glasses which contain only main valences have a thermal conductivity which is five to ten times as large as that of plastics. 2. According to Ueberreiter, the thermal conductivity of polystyrene with short chains is smaller than that of polystyrene with long chains. [16, 17] Apparently this is because in a substance with shorter chains a larger number of energy transitions

must take place between molecules. 3. When amorphous plastics are heated there is also a break in the volume versus temperature curve at the second order transition point.

The orientation model used by Eiermann in this analysis is pictured in Fig. 1. This model is equivalent to the parallel combination resistance of three series resistances.

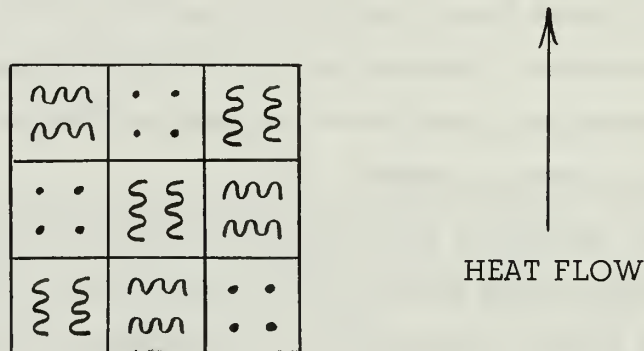


Fig. 1. Model for the effects of orientation

The lines and dots within Fig. 1 indicate the direction of orientation of the stretched samples with respect to the heat flow. The thermal conductivity evaluated from this model is:

$$\frac{1}{\chi_{\parallel}} + \frac{2}{\chi_{\perp}} = \frac{3}{\chi_{iso}}$$

where  $\chi_{\parallel}$  is the thermal conductivity in the direction of stretch;  $\chi_{\perp}$  is the thermal conductivity perpendicular to the stretch; and  $\chi_{iso}$  is the thermal conductivity of an unstretched sample. [6]

The previously described model is plausible except at low temperatures where it indicates that one-dimensional vibrations would dominate. Experimentally, this is not the case and the model must be modified to include the point that at very low temperatures the contribution of one-dimensional vibrations goes to zero to indicate that these high frequencies are no longer excited. This modification could result from analysis of the model as the

series combination resistance of three parallel resistances. The relationship would then be consistent with the tensor nature of thermal conductivity and would be:

$$\kappa_{iso} = \frac{1}{3} [\kappa_{||} + 2 \kappa_{\perp}] .$$

In summary, a combination and extension of previous theories will be used to create a model for the effect of polymer chain alignment on the thermal conductivity of polymethyl methacrylate at liquid nitrogen temperatures. The previously indicated expression due to Klemens will be assumed for the contribution of longitudinal vibrations:

$$\kappa_L = \frac{k^2}{3\pi h} \frac{A}{a} T \left(\frac{T_0}{T}\right)^3 \int_0^{\infty} \frac{e^x}{(e^x - 1)^2} \frac{x^2}{x^2 + \left(\frac{T_0}{T}\right)^3} dx .$$

The contribution of transverse vibrations will be divided into one-dimensional and three-dimensional components:

$$\kappa_3 = \frac{1}{3} s_{T3} c_3 B a$$

and

$$\kappa_1 = \alpha s_1 c_1 \lambda .$$

Reese has shown that at liquid nitrogen temperatures the total thermal conductivity of PMMA is composed of approximately 14.6%  $\kappa_L$ , 7.8%  $\kappa_3$  and 77.6%  $\kappa_1$ . [13] These figures indicate that any change in  $\kappa_1$  caused by chain orientation will greatly influence the overall thermal conductivity.

The parameter  $\alpha$ , which is dependent upon chain orientation, is a direct proportionality constant relating the effective mean free path to the mean free path of the one-dimensional component as

$$\lambda_{eff} = \alpha \lambda .$$



This model indicates that the  $\alpha_1$  component will depend directly upon chain alignment and  $\alpha$  will vary as the average of the absolute value of the cosine of the angle between the direction of stretch and the mean free path.

The value of  $\alpha$  will be developed on the basis of an equivalent ellipsoidal distribution. [1] An ellipsoidal distribution was chosen to maintain the volume constant in order to relate the initial to the stretched configuration. [12] As illustrated in Fig. 2, the major and minor axes of the ellipsoid are  $a$  and  $b$  respectively. The volume is:

$$V = \frac{4}{3} \pi a b^2 = \frac{4}{3} \pi r_0^3$$

where  $r_0$  is the characteristic unstretched length. If  $a/r_0$  is defined as the degree of stretch,  $s$ , it is related to the axes as:

$$a/b = \sqrt{s^3} .$$

$\alpha$  can then be simply calculated as follows:

$$\alpha = \langle |\cos \theta| \rangle = \frac{2}{V} \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos \theta \sin \theta d\theta \int_0^{r_0} r^2 dr$$

where

$$r_0 = \sqrt{\frac{a^2 b^2}{a^2 \sin^2 \theta + b^2 \cos^2 \theta}}$$

$$\alpha = \frac{a}{a + b} .$$

Numerically,  $\alpha$  varies from zero for a compressed polymer to one-half for the equilibrium state to one for an infinite degree of chain orientation. Fig. 3 is a plot of  $\alpha$  versus degree of stretch. (Degree of stretch is equivalent to times original length.)

A comparison of this model with experiment will be made later.

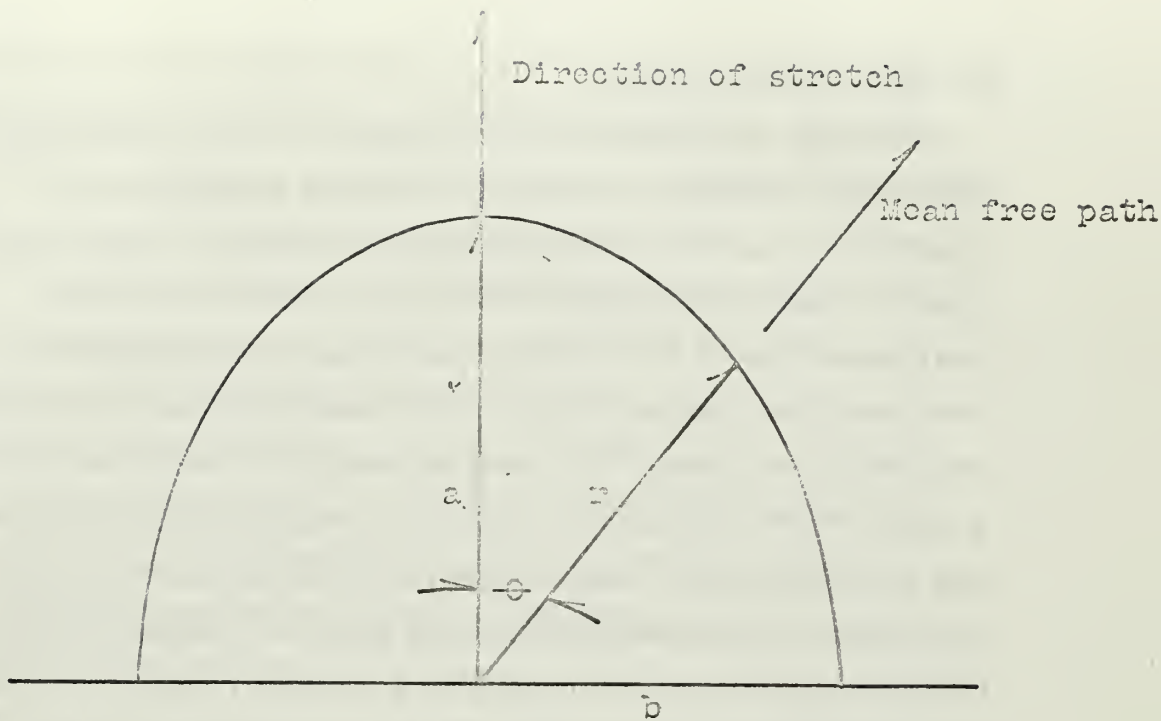


Fig. 2. Equivalent ellipsoidal distribution.

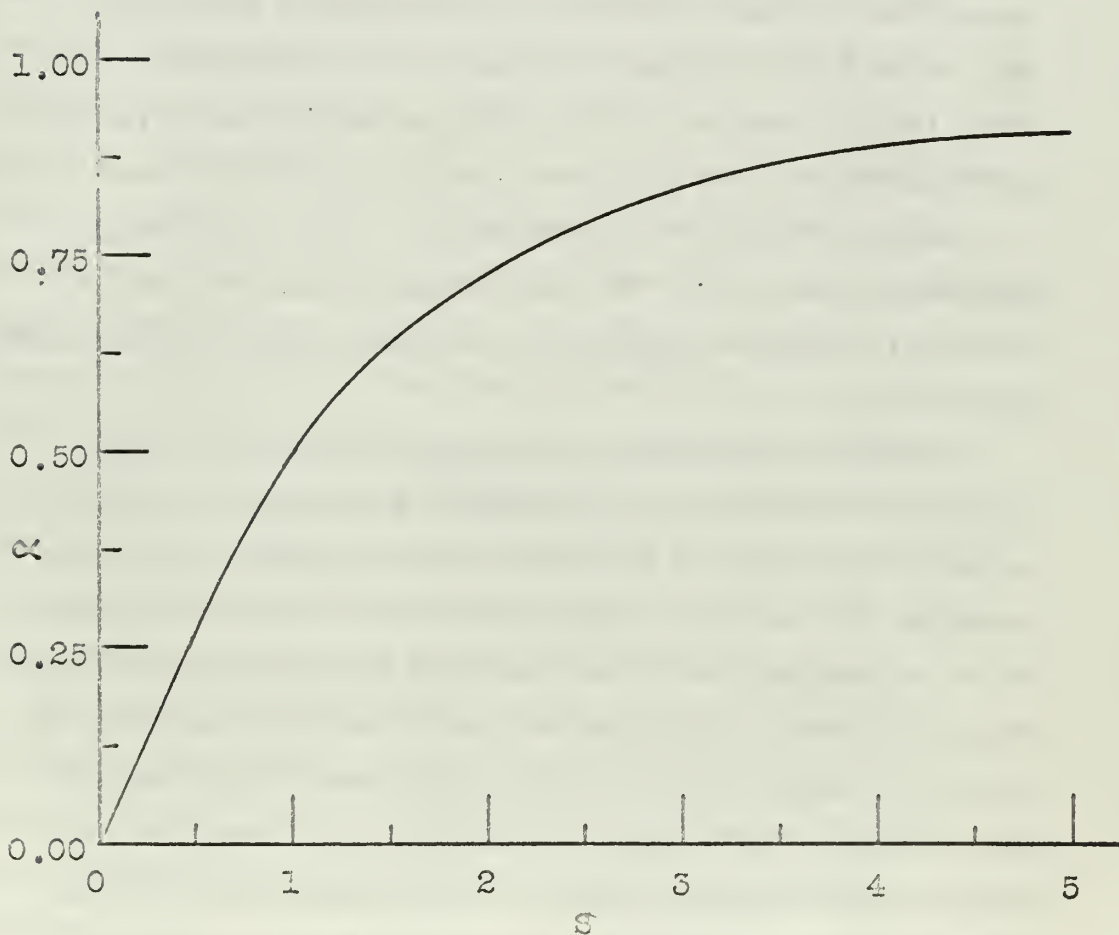


Fig. 3. Stretch parameter versus stretch degree.

## 2. Experimental Matters

To study the effects of chain alignment on the thermal conductivity of polymers, a number of separate samples must be employed. Thus the experiment must be such that sample interchange is reasonably simple, and more important, that the measurement be of fairly high accuracy and as independent as possible of the detailed conditions of those surfaces at which heat exchange takes place. The third requirement dictates the choice of a steady state experiment. The second requirement necessitates that the sample have considerable length between thermometers which sense the temperature gradient along the sample and also that the total temperature change be sufficiently small that first order calculations can be used. This requirement means that highly sensitive thermometers should be employed. As it is desired that the heat flow through the sample be sufficiently large so as to be measured accurately and not disturbed by external factors, samples with large cross-section had to be employed because of the low thermal conductivity of polymers.

Based on the above considerations, a bulk of the design requirements were set. The chief design problem was that of insuring that the heat supplied to the sample would all flow down the sample.

Preliminary calculations indicated that the most critical energy loss would be due to radiation by the sample at liquid nitrogen temperature; a loss of 5% of the heat input. This loss would be much higher at higher temperatures. To minimize this effect an adiabatic shield was designed and constructed on the basis of a thermal resistance one-tenth that of the sample. The shield was constructed from 0.020 inch sheet brass to enclose the top and all four sides of the sample. A slot was cut up one side to provide wiring clearance for the sample heater and thermometry wiring. A 100 ohm 0.002 inch diameter manganin wire

provided electrical heating for the shield. The shield was regulated to have the same temperature gradient as the sample. The shield heater was glued to the top of the shield with General Electric 7031 varnish mixed 50-50 by volume with toluene. Heat input to the shield was not measured. A thermometer for shield temperature sensing was glued to the side of the shield at a position midway between sample temperature sensors with the varnish and toluene mixture described previously. Prior to assembly the shield base was lightly coated with Apiezon type N grease and inserted into a machined slot in the copper bottom of the sample holder can.

The sample holder was designed with the principal objective of ease of changeability of the sample. It was a copper bottomed brass vacuum case pumped to a pressure of less than  $10^{-6}$  torr to provide thermal isolation of the sample from the nitrogen bath except through the copper bottom. As shown in the sectioned drawing of the sample holder, Fig. 4, the copper bottom was machined to provide precise location for the sample and the adiabatic shield which surrounded it. Centered in the sample location is a copper washer which provides good thermal contact between the sample and bath by the action of the sample shrinking around the washer during cooling. The need to provide an extra measure of thermal contact became apparent during the first measurement of the initial sample, which only rested on the copper bottom, when an equilibrium state could not be reached because of high thermal resistance between the sample and bath. This washer solved this thermal resistance problem. Also in the copper bottom is a hermetic feedthru for electrical wiring.

The upper and lower sections of the holder are sealed by low melting temperature solder to facilitate sample changing. The vacuum piping exits through the top of the holder through two 90 degree turns to eliminate the intrusion of energy by radiation.

System wiring consisted of two 0.005 inch manganin leads to each the sample and adiabatic shield heaters and seven 0.002 inch manganin leads. Two of these seven leads were for measurement of the voltage to the sample heater with the remainder for thermometry. All leads were approximately ten inches in length and mechanically secured and thermally grounded through a binding post to the copper bottom. The binding post was covered by a thin mylar film to eliminate the possibility of electrical short circuiting should the varnish coating of the leads break down. It was calculated that less than 0.25% of the heat supplied to the heater could be expected to pass up the leads, the remainder passing through the sample.

Two resistance thermometers were glued with a varnish-toluene mixture to two temperature sensing wires which protruded from the sample, to measure the temperature gradient of the sample. As stated previously, a third thermometer was attached to the adiabatic shield. All three low temperature thermistors were Keystone Carbon Company type RL 10X04-10K-315-S5 which have a nominal resistance of 31.5 kilo-ohms at liquid nitrogen temperature.

In an early calibration attempt with one measurement at acetone-dry ice temperature, the protective film enclosing the thermistors was damaged. This damage made reproducible results unavailable. After coating the thermistors with an epoxy (Epibond 104 with Hardner 951, of Furane Plastics Inc.) covering, consistent calibration was obtained.

Thermometer calibration consisted of measured resistance at various oxygen bath vapor pressures. The pressures were measured by a manometer using a cathetometer. Temperatures were obtained graphically from temperature-liquid oxygen vapor pressure data of H. J. Hoge. [9] The log of the resistance

when plotted versus the inverse temperature yielded a straight line for all three thermometers. Analytic expressions were calculated for each thermometer from the exponential form

$$R = R_0 e^{\tau/T}$$

where R is the resistance at a temperature T. Solution of the above equation for shield, sample upper and sample lower thermometers yielded values for  $R_0$  of 11.484, 10.336 and 10.274 ohms and for  $\tau$  of 597.41, 605.24 and 607.89 degrees K respectively.

These values were programmed for the Control Data Corporation 1604 computer to obtain temperature equivalents for the three thermometers at ten ohm intervals over the temperature range of interest. By using these temperature equivalents, shield heat adjustments could rapidly be made to regulate center shield temperature midway between sample temperature values.

The heat supplied to the sample heater was measured potentiometrically using a Leeds and Northrup type K-3 potentiometer. The resistance of the three thermometers was determined by an a-c Wheatstone bridge operating at 37 Hz. The bridge employed the use of an EMC Model JRB lock-in amplifier as a null detector. This apparatus was capable of determining the resistance of the thermometers to better than 0.1% while dissipating less than one nanowatt of power in the thermometers.

A measurement proceeded by allowing the whole apparatus to come to equilibrium at a fixed input heat to the sample. The sample time constant was calculated to be slightly less than 30 minutes for a one degree temperature change. The shield had a much shorter time constant. After about eight time constants of the sample a preliminary thermometer resistance measurement and trend recording were made to check equilibrium conditions. The computer print out enabled rapid resistance to temperature conversion so that the temperature gradient of the sample could

be determined and the adiabatic shield heat input adjusted to make the shield temperature that of the average of the sample. It was assumed that the sample gradient was linear for this purpose. After equilibrium was reached readings of the three resistances and the voltage and current input to the sample heater were recorded. These temperatures and the heat input, together with sample dimensions allowed calculation of the thermal conductivity by the relation:

where  $\kappa = \frac{\dot{Q}}{\Delta T} \frac{l}{A}$  is the heat input to the sample,  $\Delta T$  is the temperature gradient and  $l$  and  $A$  are the length and cross-sectional area of the sample respectively.

Design calculations were for a temperature gradient of one degree for the sample. A minimum of five measurements, and usually more, per sample were made over a temperature gradient of from 0.75 to 1.25 degrees K.

In addition to random resistance and power measurement error, one systematic error entered into the calculations from the fact that room temperature values of the sample length and cross-sectional area were used rather than the liquid nitrogen temperature values. These values could tend to make the values of thermal conductivity low by as much as 3% when also considering actual measurement error. Neglected completely was any possible boundary resistance between the sample and the temperature sensing leads.

Commercial samples of polymethyl methacrylate, PMMA, in the form of 0.875 inch diameter cast rods 12 inches long and 0.750 inch diameter extruded rods 12 inches long were obtained from Illumitronics Engineering Corporation, Sunnyvale, California. Such samples, especially after stretching, were not consistent with the large cross-sectional area desired. Thus samples were

prepared by cementing a number of relatively small sections together to provide a heat flow path of the desired cross-section. The cement used to assembly the sample components was ethylene chloride and is hereafter referred to as cement.

The first sample, the design of which proved unsatisfactory, was constructed of unstretched cast PMMA. The rod was milled to have a one-half inch square cross section. Four sections were then cemented together to form a rectangular parallelopiped one-by-one by 1.25 inches long. Two copper foils 0.002 inches thick, one inch square with a one-quarter by three-quarter inch long extension from the center of one side were formed with nine holes comprising approximately one-tenth of the total area drilled out for cement penetration. These foils were for temperature sensing and thermometer attachment. The foils were cemented to the top and bottom of the sample with one-by-one inch PMMA pieces adjacent outward. These pieces were 0.125 and 0.300 inches thick respectively on the top and bottom of the sample. The assembled sample is shown in Fig. 5. Steady state thermal conductivity measurements weren't obtainable with this sample because of high thermal resistance at the thermometer and bath boundaries.

To eliminate thermal resistance problems, subsequent samples were constructed with copper wire leads for thermometer attachment to omit the necessity for sectioning the sample for temperature sensing. A copper washer around which the sample shrunk when cooling was added to provide good thermal contact between the sample and bath.

All samples subsequent to number one have the same basic geometry as sample two, an unstretched cast sample which is shown in Fig. 6. This basic geometry consists of a rectangular parallelopiped of length 1.625 inches and one-by-one inch cross section. The temperature sensing leads are two number 26 uncoated copper wires one inch apart which protrude 0.375 inch from the sample face.



The upper wire is 0.125 inch from the top of the sample. This 0.125 inch length is for equilibrium distribution of the heat input from the sample heater. The remaining 0.500 inch length below the lower thermometer lead is for equilibrium outflow of heat to the sink. The center bottom of the sample is bored out one-half inch in diameter by one-eighth inch deep to shrink upon cooling around the copper washer in good thermal contact with the bath. There is 0.001 inch clearance in this fit at room temperature. The copper washer was coated for thermal contact purposes before sample insertion with Apiezon type N grease manufactured by Associated Electrical Industries Ltd.

Piecing requirements of samples three, four, five and six were 4, 12, 16 and 12 components respectively. The amount of stretch associated with the extruded sample, sample three, is unknown. The respective stretch of samples four, five and six is 300, 400 and 200 percent. In all cases the direction of stretch was in the longitudinal direction of heat flow.

The temperature leads protruding from the samples were bent to cradle the resistance thermometers which were glued in place with the varnish-toluene mixture.

The heat to the sample was supplied electrically to a resistance wire of about 100 ohms consisting of 0.002 inch diameter manganin wire. The heater wire was glued to a 0.002 inch thick copper foil which was in turn glued to the top of the polymer sample with varnish-toluene glue.

For stretching purposes, cast PMMA rods were machined into blanks. These blanks were then installed in the stretching assembly shown in Fig. 7. This assembly was then inserted in an electrically heated oven.

The oven consisted of a two inch diameter copper tube 18 inches long wrapped with fiber glass. Over the fiber glass was coiled a resistance wire connected to a variac for heat input control. Another coating of fiber glass covered the wire and was surrounded by a

coating of glass wool. This was all contained in a five inch diameter aluminum tube 20 inches long.

One end of the oven was secured to an angle iron frame which extended 16 inches beyond the other end of the oven for leverage in stretching. The copper tube was closed at both ends by cork stoppers. These stoppers didn't burn although heated to  $140^{\circ}$  C. The stopper at the end of the oven which was secured was drilled out to permit a glass mercury thermometer to enter the region near the PMMA. The other stopper was bored out to permit the stretching assembly to pass through.

The initial attempt at  $140^{\circ}$  C. failed because this excess temperature melted the PMMA and caused it to bubble. A working temperature of  $119^{\circ}$  C. was determined through trial to be the best for plastic movement without thermal degradation. The assembled apparatus, which was hung vertically with the secured end of the oven up, was allowed to come to equilibrium over a period of 12 hours to ensure constant temperature of the PMMA before stretching by pulling down on the blank holder assembly.

The greatest liability of this oven assembly was the inability to physically see the form the blank was taking upon being stretched. In order to achieve macroscopic consistency of polymer orientation, a uniform cross-section of the sample while being stretched is necessary. During stretching the obvious tendency of the blank to yield most at its weakest point and thereby neck down even further was ever present. To eliminate this disastrous tendency the samples were stretched only partially in the oven and then allowed to cool. The oven was then removed and the sample heated locally with an electrically heated air blower. Upon reaching a temperature suitable for stretching, which was just below the point where internal bubbles formed, the PMMA became somewhat glossy and emitted a characteristic odor. By heating locally and closely observing the degree of stretch a uniform sample could be obtained after some tedious labor. These pieces were then milled and cemented as previously described.

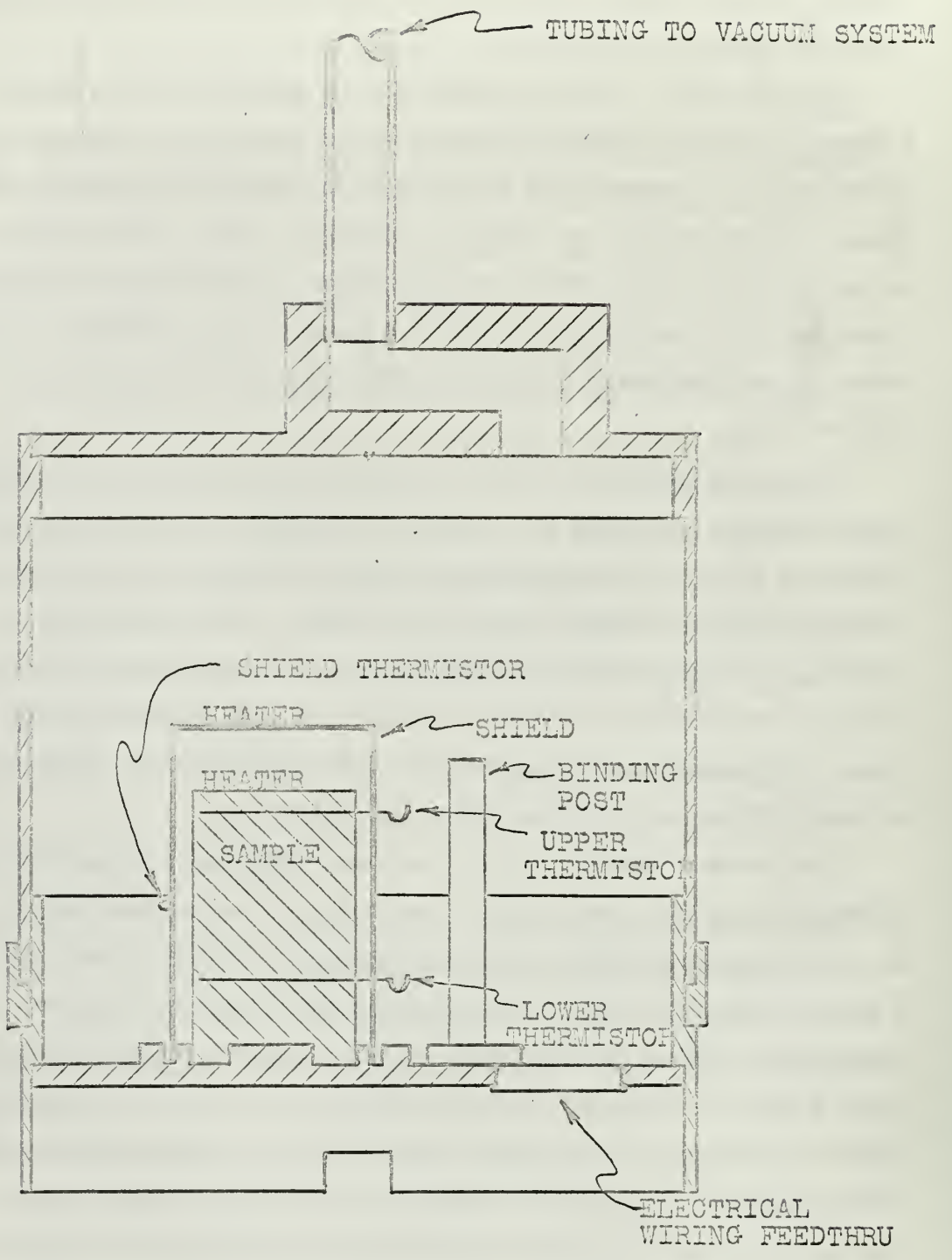


Fig. 4. Sectioned view of the sample holder.

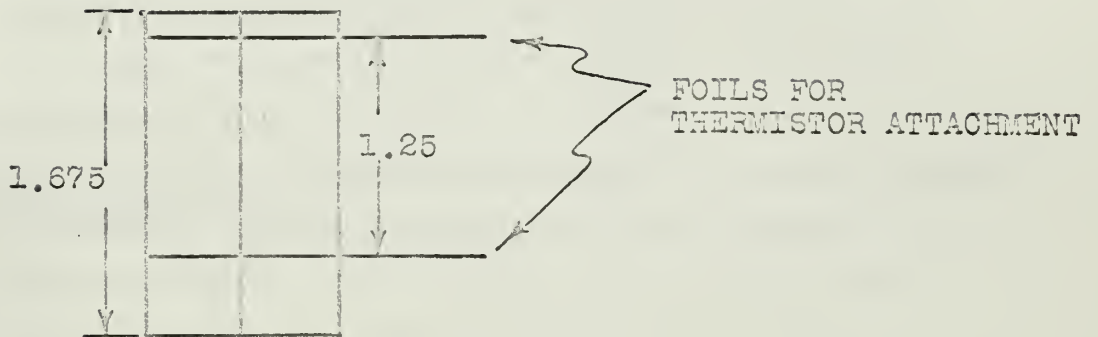
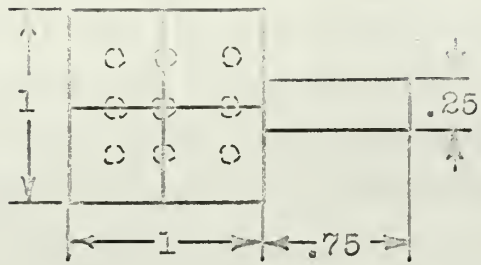
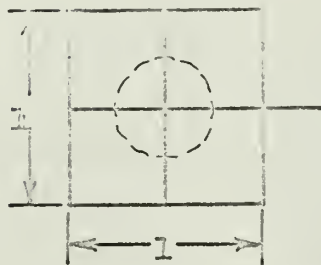


Fig. 5. Sample number one design.



Note: All dimensions in inches.

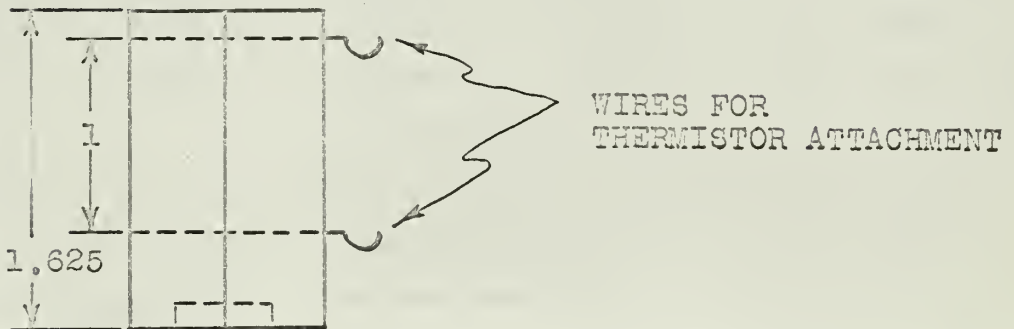


Fig. 6. Final sample design.

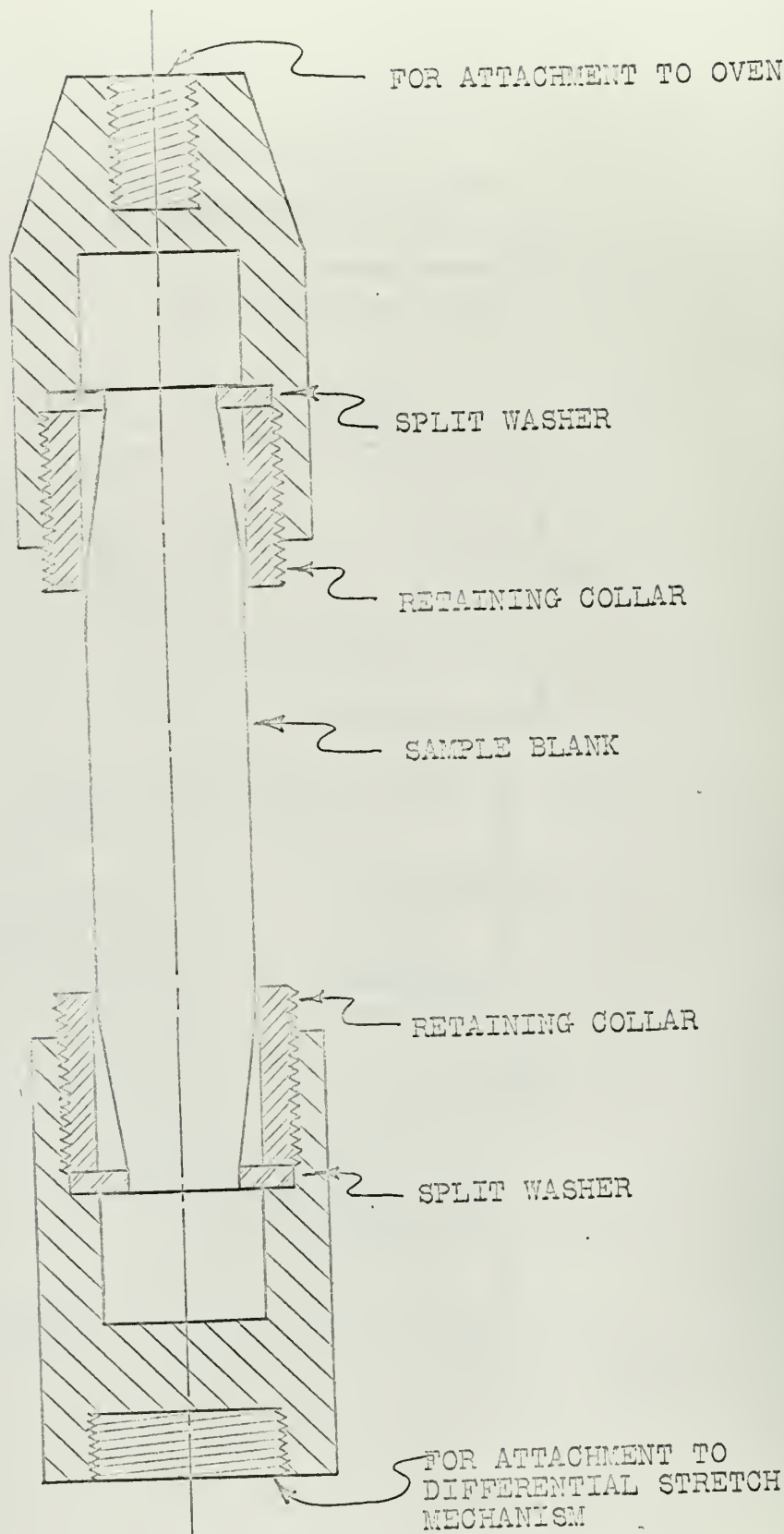


Fig. 7. Stretching blank and assembly design.

### 3. Results and Conclusions

The thermal conductivities as measured in the steady state of unstretched, extruded and stretched samples of polymethyl methacrylate are listed in Table 1 along with values computed using the previously described model. The empirical values were computed by assigning 67.1% of the total thermal conductivity to the combined  $\chi_L$  and  $\chi_3$  components and the remaining 32.9% to  $\chi_1$  in the unstretched configuration. The combined  $\chi_L$  and  $\chi_3$  components remain constant and  $\chi_1$  varies with the stretch parameter  $\alpha$  as previously developed as the polymer chain is oriented.

It must be noted that the above percentages are markedly different than the components of thermal conductivity at liquid nitrogen temperature reported by Reese of 14.6%  $\chi_L$ , 7.8%  $\chi_3$  and 77.6%  $\chi_1$ . [13]

Table 1. Measured and Calculated Thermal Conductivities

Sample Number	Fabrication	Stretch % original length	Measured	Calculated
			Thermal conductivity mwatt/cm-°K	
2	cast	100	1.67	1.67
3	extruded	(200)	1.92	
6	cast	200	1.91	1.92
4	cast	300	2.05	2.04
5	cast	400	2.10	2.10

Plotted in Fig. 8 are experimentally observed and empirically calculated curves of the thermal conductivity as functions of the degree of stretch. The agreement of these curves appears almost exact, indicating that the model developed holds for at least this limited range of specific investigation. In general terms, this model indicates the correctness of partitioning the thermal conductivity into longitudinal

and transverse terms. More specifically, it lends acceptance to dividing the contribution of transverse vibrations into one- and three-dimensional components of thermal conductivity with the assignment of an orientation dependent variable to the one-dimensional component.

An attempt was made to determine the degree of stretch of the extruded sample by heating it above the glass point and allowing it to contract to its equilibrium length. Although heated in small increments of temperature change beyond the point of thermal degradation, no contraction was observed. By comparison of thermal conductivity values it appears that the extrusion process aligns the chains an equivalent amount to a stretch of 200%.

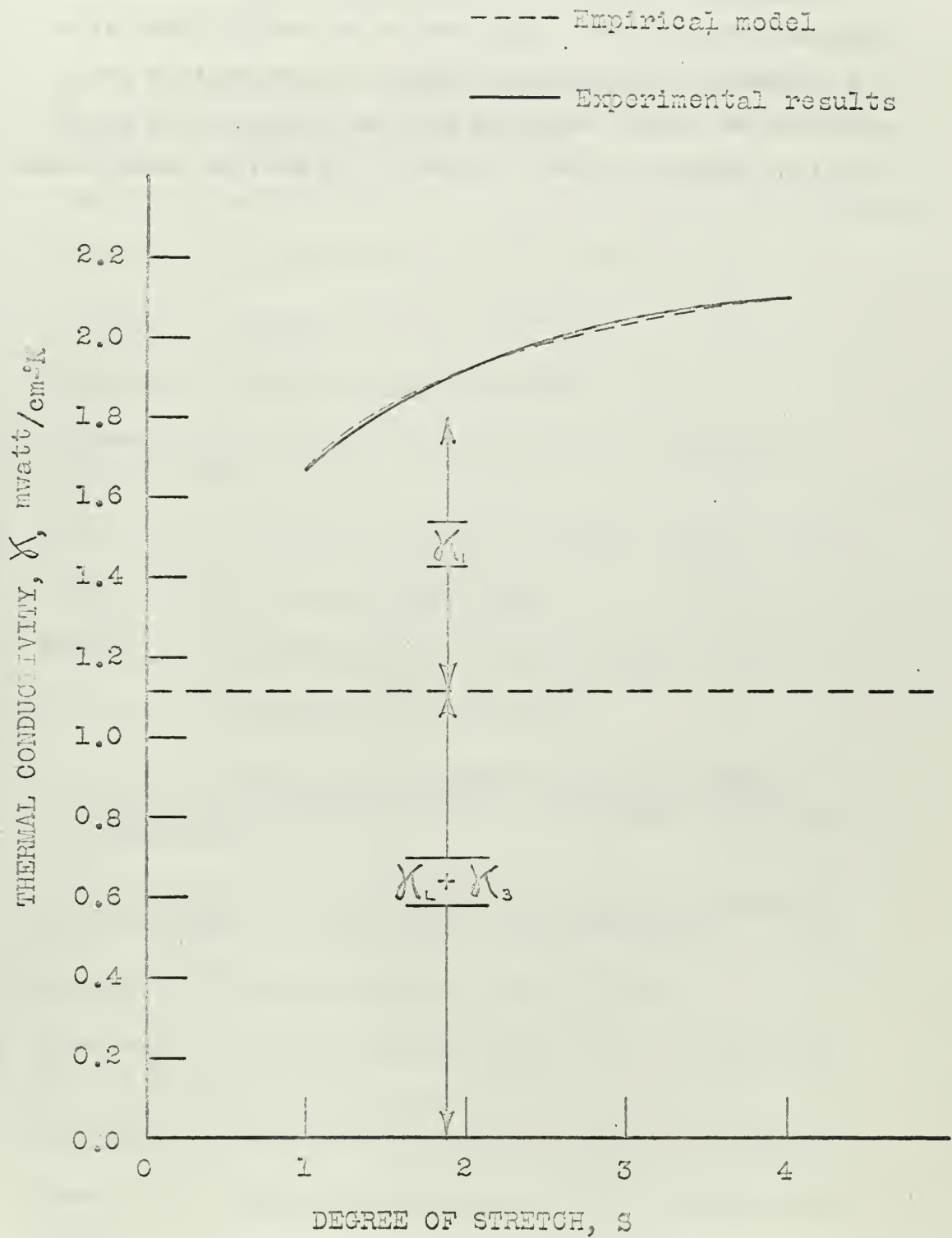


Fig. 8. Orientation effect on thermal conductivity.



#### 4. Acknowledgments

I wish to thank Professor William Reese for his enthusiastic direction in this project. I also wish to express my appreciation to Mr. Lynwood F. May, who assisted in the assembly of the apparatus; Mr. Robert Molar who built the vacuum system and machined the samples; and Mr. Tom Maris who built the sample holder.

## BIBLIOGRAPHY

1. Bueche, F. Physical Properties of Polymers. Interscience Publishers (1962).
2. Chang, G. K. and Jones, R. E. Phys. Rev. 126, 2055 (1962).
3. Eiermann, K. Kunststoffe, 51, 512 (1961).
4. Eiermann, K. and Hellwege, K. H., J. Polymer Sci. 57, 99 (1962).
5. Eiermann, K., J. Polymer Sci. 6c, 157 (1963).
6. Eiermann, K., Kolloid Z. 198, 5 (1964).
7. Eiermann, K., Kolloid Z. 199, 125 (1964)
8. Hellwege, K. H., Hennig, J. and Knappe, W., Kolloid Z. 188, 121 (1963).
9. Hoge, H. J., J. Research Natl. Bur. Standards, 44, 321 (1950).
10. Kittel, C., Phys. Rev. 75, 972 (1949).
11. Klemens, P. G., Proc. Roy. Soc. (London) A208, 108 (1951).
12. Kuhn, W., J. Polymer Sci. 1, 380 (1946).
13. Reese, W., On the temperature dependence of the thermal conductivity of amorphous polymers: polymethyl methacrylate. (To be published).
14. Reese, W., On the low temperature excess heat capacity in glassy polymers. J. Appl. Phys. (To be published).
15. Tarasov, V. V., Zhur. Fiz. Khim. 24, 111 (1950).
16. Ueberreiter, K. and Otto-Lampenmuhlen, E., Z. Naturforsch. 8a, 664 (1953).
17. Ueberreiter, K. and Nens, S., Kolloid Z. 123, 123 (1951).
18. Ziman, J. M., Electrons and Phonons. Oxford University Press, (1963).

## INITIAL DISTRIBUTION LIST

	No Copies
1. Defense Documentation Center Cameron Station Alexandria, Virginia 22314	20
2. Library U. S. Naval Postgraduate School Monterey, California 93940	2
3. U. S. Naval Material Command Department of the Navy Washington, D. C.	1
4. Professor William Reese Department of Physics U. S. Naval Postgraduate School Monterey, California 93940	1
5. Lt. Gerald N. Galstan, USN 102 Moran Circle Monterey, California 93940	1

**DOCUMENT CONTROL DATA - R&D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

1. ORIGINATING ACTIVITY (Corporate author) U. S. Naval Postgraduate School Monterey, California 93940	2a. REPORT SECURITY CLASSIFICATION Unclassified
	2b. GROUP

3. REPORT TITLE  
Effects of Polymer Orientation upon the Thermal Conductivity of Polymethyl Methacrylate at Liquid Nitrogen Temperatures

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)  
Masters' Thesis in Physics, May 1966

5. AUTHOR(S) (Last name, first name, initial)  
Galstan, Gerald Needham                      Lieutenant                      U. S. Navy

6. REPORT DATE May 1966	7a. TOTAL NO. OF PAGES 35	7b. NO. OF REFS 18
----------------------------	------------------------------	-----------------------

8a. CONTRACT OR GRANT NO.  b. PROJECT NO.  c.  d.	9a. ORIGINATOR'S REPORT NUMBER(S)
	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES  
~~\_\_\_\_\_~~  
This document has been approved for public release and sale; its distribution is unlimited. (CPL 9/15/69)

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Naval Material Command
-------------------------	--

13. ABSTRACT

Measurements of the thermal conductivity of commercial samples of polymethyl methacrylate (Plexiglas) with random and partially oriented polymer chains were made at liquid nitrogen temperatures to provide empirical guidelines into relationships of heat transfer mechanisms of amorphous polymers. Cast samples were formed to have degrees of stretch of one, two, three and four times original length. These samples were found to have thermal conductivities of 1.67, 1.91, 2.05 and 2.10 ± .04 mwatt/cm-K respectively. An extruded sample was determined to have an effective degree of stretch of two. Comparison was made with an empirical model based on component thermal conductivities obtained by partitioning with respect to vibrational modes into longitudinal and one- and three-dimensional transverse components.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymethyl methacrylate Thermal conductivity						

**INSTRUCTIONS**

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project/code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.













thesG1408

Effects of polymer chain orientation upo



3 2768 002 01014 2

DUDLEY KNOX LIBRARY