

A STUDY OF THE EFFECT OF DRAWING ON THE
THERMAL CONDUCTIVITY OF POLYPROPYLENE
AND POLYSTYRENE

BY

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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*A study of the effect
of drawing on the*



92/201108

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This thesis is my original work and has not been presented for a degree in any other University.

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This thesis has been submitted for examination with my approval as University Supervisor.

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ACKNOWLEDGEMENT

As I recall with gratitude the patience shown by my supervisor at the difficult moments of this work, I wish to thank most sincerely Prof. S.K. Katia, who not only offered untiring help through valuable advice and suggestions, but also induced valuable academic exploration, all of which made more concise and general exposition I needed. His efforts and support have made this piece of work a pride. On the same note, I am grateful to Kenyatta University and DAAD who made it a privilege for me to take the M.Sc. course at the earliest opportune time. The offer contributed alot in making my determination a reality.

I am very thankful to the East Africa Bag and Cordage Co. Ltd., Juja, for supplying the polymeric materials used in this study. I am also grateful to the deparment of Mechanical Engineering, University of Nairobi, for allowing me to use their equipment for the preparation of my samples. I also thank the chemistry department, Kenyatta University, for the use of the infrared spectrophotometer.

Lastly, but not least. I would like to thank Mrs. M., Nyawade and Miss Irene Nyambura for their tireless and dedicated efforts in typing this work.

DEDICATION

This work is dedicated to my parents, my wife and daughter.

To others I say, the mind of the rash may not know or understand the difference between the wise man, the philosopher and the scholar.

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ABSTRACT

The stretching effect on the thermal conductivity of isotactic polypropylene and atactic polystyrene samples, in the temperature range of 273K-333K, has been studied using the flash light method for measuring thermal conductivity. The processes and features involved in the heat conduction mechanism in polymeric materials have been analysed by considering factors like molecular chain conformation, bond strength, degree of crystallinity, the crystalline-amorphous boundary scattering effects and the contribution of the thermal conductivities of the individual phases.

The results have shown that stretching caused the thermal conductivity in both polypropylene and polystyrene samples to increase along the draw direction, with the increasing draw ratio, while that in the perpendicular direction decreased. The thermal conductivity in isotropic and drawn polypropylene and polystyrene samples also increased with the increasing temperature, both along and perpendicular to the draw direction. It has also been observed that the thermal conductivity of polypropylene increases with the increasing degree of crystallinity.

A model for analysing heat conduction in drawn semicrystalline polymers has also been proposed, based on the results for polypropylene obtained in this study. The model has been found to provide very good agreement with the experimental results obtained in this study, and for other semicrystalline polymers reported in the literature. It points that the thermal conductivity of an isotropic semicrystalline polymer is not dependent on the thermal conductivity of the crystalline phase, at high temperatures, and that the boundary effects are negligible at high temperatures such as in the range of 273K-333K.

CHAPTER 1

INTRODUCTION

Polymeric materials have made a great contribution to the improvement of the modern life style which has depended to a large extent on the polymer products ranging from plastic articles found in almost every home to highly specialized applications in technology. The significant economic advantage and technological flexibility perceived in polymeric materials are in the low cost energy of their fabrication into products of any shape. The industrial applications and the performance of polymer products are deduced from the response of their desired properties to a variety of phenomena familiar in everyday life, such as temperature changes. To this effect, the applications of polymers require the understanding of their unique structure-property relationship in order to modify, or select wisely from the huge range of available polymeric materials.

The mechanisms of heat transfer and thermal balance in polymeric materials are some of the

important properties normally taken into account when considering engineering applications of this class of materials. Innumerable engineering uses of polymers involve the transmission of heat and in some cases this is incidental, such as in the case of vehicle tyres becoming hot during use. In other situations the control of heat flow is a primary consideration, such as when polymeric materials are used as thermal insulators. They are also used for making electrical cables and in such cases heating up of the wires can sometimes be so severe as to cause insulation breakdown and hence lead to power failure.

The complicated physical structure of polymers, sometimes composed of crystalline and amorphous phases, and the characteristic molecular conformation introduced during the manufacturing process have since made it more difficult to relate their thermal properties to the chemical constitution alone. Consequently, theories used as phenomenological tools to provide the framework for optimizing agreement between theory and experimental results have ranged in complexity. Within the past decade or two, much research has been concentrated on the microstructure and structure-property relationship of polymeric materials.

Although substantial progress has been made in both experimental capability and theoretical explanations of the heat conduction in polymeric materials, it has not been possible as yet to describe accurately the relationship between the morphological changes in polymers and the thermal conductivity. For this reason many diverse ideas are actively being pursued and the study of the thermal conductivity behaviour in drawn polymeric materials is of theoretical and experimental value in following the understanding of the effect of morphological or structural changes on the thermal conductivity of this class of materials.

The structure-property models proposed so far, for analysing heat conduction in drawn polymers, also seem unsatisfactory in giving the relationship between the microscopic changes in semicrystalline polymers and the high temperature thermal conductivity [1, 2, 3]. For example, they do not show the extent to which the chain conformation changes in a semicrystalline polymer on stretching, and how this affects the thermal conductivity. It is therefore not clear from the models as to what draw ratio should one stretch a semicrystalline polymer to make its thermal conductivity change to a desired value. Tie molecules have also been inferred in some thermal conductivity results [3, 4] but how much contribution they make

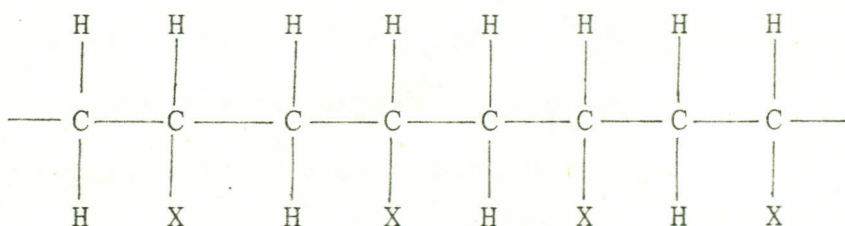
to the thermal conductivity has not been established and seem to depend on the model used for the analysis. Thermal conductivity studies in polymeric materials would therefore include attempts to propose a general model which would not only relate thermal conductivity to the microscopic changes in the material, but should also give good or precise estimate of the experimental reality presented by polymeric materials. It would then be useful to have a conception of the morphological puzzle presented by the results of the real material. To this end, a recently developed composite model for determining the effective thermal conductivity of a two-phase composite material consisting of spherical particles of one material suspended or embedded in a continuous medium of another material [5], together with a model based on the bond strength and conformational changes [6, 7], have been extended to semi-crystalline polymers, by modification, on the basis of the predictions of the results obtained in this study. A model which has the characteristics of both theories, expected to account comprehensively for the high temperature thermal conductivity of drawn and undrawn semi-crystalline polymers in terms of draw ratio, volume concentration of crystallites in the amorphous matrix and thermal conductivities of the individual phases, has been suggested by combining the two

models. The predictions of the new proposal have been compared with some of the existing models such as the modified Maxwell model [3].

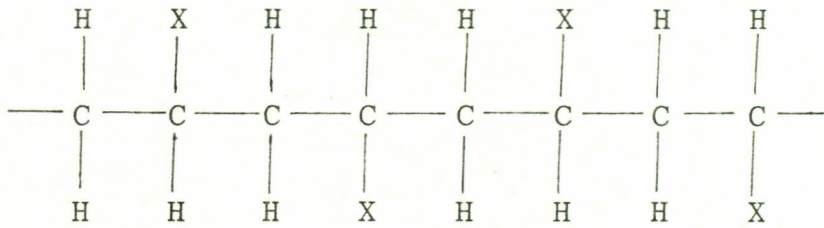
The general concern in this study has been to examine the role of polymer chain molecules, chain conformation, crystallites and boundary effects on the thermal conductivity in the temperature range of 273K - 333K. Attention has been paid to the combination of morphological forms (sphere, lamellar, etc.) of crystallites distributed within the general structure of the bulk material. The study, therefore, involved the following investigations:-

- (i) The variation of thermal conductivity with draw ratio, for measurements along and perpendicular to the draw direction.
- (ii) The variation of thermal conductivity of isotropic semicrystalline polypropylene with the degree of crystallinity.
- (iii) The variation of thermal conductivity with temperature, in the temperature range of 273K - 333K, for both isotropic and drawn samples.
- (iv) The variation of thermal conductivity with draw temperature.

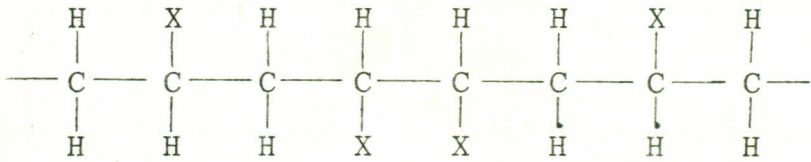
The materials used in this study were commercial thermoplastics, isotactic polypropylene and atactic polystyrene. In terms of microstructure, thermoplastics can be divided into amorphous and semicrystalline solids, with semicrystalline thermoplastics regarded as two-phase materials with an amorphous phase and crystalline phase. Arrangement of the pendant groups along the chain molecules, obtained on polymerization, determines the tacticity of the material. When the arrangement along the backbone is random the form is atactic. When a regular arrangement occurs on one side of the chain molecule the form is isotactic, while the syndiotactic form is obtained when the pendant groups are alternately arranged on both sides of the chain molecule. The forms have been illustrated by the structures below, X being the substituents.



isotactic



syndiotactic



atactic

Polypropylene, because of its high melting point, 165°C-175°C, is preferred for applications such as hot water pipes, wire and cable coverings. Polystyrene on the other hand has its softening point slightly above 100°C, which limits its use, however, it is used in making items such as wall tiles, heat insulating materials, electrical insulating materials and packaging materials.

CHAPTER 2

LITERATURE REVIEW

A review of thermal conductivity for polymers reveals that useful theoretical and experimental contributions have been made towards explaining the heat conduction mechanism in polymeric materials.

Several researchers [8, 9] have pointed out that the thermal conductivity of amorphous polymers are different from the thermal conductivity of semi-crystalline polymers, and that the difference can be attributed to imperfections which decrease the symmetry or order, which in turn is expected to lower the thermal conductivity in amorphous polymers.

In an attempt to increase order in an amorphous polymer, Eierman [10] made measurements on a stretched amorphous polymer and the thermal conductivity of the stretched polymethylmethacrylate increased in the direction of stretch but decreased in the direction perpendicular to the direction of stretch. He asserted that the increase in heat conduction in the stretch direction could not have been due to crystallization because, in that case, the heat conduction would also increase in the

direction perpendicular to the direction of stretch. He concluded that thermal energy is transported more easily along the main chain valences than along the secondary valences.

With regard to the thermal conductivity results reported by Choy and Greig [2], in the temperature range of 2K to 100K, there is evidence that the thermal conductivity in an amorphous polymer becomes anisotropic on extrusion. In a similar study, Burgers and Greig [11] reported the variation of thermal conductivity with temperature in several samples of extruded high density polyethylene, for extrusion ratio as high as 20. In all cases the values of thermal conductivity along the extrusion direction were roughly comparable between the temperature range of 2K and 20K. Above 20K, however, the values of the thermal conductivity along the extrusion direction increased markedly with the increasing draw ratio. At temperatures approximately equal to 100K a large anisotropy was reported, with the magnitude of the thermal conductivity in the extrusion direction roughly five times greater than in the perpendicular direction. The anisotropy was explained in terms of orientation of the crystallites on extrusion.

A study of the heat conduction in natural and synthetic rubbers in the temperature range of 113K to 323K and 0% to 100% stretch, reported by Dauphine, Ivery and Smith [12], showed that the values of thermal conductivity in the perpendicular direction were lower than that in the unstretched state while that in the draw direction were higher. Tantz also measured the change of thermal conductivity with draw ratio, in the direction of stretch, in a number of stretched vulcanized rubbers [13]. In all the samples investigated a considerable increase in the thermal conductivity was reported.

Silas Gustafsson and Enerst Karawachi, by determining the thermal conductivity along the direction of the molecular orientation in drawn insulating materials, reported a registered increase in the thermal conductivity along the orientation direction [14].

A study of the thermal conductivity in polyethylene at 323K, by Hansen and Bernier, also revealed that on orientation by mechanical shearing the thermal conductivity in the oriented polyethylene samples increased in the direction of molecular orientation but decreased in the perpendicular direction [9]. They also reported

that the thermal conductivity increased with the increasing lamellar crystal thickness, in polyethylene samples crystallized at different temperatures to vary the crystal size.

Mueller [1] suggested that thermal conductivity is related to the strength of the interatomic bonding forces. He asserted that when a semicrystalline polymer is oriented by stretching the thermal conductivity in the orientation direction increases while that in the perpendicular direction decreases and this can be explained in terms of the bonding strength. Hattori and Bull [15, 16] also argued that because the intrachain covalent bonds are much stronger than the interchain van der waals' forces, thermal conductivity along the chain direction is expected to be much larger than that across the chain segments.

In another study, involving measurements of the thermal conductivity in drawn amorphous polymer samples in the temperature range of 1K to 4.5K, the thermal conductivity in oriented samples of polymethylmethacrylate were reported to be only slightly higher along the direction of stretch, compared to that in the unoriented sample. It was then concluded that the thermal vibrations along the

polymer chain molecules do not play a dominant role in the transport of heat in that temperature range [17]. All these works appear to suggest that the polymer chain molecules, crystallinity and temperature have roles to play in the heat conduction mechanism in polymeric materials.

In semicrystalline polymers the boundary resistance, between crystalline and amorphous regions, has been considered by Choy and Greig to have significant effect on the thermal conductivity of polyethylene terephthalate (PET) in the temperature range of 2K to 100K. The thermal conductivity was also reported to increase with the increasing crystallinity, in that temperature range [18].

Because of the crystalline and the amorphous phases semicrystalline polymers have been imagined to be like composite materials [2, 3, 9], and some of the models used to analyse heat conduction in semicrystalline polymers have been adopted from the models proposed for analysing heat conduction in composite materials such as polymers containing fillers [19, 20, 21, 22]. The thermal conductivity of a rubber filled with aluminium spheres and rods, reported by Hamilton and Crosser, was analysed using Hamilton's equation [20]. Choy and Greig

[2], on the low temperature thermal conductivity of isotropic and oriented semicrystalline polymers, also analysed their thermal conductivity results in terms of an expression derived from Hamilton's equation [20] and the work of Maxwell [21].

The Maxwell's model [22], originally proposed for analysing heat conduction in composite materials with one material of low concentration embedded in a uniform matrix of another material, has also been modified by Choy and Young for analysing heat conduction in oriented semicrystalline polymers [19]. Choy, Luk and Chen [3] reported thermal conductivity behaviour in highly oriented polyethylene samples, in the temperature range of 120K to 320K, and analysed their results using the modified Maxwell model given in reference (19).

CHAPTER 3

THEORY

3.0.0 INTRODUCTION

In this Chapter, the heat conduction mechanism in solid materials and the flash light method for measuring thermal conductivity have been briefly outlined. Some general characteristics of polymeric materials, which make them different from other classes of materials, and the characteristics of some models proposed for analysing heat conduction in polymers and composite materials have also been reviewed.

3.1.0 HEAT TRANSFER BY CONDUCTION

Heat added to one face of a material is an additional thermal energy which, at the atomic level, increases the amplitude of thermal vibration of the atoms on that face and leads to temperature gradients, or energy difference between the receiving face and regions of the material far from the heat source. This additional thermal energy diffuses in the direction of the low temperatures, through the material, at a rate which depends on how

strong the vibrational motion of the adjacent atoms and groups is coupled, and on the temperature gradient. An abrupt change of condition on one face of the material does not usually produce instantaneous corresponding change in the whole material, but equilibrium is approached over a period of time. Therefore, the response to an abrupt change of condition is often a time measurable approach to equilibrium, frequently exponential, and may be used to determine the thermal diffusivity of a material [23, 24] from which the thermal conductivity can be calculated.

The thermal conductivity of a material may be regarded as a parameter which describes the way the thermal energy is transferred in a material where a temperature gradient exists. In other words, a net transfer of the thermal energy in a unit time, through a unit length of the material between which a temperature gradient of 1°C is maintained, can be characterized by thermal conductivity, designated by a parameter K .

The response of other regions of the material to the additional thermal energy can be monitored through temperature changes at those points. Fundamentally, temperature is a manifestation of

the average translational kinetic energy of the molecules of a substance due to heat or thermal agitation, and is measurable by any one of many physical effects due to changes or differences in energy. The thermal diffusivity of a material has been reported to depend on the heat capacity and density of the material, it varies inversely as the product of the two quantities [25].

3.2.0 FLASH LIGHT METHOD FOR DETERMINING THE THERMAL CONDUCTIVITY

Although the evaluation of thermal conductivity, K , for steady state experiments is mathematically simple [26], such experiments, particularly on substances of low and medium thermal conductivities, require long periods of time for the attainment and control of the thermal equilibrium. The flash light method for measuring the thermal conductivity, however, eliminates the thermal contact problem between the heater and the sample [27], and would be suitable for materials with poor thermal conductivity.

Using a high intensity source of flash light, not in contact with the sample, a short duration light pulse is absorbed on one face of an insulated

cylindrical sample, causing transient departures from the ambient temperature as a result of the change in thermal energy of the irradiated face. Because of the expected flow of energy in the direction of low temperatures, the other face (back surface) of the material is expected to show rise in temperature with time. This expected change in temperature of the back surface can be recorded and used to determine the thermal diffusivity of the material, and hence the thermal conductivity from the expression give by equation 3.1 [25, 28].

$$K = C_p \alpha \rho \quad \dots\dots(3.1)$$

where;

α is the thermal diffusivity

C_p is the heat capacity at constant pressure

ρ is the density of the material.

The expression for determining the thermal diffusivity of a material, using flash light method, can be obtained from Carslaw and Jaeger equation [27]. Consider a sample illuminated with a pulse of irradiation incident on the front face and denote the front and back surfaces of the sample as $x = 0$ and $x = L_0$ respectively. If $T(x, \theta)$ is the initial temperature distribution within a solid of uniform cross-sectional area, then Carslaw and Jaeger equation

gives the temperature distribution at any later time t by equation 3.2 [27].

$$T(x, t) = \frac{1}{L_0} \int_0^{L_0} T(x, 0) dx + \frac{2}{L_0} \sum_{n=1}^{\infty} \exp\left(-\frac{n^2 \alpha \pi^2 t}{L_0^2}\right) \cos\left(\frac{n \pi x}{L_0}\right) \int_0^{L_0} T(x, 0) \cos\left(\frac{n \pi x}{L_0}\right) dx \quad \dots(3.2)$$

where α is the thermal diffusivity.

If a pulse of energy Q J/m² is instantaneously and uniformly absorbed in the small depth, g , at the front surface of the solid, the temperature distribution at that instant is given by equations 3.3a and 3.3b [27].

$$T(x, 0) = \frac{Q}{DC_p g} \quad \text{for } 0 < x < g \quad \dots(3.3a)$$

$$T(x, 0) = 0 \quad \text{for } g < x < L_0 \quad \dots(3.3b)$$

where D is the density of the material.

Equations 3.3a and 3.3b give conditions which when substituted into equation 3.2 gives equation 3.4a. Assuming that g is a very small value for opaque materials, equation 3.4b holds.

$$T(x, t) = \frac{Q}{L_0 DC_p} + \frac{2}{L_0} \sum_{n=1}^{\infty} \exp\left(-\frac{n^2 \alpha \pi^2 t}{L_0^2}\right) \cos\left(\frac{n \pi x}{L_0}\right)$$

$$\cos \frac{n \pi x}{L_0} \left[\frac{Q}{DC_p} \left(\frac{\sin \frac{n \pi g}{L_0}}{n \pi g/L_0} \right) \right] \dots (3.4a)$$

$$\sin \frac{n \pi g}{L_0} \approx \frac{n \pi g}{L_0} \text{ and } \left(\frac{\sin \frac{n \pi g}{L_0}}{n \pi g/L_0} \right) \approx 1 \dots (3.4b)$$

On substituting $x = L_0$, for the back surface temperature, and taking the maximum temperature rise of the back surface as $T_M = Q/DCL_0$, equation 3.4a reduces to equation 3.5a. On plotting $T_{(L_0, t)}/T_M$ versus ω of equation 3.5a one obtains a curve from which the expression for the thermal diffusivity, α , can be determined with the help of equation 3.5b.

$$\frac{T_{(L_0, t)}}{T_M} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \omega) \dots (3.5a)$$

where $\omega = \frac{\alpha \pi^2 t}{L_0^2} \dots (3.5b)$

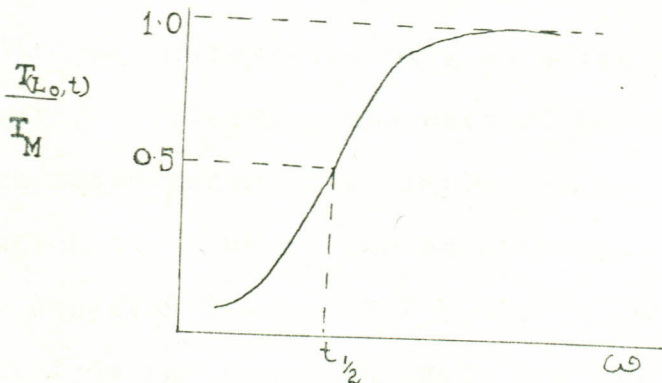


Fig. 1.

When $T(L_0t)/T_M = 0.5$ from the curve (that is when the back surface temperature is a half the maximum temperature rise) $\omega \approx 1.38$, and the time taken to come to that temperature is $t_{\frac{1}{2}}$. On substituting for ω and t in equation 3.5b, an expression which gives the thermal diffusivity of the material in terms of length of the sample and time $t_{\frac{1}{2}}$ is obtained, equation 3.6 [27, 28].

$$1.38 = \frac{\gamma^2 \alpha t_{\frac{1}{2}}}{L_0^2} \quad \text{giving } \alpha = \frac{1.38L_0^2}{\gamma^2 t_{\frac{1}{2}}} \quad \dots(3.6)$$

Another expression for α can be obtained by extrapolating the straight portion of the curve to the ω -intercept, which yields equation 3.7 [27].

$$\alpha = \frac{0.48L^2}{\gamma^2 t_x} \quad \dots(3.7)$$

where t_x is the time axis intercept of the straight portion of the curve for the variation of the back surface temperature versus time.

Thermal diffusivity of a material can then be determined by plotting the data of how the back surface temperature of a sample changes with time, from which t_x and $t_{\frac{1}{2}}$ can be obtained and used in either equation 3.6 or 3.7 to obtain α . It is evident from the equations 3.1, 3.6 and 3.7 that it is not necessary, in the flash light method, to know

the amount of heat absorbed by the sample in order to determine its thermal conductivity.

3.3.0 SOME GENERAL CHARACTERISTICS OF POLYMERS

Polymeric materials are distinguished from other classes of materials by their long continuous chain molecules. In polymeric materials the repeat units are anisotropically bonded, covalent bonds join adjacent units along the macromolecule but only weak secondary bonds join units on different macromolecules. The substituent groups attached to the main backbone vary in size from one material to the other, and cause steric interferences which dictate the chain conformation and the packing geometry. The conformation of a chain represents the orientation with the lowest energy that a chain molecule can assume, depending on the size and regularity in the placement of the substituent groups along the backbone. The conformation taken by a chain molecule is aimed at alleviating the steric difficulties experienced in the molecules, and this occurs by a combination of bond rotation which may be restricted to the trans or gauche states [29].

Because of the differences in the size and

placement of the substituent groups along the backbone of a chain molecule, one would expect conformation of the chains, packing geometry and modes of vibration to vary from one material to the other, and to cause differences in the thermal conductivity of polymeric materials. For example, polyethylene whose thermal conductivity has been reported to be higher than those of polymeric materials with bulky pendant groups has been known to assume the all-trans conformation. All-trans conformation represents the orientation with the lowest energy, and is excluded in polymers with large pendant groups because of steric interference between the neighbouring substituent groups [29].

In the trans state, successive substituent groups are within 2.5\AA to 2.6\AA of each other [29]. This distance is too small leading to gross overcrowding of the large substituent groups. This can be alleviated by having alternate bonds assume gauche position, a geometric pattern in which the substituent groups are adequately separated. If the required rotations are adequately executed in a regular manner so that the bond orientation sequence of trans-gauche-trans is followed, then a helical chain structure is followed [29]. This helical chain conformation allows the substituent

groups to be sufficiently far apart, with the nearest distance between non-bonded atoms being about 3.2\AA in isotactic polypropylene for example [29]. The path along the backbone of the polymer chain thus follows a regular helix in isotactic polypropylene. Conformation of chain molecules in amorphous polymers are as random as the arrangement of the substituent groups along the backbone of the chain molecules of amorphous polymers. The conformation affects the packing geometry which in turn affects the interchain molecular forces in the material, it also affects the path followed by the backbone of the chain molecule. The effect of the molecular chain conformation on the thermal conductivity of polymeric materials then seems to be based on the role of the backbone of chain molecules, or the covalent bonds, in the heat conduction mechanism.

The thermal conductivity in polymeric materials may also be affected by defects like voids and microcracks which cause boundary effects. Boundary effects are also expected to result from the existence of the amorphous and crystalline phases in semicrystalline polymers. Crystallites that are grown from the polymer melt, however, are not definite entities with sharp boundaries separating them from the surrounding amorphous phase. They are

small volume elements in which chain segments have crystalline arrangement and are connected to the surrounding amorphous medium by chain segments in which the crystalline order is partially maintained [29]. Therefore, there may not be a sharp discontinuity in the values of any physical parameters between the amorphous and the crystalline regions. However, a study of the thermal conductivity in polymeric materials should consider the dependence of the thermal conductivity of a semicrystalline polymer on the individual thermal conductivities of the phases.

At the time of crystallization, molecular chains in the melt are highly entangled and sections of a chain which lead from the developing portions of a crystallite to the regions where the chain is highly entangled with its neighbours become strained. The stresses and the associated strains slow down the crystallization process and also create crystal defects. The crystallites which are formed under such conditions do not have perfect geometric regularity since the alignment of the neighbouring helices become disturbed as a result of the stresses and strains set in the material.

Nevertheless, it is generally recognized that the morphology of a bulk crystallizable polymeric material is spherulitic in texture [2, 3, 11, 17]. Spherulites are formed by many substances of simple molecular structure when crystallizing from a medium of high viscosity, and spherulites formed by low molecular weight materials have been reported to be very similar to those formed by high polymers [29]. When polymers are crystallizing from a melt they are in a high viscous medium and the spherulitic habit is therefore expected. Most of the existing models that have been proposed for analysing heat conduction mechanism in semicrystalline polymers have recognized the spherulitic nature of crystallites in polymers [2, 3, 11, 17], and polypropylene has been reported to have large scale spherulites [30].

3.3.1 ANNEALING OF POLYMERIC MATERIALS

As already pointed earlier, during the forming and fabricating processes stresses and strains are introduced in polymeric materials as a result of the entanglement of chains. The stresses and strains are mostly significant in rapidly cooled samples, tending to lower the degree of crystallinity and causing defects in the material. When polymeric materials are subjected to annealing treatment,

conditions such as residual stresses and strains, non equilibrium crystals and dislocation will tend to be resolved by segment diffusion. According to Fischer and Schmidt [31], a considerable disordering followed by reorganization takes place on annealing. On annealing, the degree of crystallinity also increases by the increasing size and number of spherulites [9]. The annealing treatment may then be regarded as a means for adjusting the degree of crystallinity in polymeric materials, and for the removal of the residual strains and stresses which may create defects and dislocation of the spherulites and chain segments in the material.

During the annealing process, the polymeric material is brought upto a certain temperature, kept at that temperature for a definite period of time and then slowly cooled to room temperature. At high temperatures the molecular chain segments of polymers are highly mobile, and the degree of crystallinity depends on the thermal history of the material. Slow cooling gives the disorganized polymer molecules enough time to pack regularly, or adopt an orderly arrangement in the bulk material and causes the crystals to further increase in size. Rapid cooling does not allow enough time for chains to completely

reorganize themselves in an orderly fashion.

3.3.2 EFFECTS OF STRETCHING ON POLYMERIC MATERIALS

Stretching is a process normally used on textile fibres to enhance their textile strength and elastic modulus properties which are desirable in a number of textile applications. In such cases it is desired to have the highest degree of orientation of the crystallites so that particular crystallographic axes or planes are arranged as nearly as possible [32]. Stretching may then be regarded as a process which brings orientation of the molecular chain axes or crystallographic plans in the desired direction.

Stretching of crystallizable rubber samples has been reported to produce an increase in crystallinity, and a remarkably sharp orientation of crystallites in the direction of stretch results [29]. F. Rodrigues reported that crystallization of polymers from melt results in a peculiar form of crystallite growth with a preferred chain orientation. He also said that when a highly crystalline polymer is stressed, a certain amount of energy can be stored in bond bending and stretching, and other lattice distortions may result. Beyond the elastic limit, he added, rearrangement of the polymer chain

molecules takes place with chains oriented in the direction of stress and the spherulitic pattern is destroyed [33]. Mechanically working a crystalline polymer sample by stretching has been reported to distort the spherulites in polyethylene and nylon 6,6 by pulling as many molecules as possible into line with the direction of stretch [34]. Light and electron microscope studies of deformed low density polyethylene and nylon 6,6 were reported by Stein, Rhodes and Wilson to indicate that stretching is initially accompanied by the deformation of spherulites into ellipsoidally shaped objects with their principal axes lying in the direction of stretch. A microscopic study on the spherulitic deformation in polypropylene has been reported to show inhomogeneous deformation, and microcracks or crazing were reported to be inhomogeneously distributed within each spherulite [35].

Charles Price asserted that the equilibrium molecular chain conformation is a random coil which, on stretching, can be extended to a more linear conformation by increasing the number of trans conformations at the expense of gauche [36]. In this case the conformation would be expected to become more linear as the draw ratio increases.

3.4.0 CHARACTERISTICS OF SOME OF THE PROPOSED
THERMAL CONDUCTIVITY MODELS

Many relationships for analysing the thermal conductivity of materials with non-homogeneous phases, such as composite materials, in terms of volumetric concentration and thermal conductivities of the individual components have been proposed. Some of these relationships have been adopted for analysing heat conduction in semicrystalline polymers, on the basis that semicrystalline polymers can be regarded as two-phase materials with crystallites as the one phase embedded in the amorphous phase [2, 4, 37]. Hamilton's equation [20], for example, would consider semicrystalline polymers to consist of the crystalline phase of volume fraction ϕ dispersed in amorphous phase of volume fraction $(1-\phi)$. The crystallites may be of different shapes and distributed in either regular or irregular array. The amorphous and the crystalline phases may be considered to be of different thermal conductivities given by K_a and K_c respectively. In this case the Hamilton's equation can be expressed as equation 3.8.

$$K = \frac{K_a(1-\phi) \left(\frac{dT}{dX}\right)_a + K_c \phi \left(\frac{dT}{dX}\right)_c}{(1-\phi) \left(\frac{dT}{dX}\right)_a + \phi \left(\frac{dT}{dX}\right)_c} \quad \dots(3.8)$$

where $(dT/dx)_a$ and $(dT/dx)_c$ are the average temperature gradients in the amorphous and crystalline phases respectively. The average temperature gradients for materials with spherical particles can be obtained from the theoretical work of Maxwell and Fricke, equation 3.9[38, 39]. On substituting equation 3.9 into equation 3.8, equation given by expression 3.10 is obtained.

$$\frac{(dT/dx)_c}{(dT/dx)_a} = \frac{3K_a}{K_c + 2K_a} \quad \dots(3.9)$$

where K_a = thermal conductivity of the amorphous phase

K_c = thermal conductivity of the crystalline phase

$$\frac{K}{K_a} = \frac{1 + 2A - 2\phi(A-1)}{1 + 2A + \phi(A-1)} \quad \dots(3.10)$$

where $A = \frac{K_a}{K_c}$

The relationship given by equation 3.10 has been used by Greig and Choy for the analysis of the thermal conductivity in isotropic semicrystalline polymers at low temperatures [2]. Equation 3.10 suggests that the thermal conductivity of a semicrystalline polymer should be expressed in terms of the thermal conductivities of the individual phases and the degree of crystallinity.

One of the early models proposed for analysing the thermal conductivity in oriented polymeric materials [40] has suffered a number of criticisms from researchers [7, 19]. In this model, heat conduction in polymers has been likened to conduction through a network of large and small resistances, with heat conduction along a molecule represented by a small resistance and conduction between molecules represented by large resistances. The relationships for the thermal conductivity of oriented polymers were then given in the form of Ohm's law, equations 3.11a and 3.11b [1, 39, 40, 41].

$$K_o^{-1} = \frac{1}{3} K_{11}^{-1} + \frac{2}{3} K_{\perp}^{-1} \quad \dots(3.11a)$$

$$K_o = \frac{1}{3} K_{11} + \frac{2}{3} K_{\perp} \quad \dots(3.11b)$$

where K_o is the thermal conductivity for undrawn (isotropic) sample

K_{11} is the thermal conductivity along the direction of stretch

K_{\perp} is the thermal conductivity in the perpendicular direction.

Choy and Young [19] tested expressions 3.11a and 3.11b on their data for drawn polyethylene and reported that the values of K_o were not reasonable, especially from expression 3.11b which deviated most.

Hansen and Washo also pointed out that the basis on which the two expressions were given have no features which would deal with the effect of molecular size [7]. The model leading to equations 3.11a and 3.11b seems to be referring to the roles of chain molecules and the bonding strength in the heat conduction mechanism in polymeric materials.

Choy and Young made an attempt to relate the thermal conductivity of drawn semicrystalline polymers to the thermal conductivities of the individual phases and the volumetric concentration of the crystallites in the amorphous phase. However, their model resulted into an expression free of stretch parameter, equation 3.12 [19].

$$\frac{K_{\bullet} - K_a}{K_{\bullet} + 2K_a} = \frac{1}{3} \left(\frac{K_{11} - K_a}{K_{11} + 2K_a} \right) + \frac{2}{3} \left(\frac{K_{\perp} - K_a}{K_{\perp} + 2K_a} \right) \quad \dots(3.12)$$

where K_a is the thermal conductivity of the amorphous phase.

K_{\bullet} , K_{11} and K_{\perp} retain the same meanings given earlier.

The model treats a semicrystalline polymer as a two-phase material with spherical crystallites embedded in an amorphous matrix and occupying a volume fraction ϕ . It also considers the boundary

scattering effects at low temperatures, but neglects the effects at high temperatures ($T \geq 70\text{K}$) [3, 19]. For draw ratios not too large, the model assumes the thermal conductivity of the amorphous phase to remain approximately constant and is described by anisotropic thermal conductivity parameter K_a . The crystalline phase, however, is considered intrinsically anisotropic and is characterized by conductivities $K_{c_{11}}$ and $K_{c_{\perp}}$, parallel and perpendicular to the chain axis respectively. It is assumed, on the basis of the bonding strength, that the ratio of the thermal conductivity of the crystalline phase to that of the amorphous phase can be given by expression 3.13.

$$\frac{K_{c_{11}}}{K_a} \gg 1 \text{ and } \frac{K_{c_{\perp}}}{K_a} \approx 1 \quad \dots(3.13)$$

Considering the shape of crystallites to be an important factor, this model treats semicrystalline polymers as materials with spherical crystallites of thermal conductivity K_c , embedded in a medium of thermal conductivity K_a . The chain axis, \hat{c} , is also considered to be randomly distributed in the isotropic sample, and the process of orientation is expected to produce a strongly preferred distribution of the angle θ between \hat{c} and the draw direction \hat{n} . The orientation of the chain axis, \hat{c} , can be characterized by either $\langle \cos^2 \theta \rangle$ (the average) or crystalline orientation function, f_c , which is given by equation 3.14a [3, 19]. The orientation function, f_c ,

varies between 0, for random orientation, and 1 for full orientation of \hat{c} .

$$f_c = \frac{1}{2}[3 \langle \cos^2 \theta \rangle - 1] \quad \dots(3.14a)$$

With these quantities considered, the expressions for thermal conductivity, discussed in detail in reference 19, have been given by equations 3.14b and 3.14c, from which equation 3.12 was obtained.

$$\frac{K_{\perp} - K_a}{K_{\perp} + 2K_a} = \phi \frac{[2B_{\perp} + 1 - 3 \langle \cos^2 \theta \rangle]}{2(B_{\perp} + 2)} \quad \dots(3.14b)$$

$$\frac{K_{11} - K_a}{K_{11} + 2K_a} = \phi \frac{[B_{\perp} - 1 + 3 \langle \cos^2 \theta \rangle]}{(B_{\perp} + 2)} \quad (3.14c)$$

where $B = \frac{K_c}{K_a}$

In the case of the isotropic sample, $f_c = 0$ and $\langle \cos^2 \theta \rangle = \frac{1}{3}$ from equation 3.14a. The thermal conductivity of an isotropic semicrystalline polymer, K_o , is then given by equation 3.15, the reduced form of either equation 3.14b or 3.14c with the assumptions of equation 3.13 [19].

$$\frac{K_o - K_a}{K_o + 2K_a} = \frac{\phi}{3} \quad \dots(3.15)$$

where ϕ is the degree of crystallinity.

This model asserts that the thermal conductivity of an isotropic semicrystalline polymer depends only

on K_{c_1} , thermal conductivity in the direction perpendicular to the axis of the chains in the crystallite. The effect of the thermal conductivity along the chain axis is assumed to be saturated and does not influence the thermal conductivity of an isotropic sample. Equation 3.12 was obtained from equations 3.14b and 3.14c on the assumption that the degree of crystallinity remains approximately constant on stretching [19].

A relationship containing draw ratio, aimed at analysing the effect of drawing on the thermal conductivity of amorphous polymers, was proposed by Hansen and Washo [7], based on the theory advanced by Hansen and Ho [6]. The model starts with the geometry, or conformation of the molecules, and employs other characteristics of the molecules to analyse the influence of orientation on the thermal conductivity. It assumes that a segment exchanges thermal energy with each of its nearest neighbouring segments at a rate which is proportional to the energy (or temperature) difference between them. The specific nature of polymers is recognized in this model by considering two types of nearest neighbour interactions for a chain segment; interaction with bonded neighbours (on the same molecule), and interaction with the unbonded neighbours (on

different molecules). The energy, or temperature, of a given segment then becomes a function of its location in the temperature field and the location of all other segments on the same molecule, that is on the chain conformation.

By determining the geometry or conformation of a molecule in terms of segment location or position, x_i , relative to the centre of gravity of the molecule, for 600 molecules of varying sizes, Hansen and Washo [7] determined the thermal conductivity of each molecule, following the procedure laid down by Hansen and Ho [6], for different conformations. For each molecule the average absolute segment position relative to the centre of gravity of a molecule, \bar{X} , was used as a measure of the conformation. \bar{X} was determined from the construction of a molecule on a computer by random walk procedure. This dimension statistic, \bar{X} , was considered an appropriate correlating parameter such that for the deformation of a mass of molecules it is to be expected that \bar{X} would increase, in the direction of elongation, proportional to the elongation or draw ratio. A regression analysis of the correlation between the relative thermal conductivity of each molecule, K/K_{av} , and \bar{X} was reported to give linear relationships which

led to the prediction of equation 3.18 from equation 3.17, for the thermal conductivity along the draw direction, K_{av} is the average thermal conductivity of the 600 molecules before deformation, which is equivalent to the thermal conductivity of the isotropic sample, K_o .

$$\frac{K}{K_{av}} \propto \bar{X} \text{ and } \bar{X} \propto \lambda \quad (3.17)$$

where $K \equiv K_{11}$ (defined earlier)

λ is the draw ratio.

$$\left(\frac{K_{11}}{K_o} - 1 \right) = C(\lambda - 1) \quad \dots(3.18)$$

where C = gradient of the curve for the relative thermal conductivity along the draw direction versus draw ratio.

Similarly, a linear relationship was reported for the variation of the relative thermal conductivity in the perpendicular direction with the inverse square root of the draw ratio, equation 3.19 [7]. The linear relationship between the relative thermal conductivity along the draw direction and the draw ratio has been confirmed in some amorphous polymers [10, 40, 42, 43].

$$\left(\frac{K_1}{K_0} - 1\right) = C \left(\lambda^{-\frac{1}{2}} - 1\right) \quad \dots(3.19)$$

According to Hansen and Washo, C is the same in equations 3.18 and 3.19 for monodisperse molecules. That is, C is a characteristic of a particular polymer which when determined by other methods and substituted in equations 3.18 and 3.19 [7], a good agreement between the experimental and theoretical thermal conductivity values should be obtained, especially in monodispers polymers. Good agreement between the experimental and theoretical thermal conductivity values derived from equations 3.18 and 3.19 was reported for PMMA [7]. Hansen and Washo then concluded by pointing bond strength and relative length or molecular chain conformation in the deforming network as the likely major determinants of the models given by equations 3.18 and 3.19.

Sangani and Yao [5] recently developed a model for determining the effective thermal conductivity of two-phase composite materials consisting of spherical particles of one material suspended or embedded in a continuous medium of another material. The effective thermal conductivity was

considered to depend on the detailed microstructure of the composite materials, such as size and spatial distribution of the particles. The expression for the effective thermal conductivity was obtained by solving Laplace equation for heat conduction, subject to the conditions of continuity of the temperature and heat flux at the interface of each particle and the surrounding matrix [5]. Only the summary of the whole derivation has been presented here, other details have been given in reference (5).

To solve the Laplace equation for heat conduction, relatively simple microstructures which include cases such as those studied by McPhedran and Milton [44] and Maxwell [21] were considered. Maxwell showed that when the volume fraction, ϕ , of the particles in a continuous medium is very small, the effective thermal conductivity can be given by equation 3.20 [21] regardless of the size and spatial distribution of the particles.

$$\frac{K^*}{K} = 1 + 3\phi \left(\frac{B-1}{B+1} \right) + \phi^2 \dots (3.20)$$

where K^* is the effective thermal conductivity of the composite material

K is the thermal conductivity of the matrix

B is the ratio of the thermal conductivity of the particles to that of the surrounding matrix.

ϕ_c is a function of ϕ (crystallinity)

Sangani and Yao [5] presented a numerical method to estimate K^* for composite materials whose microstructure can be approximated to a spatially periodic array with each unit cell containing N spherical particles whose size and location of the centres are completely arbitrary. They evaluated K^* in powers of ϕ , as given by equation 3.21.

$$\frac{K^*}{K} = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} Q_n \phi^n \quad \dots(3.21)$$

$$\phi = \left(\frac{B-1}{B+1} \right)$$

Q_n is a function of ϕ (volume fraction)

$$n = (1, 2, 3, \dots)$$

On the assumption that the particles are uniformly distributed throughout the unit cell, and that N is very large ($N \gg 1$), Sangani and Yao evaluated Q_n in terms of ϕ , following the procedure whose details are given in reference (5).

Equations 3.22a and 3.22b are obtained from equation 3.21, for Q_1 and Q_2 respectively [5]

$$Q_1 = 2\phi; (n=1)$$

giving
$$\frac{K^*}{K} = 1 + 2\phi \left(\frac{B-1}{B+1} \right) \quad (3.22a)$$

$$Q_2 = \frac{4}{3} (\phi + 2\phi^2); (n=2)$$

giving
$$\frac{K^*}{K} = 1 + 2\phi\left(\frac{B-1}{B+1}\right) + \frac{2}{3}(\phi + 2\phi^2)\left(\frac{B-1}{B+1}\right)^2 \dots (3.22b)$$

The third term on the right hand side of equation 3.22b has been reported to be size and distribution dependent, while equation 3.22a is in agreement with the Maxwell's proposal for equation 3.20. If the composite model of equation 3.21 were to be applied to semicrystalline polymers, the terms containing higher powers of β may have to be neglected. This is to be expected when one considers semicrystalline polymers as materials with the crystallites connected to the surrounding amorphous phase by chain segments in which crystalline order is partially maintained and, therefore, no sharp discontinuity in the value of any physical parameter between the amorphous and the crystalline phases would be expected [29]. This way, the difference in the thermal conductivities of the amorphous and the crystalline phases would not be expected to be so big and the ratio $B = K_c/K_a$ is expected to be close, but not equal, to unity, making the higher powers of β very small such that the terms containing β^n (for $n \geq 3$) may be neglected.

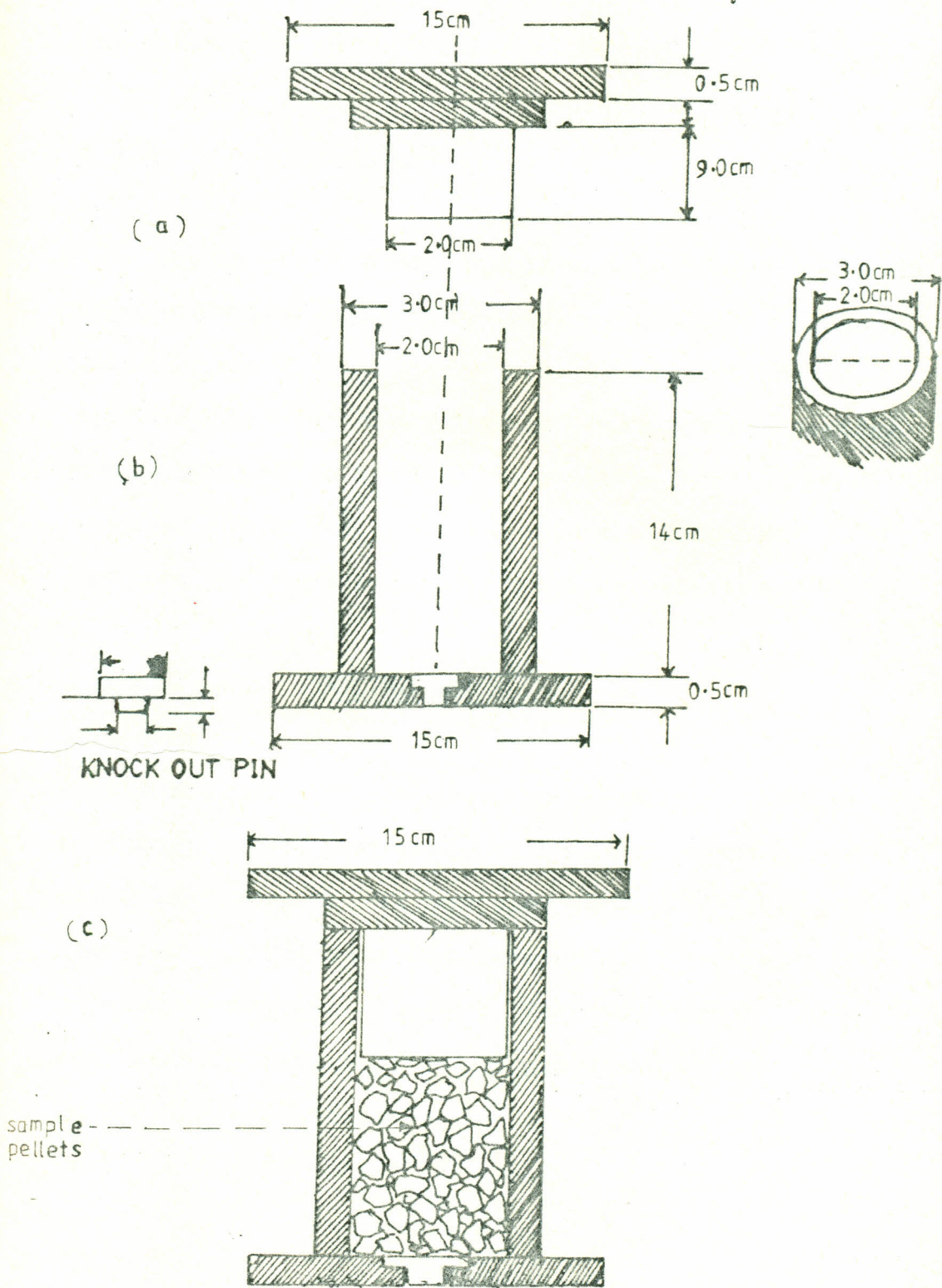


Fig.2 The mold : (a) - Plunger (b) - cylinder
(c) cylinder with the plunger

the study were prepared using this mold.

4.0.2 THE OVEN

An oven with a maximum temperature of 300°C and temperature fluctuation of about $\pm 2^\circ\text{C}$, having a motor that rotates a disc in the heating compartment to regulate the heat distribution, was used for heating sample pellets to melting temperature, and to anneal samples. This was obtainable at the Mechanical Engineering Department, Nairobi University.

4.0.3 COOLING BOX

A cooling box (chamber) was made from a frame of timber and plywood, the dimensions of which are given in figure 3. It was used mainly to provide the slow cooling rate for samples, and to reduce the effects of weather changes. This was done by lining the box with layers of fiber glass and cotton wool as the lagging materials.

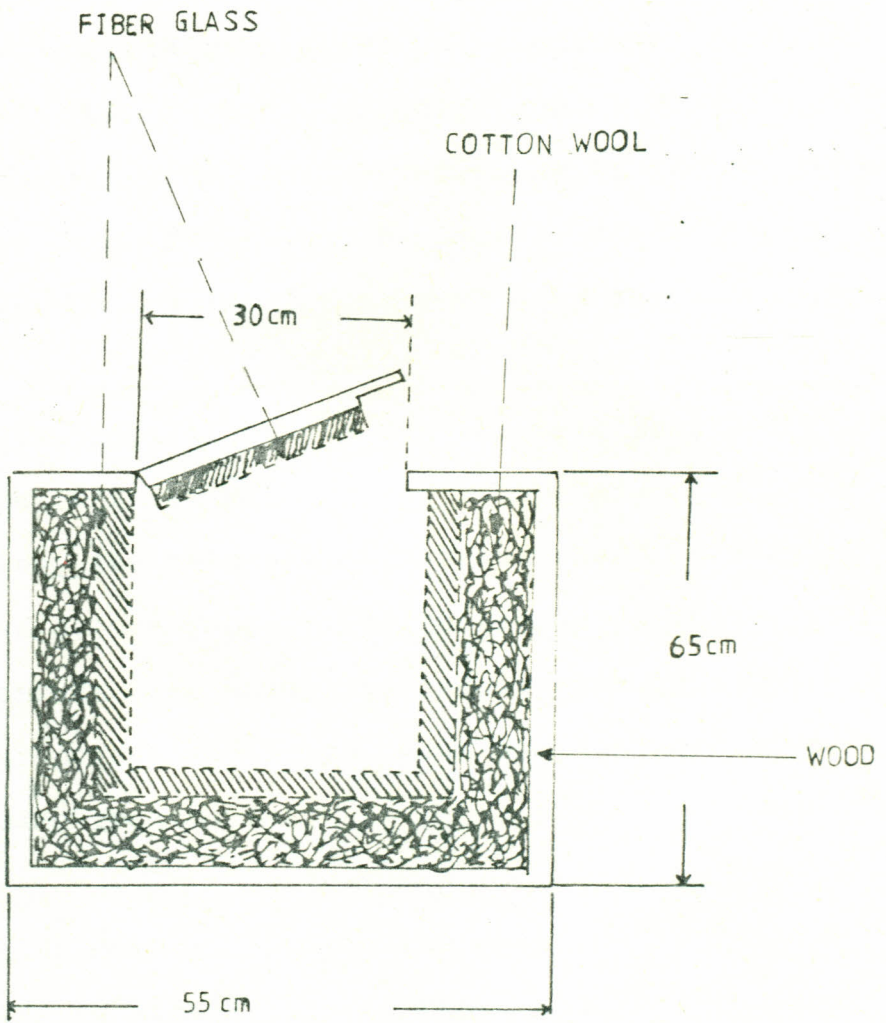


Fig 3 COOLING BOX

4.1.0 SAMPLE PREPARATION AND TREATMENT

Commercial isotactic polypropylene, labelled as FINAPROP PPH 30605 of melt index 1.7, and amorphous polystyrene, labelled as PS 158K, supplied in the form of pellets, by East Africa Bag and Cordage Co., Juja, Kenya, were used for the study.

Cylindrical shaped samples were prepared from the pellets, by melting and compressing. After melting, the melt was either quenched or slowly cooled before subjecting the sample to any further treatments like annealing and stretching. The polypropylene and polystyrene samples were given the same treatments.

The mold was put in the oven set at 240°C, resting vertically on its base, and left to warm for about 20 minutes before packing it with a given quantity of sample pellets, 20gm. It (mold) was supported on 4 pieces of blocks of wood measuring 5cm x 5cm x 7cm, at the four corners of the base, raising it 7cm from the oven's base to avoid contact heating of the base. It was also positioned at a corner in the oven, about 7cm from two converging walls of the oven, in an attempt to keep all parts, vertical column and base, equal distance from the

heat source.

After 60 minutes of heating the pellets, the top of the mold (plunger) was replaced and a weight of 16kg put on it for about ten minutes before the mold was removed from the oven and quickly transferred (with 16kg weight on it) into the cooling box, or into a water bath with water at 25°C kept flowing to avoid high rise of the temperature. Quenching was aimed at producing low degrees of crystallinity required for the study of the effect of crystallinity on the thermal conductivity.

4.1.1 ANNEALING TREATMENTS

The polypropylene and polystyrene samples that were to be stretched were annealed in the oven at 140°C for 6 hours, during which they were rotated after every 15 minutes. The oven was then switched off and samples allowed to cool to room temperature, in the oven, a process which took 2½ hours. The samples used for the stretch-thermal conductivity study were the ones given slow cooling treatment and subsequently annealed at 140°C for 6 hours.

For the study of the crystallinity effect on thermal conductivity, some quenched polypropylene samples were annealed for varying times, at a fixed temperature, to raise the degree of crystallinity. However, annealing was not only aimed at increasing crystallinity in polypropylene samples, for even polystyrene samples were annealed. It was also aimed at adjusting the residual stresses and strains developed in the samples to approximately the same level, before stretching. The treatments given to the polypropylene samples to vary the degree of crystallinity, and the crystallinity results, have been summarized in table 6.

4.1.2

STRETCHING OF THE SAMPLES

Samples were stretched at temperatures above their glass transition temperatures, but below their melting points, in the oven, using a stretching frame shown in figure 4. The oven was first set at the required temperature and left to attain the temperature before introducing into it the stretching frame and the sample.

A sample was clumped with its ends between the grips of the stretching frame, with a gauge length

of 3.0 cm, and emery cloth placed between the samples and the grips to improve the gripping and to prevent over-heating from the hot metal grips. The sample was first loosely clamped and left to warm for 10 minutes, during which it was rotated after every 1 minute for a uniform temperature distribution, after which the ends were locked and the stretching process started.

Polypropylene and polystyrene samples were stretched to the required length, or draw ratio, by rotating the lever arm of the stretching frame. At the end of every stretch, every sample was left to stay in the oven for another five minutes before removing the frame. The draw rate was determined by dividing the extension by the time taken to stretch the sample to the required length. Four samples of each material were used as trial samples, and in doing so the rate of stretch was controlled such that the mean rate of stretch of the samples was about 0.005cm/sec.

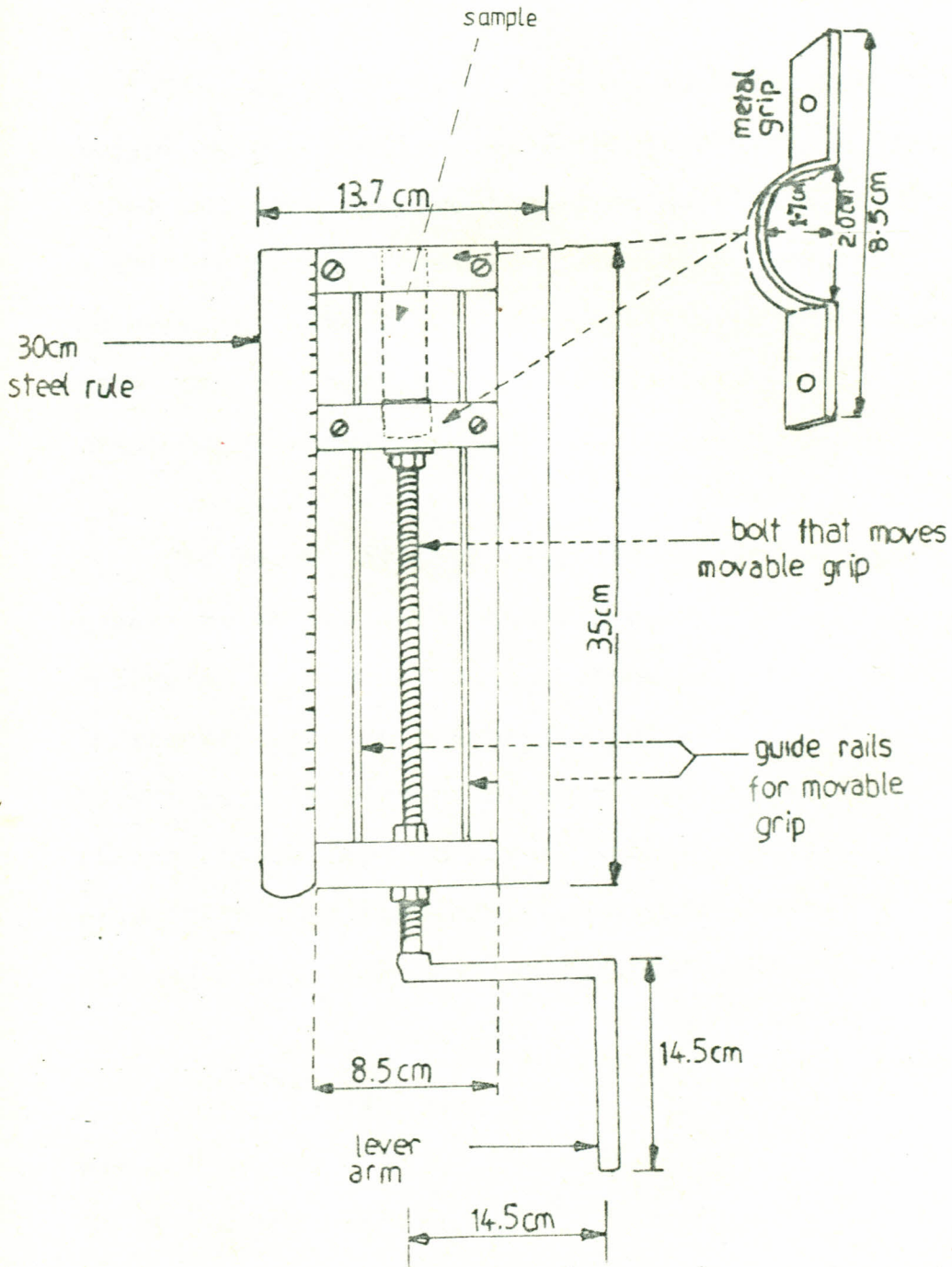


Fig.4

stretching frame.

I is the infrared radiation transmitted through the sample

When the infrared light is passed through a polymer sample, some of the frequencies are absorbed while others are transmitted. The intensity of the light frequencies absorbed by amorphous phase are expected to be different from the absorption of the crystalline phase. These absorbed frequencies provide the phase identification characteristic bands for a particular material.

The infrared analysis is based on Bouguer-Beer law [45], which assumes that each layer of equal thickness, or phase, absorbs a constant fraction of the radiation energy passing through it, and the absorption by any phase of the material is proportional to its concentration.

From the infrared spectrum, the phase identification bands for crystalline and amorphous absorptions can be identified [28, 46] and absorbances determined from the measurements of I_0 and I . The measurements of I_0 and I can be obtained using an ordinary millimeter scale [45] and the natural logarithm of the ratio I_0/I taken, from which the degree of crystallinity is defined by equation 4.1b [47].

$$X_c = \frac{A_c}{A_c + A_a} \times 100\% \quad \dots\dots(4.1b)$$

where A_a and A_c are absorbances of the amorphous and crystalline regions respectively .

For isotactic polypropylene, the absorption bands for crystalline and amorphous regions have been given in the literature [28, 46]. The crystalline absorption frequencies (cm^{-1}) are, 809, 842, 894 and 998, while the amorphous absorption frequencies (cm^{-1}) are 790 and 1158.

Any strong or weak analytical band can be used for determining the degree of crystallinity, provided its absorbance is brought into a suitable range. For minimum error in the absorbance reading, a thickness should be chosen to give analytical band absorbances near 37% transmittance. In practice, a range of 20-60% transmittance is satisfactory [45].

The use of the millimeter scale to measure I_0 and I assumes that the height of the transmittance recorded, from the zero point transmittance, is proportional to the transmitted radiation. The criteria used is to draw the baseline, as nearly as possible, through where the pen tracing would go if

the bands were not present, figure 5.

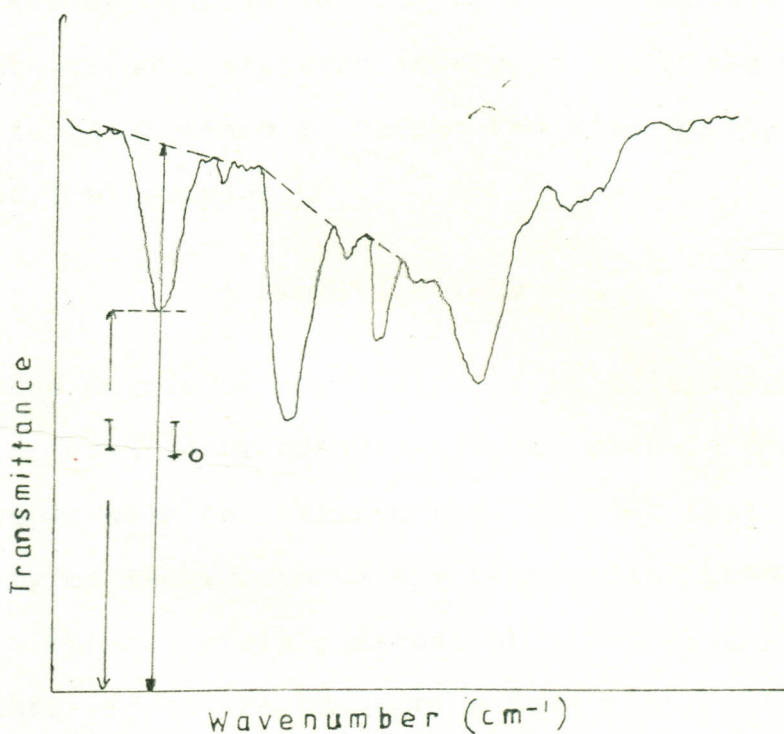


Fig. 5

For the infrared spectroscopy crystallinity measurements, 5-micron thick rectangular pieces of specimens were prepared from the curved surfaces, on the outermost surface and near the centre (at a radius of 0.5 cm) of the cylindrical isotropic and drawn samples. The value of the crystallinity near the centre was always slightly higher by some value ξ , ($\xi \leq 1\%$). This could be attributed to the difference in the cooling rates of the two regions.

The degree of crystallinity in experimental samples was assumed to be the values obtained from the specimens taken from near the centers of the samples. This was so because for the thermal conductivity measurements the prepared isotropic and drawn samples were to be machined to reduce the size of the cylindrical samples.

4.2.1 DENSITY METHOD

The degree of crystallinity in polypropylene was also determined by density method, both in drawn and isotropic samples. This method assumes that the density of the amorphous and crystalline phases remain approximately constant on stretching [48], and was obtained on the assumption that the density of the crystalline phase and the amorphous phase in isotactic polypropylene are 0.9359 g/cm^3 and 0.8535 g/cm^3 respectively [48]. The expression for calculating the degree of crystallinity is given by equation 4.2 [31].

$$\phi = \frac{\rho_x - \rho_a}{\rho_c - \rho_a} \text{ (volume fraction crystallinity).} \quad \dots(4.2)$$

where

ρ_x is the density of the samples of unknown crystallinity

ρ_a is the density of the amorphous phase

ρ_c is the density of the crystalline phase.

The density, ρ_x , was determined at room temperature using a graduated density gradient column, available at Kenya Bureau of Standards. The column has on it a movable ring with a window opened to a microscopic lens for locating the marks. When a sample is dropped into the graduated column, it settles itself around the position of its own density, and a mark around the mid-point of the sample is taken as the value of the density. The mid-points of the samples were marked with black ink, before dropping them into the column.

The samples used for the determination of the density were machined into cylindrical pieces, 1.0 cm in diameter and 1.0 cm long. The density results obtained were to be used for the determination of crystallinity, in the case of polypropylene, and for the calculation of the thermal conductivity using equation 3.1 .

4.3.0 THERMAL CONDUCTIVITY MEASUREMENTS

The flash unit used for the determination of the thermal diffusivity was commercially available in parts, the main unit being the Altai variable flash controller to which a bulb of any rating could be connected. A 500-watt bulb was used as the source of

of energy, to form the complete unit. The unit had a manual switch and knobs for varying the frequency or pulse time of the flash light. The flash method requires that the flash duration, or the sample size, or both be varied to ensure that the pulse time is short compared to the time the back surface temperature of a sample starts to rise. It was also necessary that the sample size chosen should minimize the cooling rate of the sample at the time of heating, so as to suit the Carslaw-Jaeger equation for determining thermal diffusivity [27].

The sample size was determined in the trial runs, and a sample length $L_0 = 0.95 \pm 0.01$ cm was used for all the experimental samples. An isotropic polystyrene sample of that length, tested at 273K, produced results which compared well, with an error of about 5% less, to the value of thermal conductivity given in the literature [46]. All the samples were machined from the prepared isotropic and drawn samples, into cylindrical samples of diameter $d = 1.25$ cm and length $L_0 = 0.95$ cm. The trial runs revealed that diameters upto 2 cm and lengths within the range of $0.3 \leq L_0 \leq 1.5$ cm could be used without appreciably affecting the values obtained for the thermal conductivity, both in the isotactic polypropylene and polystyrene. This may be

understood from the boundary conditions for the Carslaw and Jaeger equation [27]. The diameter chosen was hoped to suit the experimental conditions for the set up, aimed at reducing the radial temperature gradient and to ensure that the energy arriving at the irradiated face was uniformly concentrated over the area, for uniform absorption by the sample surface. The front surface of each sample was also blackened with a blackboard paint (matt black) to increase the amount of energy absorbed, and to ensure that all parts of the sample surface had equal absorption and that the absorptivity of all samples were identical [24].

For the thermal conductivity measurements along and perpendicular to the draw direction, two samples were cut from the cylindrical isotropic or drawn samples and machined into cylindrical samples in such a way that one had its front face being the plane perpendicular to the draw direction and the other had its front face being the plane parallel to the draw direction. Each sample was then enclosed, in turn, in the cylindrical shaped sample holder for measurements, figure (6a). The sample holder had a cotton and fiber glass lining for the insulation of the samples. Fixed at a position in the sample

holder was also a disc (made of wood) on which the thermocouple junctions were fixed, 3 mm apart (one at the centre), for the measurements of the back surface temperature of the sample. Figure 6b shows how the junctions appeared from front. The diameter of the disc was made slightly less than that of the samples used. The position of the disc was also adjustable. After a sample made good contact with the thermocouple junctions, the sample holder was tightened to hold the sample in position. The sample holder could also be removed or fixed at a position in the heating chamber where the bulb envelope was fixed, figure (6b). There were adjustable metal strips at the corners of the bulb envelope, to keep the desired distance between the sample and the bulb. The distance between the sample and the bulb was chosen to be about 1.0 cm.

With the insulation, average sample size and the flash duration made short enough, the amount of heat lost during the experiment was assumed negligible. The amount of heat lost by samples, between two heat pulses, and the amount of heat lost at the time of the heat transfer to the back surface were also assumed negligible. The time taken by heat to transfer from the front to the back surface, at room temperature, was about 20 and 25 seconds in

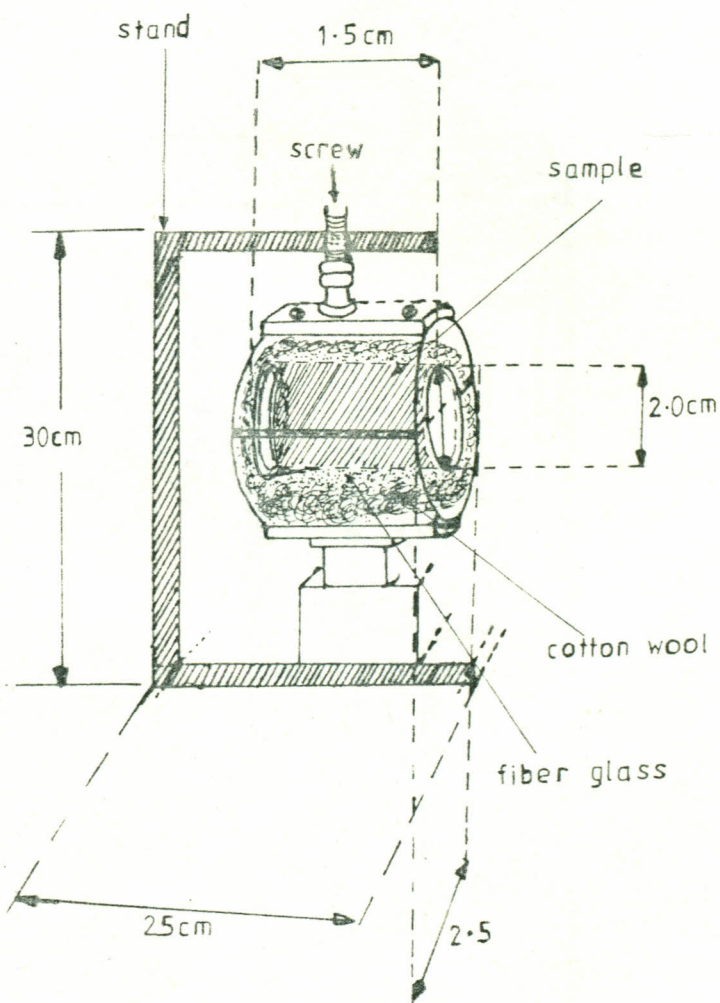


Fig. 6a Sample holder

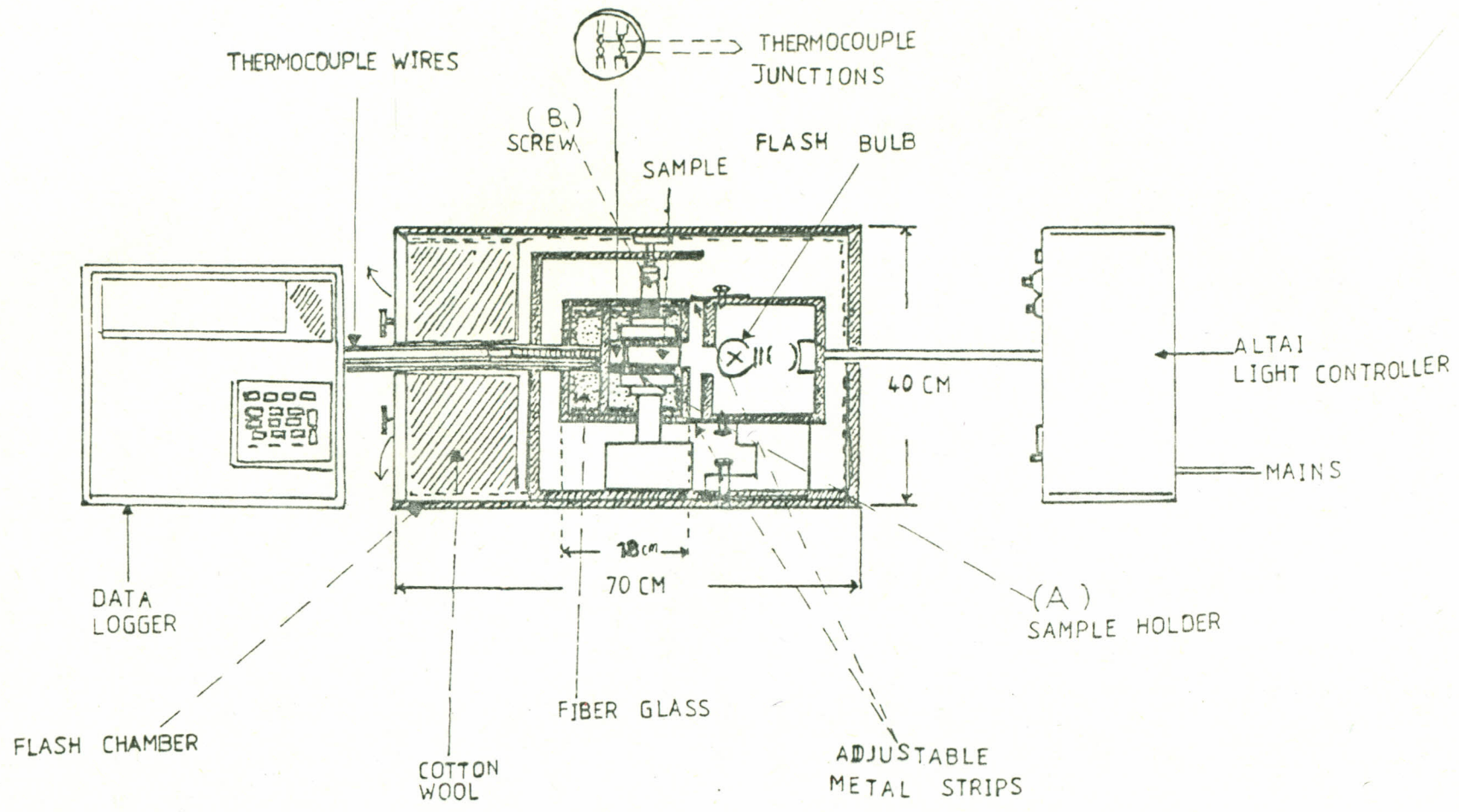


Fig.6b The apparatus for measuring thermal diffusivity

isotropic polypropylene and polystyrene samples, respectively, of length $L_0 = 0.95 \pm 0.01$ cm. Every sample was flashed for the same duration of 4 minutes using the flash duration of $\tau = 0.67$ sec.; after which the flash light was switched off. Temperature readings of the back surface were displayed and printed by the data logger after every 15 seconds. The temperature readings obtained were plotted against time, from which the thermal diffusivity was calculated using equations 3.7 and 3.8 and the average of the two taken. Variations between the values obtained from equations 3.7 and 3.8 were very small, in most cases the values were reproducible to the second decimal place. The differences could be attributed to the accuracy with which the tangent, or t_x , was obtained. In some cases the temperature versus time curves may reflect deviation from the ideal boundary conditions of the experiment [24]. If the final temperature is approached very slowly after an initial fast rise, or if the curve has a peak before seeking a low temperature plateau, then a non-uniform distribution of irradiation on the front surface is suggested. Given in the appendix are some representative temperature versus time curves obtained during the measurements.

The back surface temperature readings were also

used to determine the heat capacity for isotropic polystyrene, at various temperatures. The heat capacity for isotropic isotactic polypropylene has been reported to be changing with temperature according to equation 4.3 [28, 46].

$$C_p = 4.184 (0.3669 + 0.00242T) \text{J/g}^\circ\text{C} \quad \dots\dots(4.3)$$

where T is in $^\circ\text{C}$ and varies between 0°C and 100°C .

The heat capacity of $1.789 \text{J/g}^\circ\text{C}$ for isotropic isotactic polypropylene at 25°C [28, 46] is in good agreement with equation 4.3. The validity of equation 4.3 at other temperatures was verified, in this part of the study, by comparing the back surface temperature rise at a particular temperature with that at room temperature (25°C). This was done by taking the ratio of the expression for C_p' given by equation 3.3a, at one temperature and the value of C_p at room temperature. The polypropylene results were in good agreement with equation 4.3, table (3a). The ratio method of determining C_p from equation 3.3a, at any temperature, was used to determine C_p for polystyrene at other temperatures. The values of C_p for polystyrene have been given in table (3b). For drawn polypropylene and polystyrene samples, the values of C_p were also

determined using the same ratio method. However, in this case the expression for C_p , equation 3.3a, for a drawn sample, is compared with that for the isotropic sample at the same temperature.

CHAPTER 5

EXPERIMENTAL RESULTS

5.0.0 INTRODUCTION

In this chapter curves and tables relating to the crystallinity, heat capacity and thermal conductivity results have been presented for analysis. Theoretical thermal conductivity values derived from some of the models presented in chapter 3 have been graphically compared with the experimental results, but the discussion of the results has been presented in chapter 6. The results are as given below.

5.0.1 CRYSTALLINITY CHANGES IN DRAWN POLYPROPYLENE SAMPLES

The degree of crystallinity in drawn samples, obtained by the infrared spectroscopy and density methods described in chapter 4, are graphically represented in figure 7 while table 1 contains the actual corresponding data. The infrared diagrams used for the determination of the degree of crystallinity have been given in the appendix, figures 20(a-g). The samples were drawn at 120°C.

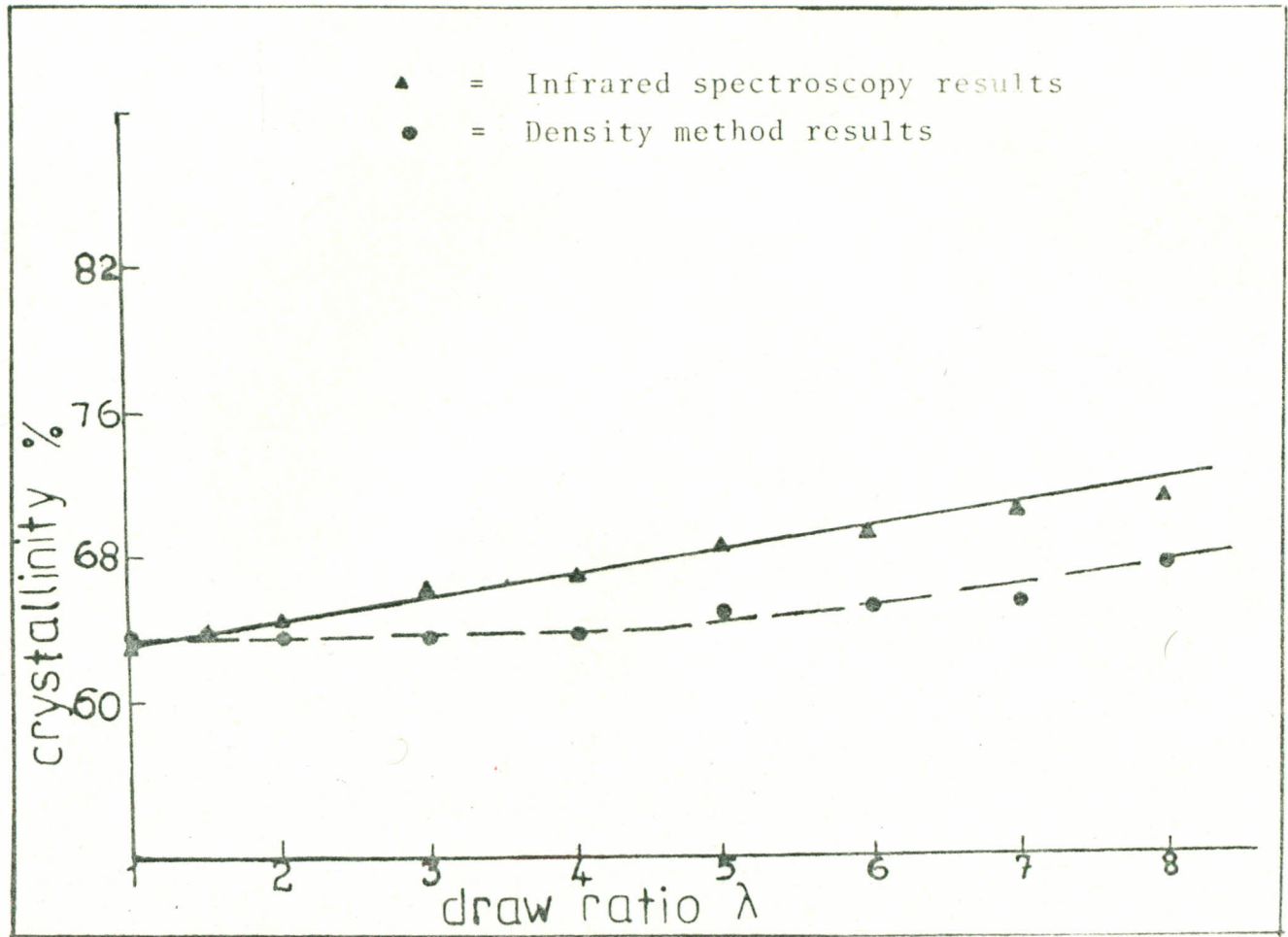


Fig. 7 : Variation of the degree of crystallinity in polypropylene with the increasing draw ratio.

Table 1 : The Variation of crystallinity in polypropylene with draw ratio

| Draw Ratio | Density /gcm ⁻³ | Percent Crystallinity Density Method % | Percent Crystallinity IR-Spectroscopy % |
|------------|-------------------------------|--|---|
| 1 | 0.9064 | 64.2 | 63.6 |
| 1.5 | 0.9062 | 64.0 | 64.0 |
| 2 | 0.9060 | 63.7 | 64.6 |
| 3 | 0.9058 | 63.5 | 66.3 |
| 4 | 0.9058 | 63.5 | 66.9 |
| 5 | 0.9068 | 64.7 | 68.4 |
| 6 | 0.9068 | 64.7 | 68.7 |
| 7 | 0.9071 | 65.0 | 70.6 |
| 8 | 0.9084 | 66.6 | 71.8 |

5.0.2 HEAT CAPACITY RESULTS

- (i) The results for the variation of the heat capacity with draw ratio, for polypropylene and polystyrene samples drawn at 120°C, are graphically represented by figures 8a and 8b respectively. The corresponding data are given by tables 2a and 2b respectively.

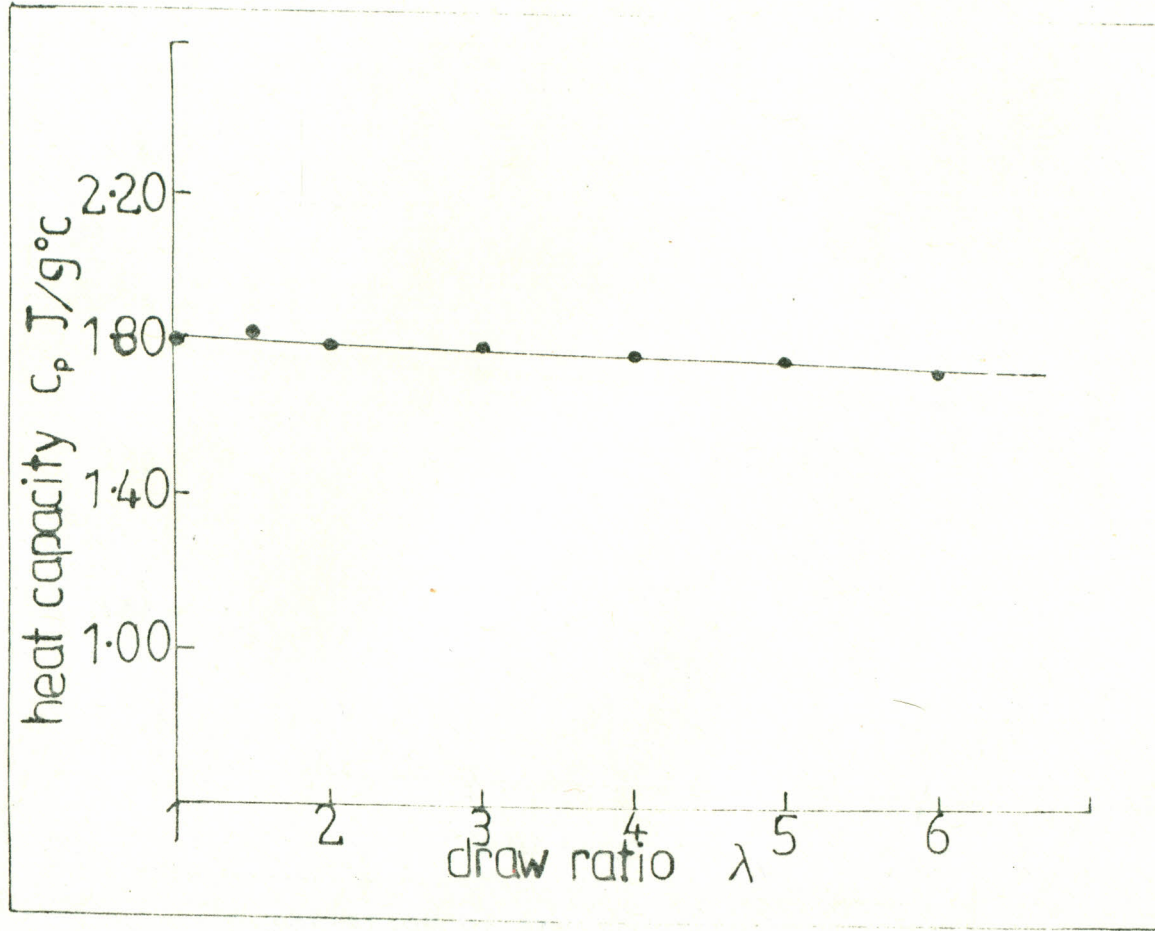


Fig. 8a : The variation of the heat capacity of polypropylene at 298K with the draw ratio.

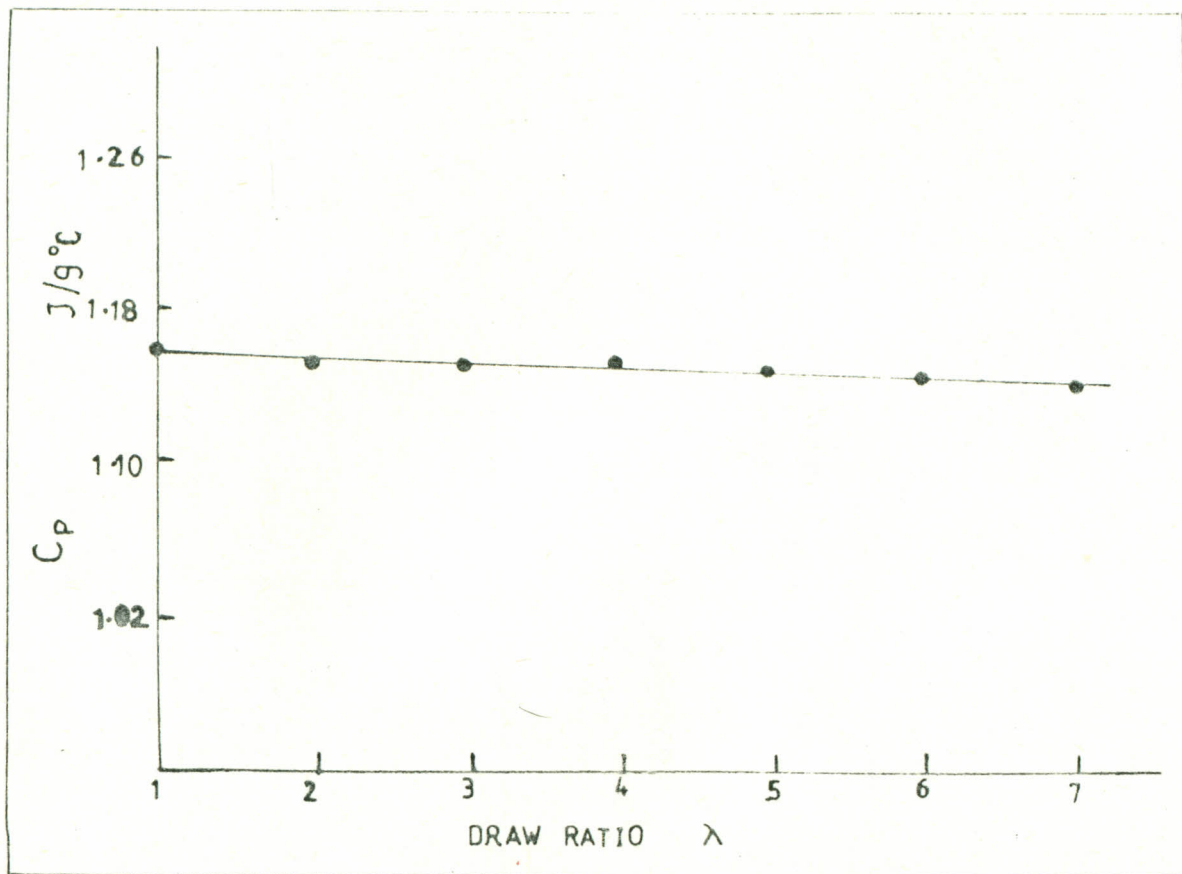


Fig 8b : The variation of the heat capacity of polystyrene at 298K with the draw ratio.

The variation of the heat capacity at 298K with draw ratio, for samples drawn at 120°C

Table 2a : Polypropylene

| Draw Ratio | Heat Capacity C_p / J/g°C |
|------------|--------------------------------|
| 1 | 1.786 |
| 1.5 | 1.797 |
| 3 | 1.793 |
| 4 | 1.771 |
| 5 | 1.726 |
| 6 | 1.680 |

Table 2b : Polystyrene

| Draw Ratio | Heat Capacity |
|------------|---------------|
| 1 | 1.157 |
| 2 | 1.152 |
| 3 | 1.150 |
| 4 | 1.149 |
| 5 | 1.147 |
| 6 | 1.142 |
| 7 | 1.139 |

- (ii) The variations of the heat capacity with temperature, for polypropylene and polystyrene samples in the temperature range of 273K-333K, have been shown in tables 3a and 3b respectively.

The variation of the heat capacity with temperature

Table 3a : Polypropylene

| Temperature /K | Heat Capacity (experimental) C_p J/g°C | Heat Capacity (Theoretical) Eq. 4.3 C_p J/g°C |
|-------------------|--|--|
| 273 | 1.494 | 1.535 |
| 293 | 1.723 | 1.738 |
| 313 | 1.920 | 1.940 |
| 323 | 2.006 | 2.041 |
| 333 | 2.068 | 2.143 |

Table 3b : Polystyrene

| Temperature /K | Heat Capacity C_p J/g°C |
|-------------------|------------------------------|
| 273 | 1.138 |
| 293 | 1.152 |
| 298 | 1.157 |
| 303 | 1.166 |
| 313 | 1.201 |
| 333 | 1.332 |

5.0.3 THERMAL CONDUCTIVITY RESULTS

- (i) Figures 9a and 9b given below show the variation of thermal conductivity with draw ratio , at 298K, for polypropylene and polystyrene samples, respectively, that were drawn at 120°C at the draw rate of 0.005cm/sec. Tables 4a and 4b give the corresponding data.

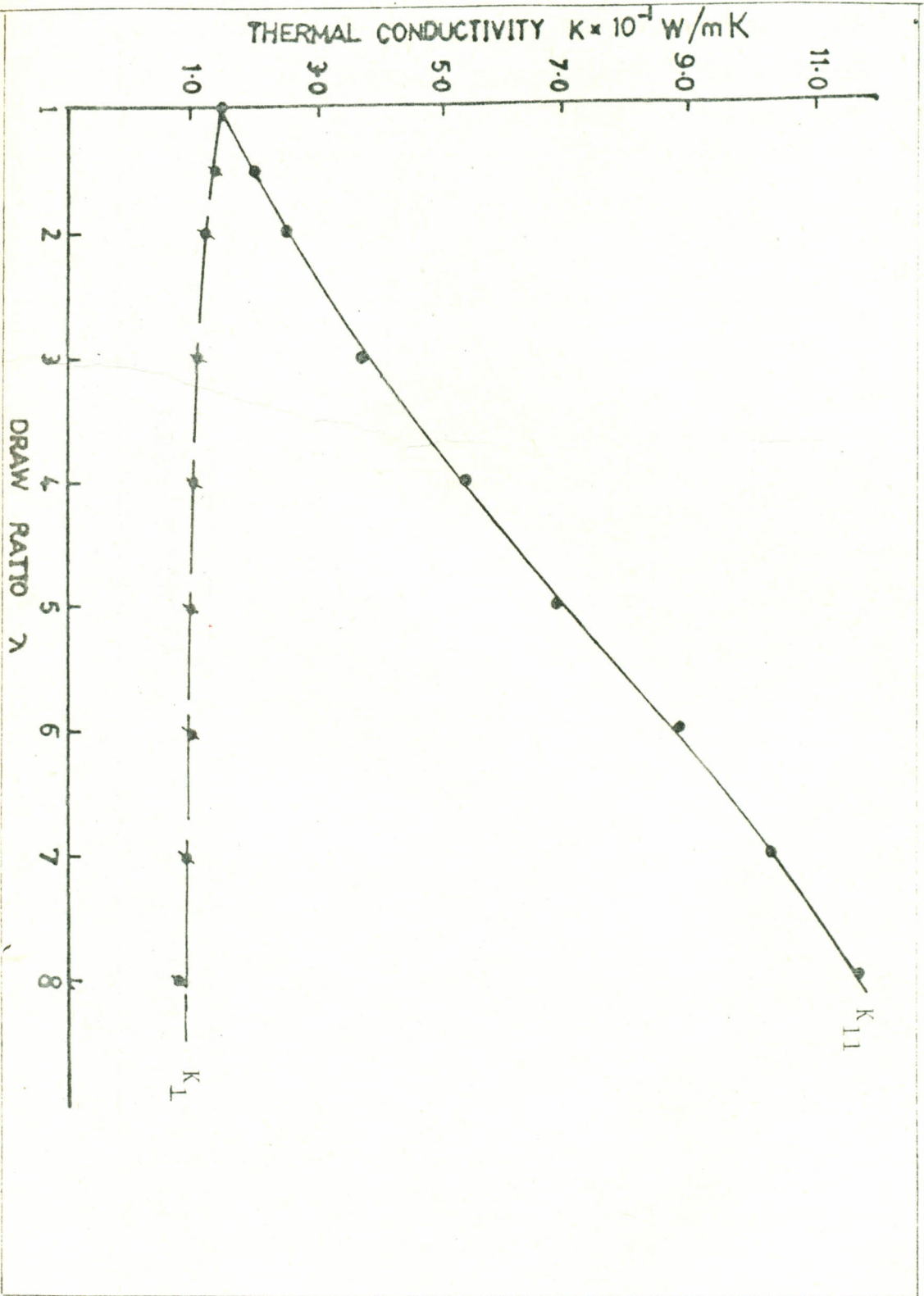


Fig. 9a : The variation of the thermal conductivity of polypropylene at 298K with draw ratio, for samples drawn at 120°C.

K_{11} —●—●— results along the draw direction

K_{\perp} —*—*— results in the perpendicular direction

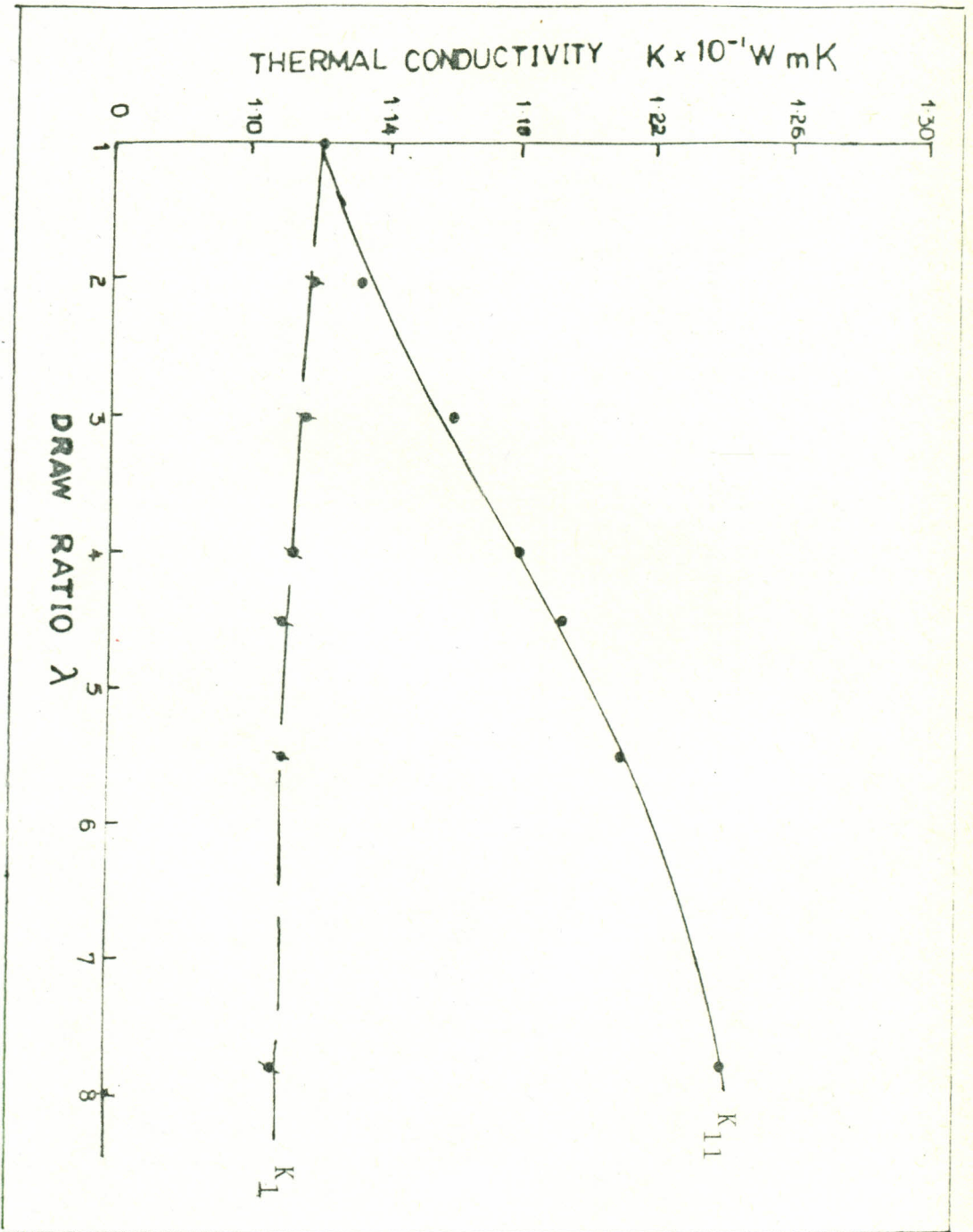


Fig. 9b : The variation of the thermal conductivity of polystyrene at 298K with draw ratio, for samples drawn at 120°C.

K_{11} —●—●—

results along the draw direction

K_1 —◐—◐—

results in the perpendicular direction

Table 4a : The variation of thermal conductivity for polypropylene with draw ratio, at 298K, for samples drawn at 120°C

| Draw Ratio λ | Thermal Cond. (EXP) | Thermal Cond. (EXP) | Theoretical values of K_{11} , $\times 10^{-1}$ w/mK, based on:- | | | |
|-------------------------|---------------------------------|------------------------------|--|-----------|--------------------|-------------|
| | $K_{\perp} \times 10^{-1}$ w/mK | $K_{11} \times 10^{-1}$ w/mK | Eq. (5.13) $\phi \rightarrow$ table 1 | Eq. (5.6) | Maxwell Eq. (3.12) | Eq. (3.11a) |
| 1 | 1.504 | 1.504 | | - | - | - |
| 1.5 | 1.369 | 2.023 | 2.148 | 1.872 | 1.800 | 1.774 |
| 2 | 1.224 | 2.462 | 2.760 | 2.460 | 2.260 | 2.064 |
| 3 | 1.057 | 3.721 | 3.992 | 3.619 | 3.064 | 2.398 |
| 4 | 0.972 | 5.468 | 5.151 | 4.696 | 3.677 | 2.568 |
| 5 | 0.921 | 6.852 | 6.447 | 5.723 | 4.150 | 2.670 |
| 6 | 0.803 | 8.863 | 8.259 | 7.427 | 4.988 | 2.906 |
| 7 | 0.736 | 10.335 | 9.902 | 8.912 | 7.413 | 3.040 |
| 8 | 0.733 | 11.661 | 11.319 | 9.853 | 7.503 | 3.779 |

Table 4b: The variation of thermal conductivity with draw ratio, at 298K, for polystyrene samples drawn at 120°C.

| Draw Ratio | Density g/cm ³ | Thermal Cond. $K_{\perp} \times 10^{-1} \text{ w/mk}$ | Thermal Cond. $K_{11} \times 10^{-1} \text{ w/mk}$ | Theoretical Values of K_{11} , based on equation 5.6 $K_{11} \times 10^{-1} \text{ w/mk}$ |
|------------|------------------------------|--|---|--|
| 1 | 1.043 | 1.121 | 1.121 | - |
| 2 | 1.042 | 1.118 | 1.131 | 1.131 |
| 3 | 1.040 | 1.114 | 1.160 | 1.154 |
| 4 | 1.040 | 1.112 | 1.180 | 1.175 |
| 4.5 | 1.040 | 1.110 | 1.194 | 1.194 |
| 5.5 | 1.040 | 1.110 | 1.211 | 1.207 |
| 7.8 | 1.041 | 1.108 | 1.242 | 1.259 |

(ii) Results for the variation of the thermal conductivity with temperature, for polypropylene and polystyrene samples that were annealed at 140°C and drawn at 120°C at the rate of 0.005cm/sec.; are graphically represented by figures 10a and 10b respectively. The corresponding data are also presented in tables 5a and 5b respectively.

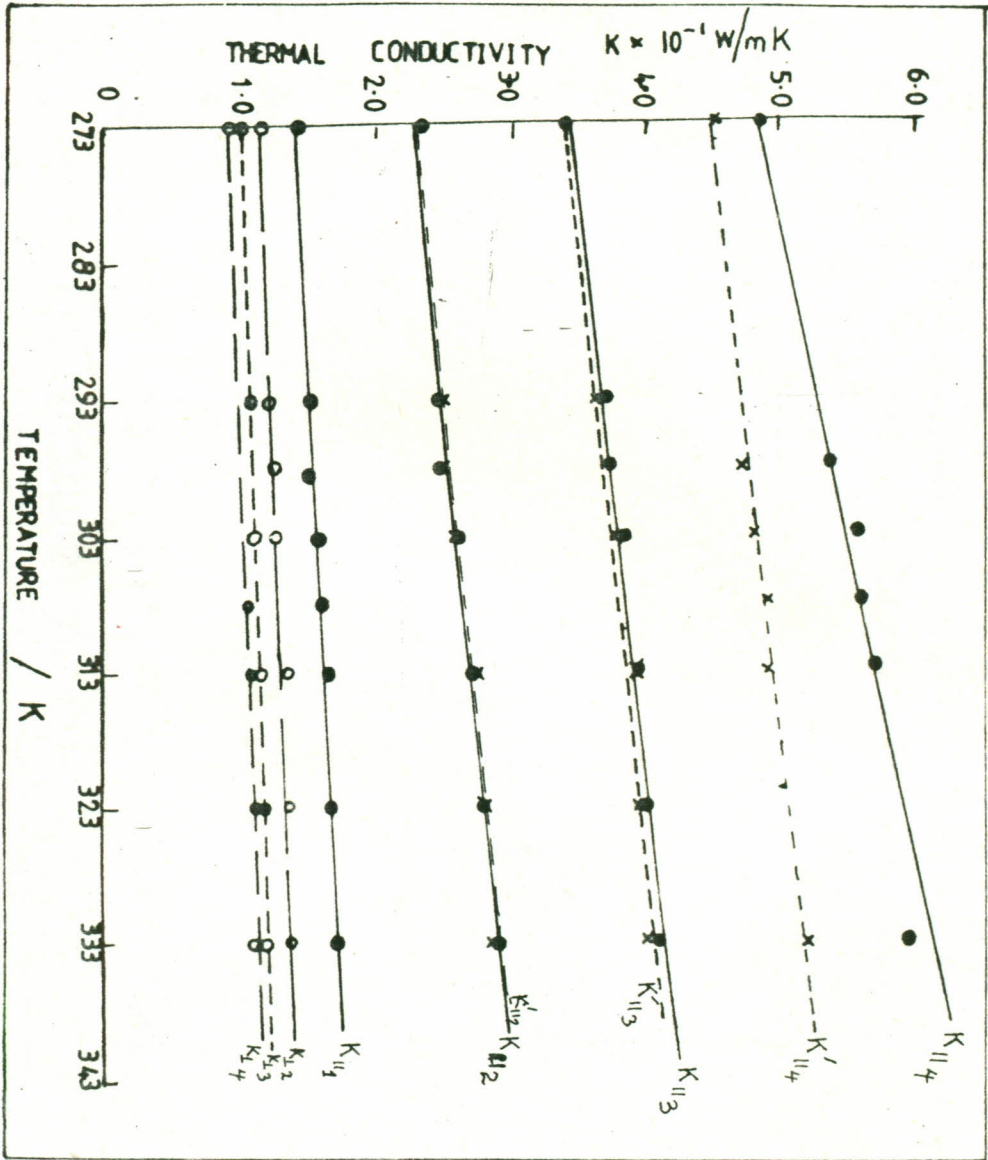


Fig. 10a : The variation of thermal conductivity with temperature, for the polypropylene samples drawn at 120°C.

$K_{11\lambda}$ —●—●— = experimental results along the draw direction, for draw ratio $\lambda=1,2,3$ and 4.

$K'_{11\lambda}$ —x—x—x— theoretical curves derived from equation 5.6, for draw ratios $\lambda=1,2,3$ and 4.

$K_{\perp\lambda}$ —○—○— experimental results in the perpendicular direction, for draw ratios $\lambda=2,3$ and 4.

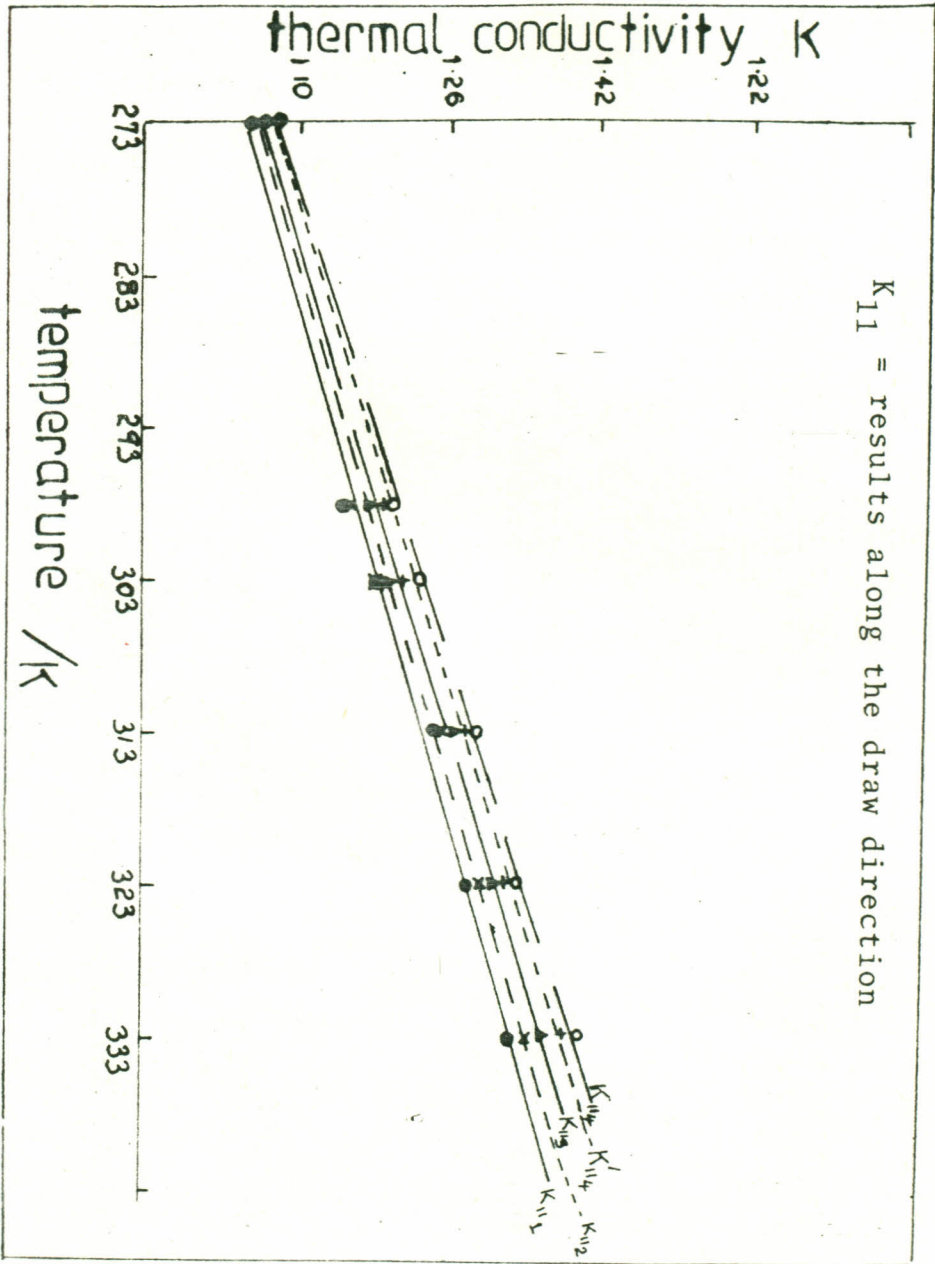


Fig. 10b : The variation of thermal conductivity with temperature, for the polystyrene samples drawn at 120°C.

$K_{11\lambda}$ experimental results along the draw direction, for draw ratios $\lambda=1, 2, 3$ and 4.

$K_{11\lambda}^1$ theoretical curve derived from equation 5.6,

Table (5 a)

The variation of thermal conductivity with temperature, for polypropylene samples drawn at 120°C

| Draw Ratio λ | Temperature /°K | Thermal Conductivity $K_{\perp} \times 10^{-1} \text{ w/mK}$ | Thermal Conductivity $K_{\parallel} \times 10^{-1} \text{ w/mK}$ |
|-------------------------|--------------------|---|---|
| 1 | 273 | 1.424 | 1.420 |
| | 293 | 1.504 | 1.504 |
| | 298 | 1.504 | 1.504 |
| | 303 | 1.574 | 1.575 |
| | 313 | 1.622 | 1.625 |
| | 323 | 1.667 | 1.675 |
| | 333 | 1.688 | 1.720 |
| 2 | 273 | 1.150 | 2.303 |
| | 293 | 1.202 | 2.450 |
| | 298 | 1.224 | 2.462 |
| | 303 | 1.251 | 2.602 |
| | 313 | 1.331 | 2.703 |
| | 323 | 1.341 | 2.770 |
| | 333 | 1.350 | 2.901 |
| 3 | 273 | 1.003 | 3.401 |
| | 293 | 1.061 | 3.702 |
| | 298 | 1.057 | 3.721 |
| | 303 | 1.101 | 3.851 |
| | 313 | 1.163 | 3.950 |
| | 323 | 1.171 | 4.010 |
| | 333 | 1.204 | 4.100 |
| 4 | 274 | 0.903 | 4.840 |
| | 298 | 0.972 | 5.468 |
| | 303 | 1.032 | 5.580 |
| | 308 | 1.051 | 5.601 |
| | 313 | 1.101 | 5.702 |
| | 333 | 1.103 | 5.950 |
| | 5 | 273 | 0.871 |
| 293 | | - | 6.821 |
| 298 | | 0.921 | 6.852 |
| 303 | | 0.986 | 7.150 |
| 308 | | - | 7.302 |
| 313 | | 1.047 | 7.453 |
| 323 | | 1.051 | 8.001 |

Table (5b)

The variation of thermal conductivity with temperature, for polystyrene samples drawn at 120°C

| Draw Ratio λ | Temperature /°K | Thermal Conductivity $K_{\perp} \times 10^{-1} \text{ w/mK}$ | Thermal Conductivity $K_{11} \times 10^{-1} \text{ w/mK}$ |
|-------------------------|--------------------|---|--|
| 1 | 273 | 1.046 | 1.046 |
| | 298 | 1.121 | 1.121 |
| | 303 | - | 1.152 |
| | 313 | 1.218 | 1.218 |
| | 323 | 1.267 | 1.267 |
| | 333 | 1.326 | 1.327 |
| 2 | 273 | 1.046 | 1.056 |
| | 298 | 1.118 | 1.131 |
| | 303 | 1.143 | 1.189 |
| | 313 | 1.212 | 1.239 |
| | 323 | 1.264 | 1.278 |
| | 333 | 1.323 | 1.345 |
| 3 | 273 | 1.044 | 1.059 |
| | 298 | 1.114 | 1.160 |
| | 303 | 1.142 | 1.199 |
| | 313 | 1.211 | 1.256 |
| | 323 | 1.263 | 1.287 |
| | 333 | 1.319 | 1.369 |
| 4 | 273 | 1.043 | 1.069 |
| | 298 | 1.112 | 1.151 |
| | 303 | 1.140 | 1.229 |
| | 313 | 1.210 | 1.269 |
| | 323 | 1.259 | 1.316 |
| | 333 | 1.318 | 1.392 |

(iii) Figures 11a and 11b, shown below, show the graphical representations of the variation of the anisotropy with draw ratio,, for the thermal conductivity results referred to in 5.0.3 (ii).

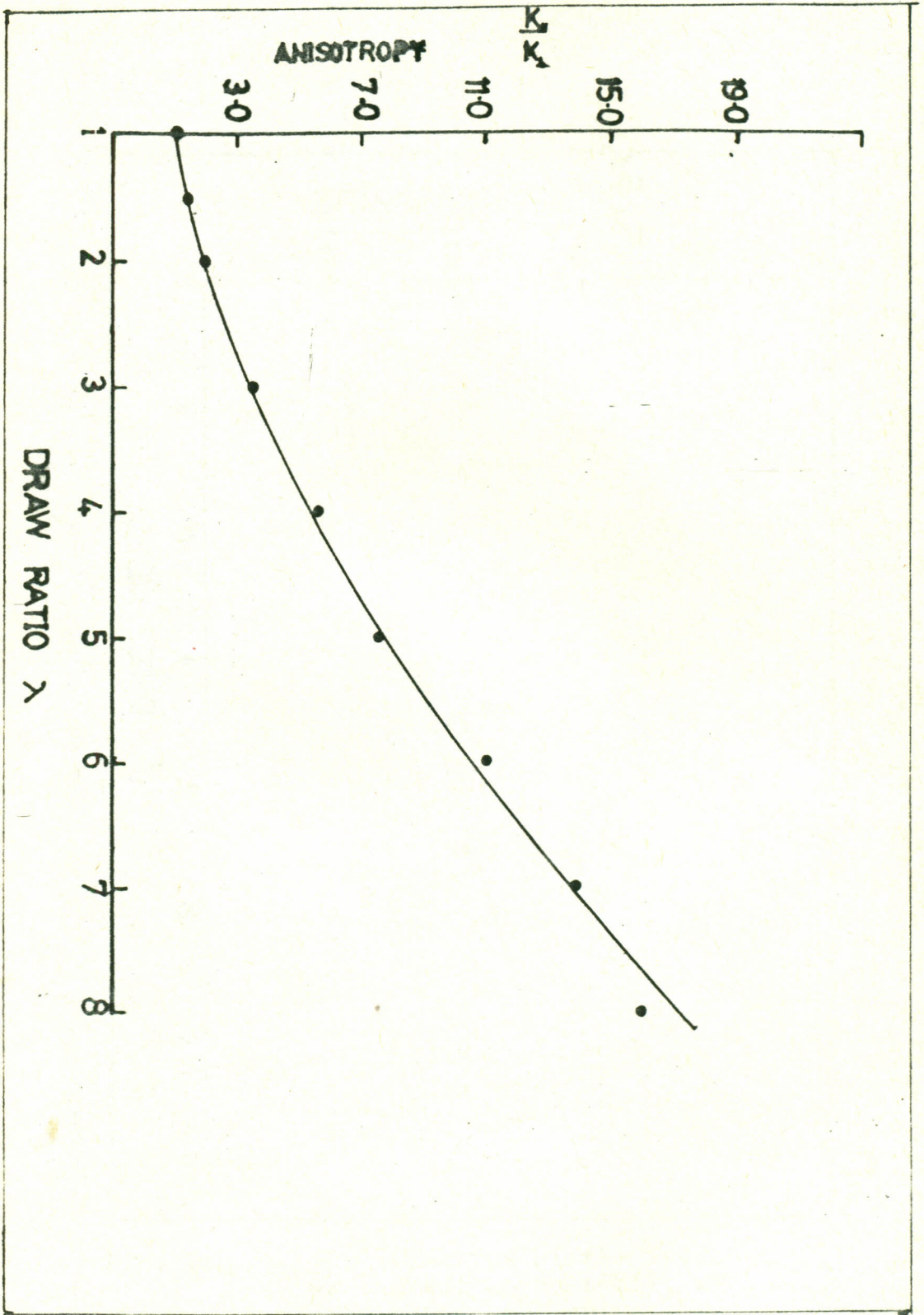


Fig. 11a : The variation of the anisotropy in thermal conductivity with draw ratio, for polypropylene samples drawn at 120°C.

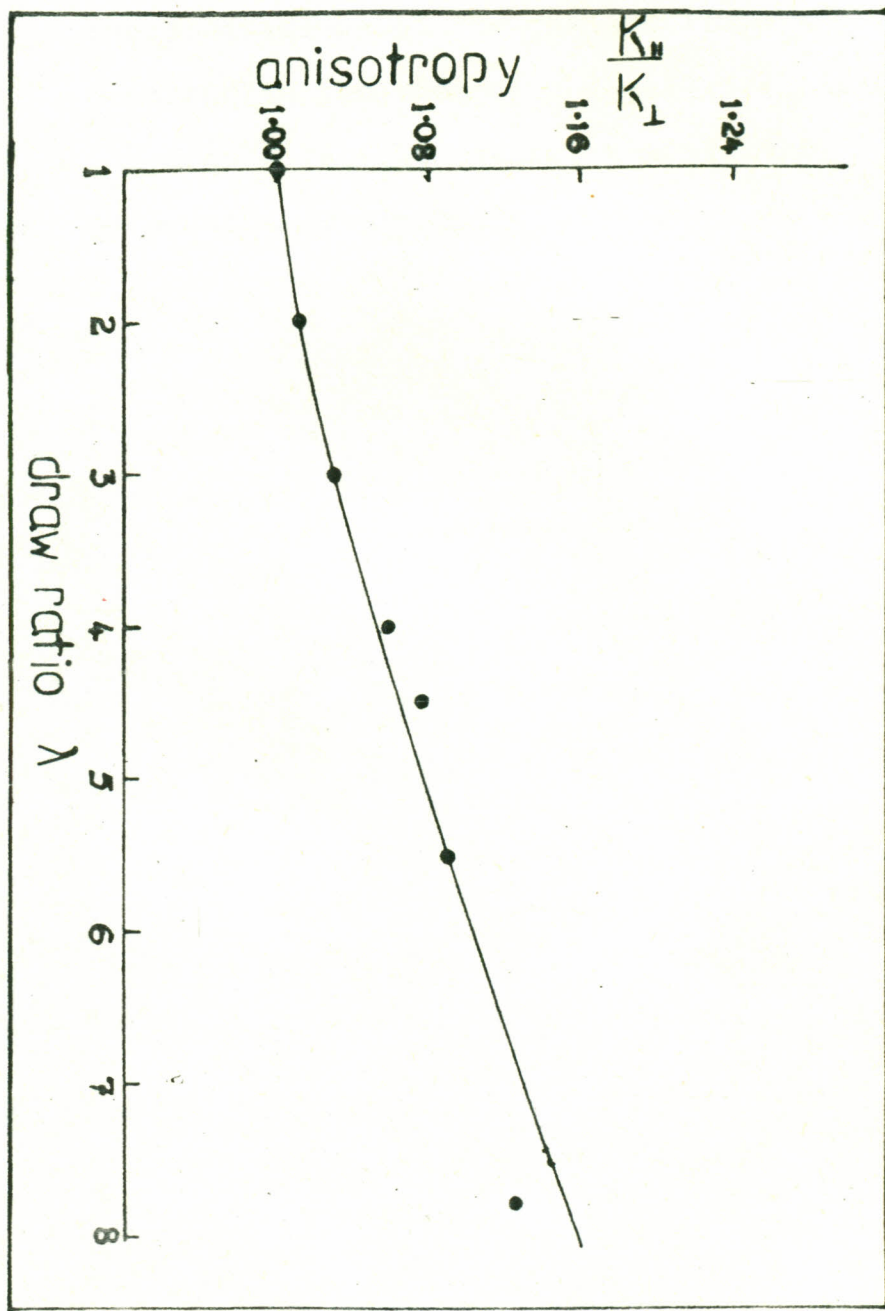


Fig. 11b : The variation of the anisotropy in thermal conductivity with draw ratio, for polystyrene samples drawn at 120°C.

(iv) Figures 11c and 11d show the graphical representations of the changes that occurred in the thermal conductivity along the draw direction against that in the perpendicular direction.

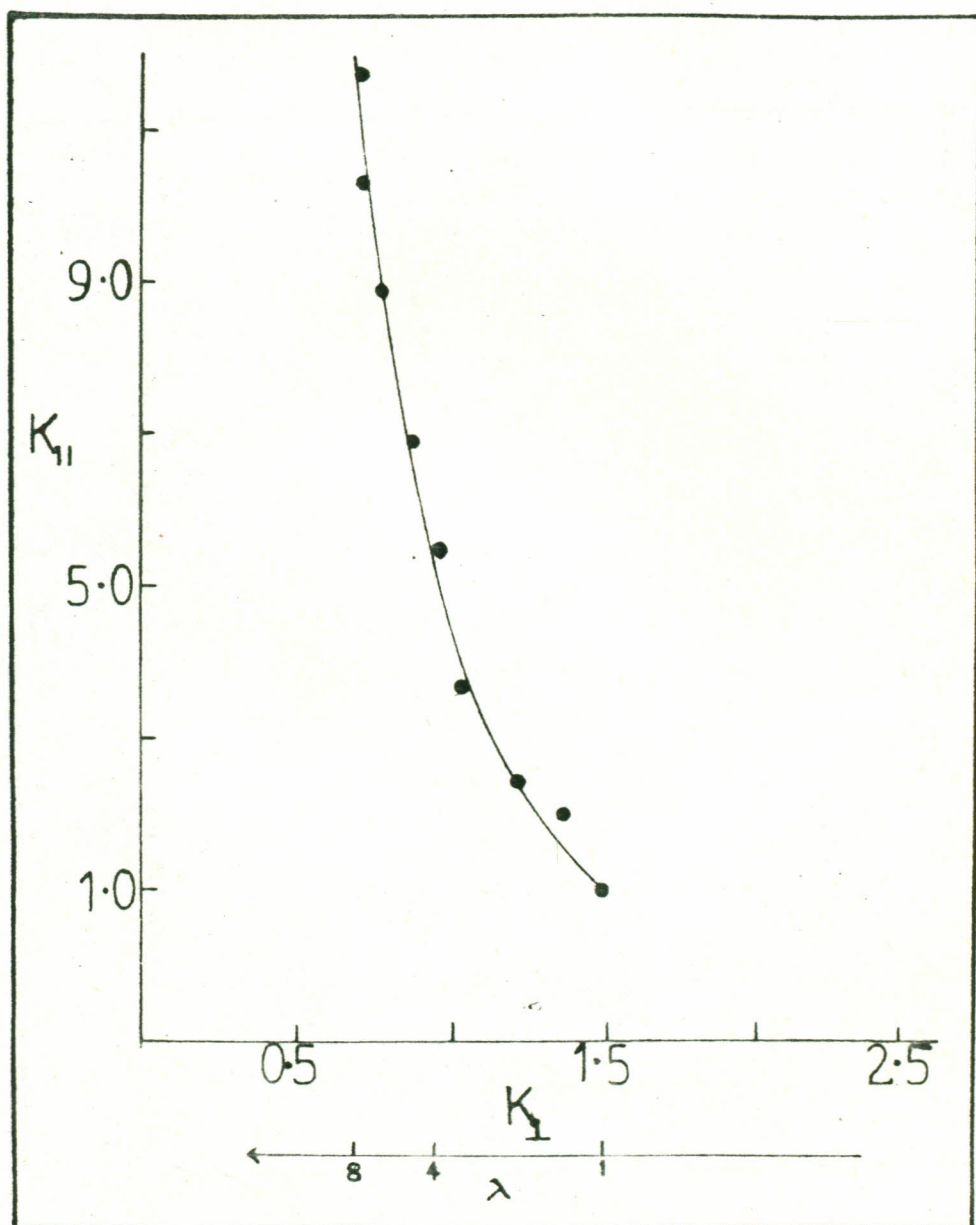


Fig. 11c : Thermal conductivity along the draw direction versus thermal conductivity in the perpendicular direction, for the polypropylene samples drawn at 120°C.

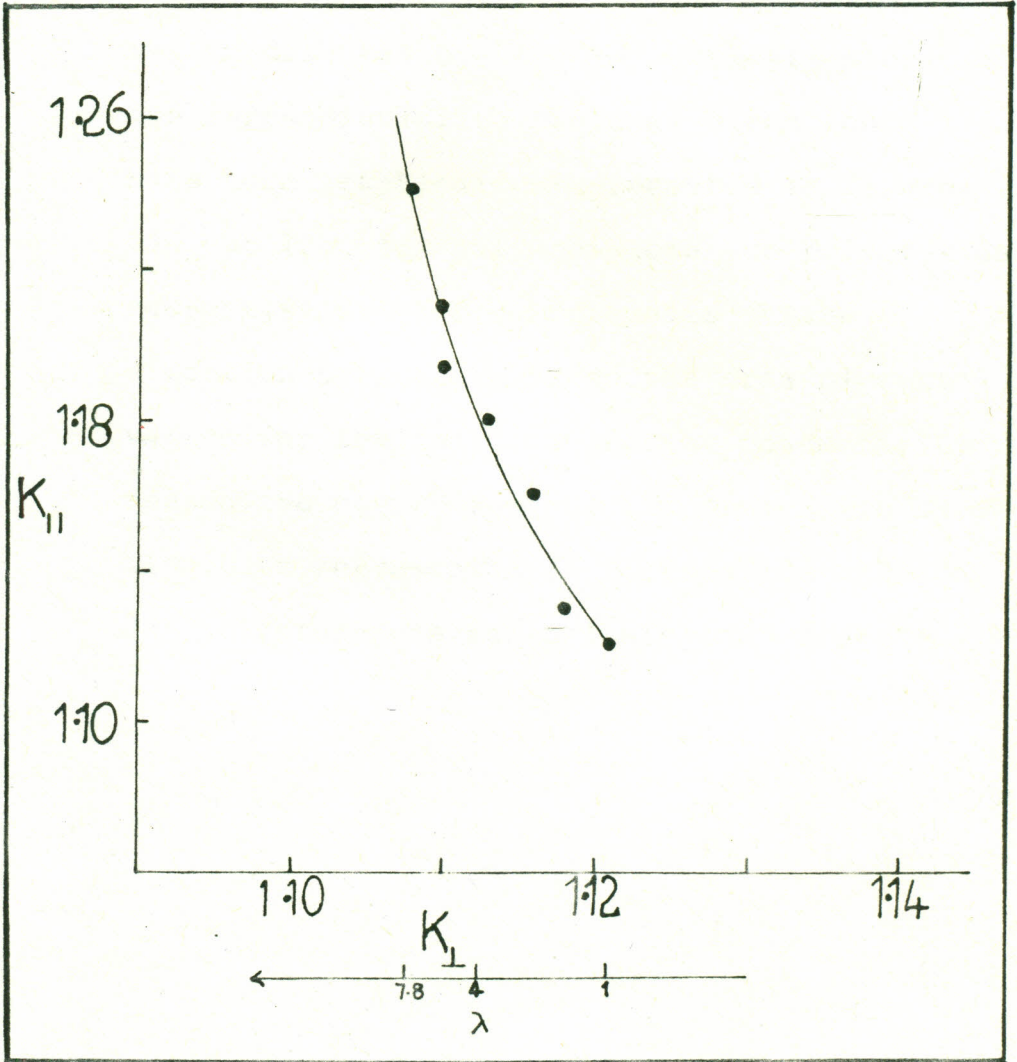


Fig. 11d : Thermal conductivity along the draw direction versus thermal conductivity in the perpendicular direction, for the polystyrene samples drawn at 120°C.

- (v) As another method of analysing the variation of the thermal conductivity with draw ratio, from the results presented in 5.0.3(ii), values for the relative thermal conductivity versus draw ratio, for measurements along and perpendicular to the draw direction, have been graphically represented in figures 12a and 12b, for polypropylene and polystyrene respectively. For measurements in the direction perpendicular to the draw direction, values for the relative thermal conductivity versus the square root of the draw ratio have also been represented in figures 13a and 13b, for polypropylene and polystyrene respectively.

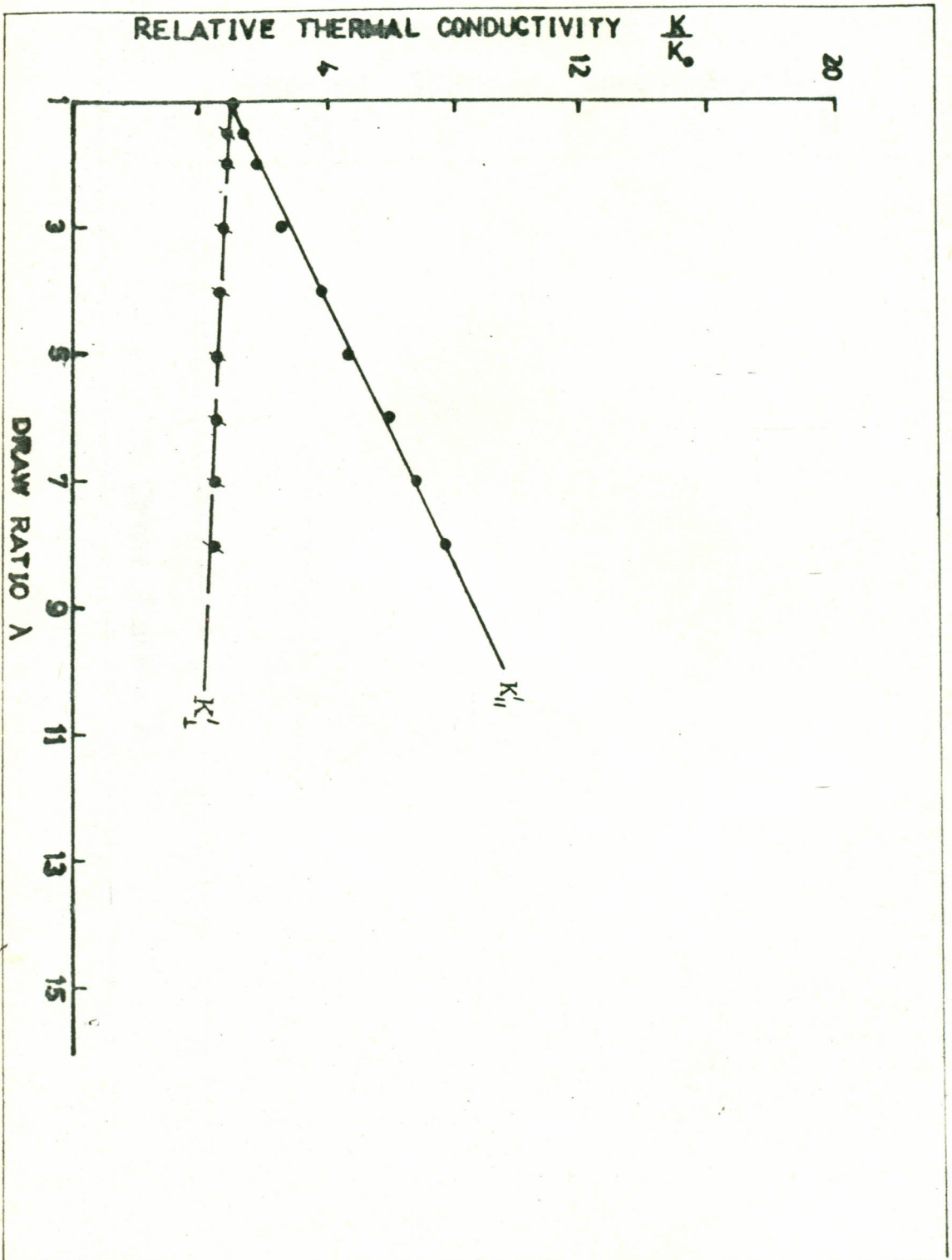


Fig. 12a : Relative thermal conductivity versus draw ratio, for the polypropylene samples drawn at 120°C.

K_{11}^1 —●—●— results along the draw direction

K_{\perp}^1 —■—■— results in the perpendicular direction

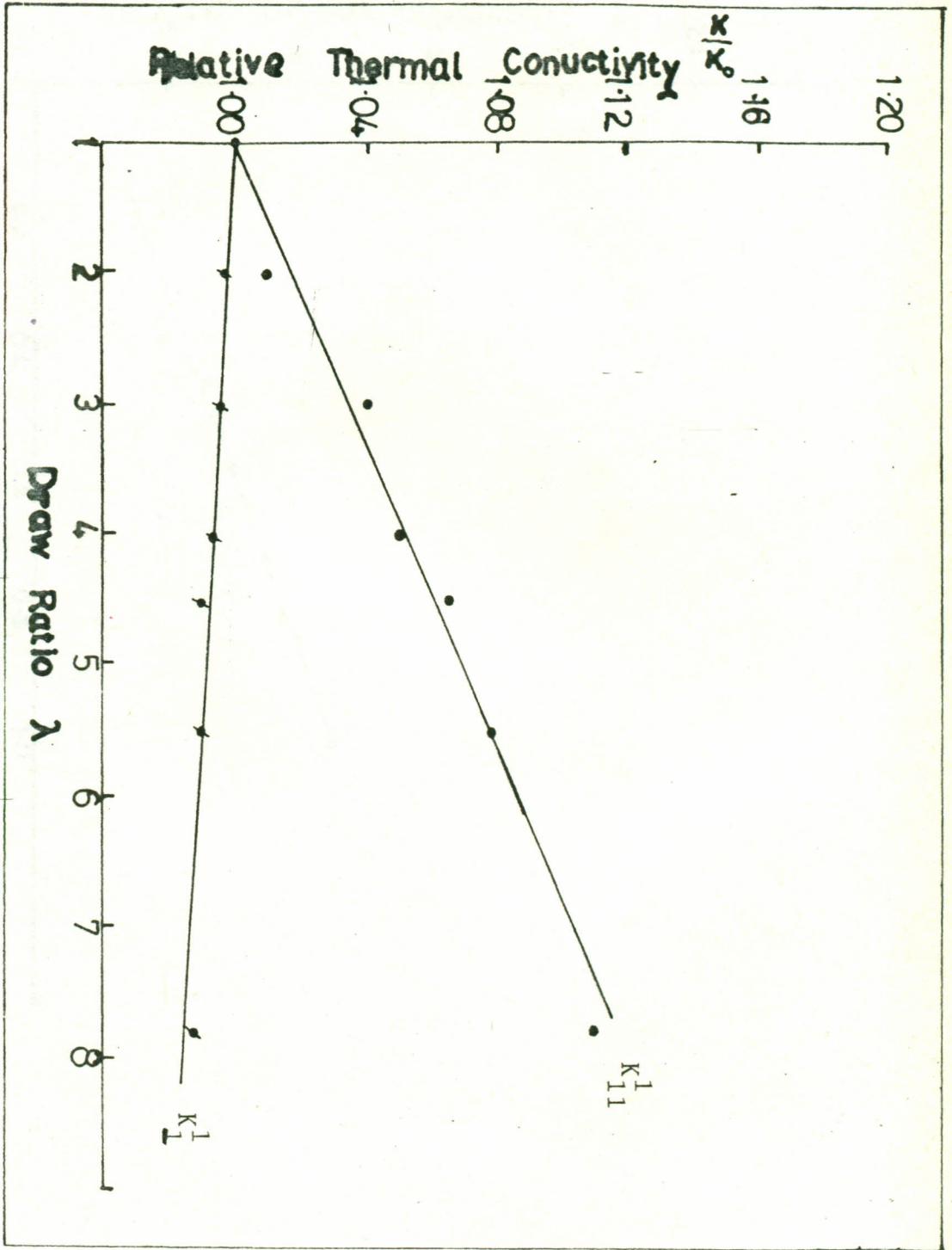


Fig. 12b : Relative thermal conductivity versus draw ratio, for the polystyrene samples drawn at 120°C.

K_{11}^1 —●—●—

results along the draw direction

K_1^1 —◄—◄—

results in the perpendicular direction

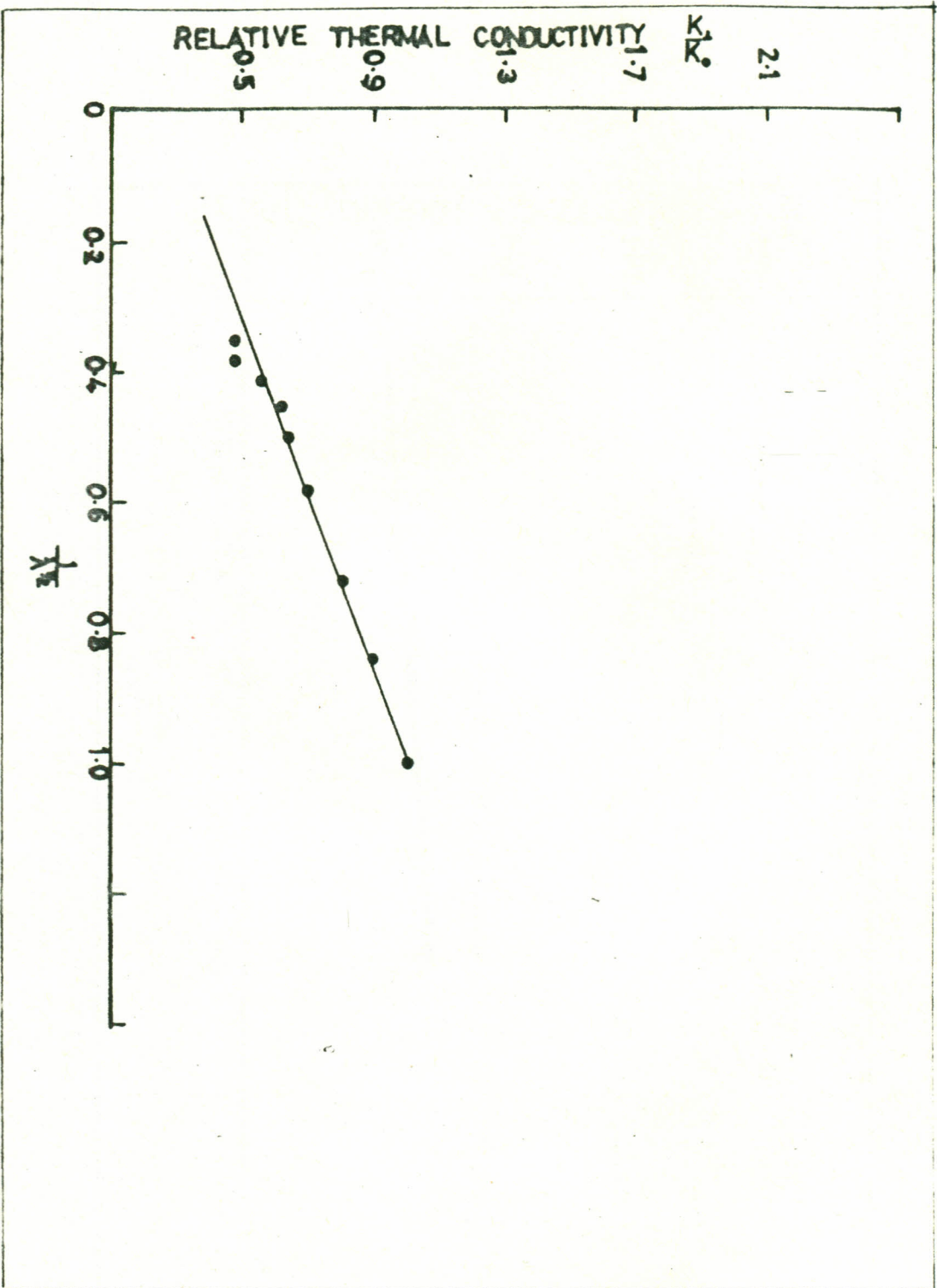


Fig. 13a : Relative thermal conductivity in the perpendicular direction versus the inverse square root of the draw ratio, for polypropylene samples drawn at 120°C.

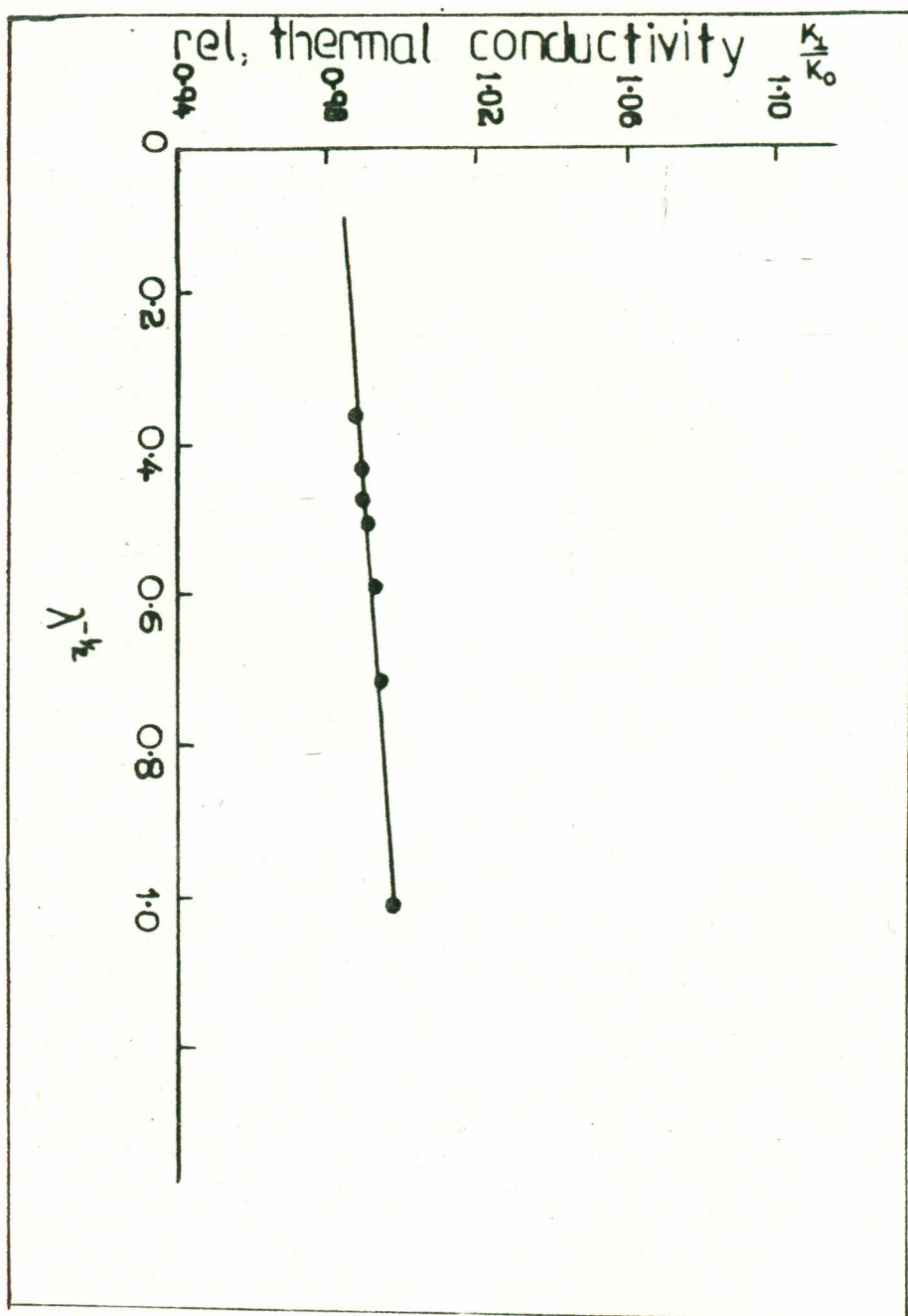


Fig. 13b : Relative thermal conductivity in the perpendicular direction versus the inverse square root of the draw ratio, for polystyrene samples drawn at 120°C.

(vi) A graphical representation of the variation of thermal conductivity with the increasing crystallinity in isotropic polypropylene, at 298K, is given in figure 14, and the corresponding data are summarized in table 6 below.

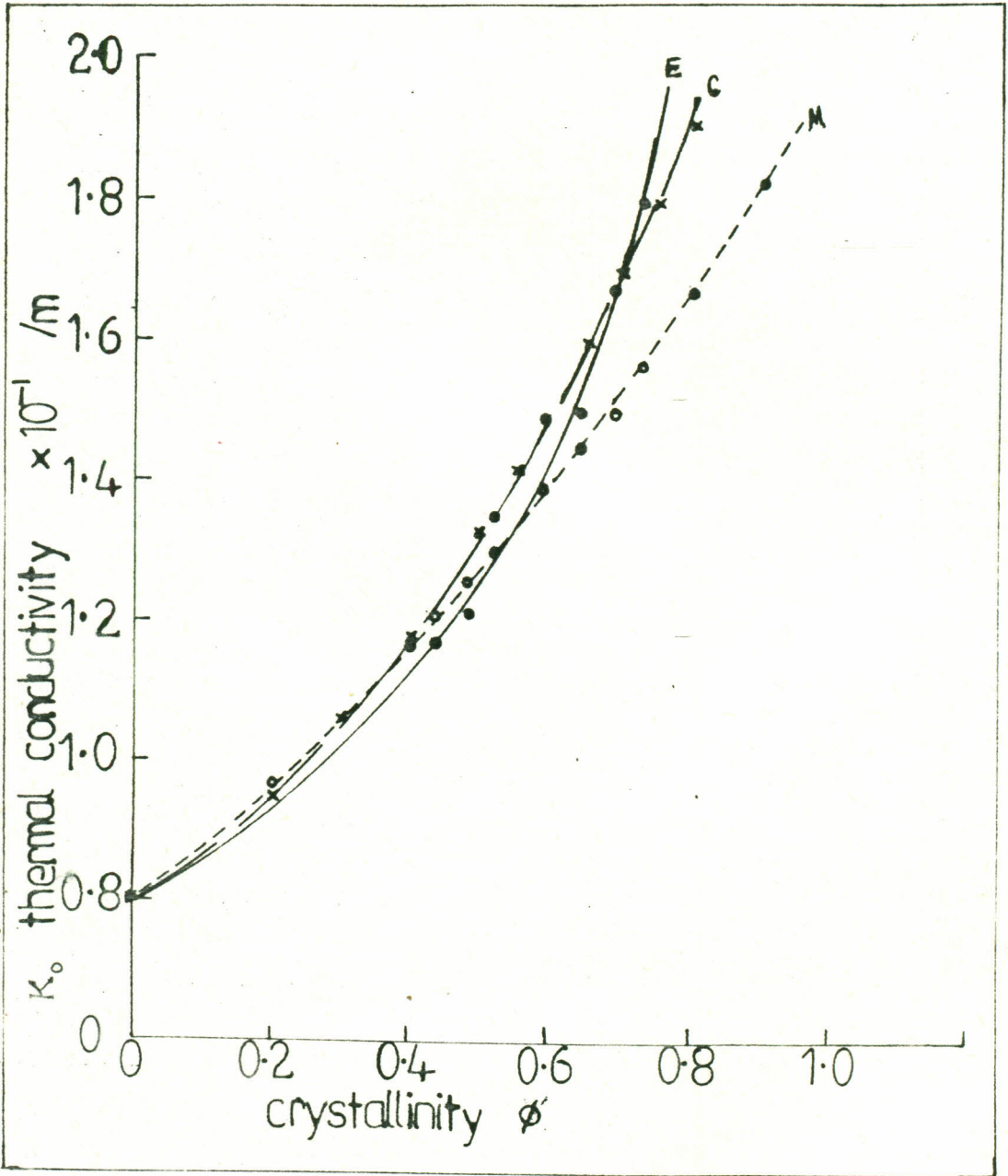


Fig. 14 : The variation of the thermal conductivity of polypropylene at 298K with crystallinity, isotropic samples

E —●—●— experimental curve

C —*—*— curve derived from the proposed model of equation 5.12

M —○—○— curve derived from the Maxwell model of equation 3.15

Table 6 : The variation of thermal conductivity, at 298K, with crystallinity in polypropylene samples

| Sample Treatment | Density /gcm ⁻³ | Percent Crystallinity % | Thermal cond. K _o x10 ⁻¹ w/mK |
|---|-------------------------------|-------------------------------|---|
| (i) Quenched in water at 25°C | 0.8893 | 43.5 | 1.172 |
| (ii) Quenched as in (i) and annealed at 140°C for ½ hr | 0.8931 | 48.3 | 1.207 |
| (iii) Air cooled to room temperature | 0.8964 | 52.1 | 1.354 |
| (iv) Treated as in (iii) and annealed at 140°C for 2½ hr | 0.9021 | 59.0 | 1.494 |
| (v) Treated as in (iii) and annealed at 140°C for 6 hr | 0.9064 | 64.0 | 1.502 |
| (vi) Treated as in (iii) and annealed at 140°C for 18 hr | 0.9103 | 69.0 | 1.669 |
| (vii) Treated as in (iii) and annealed at 140°C for 28 hr | 0.9136 | 73.0 | 1.804 |

(vii) Results for the variation of thermal conductivity with draw ratio, at 298K, for polypropylene and polystyrene samples drawn at different temperatures (100°C, 120°C and 140°C) at the draw rate of about 0.005cm/sec, are given below. Figures 15a and 15b show the graphical representation of the results and tables 7a and 7b give the actual corresponding data obtained.

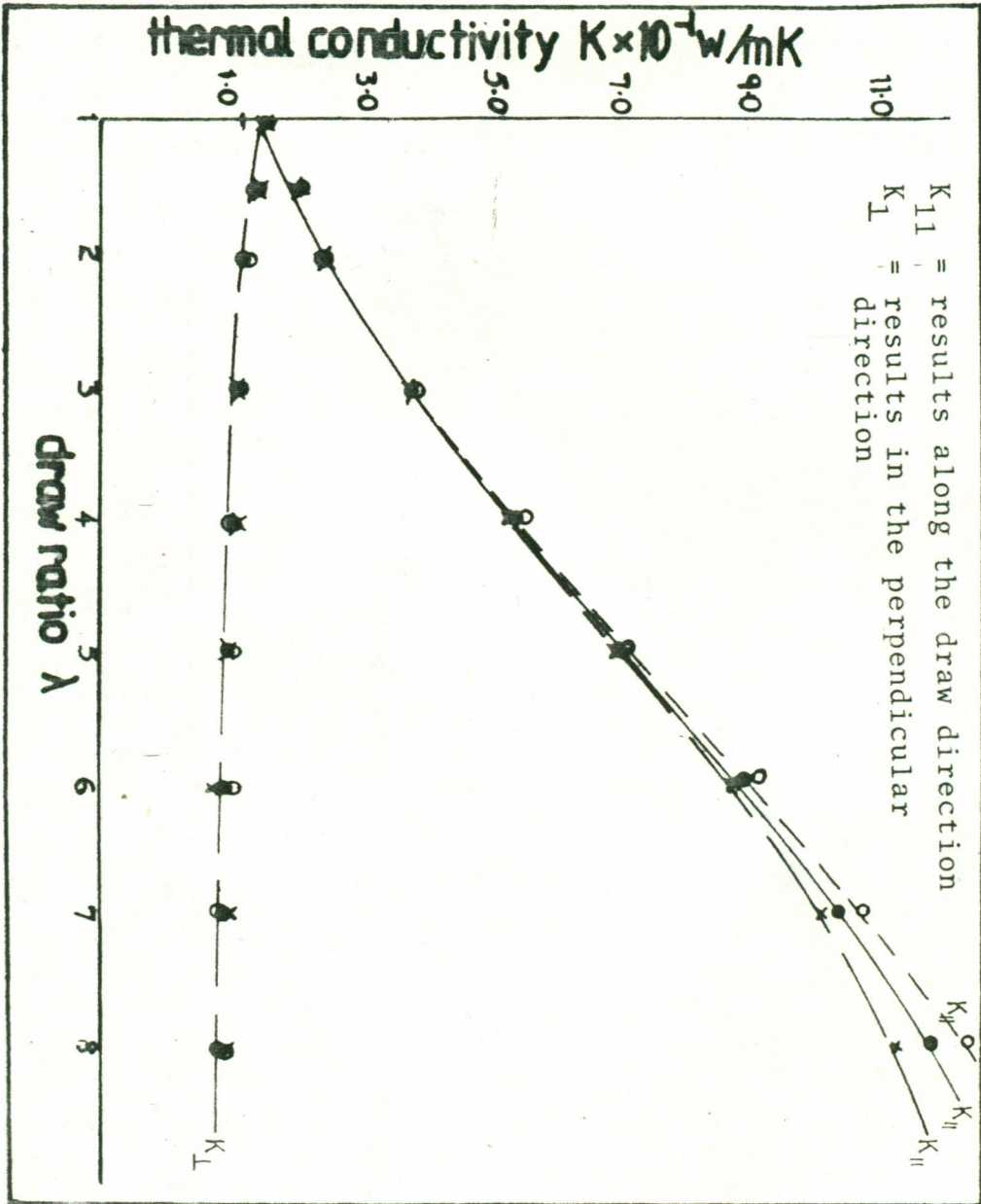


Fig. 15a : The variation of the thermal conductivity of polypropylene with draw temperature.

- $K_{||}$ — ○ — ○ — curve for the draw temperature of 100°C
- $K_{||}$ — ● — ● — curve for the draw temperature of 120°C
- $K_{||}$ — × — × — curve for the draw temperature of 140°C
- K_{\perp} — ○ — ○ — , ● — ● — , × — × — results for the draw temperatures of 100°C, 120°C and 140°C respectively.

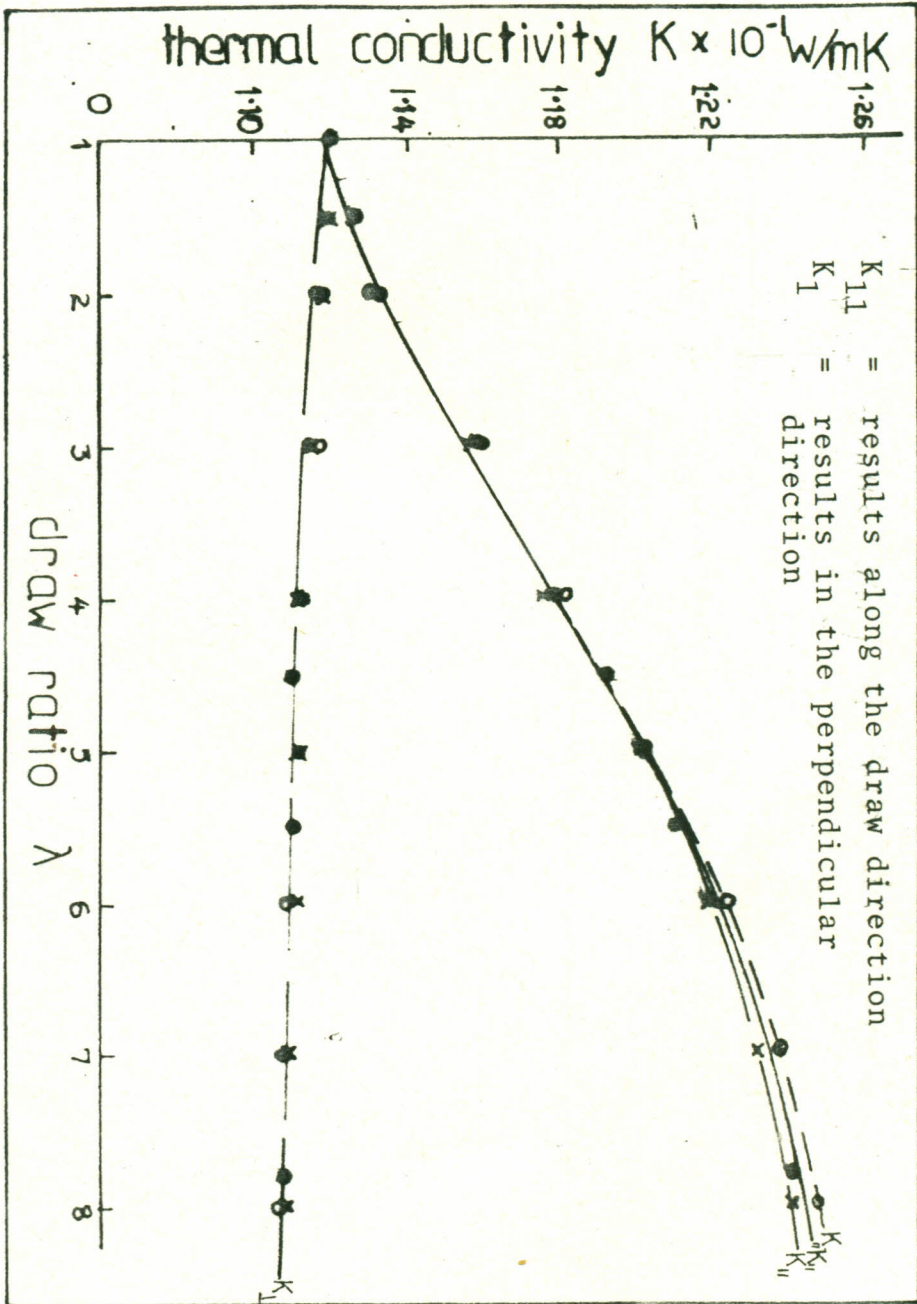


Fig. 15b : The variation of the thermal conductivity of polystyrene with draw temperature.

$K_{1,1}$ —○—○— curves for the draw temperature of 100°C
 $K_{1,1}$ —●—●— curves for the draw temperature of 120°C
 $K_{1,1}$ —x—x— curves for the draw temperature of 140°C
 K_{\perp} —○—○—, —●—●—, —x—x— results for the draw temperatures of 100°C, 120°C and 140°C respectively.

Table 7a : The variation of thermal conductivity, at 298K, with draw temperature, for drawn polypropylene samples

| Draw Temp. /°C | Draw Ratio λ | Density /gcm ⁻³ | Thermal cond. K ₁ x10 ⁻¹ w/mK | Thermal Cond. K ₁₁ x10 ⁻¹ w/mK |
|-------------------|-------------------------|-------------------------------|--|---|
| 100 | 1 | 0.9064 | 1.504 | 1.504 |
| | 1.5 | 0.9063 | 1.371 | 2.024 |
| | 2 | 0.9060 | 1.226 | 2.461 |
| | 3 | 0.9058 | 1.057 | 3.721 |
| | 4 | 0.9057 | 0.970 | 5.470 |
| | 5 | 0.9068 | 0.923 | 7.051 |
| | 6 | 0.9068 | 0.805 | 9.332 |
| | 7 | 0.9070 | 0.734 | 10.734 |
| 140 | 8 | 0.9082 | 0.734 | 12.218 |
| | 1 | 0.9064 | 1.504 | 1.504 |
| | 1.5 | 0.9062 | 1.371 | 2.023 |
| | 2 | 0.9061 | | 2.462 |
| | 3 | 0.9057 | 1.057 | 3.720 |
| | 4 | 0.9057 | 0.972 | 5.466 |
| | 5 | 0.9068 | 0.923 | 6.852 |
| | 6 | 0.9068 | 0.803 | 8.820 |
| 7 | 0.9071 | 0.737 | 9.931 | |
| | 8 | 0.9082 | 0.736 | 10.054 |

Table 7b : The variation of thermal conductivity with draw temperature, for drawn polystyrene samples, at 298K

| Draw Temp. /°C | Draw Ratio λ | Density /gcm ⁻³ | Thermal Cond. K ₁₁ x10 ⁻¹ w/mK | Thermal Cond. K _⊥ x10 ⁻¹ w/mK |
|-------------------|-------------------------|-------------------------------|---|--|
| 100 | 1 | 1.043 | 1.121 | 1.121 |
| | 1.5 | 1.042 | 1.126 | 1.120 |
| | 2 | 1.042 | 1.133 | 1.118 |
| | 3 | 1.040 | 1.161 | 1.118 |
| | 4 | 1.039 | 1.182 | 1.113 |
| | 5 | 1.039 | 1.204 | 1.112 |
| | 6 | 1.040 | 1.224 | 1.110 |
| | 7 | 1.041 | 1.238 | 1.110 |
| 140 | 8 | 1.041 | 1.248 | 1.108 |
| | 1 | 1.043 | 1.121 | 1.121 |
| | 1.5 | 1.043 | 1.126 | 1.120 |
| | 2 | 1.042 | 1.131 | 1.117 |
| | 3 | 1.040 | 1.156 | 1.116 |
| | 4 | 1.040 | 1.175 | 1.113 |
| | 5 | 1.039 | 1.201 | 1.112 |
| | 6 | 1.040 | 1.219 | 1.112 |
| 7 | 1.040 | 1.232 | 1.111 | |
| 8 | 1.041 | 1.242 | 1.109 | |

(viii) Results for the variation of the thermal diffusivity with temperature, for isotropic and drawn polypropylene samples, are shown in figure 16.

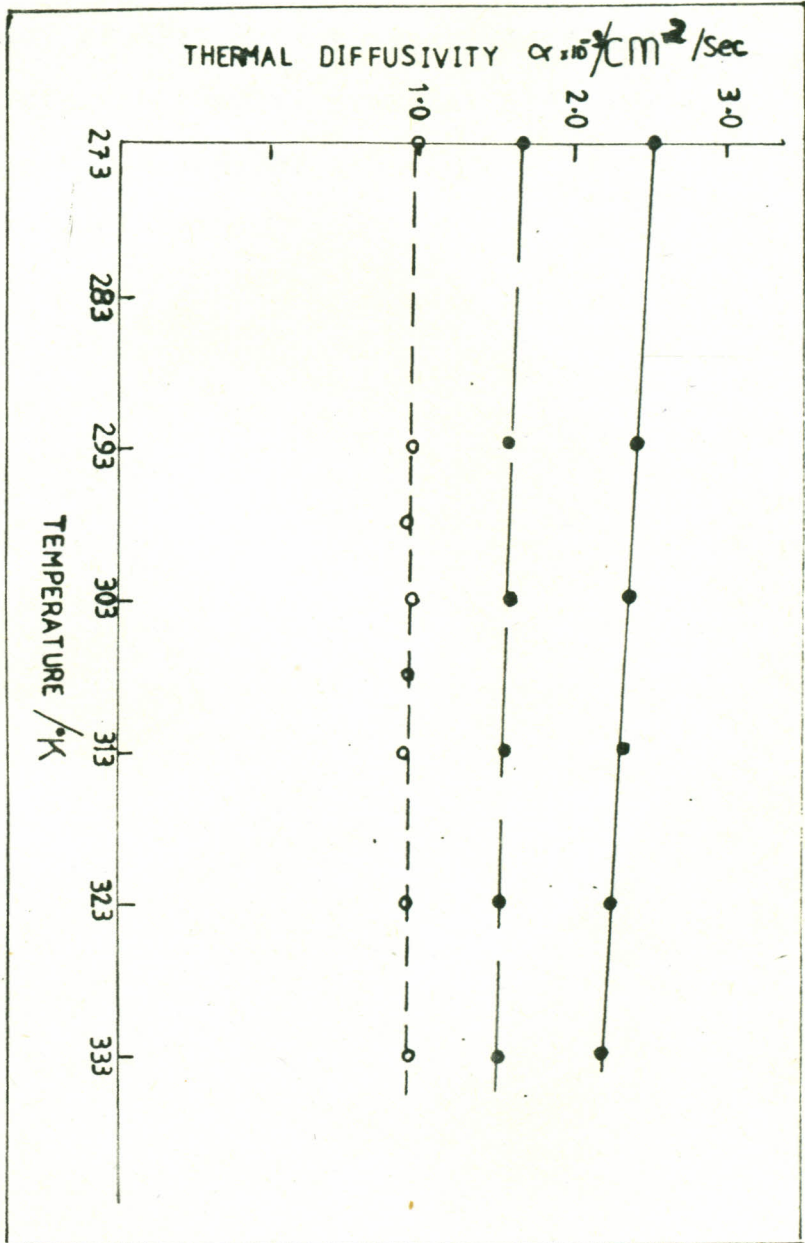


Fig. 16 : The variation of the thermal diffusivity with temperature, for drawn and isotropic polypropylene samples.

- o - o - o isotropic sample
- ● - ● - ● drawn sample $\lambda=2$
- ● - ● - ● drawn sample $\lambda=3$

- (ix) The experimental and theoretical curves for the variation of thermal conductivity with draw ratio, at 298K, for polypropylene and polystyrene samples drawn at 398K are shown in figures 17a and 17b.

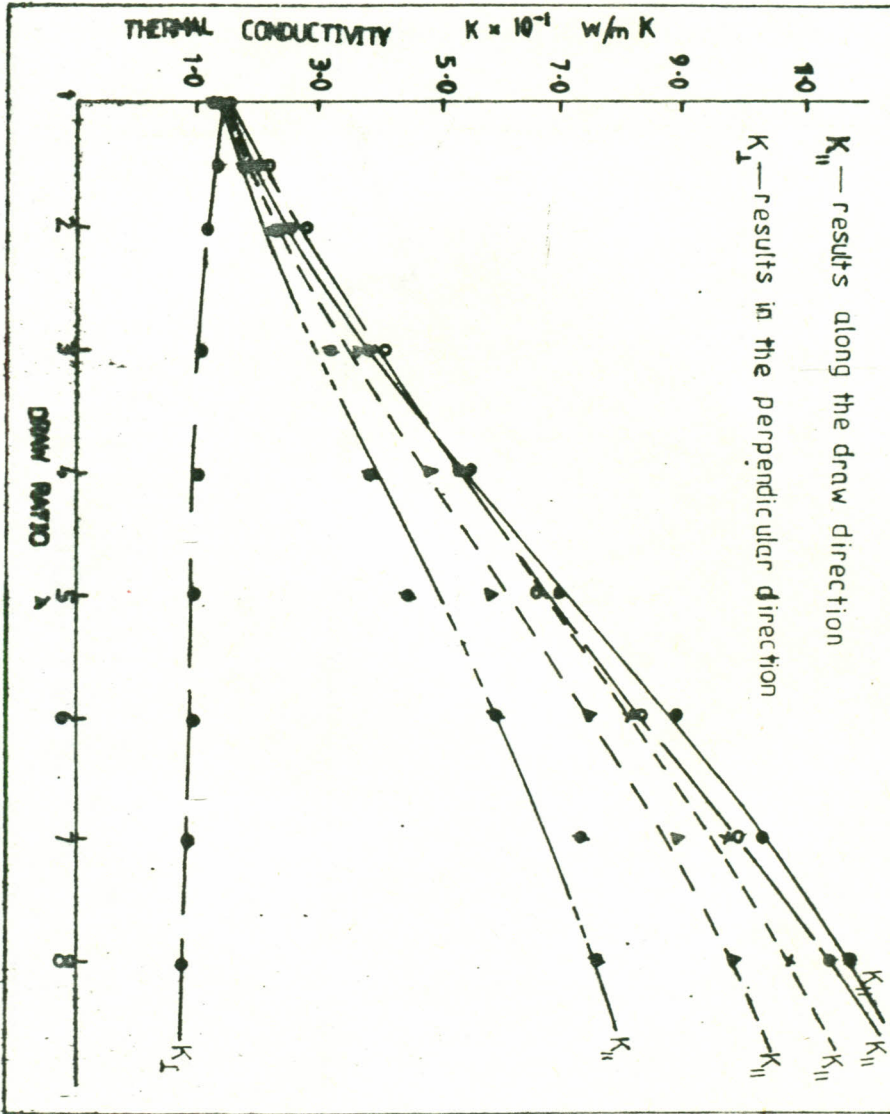


Fig. 17a : Thermal conductivity versus draw ratio, at 393K, for polypropylene samples drawn at

- K_{\parallel} —●—●— experimental curve
- K_{\parallel} —○—○— the curve derived from equation 5.13, stretch induced crystallinity included;
- K_{\parallel} —x—x— the curve derived from equation 5.13, stretch induced crystallinity neglected;
- K_{\parallel} —▲—▲— the curve derived from equation 5.6;
- K_{\parallel} —◆—◆— the curve derived from the Maxwell model of equation 3.12;
- K_{\perp} —●—●— experimental curve.

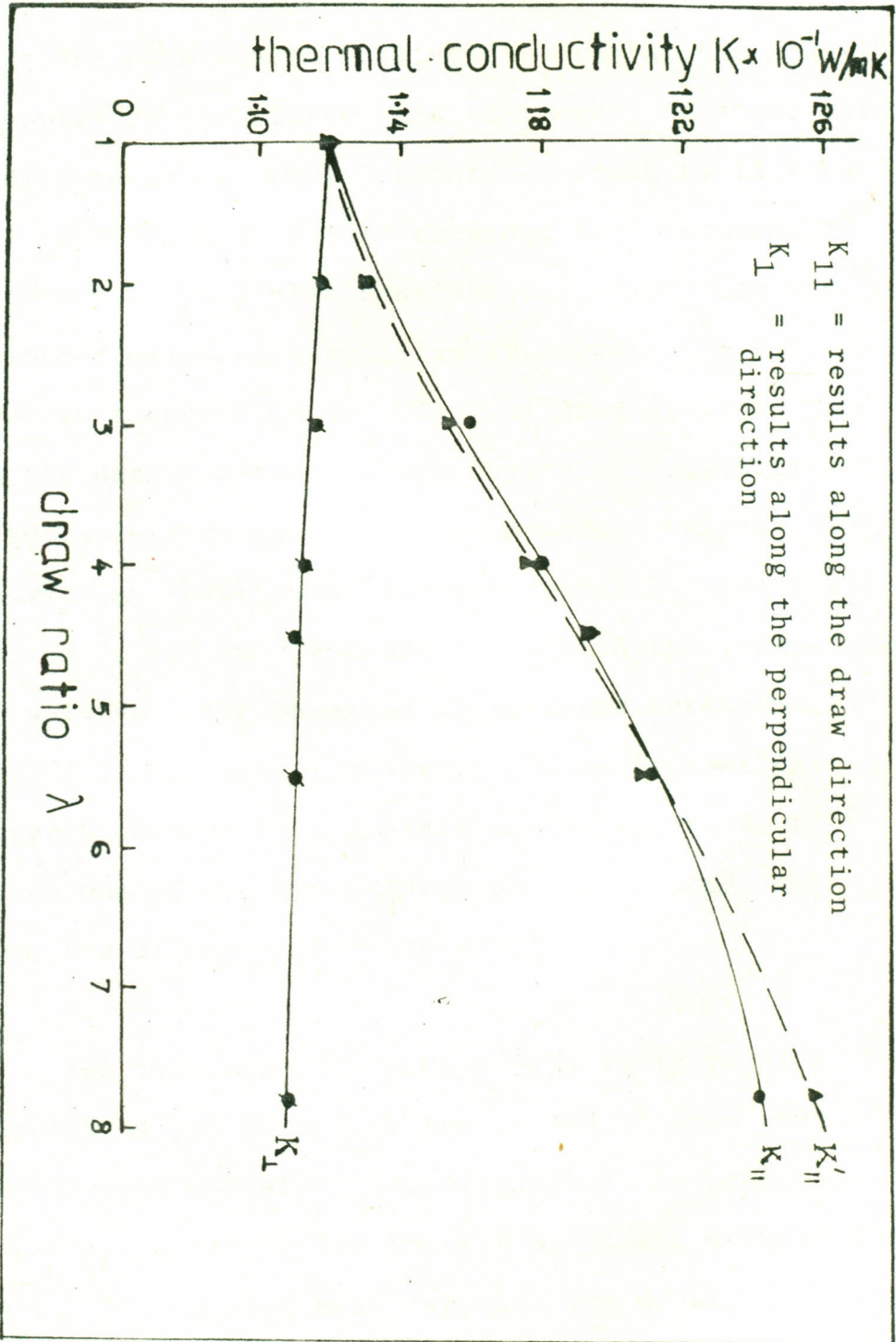


Fig. 17b : The thermal conductivity at 298K versus draw ratio, for polystyrene samples drawn at 393K.

- K_{11} ●—● experimental curve
- K'_{11} ▲—▲ the curve derived from equation 5.6
- K_{\perp} ■—■ experimental curve

Figure 7 shows that while the infrared measured crystallinity for drawn polypropylene starts to increase with the increasing draw ratio, the density measured crystallinity remains roughly constant upto a draw ratio of $\lambda \approx 4.5$ before starting to increase. The crystallinity values obtained from the density measurements are also considerably lower than the infrared measured crystallinity, except for the undrawn sample ($\lambda = 1$). The infrared diagrams used in the determination of the degree of crystallinity, figures 20(a-g) given in the appendix, exhibit increasing absorbance, in the crystalline bands at 809 cm^{-1} , 842 cm^{-1} and 894 cm^{-1} , with the increasing draw ratio. The observed differences between the crystallinity values measured by the two methods suggest changes taking place in the material, to which one of the two methods do not respond, this has been discussed in Chapter 6.

The heat capacity versus draw ratio results, figures 8a and 8b and tables 2a and 2b show that drawing did not significantly affect the heat capacity, at 298K, for the two polymeric materials used. The average heat capacity for drawn polypropylene samples, for the draw ratios of $\lambda = 1-6$, was found to be about 1% less than the value of C_p for isotropic polypropylene sample

at 298K, calculated from equation 4.3, and fairly in good agreement with the value given in the literature [46]. The graphical representations of the heat capacity versus draw ratio results, however, exhibit linear decrease. On physical grounds, one would expect orientation to have very little effect on C_p for polymeric materials in general. This has been reported to be true for draw ratios not too large [16], and Choy, Luk and Chen adopted the same view in their study, for draw ratios of $\lambda = 1 - 25$ [3]. The thermal conductivity for drawn polypropylene and polystyrene samples used in this study were also calculated on the assumption that the heat capacity for the two materials are little affected by stretching, and the values of C_p for the isotropic samples were used for all the drawn samples.

Figures 9a and 9b show that on stretching polypropylene and polystyrene samples, the thermal conductivity increased along the draw direction but decreased in the perpendicular direction. This behavior has been observed at various temperatures, in the range of 273K-333K, figures 10a and 10b. Figures 9a and 9b, however, are just showing what one would expect at any temperature within the range given above. It is also evident

from figures 9a and 9b that although the magnitudes of change in the thermal conductivity of the two materials used were different, their curves exhibit similar shapes. The differences between the thermal conductivity along the draw direction and that in the perpendicular direction, in one material, is an indication of the anisotropy in thermal conductivity. The ratio of the thermal conductivity along the draw direction to that in the perpendicular direction can be used as a measure of the magnitude of the anisotropy developed on stretching a particular material. When this ratio is unity the material is isotropic. Figures 11a and 11b show the anisotropy in thermal conductivity developed on stretching polypropylene and polystyrene samples at 120°C respectively. A comparison of the two curves shows that, the anisotropy developed in polypropylene is greater than that developed in polystyrene, for the same draw ratios.

From the graphical representations of the thermal conductivity along the draw direction versus that in the perpendicular direction it is observed that, in polypropylene the thermal conductivity along the draw direction becomes more rapid at draw ratios greater than four ($\lambda > 4$), figure 11c.

That is, for equal decreases in K_{\perp} , the corresponding increase in K_{11} is becoming rapidly larger. In polystyrene, however, the accompanying magnitudes of change in K_{11} , for equal decreases in K_{\perp} , are comparatively equal for low and high draw ratios. This observation has triggered some questions about the correlation between the draw ratio and the thermal conductivity.

From figures 12a and 12b, which show the graphical representations of the relative thermal conductivity (K/K_0) versus draw ratio (λ), where K represents either K_{11} or K_{\perp} while K_0 is the thermal conductivity of the isotropic sample, K_{11}/K_0 increases linearly with draw ratio, for both polypropylene and polystyrene. On the other hand, figures 13a and 13b show that the relative thermal conductivity in the perpendicular direction (K_{\perp}/K_0) increases linearly with the inverse square root of the draw ratio. The linear relationships for K_{11}/K_0 and K_{\perp}/K_0 may be expressed by equations 5.1a and 5.1b respectively, and the gradients of the curves, for the two materials, can be determined and compared.

$$\frac{K_{11}}{K_0} \propto \lambda \quad \dots\dots(5.1a)$$

and

$$\frac{K_{\perp}}{K_0} \propto \lambda^{-\frac{1}{2}} \quad \dots(5.1b)$$

Taking as reference the points where $K_{11}/K_0 = K_{\perp}/K_0 = 1$, the gradients of the curves in figures 12(a-b) and 13(a-b) may be expressed by equations 5.2 and 5.3 respectively. C_{11} and C_{\perp} refer to the gradients for measurements along and perpendicular to the draw direction respectively.

$$C_{11} = \frac{\left(\frac{K_{11}}{K_0} - 1\right)}{(\lambda - 1)} \quad \dots(5.2)$$

$$C_{\perp} = \frac{\left(\frac{K_{\perp}}{K_0} - 1\right)}{(\lambda^{-\frac{1}{2}} - 1)} \quad \dots(5.3)$$

The expressions given by equations 5.2 and 5.3 may also be expressed in the form of equations 5.4 and 5.5 respectively. Equations 5.4 and 5.5 are in agreement with the expressions proposed by Hansen and Washo [7] for analysing heat conduction in amorphous polymers, equations 3.18 and 3.19.

$$\left(\frac{K_{11}}{K_0} - 1\right) = C_{11} (\lambda - 1) \quad \dots(5.4)$$

$$\left(\frac{K_1}{K_0} - 1 \right) = C_1 (\lambda^{-\frac{1}{2}} - 1) \quad \dots\dots(5.5)$$

On determining the gradients of the curves, C_{11} and C_1 , regression analysis gave different values of C_{11} and C_1 for the two materials. However, the values of C_{11} and C_1 for one particular material are comparable, that is, they are nearly equal. For polystyrene $C_{11} \approx 0.014$ and $C_1 \approx 0.016$ while for polypropylene $C_{11} \approx 0.877$ and $C_1 \approx 0.826$. According to Hansen and Washo, $C_{11} = C_1 = C$ is a characteristic value for a particular material, however, it is a more accurate assumption for monodisperse polymers [7]. Because the values of C_{11} and C_1 seem to be close to one another, for the materials used in this study, it will be assumed that $C_{11} \approx C_1$ and without having to know the values of C_{11} and C_1 , equations 5.4 and 5.5 may be combined to give expression 5.6, which may be used to predict changes in either K_{11} or K_1 in terms of λ . It should be noted that the use of equation 5.6 to analyse the behaviour of thermal conductivity would not require the knowledge of C , for a particular material, as equations 5.4 and 5.5 do. Since the

thermal conductivity results for both materials have led to equations 5.2, 5.3 and 5.6, the equations appear to be a characteristic of micromolecules, irrespective of the inhomogeneity of the phases, suggesting the contribution of the chain molecules to the thermal conductivity.

$$K_{11} = \frac{(\lambda - 1)}{(1 - \lambda^{\frac{1}{2}})} \lambda^{\frac{1}{2}} [K_1 - K_0] + K_0 \quad \dots(5.6)$$

Although equation 5.6 is predicted for both polypropylene and polystyrene, and suggests the contribution of the chain molecules, the contribution of crystallinity to the thermal conductivity of drawn polypropylene should not be overlooked. For isotropic semicrystalline polymers, K_0 is crystallinity dependent [2, 3, 19].

From table 6 and figure 14, crystallinity appears to have a considerable effect on the thermal conductivity for isotropic polypropylene. On average, a 1% increase in the degree of crystallinity appears to cause about 1.8% increase in the thermal conductivity, an equivalent of approximately 0.021 w/mK. The increase in thermal conductivity along the draw direction, for drawn polypropylene samples, table 4a, however, is much higher than the change in the thermal conductivity that

would result from the accompanying stretch-induced crystallinity. Infrared spectroscopy method registered an increase in crystallinity of about 8%, for $\lambda = 8$, while the density measured crystallinity showed an increase of about 2.4%. In the study of the effect of crystallinity on the thermal conductivity, where crystallinity varied by about 30% (density measured), an increase of about 0.0632 w/mK only was realized. One might then not expect the stretch induced crystallinity to have brought the big change that occurred in the thermal conductivity for drawn samples. This observation has stirred up questions and interests of how changes in the molecular chain conformation and crystallinity, individually and collectively, relate to the thermal conductivity in polymeric materials.

From the graphical representation of the thermal conductivity versus crystallinity, figure 14, the curve obtained is of quadratic form, suggesting the relationship between the thermal conductivity and crystallinity to be of the form given by equation 5.7.

$$y = ax^2 + bx + c \quad \dots(5.7)$$

where

$y \equiv K_o$ = thermal conductivity for
an isotropic sample

$x \equiv \phi$ = volume fraction crystallinity.

In terms of K_o and ϕ , equation 5.7 has been solved for a, b and c using points on the experimental curve for polypropylene, figure 14. When $\phi = 0$ the value of $K_o = c$, which is equal to the thermal conductivity for the amorphous phase (K_a) at 298K. The value of K_a at 298K, for polypropylene, has been determined by extrapolation of the thermal conductivity results, for polypropylene crystallites, in the perpendicular direction [19], and equation 3.14b. The value of K_a obtained was approximately equal to 8×10^{-2} w/mK. The solutions for a, b and c led to equation 5.8, which becomes the predicted expression for the dependence of the thermal conductivity for isotropic isotactic polypropylene on crystallinity.

$$K_o = (0.8 + 0.451\phi + 0.929\phi^2) \times 10^{-1} \text{ w/mK}$$

or

....(5.8)

$$\frac{K_o}{K_a} = 1 + 0.564\phi + 1.161\phi^2$$

where K_a = thermal conductivity of the amorphous phase, 8×10^{-2} w/mK.

Equation 5.8 has some features that it shares with the composite model given by Sangani and Yao, equation 3.22b [5]. In equation 3.22b the term containing ϕ^2 indicates that the thermal conductivity, in composite materials with spherical inclusions, should depend on the size and spatial distribution of the spherical particles [5]. The fact that a term containing ϕ^2 has been predicted from the results for polypropylene, equation 5.8, suggests that in polypropylene the term plays the same role as the one in the composite model, pointing that in a semicrystalline polymer (polypropylene) also the thermal conductivity depends on the size and spatial distribution of the crystallites. From this result it seems possible that the composite model [5] may be applied to semicrystalline polymers, see section 5.1.1 (ii).

Figures 15a and 15b show that the thermal conductivity along the draw direction, for drawn polypropylene and polystyrene samples respectively, decreases with the increasing draw temperature while that in the perpendicular direction is not sensitive to the draw temperature. It is also observed that the thermal conductivity along the draw direction becomes sensitive to the draw temperature mainly at high draw ratios. At low draw ratios ($\lambda \leq 4$) the

thermal conductivity values are approximately equal for the three draw temperatures considered. Tables 4a, 7a and 7b show the actual data obtained for the draw temperatures. This observed dependence of the thermal conductivity on the draw temperature suggests the existence of features which have some bearing on the thermal conductivity along the draw direction.

5.1.0 EXPERIMENTAL RESULTS VERSUS THE THEORETICAL PREDICTIONS OF MODELS

The models used here have been considered in two groups; models discussing the variation of the thermal conductivity with crystallinity, for isotropic semicrystalline polymers of varying volume fraction crystallinity, and models for the variation of thermal conductivity with draw ratio.

5.1.1 THERMAL CONDUCTIVITY VERSUS CRYSTALLINITY

(i) Modified Maxwell Model

Figure 14 shows the experimental and theoretical curves for the variation of the thermal conductivity with the volume fraction crystallinity, ϕ , in isotropic polypropylene samples. The curve derived from the modified Maxwell model of

equation 3.15 [19] provides a fairly good approximation to the experimental curve at low volume fraction crystallinity ($\phi \leq 0.6$). At crystallinity values higher than 0.6, the experimental values are observed to be increasingly **becoming** much higher than the theoretical values derived from the Maxwell model. This kind of deviation of the Maxwell model from the experimental results, at high degrees of crystallinity, has not only been observed here, but a similar deviation has been reflected in the results for the thermal conductivity of high density polyethylene and polyethylene terephthalate [19]. This deviation therefore suggests that, either there are features in the material, other than the crystallites, whose contributions have not been represented in the equation, or it is the failure of the model as a means for expressing the dependence of the thermal conductivity on crystallinity.

(ii) Composite Model

The model [5] for the thermal conductivity of composite materials with spherical inclusions has been employed here. The possibility of applying this model to semicrystalline polymers had been mentioned earlier, see page 114. Some common assumptions pertaining to the amorphous — crystalline

boundary effects had to be considered in the attempt to apply this model to the data for polypropylene. It has been assumed that at high temperatures the boundary scattering effects in semicrystalline polymers can be neglected [23], and that the ratio of the thermal conductivity of the crystalline phase to that of the amorphous phase becomes much greater than unity [3,19], equation 5.9.

$$\frac{K_c}{K_a} \gg 1 \quad \dots(5.9)$$

On substituting equation 5.9 into 3.22b, expression 5.10 is obtained. On applying equation 5.10 to the data for isotropic polypropylene samples at 298K, the theoretical values of K^* were much larger than the experimental values.

$$\frac{K^*}{K} = 1 + 2\phi + \frac{2}{3} (\phi + 2\phi^2) \quad \dots(5.10)$$

where

$K^* \equiv K_o$ = thermal conductivity of the isotropic sample.

$K \equiv K_a$ = thermal conductivity of the amorphous phase.

ϕ = volume fraction crystallinity.

A comparison of equation 5.10 with equation

5.8, however, indicated that a reasonable agreement could be achieved between the two equations if and only if the second term in equation 3.22b, that is $2\phi(B-1)/(B+1)$ where $B = K_c/K_a$, was not contained in the equation. It then seemed that there are some assumptions about the model of equation 3.22b which could make it applicable to semicrystalline polymers at high temperatures. This has been considered possible by considering the significance of each term contained in the composite model of equation 3.22b.

From equation 3.22b, it was pointed that the role of the term containing ϕ^2 depends on the size and spatial distribution of the spherical particles [5]. It was also pointed that an expression containing only the first two terms in equation 3.22b, see equation 3.22a, expresses the thermal conductivity of a composite material irrespective of the size or spatial distribution of the particles. The role of the second term in equations 3.22a and 3.22b then seems to be dependent on the boundaries between the spherical particles and the surrounding matrix, since both equations are products of the Laplace equation for heat conduction subject to the conditions of continuity of temperature and heat flux at the

interface of each particle and the surrounding matrix. To this end, the term $\phi = 2\phi(B-1)/(B+1)$ may be seen to be of little significance to semicrystalline polymers at high temperatures where the boundary effects can be neglected. On this assumption equation 3.22b may be expressed as equation 5.11 and only the first two terms considered to be of significant role in this application. That is, to determine the thermal conductivity K_o in semicrystalline polymers at high temperatures, one should only be concerned about the size and spatial distribution of the spherulites and not the boundary effects.

$$\frac{K_o}{K_a} = 1 + \frac{2}{3} (\phi + 2\phi^2) \left(\frac{B-1}{B+1}\right)^2 + \theta(\phi, \beta) \dots (5.11)$$

where $\theta(\phi, \beta) = 2\phi \left(\frac{B-1}{B+1}\right)$

Minus the term $\theta(\phi, \beta)$, equation 5.11 showed a fairly good approximation to equation 5.8, for $B \gg 1$, suggesting that the thermal conductivity of isotropic semicrystalline polymers (K_o) at high temperatures would be given, from equation 5.11, by equation 5.12.

$$\frac{K_o}{K_a} \geq 1 + \frac{2}{3}(\phi + 2\phi^2)$$

or

$$\dots (5.12)$$

$$\frac{K_o}{K_a} \geq 1 + 0.667\phi + 1.333\phi^2$$

Figure 14 shows the theoretical curve derived from equation 5.12, for the case where the equality sign is used. A better approximation to the experimental thermal conductivity curve for polypropylene, compared to the Maxwell model, is obtained. The good agreement between equation 5.12 and the experimental data is a support for the assumptions made to obtain equation 5.12.

5.1.2 THERMAL CONDUCTIVITY VERSUS DRAW RATIO

(i) The Modified Maxwell Model

The experimental and theoretical thermal conductivity curves for drawn polypropylene samples have been shown in figure 17a. The theoretical values for K_{11} , derived from the modified Maxwell model of equation 3.12 using the data for K_{\perp} and K_0 , is in fairly good agreement with the experimental results upto the draw ratio of $\lambda=4$. At higher draw ratios the experimental thermal conductivity values are higher and are increasingly becoming much larger than the predictions of the Maxwell model. The thermal conductivity for the amorphous phase (K_a) at 298K, used in equation 3.12, was obtained by extrapolation of the thermal conductivity in the perpendicular direction of the polypropylene

crystallite [19] and the Maxwell equation 3.14b. The results indicate that either there are some features developed at high draw ratios which highly contribute to the thermal conductivity along the draw direction, resulting into values higher than the predicted values, or the modified Maxwell model does not adequately account for the thermal conductivity in drawn semicrystalline polymers. The existence of tie molecules have been pointed as one factor which contribute to the deviation of the experimental results from the model [3]. However, the magnitude of their contribution has not been mentioned and it is not yet clear whether the observed large difference between the experimental results and the Maxwell model can solely be attributed to the tie molecules.

(ii) Suggested Models

Using the same data for K_{\perp} and K_{\parallel} used in the Maxwell model of equation 3.12, equation 5.6 gives a much better approximation to the experimental thermal conductivity curve for polypropylene, at all draw ratios, compared to the Maxwell model, figure 17a. At high draw ratios ($\lambda > 4$), however, the experimental results are still higher than even the

theoretical values derived from equation 5.6.

On applying expression 5.6 to polystyrene, figure 17b, the agreement between the experimental and the theoretical thermal conductivity values, upto draw ratio of $\lambda = 6$, were even much better compared to the polypropylene's response to the model, except that the theoretical thermal conductivity values of polystyrene tend to be higher than the experimental results at high draw ratios, $\lambda \geq 6$. The good approximation of expression 5.6 to the experimental results, for both polystyrene and polypropylene, indicates that it is possible that expression 5.6 may largely be linked with bond strength and changes in the molecular chain conformation brought about by stretching [7], and may accurately be applied to both drawn amorphous and semicrystalline polymers, in terms of draw ratio.

For polypropylene, however, the substitution of the measured value for K_0 into equation 5.6 also adds the contribution of the crystalline phase, since K_0 for polypropylene has been observed to depend on the degree of crystallinity, figure 14. Because K_0 may be expressed by equation 5.12, the thermal conductivity along the draw direction, for semi-

equation 5.13. 7

Figure 17a shows the curve representing the predictions of equation 5.13 for the two cases above. For draw ratios less than 5 ($\lambda > 5$) the two cases follow approximately the same curve. For higher draw ratios, however, the second case (b) gives values slightly higher than the first case (a), but they are still reasonably close to one another and both give much better approximation to the experimental curve than the curves derived from the modified Maxwell model of equation 3.12 and the proposed model of equation 5.6 where the measured value of K_0 is used. The slight difference between the curves derived from equation 5.13, for the two cases (a) and (b) above, seems to point that the stretch induced crystallinity did not contribute significantly to the thermal conductivity along the draw direction, and is in agreement with the earlier analysis which pointed that the observed increase in K_{11} could not be attributed to the stretch induced crystallinity in drawn polypropylene. Although the curves from equation 5.13 show better approximation to the experimental curve, the theoretical values are lower than the experimental values at high draw ratios ($\lambda > 4$). This observed deviation, like the modified Maxwell model of

equation 3.12, also suggests the development of some stretch induced features which tend to increase the thermal conductivity along the draw direction to values higher than the expected results. This leaves a room for tie molecules to be considered as the likely features, as proposed by other researchers [3].

5.2.0 THE PROPOSED MODELS VERSUS THE DATA REPORTED FOR OTHER MATERIALS

In this section the data reported by other researchers, for other polymers, have been used to confirm the validity of equation 5.13. Its predictions for the high temperature thermal conductivity in polyethylene at 323K has been compared with the modified Maxwell model, figure 18. The validity of the assumptions which led to the proposal of equations 5.12 and 5.13 have also been examined through the application of the unmodified composite model of equation 3.22b to the thermal conductivity results in the temperature regions where boundary effects seem to be significant. Since equation 5.12 was obtained from equation 3.22b, on the assumption that at high temperatures the boundary effects can be neglected, it should follow that at temperatures where the boundary scattering effects would be considered

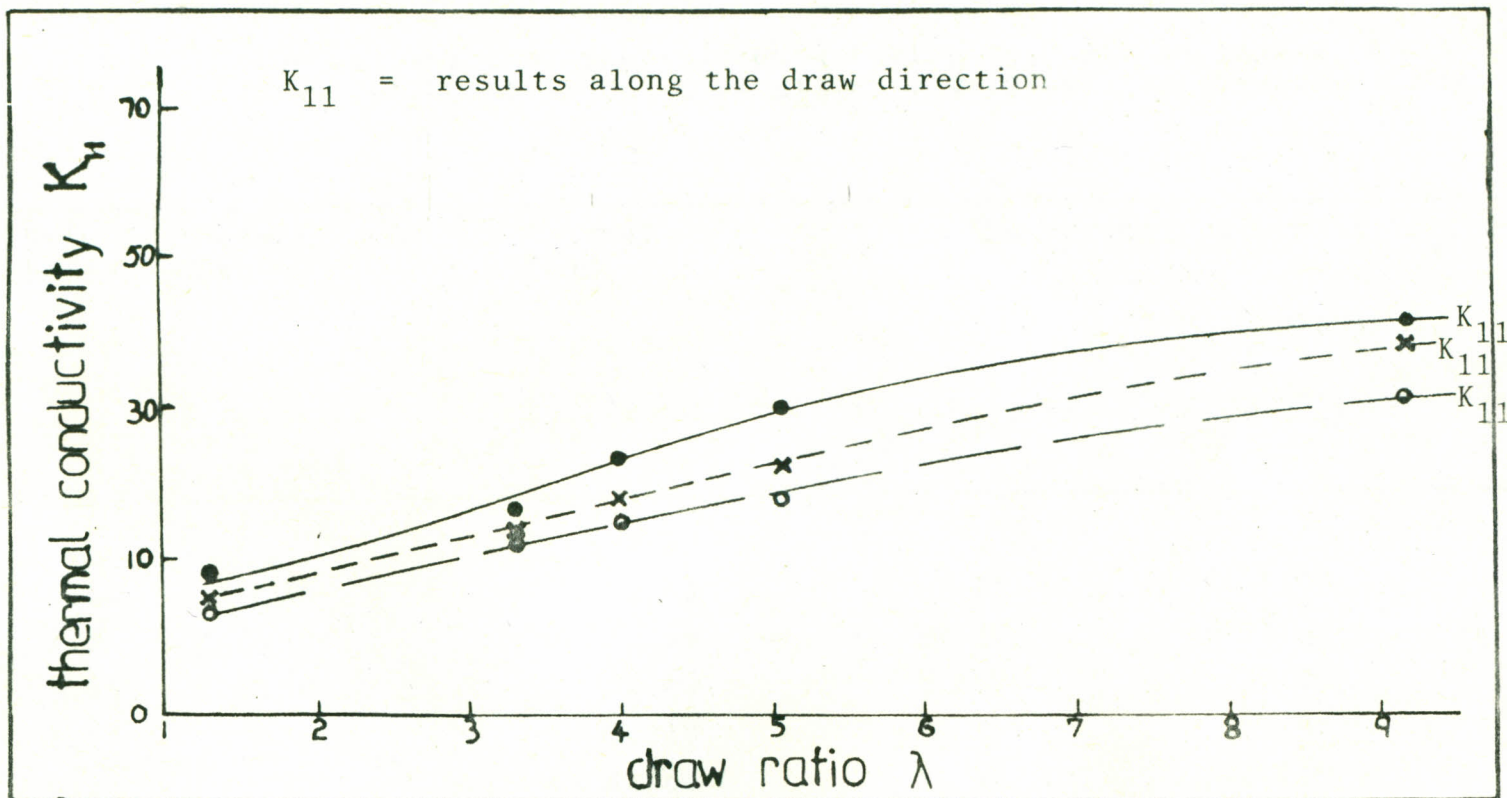


Fig. 18 : The variation of the thermal conductivity of polyethylene at 323K with draw ratio, data from ref (19), see table (8).

- K_{11} —●—●— experimental curve
- K_{11} —x—x— the curve derived from equation 5.13
- K_{11} —○—○— the curve derived from the Maxwell model of equation 3.12

Table 8 : The variation of thermal conductivity for polyethylene with draw ratio, at 323K. Crystallinity $\phi = 0.69$. Data from ref (19)

| Draw Ratio | Thermal Cond. $K_1(\text{exp}) \times 10^{-1}$ w/mK | Thermal Cond. $K_{11}(\text{exp}) \times 10^{-1}$ w/mK | Theoretical values of K_{11} based on | | |
|------------|---|--|--|---|---|
| | | | Eq. (5.13) $K_{11} \times 10^{-1}$ w/mK | Eq. (5.6) $K_{11} \times 10^{-1}$ w/mK | Maxwell model Eq. (3.12) $K_{11} \times 10^{-1}$ w/mK |
| 1 | - | 4.89 | | | |
| 1.64 | 4.86 | 8.86 | 7.51 | 6.96 | 6.71 |
| 3.3 | 3.20 | 16.50 | 14.39 | 13.54 | 11.98 |
| 4.03 | 2.90 | 23.40 | 17.89 | 16.90 | 15.25 |
| 5.14 | 2.72 | 30.30 | 22.14 | 20.96 | 20.96 |
| 9.26 | 2.30 | 40.60 | 38.62 | 36.75 | 36.75 |

$$K_a = 2.4 \times 10^{-1} \text{ w/mk}$$

(exp) = experimental

significant, equation 3.22b should show good agreement with the thermal conductivity versus crystallinity results.

A test of the composite model of equation 3.22b on the data for polyethylene terephthalate and polypropylene at 70K and 100K respectively [49], has been summarized in table 9. The values for $B = K_c/K_a$, for the two materials at those temperatures, were calculated from the data using equation 3.10, as shown by Choy and Greig [2], and substituted in 3.22b. The theoretical values obtained from equation 3.22b are in very good agreement with the experimental results.

On substituting equation 3.22b into equation 5.6, for K_o , an expression expected to show good variation of the thermal conductivity of drawn semicrystalline polymers with draw ratio, at low temperatures, is obtained as given by equation 5.14. For draw ratios not too large, $\lambda \leq 5$, the theoretical thermal conductivity values along the draw direction (K_{11}), for polypropylene at 100K, compare well with reported experimental data [19], figure 19. For draw ratios greater than five the theoretical values derived from equation 5.14 are increasingly becoming higher than the experimental values. For the

Table 9 : The variation of thermal conductivity with crystallinity, experimental versus theoretical predictions of the model of equation (3.22b). Data from reference (49)

| Material and temp. | Volume fraction crystallinity | Isotropic thermal cond. | Theoretical values based on Eq. (5.12) |
|--------------------|-------------------------------|---|--|
| | | $K_o(\text{exp}) \times 10^{-1} \text{ w/mK}$ | $K_o \times 10^{-1} \text{ w/mK}$ |
| PET 70K | 0.09 | 1.56 | 1.561 |
| | 0.17 | 1.62 | 1.624 |
| | 0.25 | 1.68 | 1.678 |
| | 0.29 | 1.74 | 1.737 |
| | 0.39 | 1.88 | 1.876 |
| | 0.51 | 2.02 | 2.003 |
| PP 100K | 0.65 | 1.80 | 1.795 |

calculation purposes, the value of K_c/K_a for the isotropic polypropylene at 100K was used for all the drawn samples on the assumption that K_c and K_a do not change significantly on stretching semicrystalline polymers [3,19]. The observed deviation of the experimental curve suggests that some features are developed on stretching polypropylene samples, which tend to lower the thermal conductivity, K_{11} , at low temperatures. The fact that the deviation becomes larger with the increasing draw ratio is a suggestion that the development of the features, and hence their effect on the thermal conductivity, is increasing with the increasing draw ratio. The modified Maxwell model of equation 3.12, however, gives low values even at high draw ratios and, as a result, any negative effects of the expected features cannot be inferred from the results.

$$K_{11} = \frac{(\lambda-1)\lambda^{\frac{1}{2}}}{(1-\lambda^{\frac{1}{2}})} \left\{ K - K_a \left[1 + 2\phi\beta + \frac{2}{3}(\phi + 2\phi^2)\beta^2 \right] \right\} + K_a \left[1 + 2\phi\beta + \frac{2}{3}(\phi + 2\phi^2)\beta^2 \right] \quad \dots (5.14)$$

where,

$$\beta = \frac{B-1}{B+1}$$

$$B = \frac{K_c}{K_a}$$

Table 10 : The variation of thermal conductivity with draw ratio, at 100K: Data from reference (19)

| Crystal- linity | Draw Ratio | Thermal Cond. $K_1(\text{exp}) \times 10^{-1}$ w/mk | Thermal Cond. $K_{11}(\text{exp}) \times 10^{-1}$ w/mK | Theoretical values of K_{11} based on:- | | |
|--------------------|---------------|--|---|---|-------------------------------------|---|
| | | | | Eq. (5.13) $\times 10^{-1}$ w/mK | Eq. (5.6) $\times 10^{-1}$ w/mK | Maxwell Eq. (3.12) $\times 10^{-1}$ w/mK |
| PP 0.62 | 3.3 | 1.5 | 3.2 | 3.03 | 2.98 | 2.33 |
| | 5.5 | 1.3 | 5.2 | 5.28 | 5.19 | 3.04 |
| | 10.5 | 1.2 | 7.8 | 11.67 | 10.9 | 3.06 |
| PET 0.42 | 3.6 | 2.0 | 3.9 | 3.30 | 3.29 | 3.06 |

CHAPTER 6

DISCUSSION, CONCLUSION AND RECOMMENDATIONS

6.0.0 INTRODUCTION

In this chapter, the discussion, conclusions and recommendations consider the quantitative and qualitative implications of the experimental and theoretical results presented in chapter 5. Efforts have been made to explain how crystallinity, temperature and stretching, individually and collectively, affected the thermal conductivity behaviour in polypropylene and polystyrene samples.

6.1.0 DISCUSSION

(a) Crystallinity Effect

It is generally accepted that a semicrystalline polymer is composed of crystallites of spherulitic nature [2, 3, 4], and may be regarded as a two-phase material with amorphous and crystalline phases whose thermal conductivities may be denoted by K_a and K_c respectively. The thermal conductivity of a semicrystalline polymer, like composite materials, may then be expected to depend on the thermal conductivities of the amorphous and the

crystalline phases, and also to be affected by the boundaries between the phases. However, unlike in composite materials, crystallites are just small volume elements in which chain segments have a crystalline order and are connected to the surrounding amorphous phase by chain segments, therefore sharp boundaries are not to be expected [29].

Considering the theoretical thermal conductivity versus crystallinity results for isotropic polypropylene samples at 298K, both Maxwell model of equation 3.15 and the proposed model of equation 5.12 have shown good approximations to the experimental results, thereby seeming to confirm the assumptions and implications of the models. Both models assume that the boundary effects on the thermal conductivity of semicrystalline polymers are negligible at high temperatures. The model of equation 5.12 also points that the thermal conductivity of semicrystalline polymers in general and polypropylene in particular is not dependent on the thermal conductivity of the spherulites (K_c), but is dependent on the thermal conductivity of the amorphous phase (K_a), size and distribution of the spherulites in the amorphous phase. The independence of the thermal conductivity of an isotropic semicrystalline polymer on K_c , as suggested by equation 5.12, has not only been pointed

out in this study but Choy and Greig also reported that K_c increases with temperature and the thermal conductivity of an isotropic semicrystalline polymer becomes less dependent on K_c when it (K_c) becomes very large [2]. On assuming that $K_c = \infty$ at high temperatures, the thermal conductivity value for polyethylene terephthalate (PET) at 100K was reported by Choy and Greig to be only about 25% lower than the theoretical value derived from the model of equation 3.10, the difference of which was attributed to the boundary effects. The assumption of neglecting the boundary effects at high temperatures was then considered not too extreme [2]. Therefore, neglecting the boundary effects and considering the thermal conductivity of semicrystalline polymers in general, and polypropylene in particular, to be independent of K_c , how the increase in crystallinity contributes to the increase in thermal conductivity becomes a question of interest.

In semicrystalline polymers crystallinity would be expected to increase by the increasing size of the already formed spherulites and through the development of new spherulites. The variation of the thermal conductivity with the increasing crystallinity may then be regarded as the

variation of thermal conductivity with the increasing size and number of spherulites. Thermal conductivity has been reported to increase with the increasing size of the crystallites in polyethylene [20]. Also from the graphical representation of the thermal conductivity versus crystallinity results for polypropylene, obtained in this study, the derived equation of the curve contains a term which in the composite model of equation 3.22b has been pointed to imply the dependence of the thermal conductivity on the size and distribution of the spherical inclusions. The variation of the thermal conductivity with the increasing degree of crystallinity in polypropylene may then be seen to be dependent on the size and number of the spherulites, and may be explained in terms of the accompanying increase of order in the material, and not in terms of K_c .

The increasing size of the crystallites is expected to increase the order of the material by incorporating more chain segments into the crystalline structure, while increasing the number of spherulites is expected to increase the order as well as the crystalline-amorphous boundaries in the material. Thermal vibrations in the ordered structure are expected to be less unharmonic than those in the disordered structure. The increase in

the thermal conductivity of polypropylene with the increasing crystallinity is therefore seen to be expected.

(b) Temperature Effect

Equation 3.1 shows that the thermal conductivity depends on the heat capacity, thermal diffusivity and density of a material. Changes in thermal conductivity would then seem to result from changes in the heat capacity, thermal diffusivity and density of the material. In polypropylene, heat capacity has been reported to increase with the increasing temperature, according to equation 4.3 [28, 46]. The heat capacity of polystyrene also increases with temperature, table 3b. However, thermal diffusivity is inversely proportional to the heat capacity [25], and figure 16 shows the variation of the thermal diffusivity in polypropylene with temperature. Also the density of polymeric materials are assumed constant, for temperatures fairly below the melting point [48]. The observed increase in thermal conductivity, with the increasing temperature, then seems to result from the increasing heat capacity of polypropylene and polystyrene, and may be explained in terms of increasing thermal vibrations. The assembly of atoms bound together by covalent bonds and intermolecular

forces is capable of vibrating in a large number of independent modes about equilibrium. Increase in temperature would be expected to increase the thermal vibrations of the atoms, and to induce some modes of vibration. In these vibrations is stored a large proportion of the thermal energy of the solid and hence the major contribution to the heat capacity. The increase in temperature is therefore expected to cause increase in the heat capacity, and hence increase in the thermal conductivity.

Correlation coefficient values for the thermal conductivity along the draw direction versus temperature, for polypropylene, confirm the observed linear relationship shown by figure 10a. However, the values indicate that the linear relationship drops with the increasing draw ratio and may be attributed to morphological changes or structural organization which occur on stretching. For draw ratios of $\lambda = 2, 3, 4$ and 5 the correlation coefficient values, calculated from table 5a and the equation given in appendix I, are $0.986, 0.985, 0.977$ and 0.961 respectively.

(c) Stretching Effect

On comparing the thermal conductivity versus crystallinity results with the thermal conductivity versus draw ratio results, for measurements along the draw direction, it was indicated that the stretch induced crystallinity is not expected to have brought the observed big increase in the thermal conductivity of drawn polypropylene samples. For $\lambda = 8$ the stretch induced crystallinity was only about 2.4%, a quantity whose contribution to the thermal conductivity could not be expected to have been higher than the contribution of the 30% crystallinity realized in the thermal conductivity versus crystallinity study. The observed thermal conductivity versus draw ratio results for polypropylene and polystyrene samples may be explained in terms of the anisotropic bonding and orientation of the chain segments.

In polymeric materials covalent bonds join constituent groups in the same molecular chain but weaker van der Waals' forces join the constituent groups in different molecular chains. The thermal vibrations associated with strong covalent bonds are expected to be less unharmonic than those associated with weaker secondary bonds. Heat conduction in a material in which constituent groups are

anisotropically bonded would then be expected to be higher along the backbone of the chain molecules, which should follow the direction of orientation of the covalent bonds. As the magnitude of stretch increases the number of the covalent bonds aligned in the direction of stretch would also be expected to increase, and the thermal conductivity should increase in the direction of stretch but decrease in the perpendicular direction. The thermal conductivity in this case is expected to be sensitive to the magnitude and direction of stretch, irrespective of the inhomogeneity of the phases in the material. Figures 9a and 9b support this expectation.

Stretching of polymeric materials would primarily seem to be a process of straightening the chain molecules expected to bring alignment of the polymer chain segments, or covalent bonds, in the direction of stretch. The results in figure 7 would answer some of the questions touching on the straightening of the chain molecules on stretching, and hence the correlation between draw ratio and thermal conductivity. The graphical representations of the crystallinity versus draw ratio results for polypropylene, figure 7, exhibit characteristics which are in agreement with the results reported by T.M. Ward for polyethylene terephthalate [50]. On comparing the crystallinity results from X-ray,

density and infrared spectroscopy methods, Ward reported that the X-ray and the density methods responded the same way to the draw ratio. The Density and the X-ray crystallinity results were reported to have remained approximately constant for draw ratios not greater than five ($\lambda < 5$) while the infrared spectroscopy results showed a continuous increase in crystallinity even at very low draw ratios. T. Ward pointed out that the infrared results arose from the conformational changes which occur on stretching, to which the infrared spectroscopy method is sensitive. The conformational changes which occur on stretching polymeric materials have also been discussed by Charles Price [35]. According to Charles Price, the equilibrium molecular chain conformation is a random coil which on stretching can be extended to a more linear conformation by increasing the number of trans conformations at the expense of gauche. All-trans conformation is the more linear form a chain molecule can assume, which is the case for polyethylene. The infrared spectroscopy results for polypropylene, which are everywhere higher than the density crystallinity results, may then be regarded as signifying the change in molecular chain conformation. Crystallinity is then only approximated by the infrared spectroscopy method,

and the method may be considered suitable only for the determination of the crystallinity for isotropic samples ($\lambda = 1$). The crystallinity values for isotropic polypropylene, obtained from the density and infrared spectroscopy methods, are in good agreement, figure 7. The infrared spectroscopy results for drawn polypropylene samples, however, showed increase even at low draw ratios such as $\lambda = 1.5$ where even the voids which may affect the density crystallinity results are not expected to have been considerably developed.

The molecular chain conformation determines the path along the backbone of a chain molecule, which is composed mainly of the covalent bonds. Changing the molecular chain conformation is therefore changing the route for easier heat transfer. Hansen and Washo [7] considered the effect of changing the molecular chain conformation on the thermal conductivity and suggested that the thermal conductivity of amorphous polymers would increase proportionally, along the chain molecule, with the increasing draw ratio, see chapter 3. The agreement between the expressions obtained from the experimental thermal conductivity versus draw ratio results for polypropylene and polystyrene, equations 5.4 and 5.5, and the proposals by Hansen and Washo, which led to the proposal of equations 5.6 and

5.13, then seems to point that the thermal conductivity in both amorphous and semicrystalline polymers depends on the chain conformation, or geometry and the bond strength, as discussed in the derivation of the model proposed by Hansen and Washo [7].

The differences observed in the magnitudes of change in the thermal conductivity versus draw ratio results, being largest in polypropylene, is in agreement with the assertion by other researchers that the anisotropy in thermal conductivity is different for different polymeric materials and is largest in polymers with small compact repeat units such as polyethylene [9, 26]. This may be explained in terms of the differences in bond strength and packing geometry caused by the size of the substituent groups. The increasing size of the substituent groups is expected to weaken the bond strength and to affect the packing geometry, or conformation of the chain molecule. The large anisotropy developed in polypropylene, compared to polystyrene, is then seen to be expected since polystyrene has bulky substituent groups derived from benzene structure.

The deviation of the experimental thermal

conductivity versus draw ratio results, for drawn polypropylene samples, from the modified Maxwell model of equation 3.12 and the proposed models of equations 5.6 and 5.13, figure (17a), however, seems to indicate that the bond strength, orientation of chain molecules and crystallinity are only approximation of the total real situation in the qualitative and quantitative evaluation of the thermal conductivity in drawn semicrystalline polymers. The theoretical curves derived from the models seem to point that at high draw ratios, $\lambda > 4$, there are some stretch induced features which aid the thermal conductivity along the draw direction, resulting into the observed deviation of the experiment results at high draw ratios. Other researchers have suggested that taut tie molecules are developed on stretching polymeric materials and that they also aid the thermal conductivity along the chain molecules [3]. The deviation of the experimental thermal conductivity curve, for measurements along the draw direction, may then be attributed to taut tie molecules, however, how much contribution they make to the thermal conductivity (K_{11}) has not been established. While the modified Maxwell model would portray tie molecules as contributing highly to the thermal conductivity of drawn semicrystalline polymers, polypropylene in particular, the proposed model of equation 5.13 points that the contribution is

not significant at moderate draw ratios, figure 17a.

The graphical representations of the thermal conductivity versus draw temperature results, figures 15a and 15b, suggest the contributions of tie molecules to the thermal conductivity along the draw direction, K_{11} . The fact that the thermal conductivity along the draw direction drops with the increasing draw temperature, at high draw ratios, while that in the perpendicular direction follows approximately the same curve, may be explained in terms of strained chain segments expected on stretching. When a polymeric material is subjected to a deformation stress, chain segments become strained and orientation of molecules or crystallites may not take place instantaneously but lags behind the stress [29]. This may be attributed to factors such as the entanglement of chain segments and segments (tie molecules) connecting one crystallite with others or with the entanglement points. Stresses and strains developed in the segments would also be expected to depend on the distribution of the crystallites and the entanglement points. By raising temperature the mobility of the chain segments is increased and some chain segments would be expected to disentangle [29]. Drawing is also expected to aid the

disentanglement of the chain segments which, coupled with the high temperature drawing, would result into fewer entanglement points and hence fewer taut tie molecules. If taut tie molecules contribute significantly to the thermal conductivity, then the thermal conductivity would be expected to decrease with the increasing draw temperature. The results for the thermal conductivity along the draw direction, in polypropylene and polystyrene, show this expectation at high draw ratios, figures 15a and 15b. Tie molecules are expected to be considerably strained at high draw ratios and, as a result, their contribution would also be expected to be significant at high draw ratios.

The stretching of semicrystalline polymers is also expected to deform the crystallites and develop microcracks and voids [36] which, coupled with the crystalline-amorphous boundaries, would be expected to lower the thermal conductivity of drawn semicrystalline polymers. The development of the microcracks and voids would be expected to increase with the increasing draw ratio, and hence their effect on the thermal conductivity. The experimental thermal conductivity values would then be expected to be lower than the theoretical predictions of a model, especially at high draw ratios. The observed low theoretical values derived from the Maxwell model

of equation 3.12 and the proposed model of equation 5.13, figure 17a, then seems to suggest that at high temperatures the contribution of tie molecules overcompensates for the boundary effects. Following the report by Choy and Greig that the boundary effects lowered the thermal conductivity of isotropic polyethylene terephthalate by 25%, at 100K [2], it would be expected that on stretching a material the boundary effects at 100K should even increase because of the production of voids and microcracks. The model of equation 5.14, proposed for analysing the thermal conductivity in drawn semicrystalline polymers at low temperatures, confirms this expectation on the thermal conductivity values of drawn polypropylene reported at 100K [19], figure 19. It is observed from the figure that the experimental thermal conductivity values become lower than the theoretical values derived from equation 5.14, suggesting the effect of the expected increased number of voids and microcracks. The modified Maxwell model of equation 3.12, however, predicts values lower than the experimental results, figure 19, just as it does for the thermal conductivity results for polypropylene at 298K, figure 17a. The curves derived from the Maxwell model do not reflect any boundary effects, suggesting that the boundary effects are negligible even at 100K. This is in agreement with the

assumption made by Choy, Luk and Chen that the boundary effects are negligible at high temperatures, $T \gg 70K$. However, it is not clear whether the big difference between the Maxwell model and the experimental curves in figures 17a and 19 should just be attributed to the tie molecules.

6.2.0

CONCLUSION

From the analysis and discussion of the thermal conductivity results, the following conclusions have been drawn.

- (i) The thermal conductivity of a stretched polymeric material depends on the magnitude and direction of stretch, irrespective of the inhomogeneity of the phases in the material. While the thermal conductivity increases in the direction of stretch, it decreases in the perpendicular direction.
- (ii) The anisotropy in the thermal conductivity of stretched polymeric materials is different for different polymers. The anisotropy in polypropylene is larger than that in polystyrene sample of the same draw ratio, and can be attributed to the

effect of the size of substituent groups on the bond strength and chain conformation.

- (iii) At high draw ratios, $\lambda > 4$, the thermal conductivity along the draw direction becomes sensitive to the draw temperature. While the thermal conductivity along the draw direction decreases with the increasing draw temperature, in both polypropylene and polystyrene, that in the perpendicular direction is not affected by the draw temperature, for the draw temperatures considered in this study.
- (iv) The relative thermal conductivity in polypropylene and polystyrene samples show linear relationship with draw ratio, for measurements along the draw direction, and a linear relationship with the inverse square root of the draw ratio for measurements in the perpendicular direction.
- (v) The thermal conductivity in polypropylene and polystyrene samples increase with the increasing temperature, in the temperature range of 273K - 333K.

- (vi) The thermal conductivity in polypropylene increases with the increasing degree of crystallinity.
- (vii) The observations made by correlating the thermal conductivity of isotropic polypropylene and the thermal conductivities of its amorphous and crystalline phases, through models, demonstrate that it is not enough to expect the thermal conductivity of an isotropic semicrystalline polymer to relate simply with the thermal conductivities of the individual phases. The modified Maxwell model of equation 3.15 and the proposed model of equation 5.12 point that the degree of crystallinity and the temperature region in which the measurements take place must also be stated.
- (viii) The results have revealed that semicrystalline polymers are comparable to composite materials with spherical inclusions, and the model for the thermal conductivity of isotropic semicrystalline polymers can be derived from the Laplace equation for thermal conductivity, the same way

Sangani and Yao did for composite materials with spherical inclusions [5]. However, in semicrystalline polymers the boundary scattering effects are negligible at high temperatures, such as in the range considered in this study, and the thermal conductivity results for isotropic polypropylene presented in figure 14 and table 6 have agreed with the proposal that the equation for expressing the high temperature thermal conductivity of isotropic semicrystalline polymers can be expressed in the form shown below

$$\frac{K_o}{K_a} \geq 1 + \frac{2}{3} (\phi + 2 \phi^2)$$

where K_o = thermal conductivity of the sample.

K_a = thermal conductivity of the amorphous phase.

ϕ = degree of crystallinity.

(ix) The proposed expression given in (viii) above, and hence the good agreement observed between the experimental thermal conductivity results for

isotropic polypropylene with the model, shows that the thermal conductivity of a semicrystalline polymer at high temperatures, such as in the range considered in this study, does not depend on the thermal conductivity of the crystalline phase (K_c), but on the thermal conductivity of the amorphous phase, degree of crystallinity, size and distribution of the spherulites in the material.

- (x) The thermal conductivity results for drawn polypropylene and polystyrene samples have revealed that on drawing, semicrystalline and amorphous polymers are comparable in their heat conduction mechanisms, except for the contribution of the crystallites in semicrystalline polymers. There is a good agreement between the thermal conductivity results and the proposal that the thermal conductivity of drawn semicrystalline and amorphous polymers, at high temperatures, can be explained in terms of the theory advanced by Hansen and Washo and expressed in terms of draw

ratio by the equation given below.

$$K_{11} = \frac{(\lambda-1)}{(1-\lambda^2)} \lambda^{\frac{1}{2}} \left\{ K_L - K_a \left[1 + \frac{2}{3}(\phi + 2\phi^2) \right] \right\} + K_a \left[1 + \frac{2}{3}(\phi + 2\phi^2) \right]$$

where $K_a \left[1 + \frac{2}{3}(\phi + 2\phi^2) \right] = K_o =$ the thermal conductivity for isotropic sample.

$\phi =$ degree of crystallinity, for amorphous polymers $\phi = 0$

$\lambda =$ draw ratio

$K_a =$ thermal conductivity of the amorphous phase.

- (xi) The maxwell model of equation 3.12 and the proposed model given in (x) above have shown some similar deviation from the experimental thermal conductivity results for drawn polypropylene samples presented in figure 17a. From the deviation it has been deduced that on stretching, the polymer chain segments develop into taut tie molecules, especially at high draw ratios, which are believed to aid the heat conduction along the chain molecules, leading to experimental values being higher than the theoretical values.

However, how much contribution taut tie molecules make to the thermal conductivity has not been established and seems to depend on the model chosen for the analysis of the results.

6.3.0 RECOMMENDATIONS

- (i) It would be necessary to establish the magnitude of the contribution of tie molecules to the thermal conductivity, so that the models which have been proposed by researchers can be adequately evaluated. It may also give a useful information of whether tie molecules is one of the features which should be developed or eliminated in a polymeric material if its thermal conductivity is intended to be highly increased or highly reduced respectively, depending on the application for which it is intended.

- (ii) The effect of the distribution of spherulites on the thermal conductivity of semicrystalline polymers, as predicted by the models of equations 5.12 and 5.13, should be investigated. The models predict

the dependence of the thermal conductivity on the degree of crystallinity, size and distribution of the spherulites in the material, however, in this study attention was focused on the effect of the degree of crystallinity. The effects of the degree of crystallinity and size of the crystallites have also been reported in some previous studies [3, 9, 19].

- (iii) Investigations should also be carried out on the effect of drawing on the thermal conductivity of monodisperse semicrystalline polymers, so that much about the model given by equation 5.6 and hence equations 5.13 and 5.14 can be established. This way it may even be possible to use the determined values of C_{\perp} and C_{\parallel} , from equations 5.4 and 5.5, as a measure of dispersity in polymeric materials.

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APPENDIX 1

Calculation of the correlation coefficient between two variables.

The correlation coefficient measures the amount of linear relationship between two variables. For the variables x and y , the correlation coefficient (Y) is given as:

$$Y(xy) = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2\}}}$$

where $\bar{x} = \frac{1}{n} \sum x_i$

and $\bar{y} = \frac{1}{n} \sum y_i$

APPENDIX II

Infrared diagrams, figures 20(a-g)

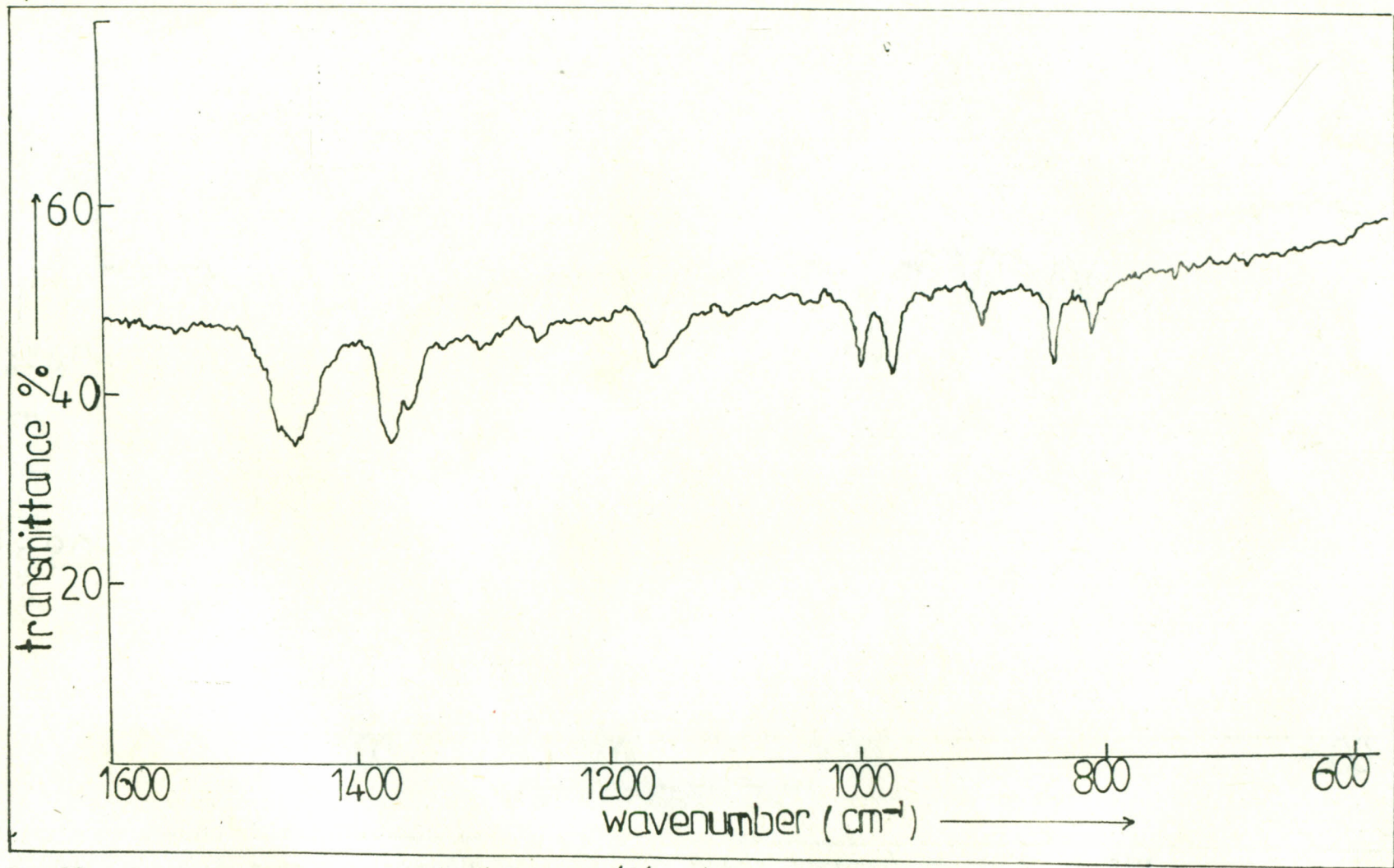


Fig. 20a. Infrared scan for isotropic unannealed polypropylene sample

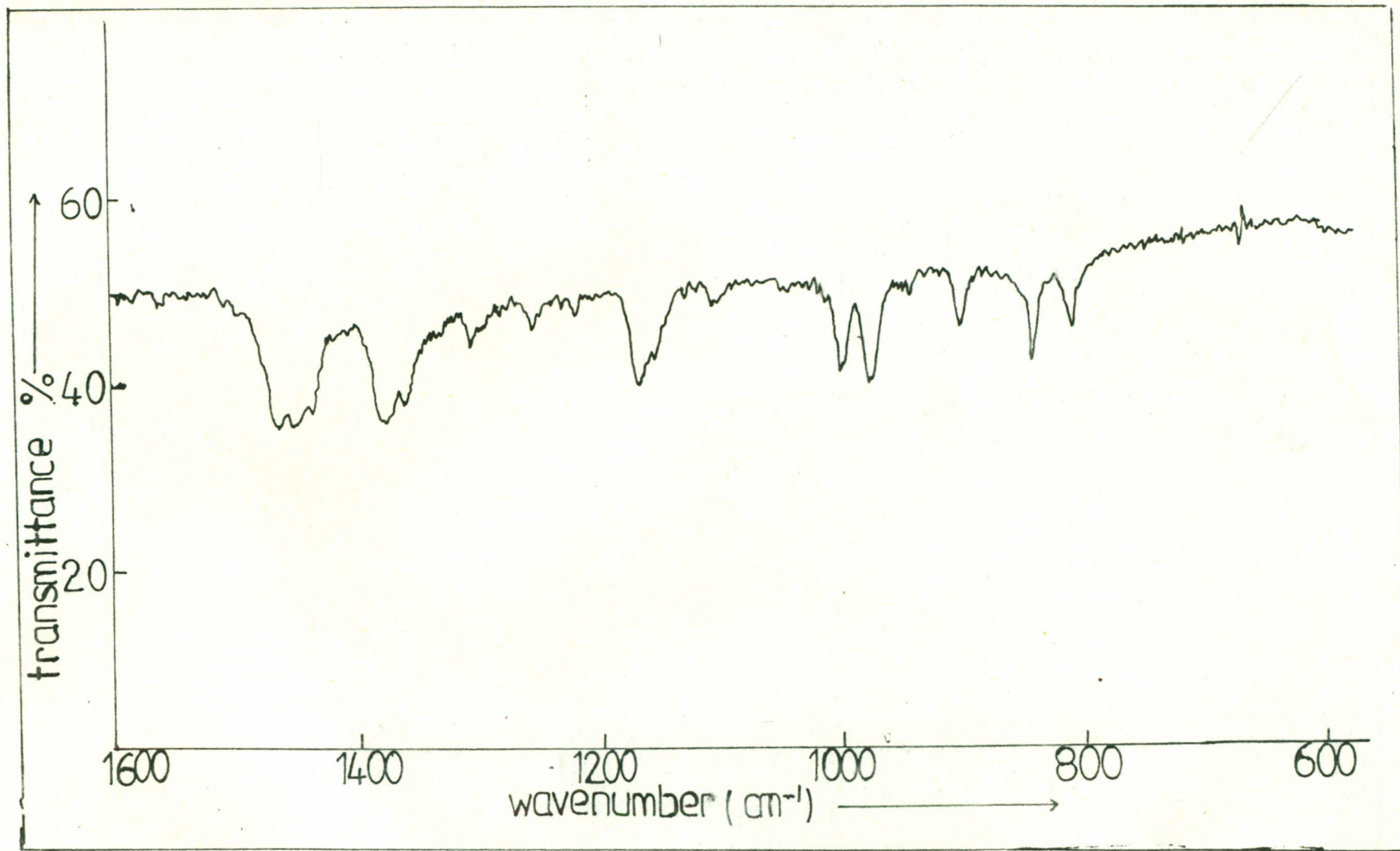


Fig.20b. Infrared scan for isotropic polypropylene sample annealed at 140°C for 6hrs.

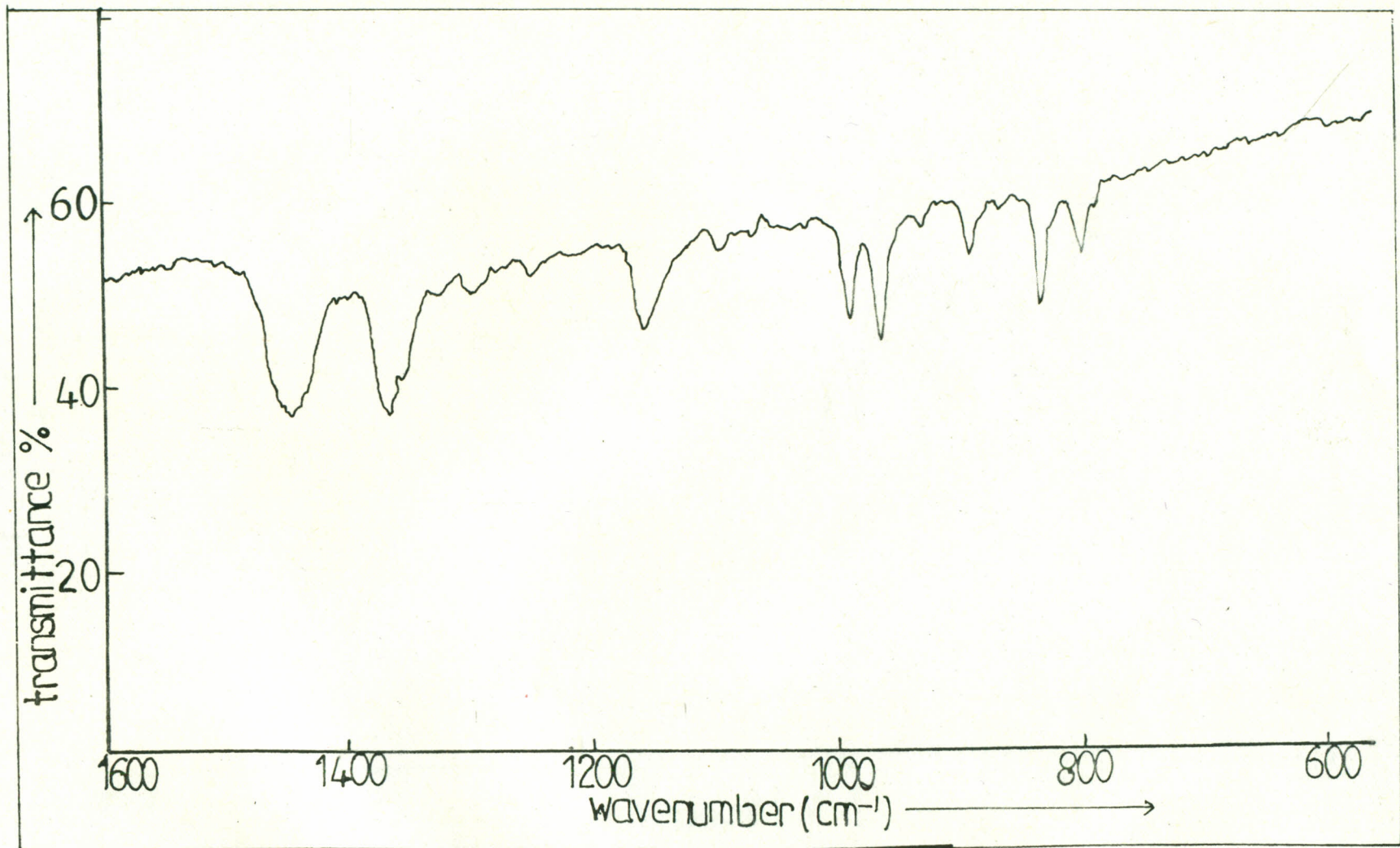


Fig. 20C. Infrared scan for polypropylene sample annealed at 140°C and drawn at 120°C to $\lambda = 1.5$

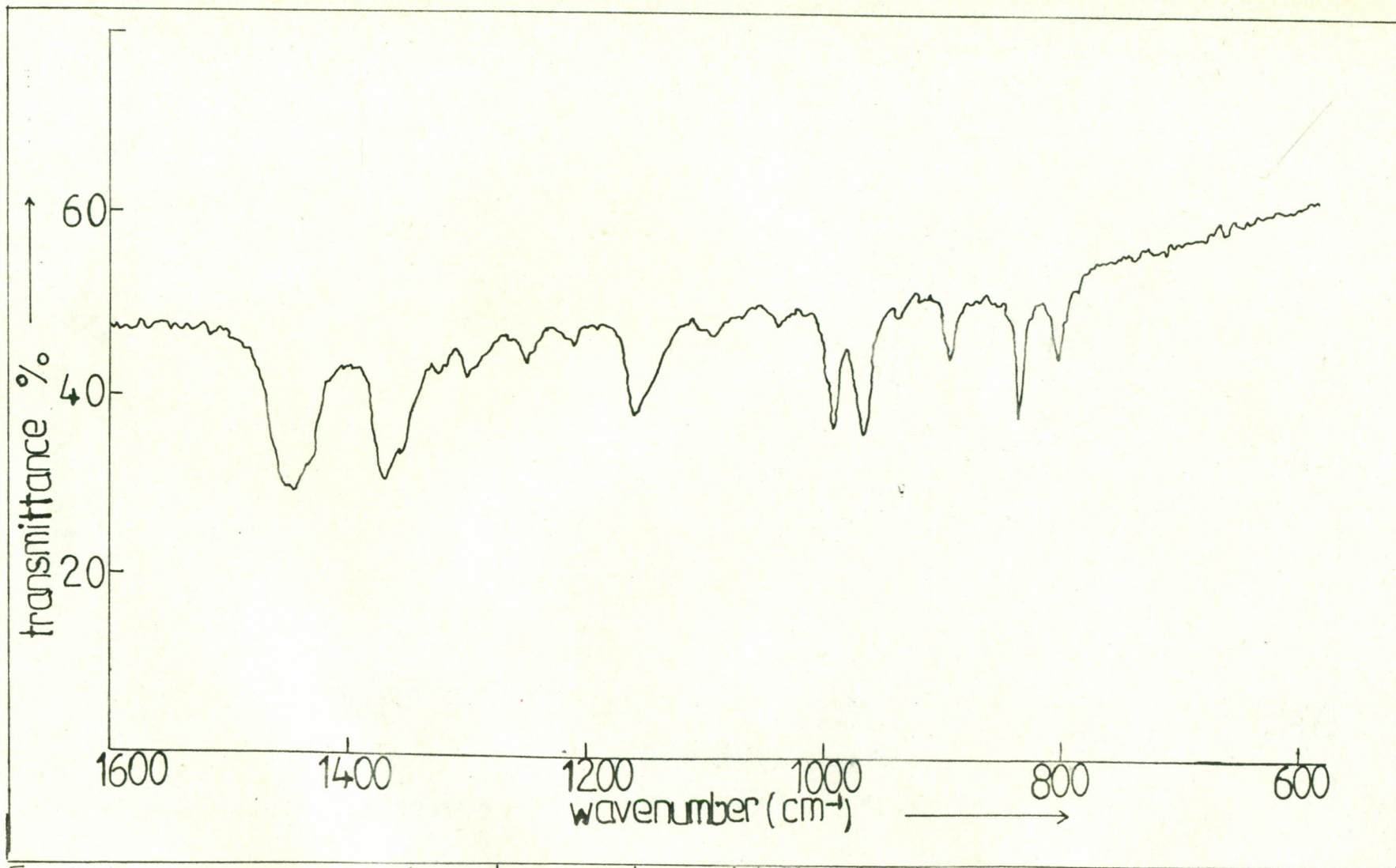


Fig. 20d. Infrared scan for polypropylene sample annealed at 140°C and drawn at 120°C to $\lambda = 2$

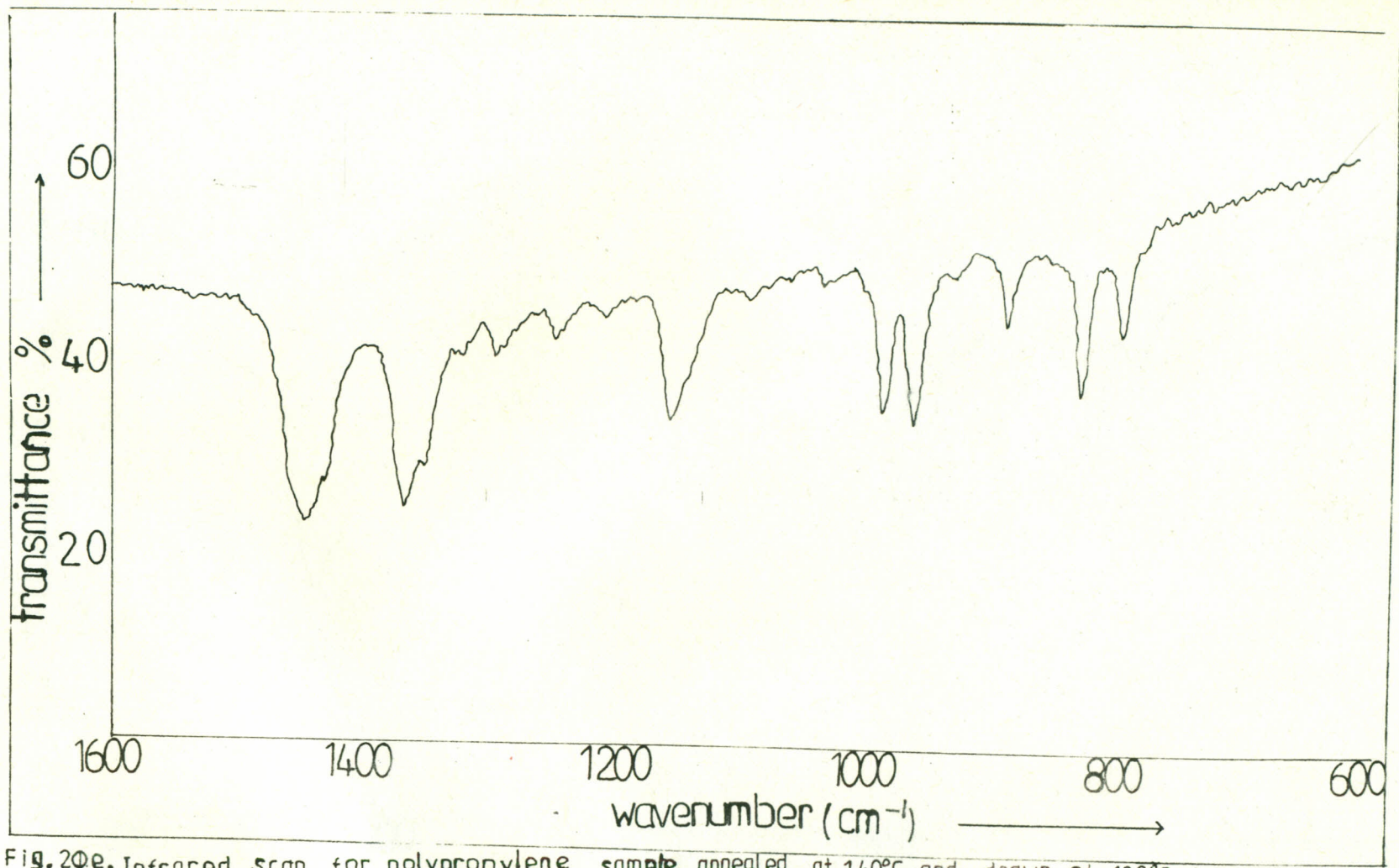


Fig. 20e. Infrared scan for polypropylene sample annealed at 140°C and drawn at 120°C to $\lambda = 4$

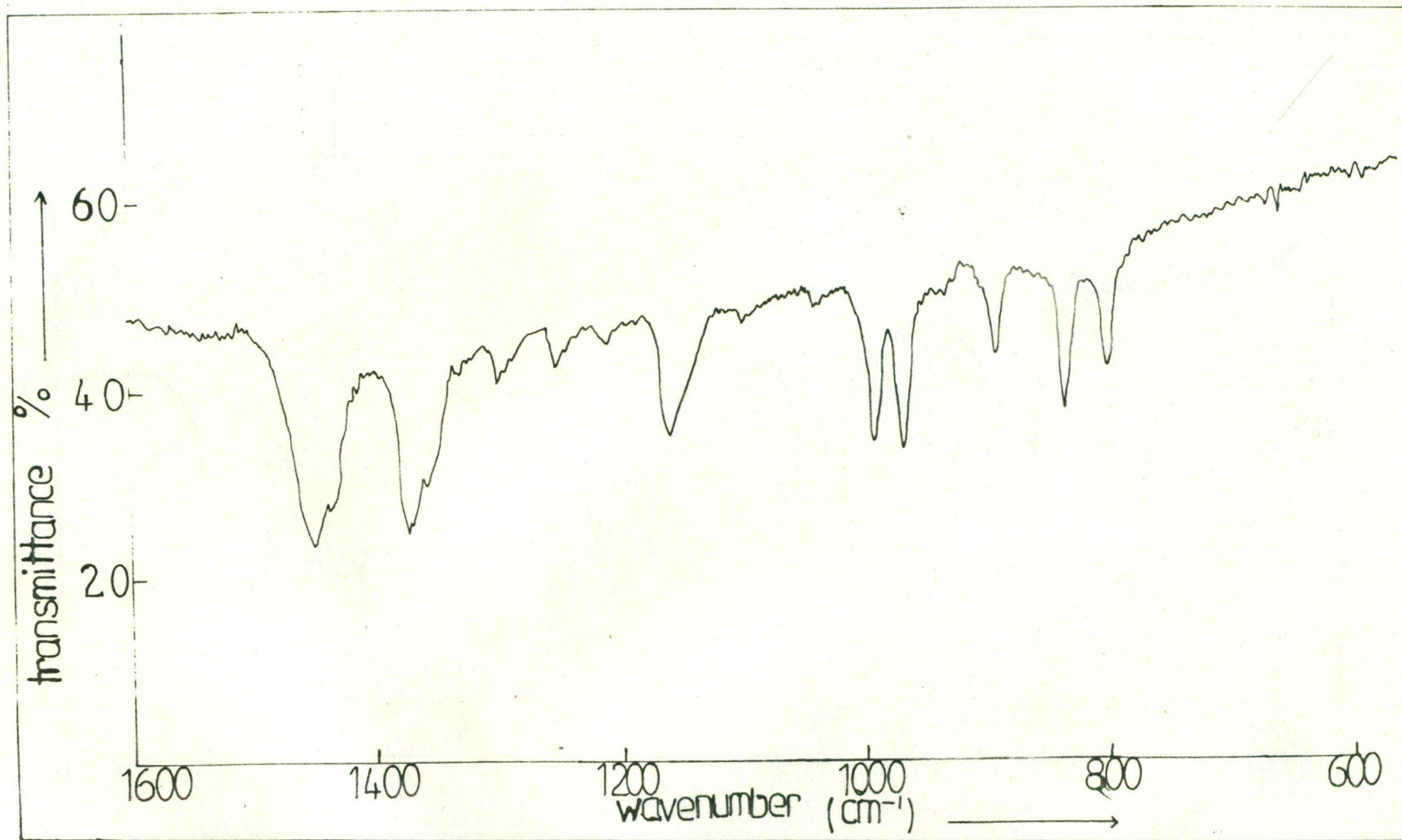


Fig. 20f. Infrared scan for polypropylene sample annealed at 140°C and drawn at 120°C to $\lambda = 6$.

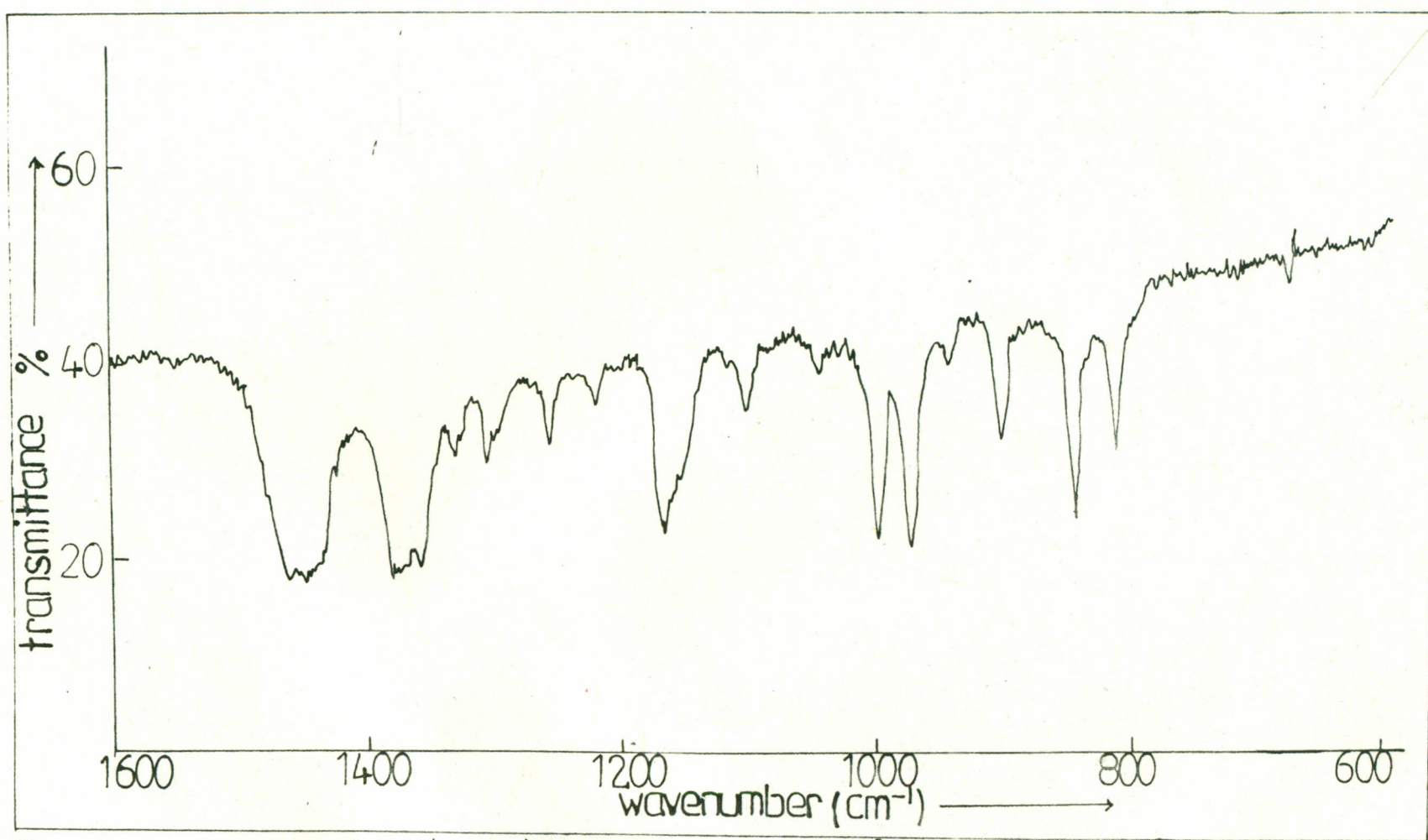


Fig. 20g. Infrared scan for polypropylene sample drawn at 140°C and drawn at 120°C to $\lambda = 8$

APPENDIX III

The back surface temperature versus time curves for the thermal diffusivity measurements, figures 21(a-i).

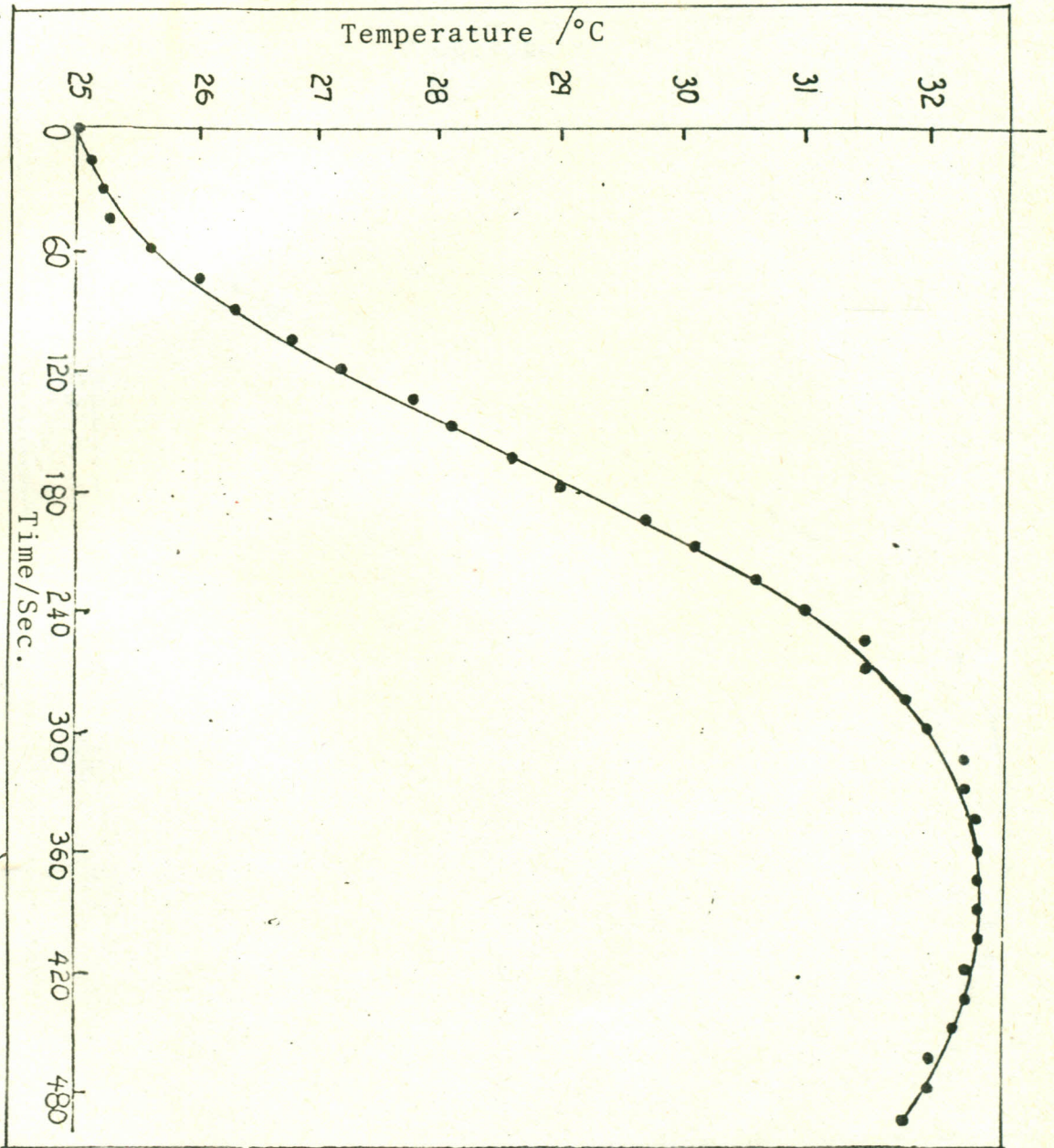


Fig. 21a : Variation of the back surface temperature with time, at 298K, for the isotropic polypropylene sample of crystallinity $\phi = 43.5\%$.

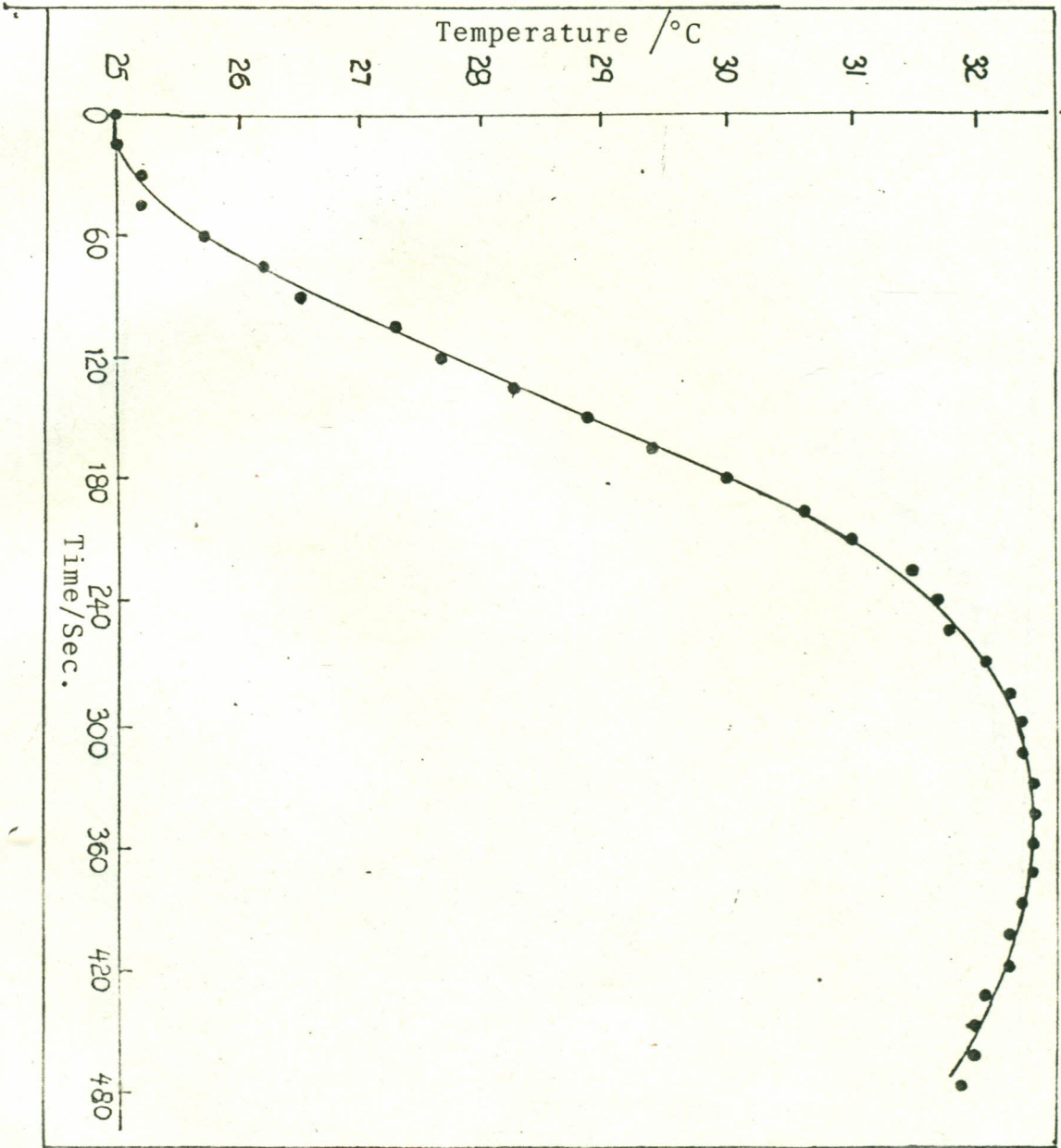


Fig. 21b : Variation of the back surface temperature with time, at 298K, for the isotropic polypropylene sample of crystallinity $\phi = 64.2\%$

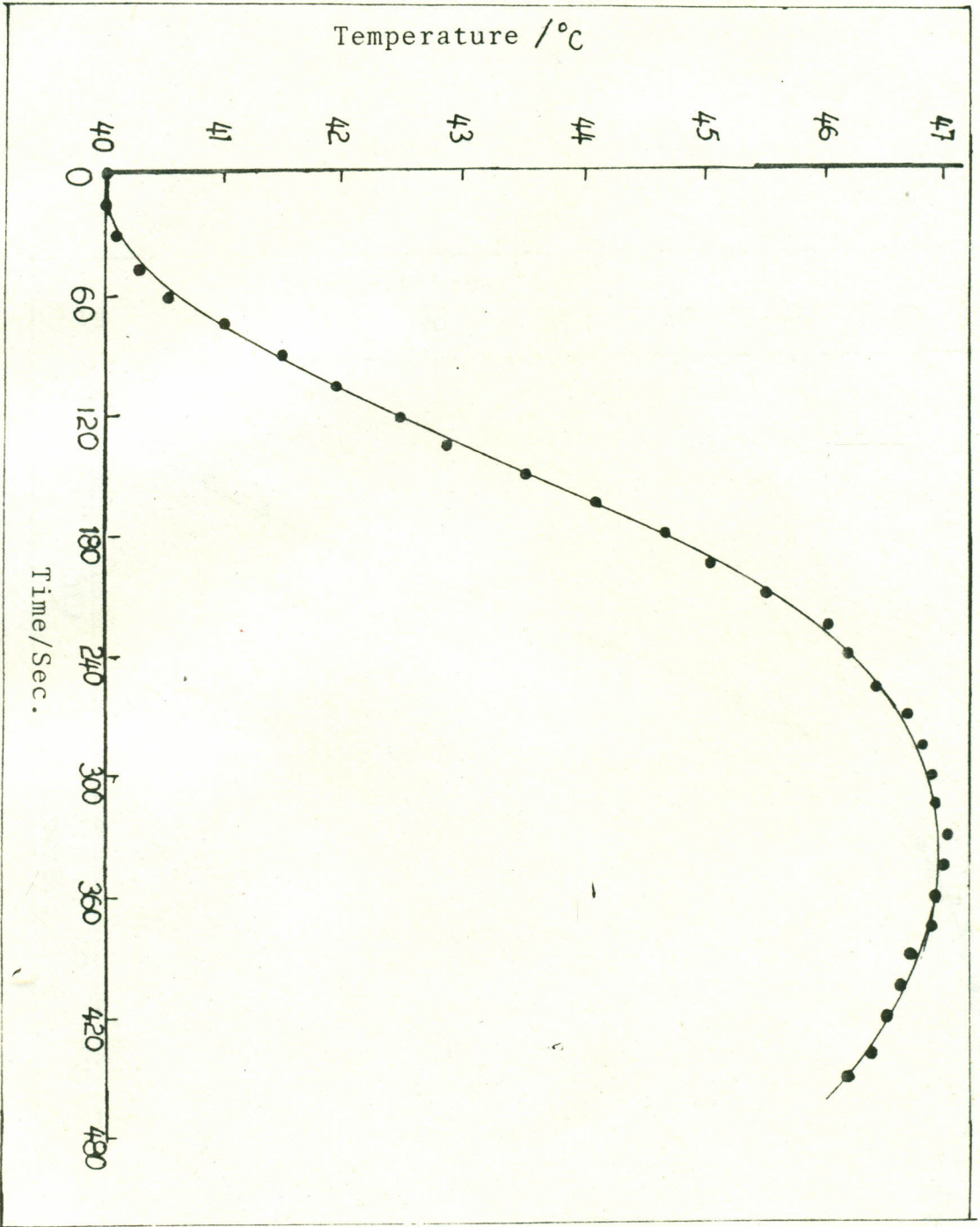


Fig.21c : Variation of the back surface temperature with time, at 313K, for isotropic polypropylene sample of crystallinity $\phi = 64.2\%$.

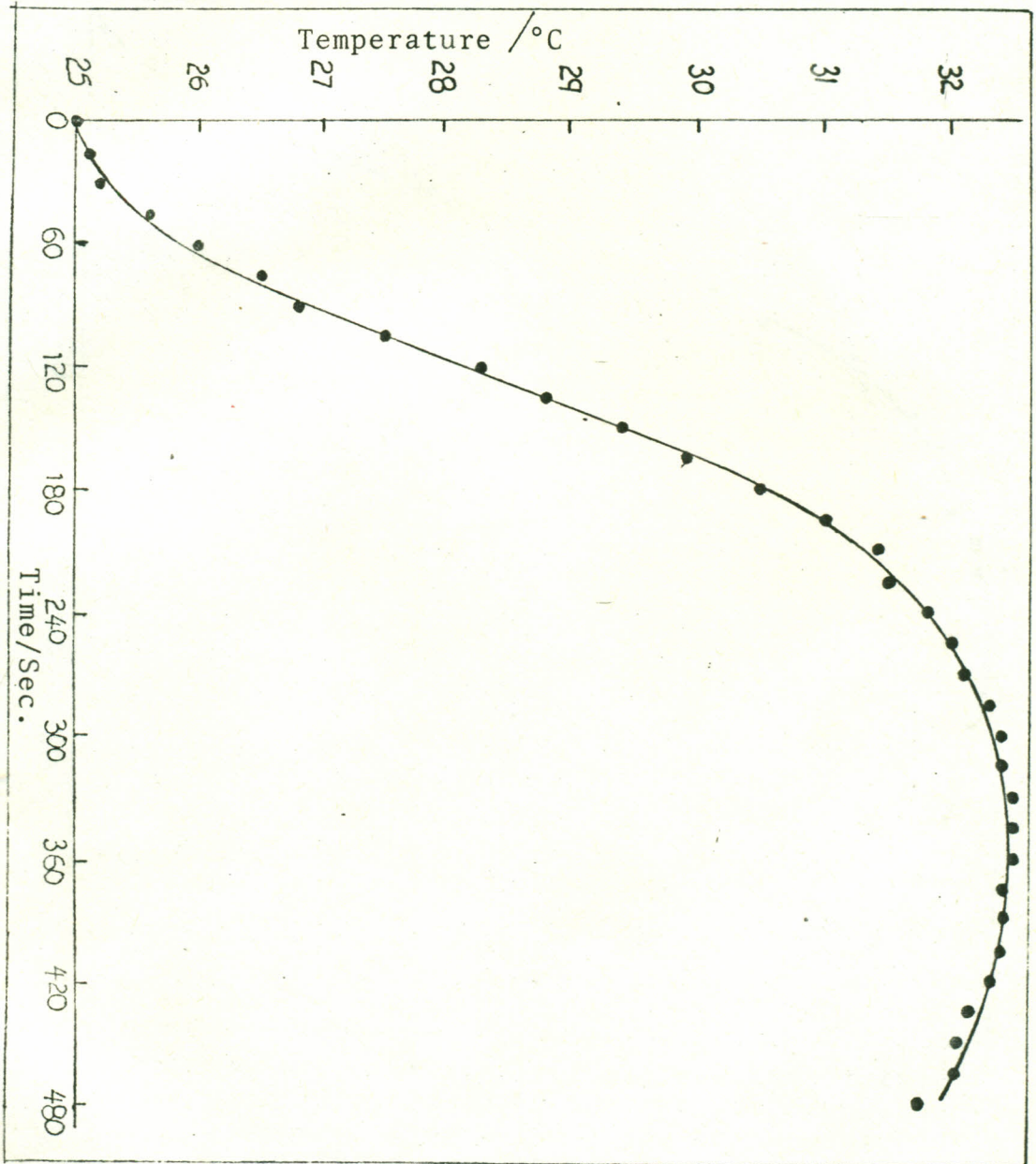


Fig. 21d : Variation of the back surface temperature with time, at 298K, for the isotropic polypropylene sample of crystallinity $\phi = 69\%$.

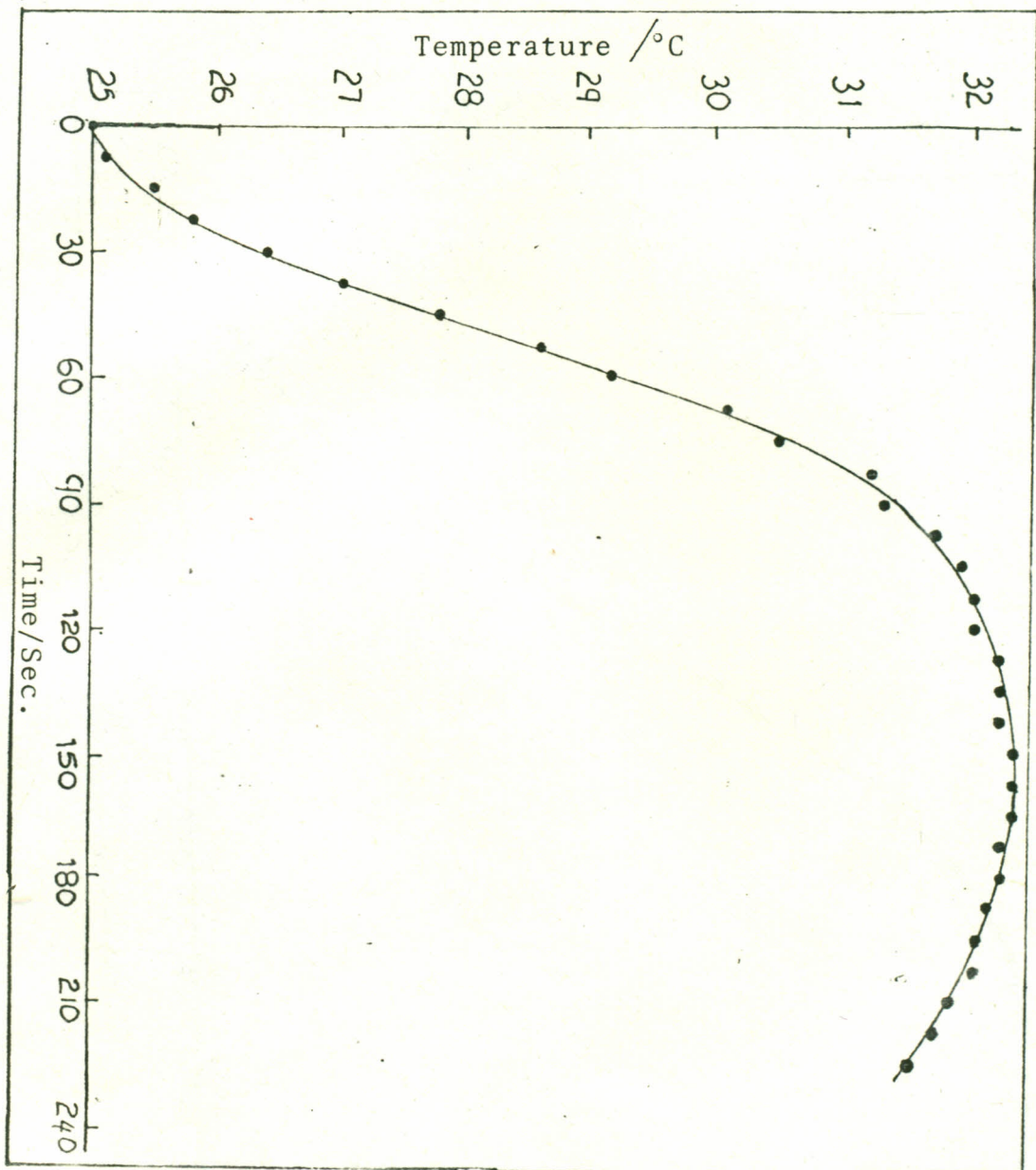


Fig. 21e : Variation of the back surface temperature with time, at 298K, for the polypropylene sample of draw ratio $\lambda = 3$, for measurement along the direction of stretch.

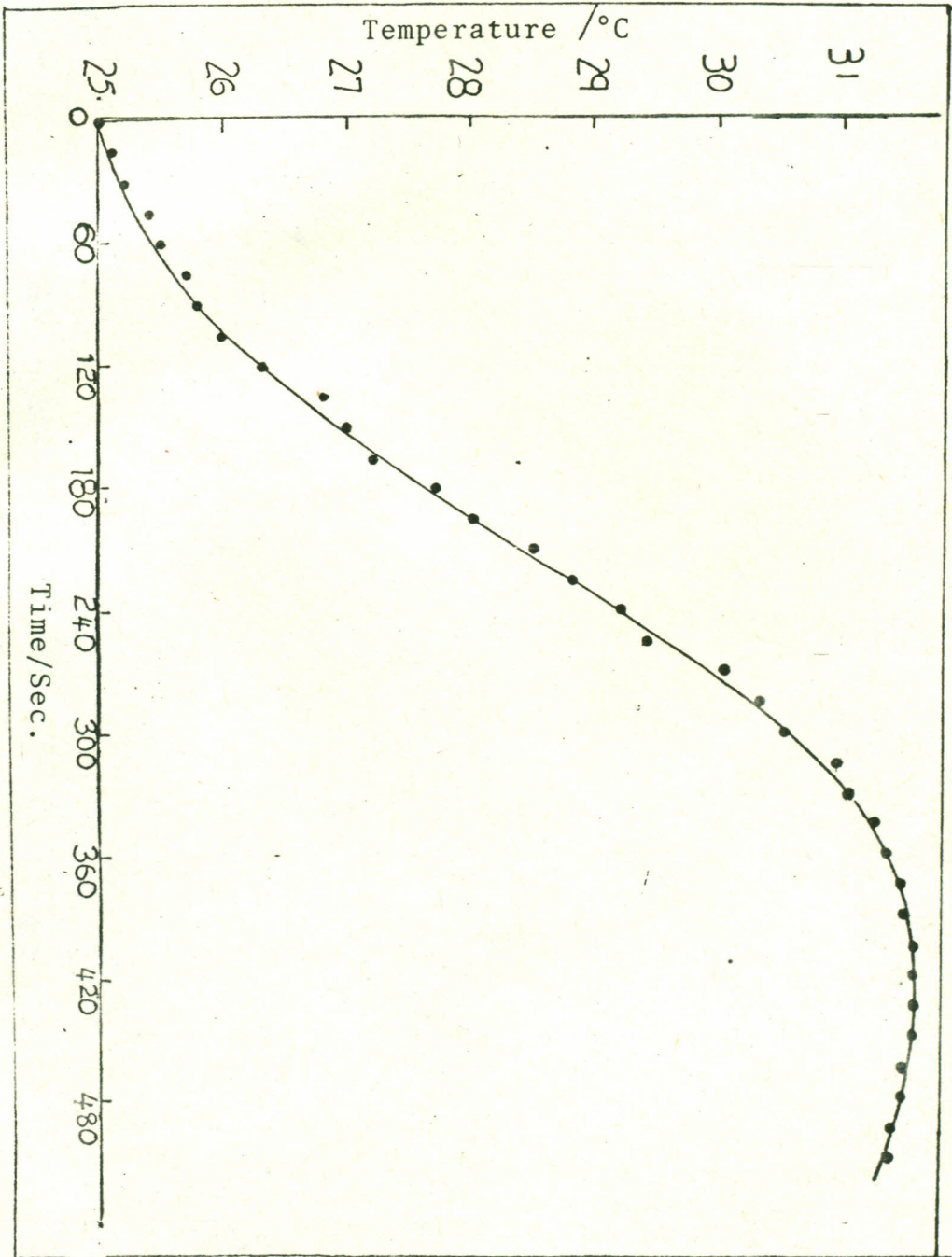


Fig. 21f : Variation of the back surface temperature with time, for the isotropic polystyrene sample at 298K.

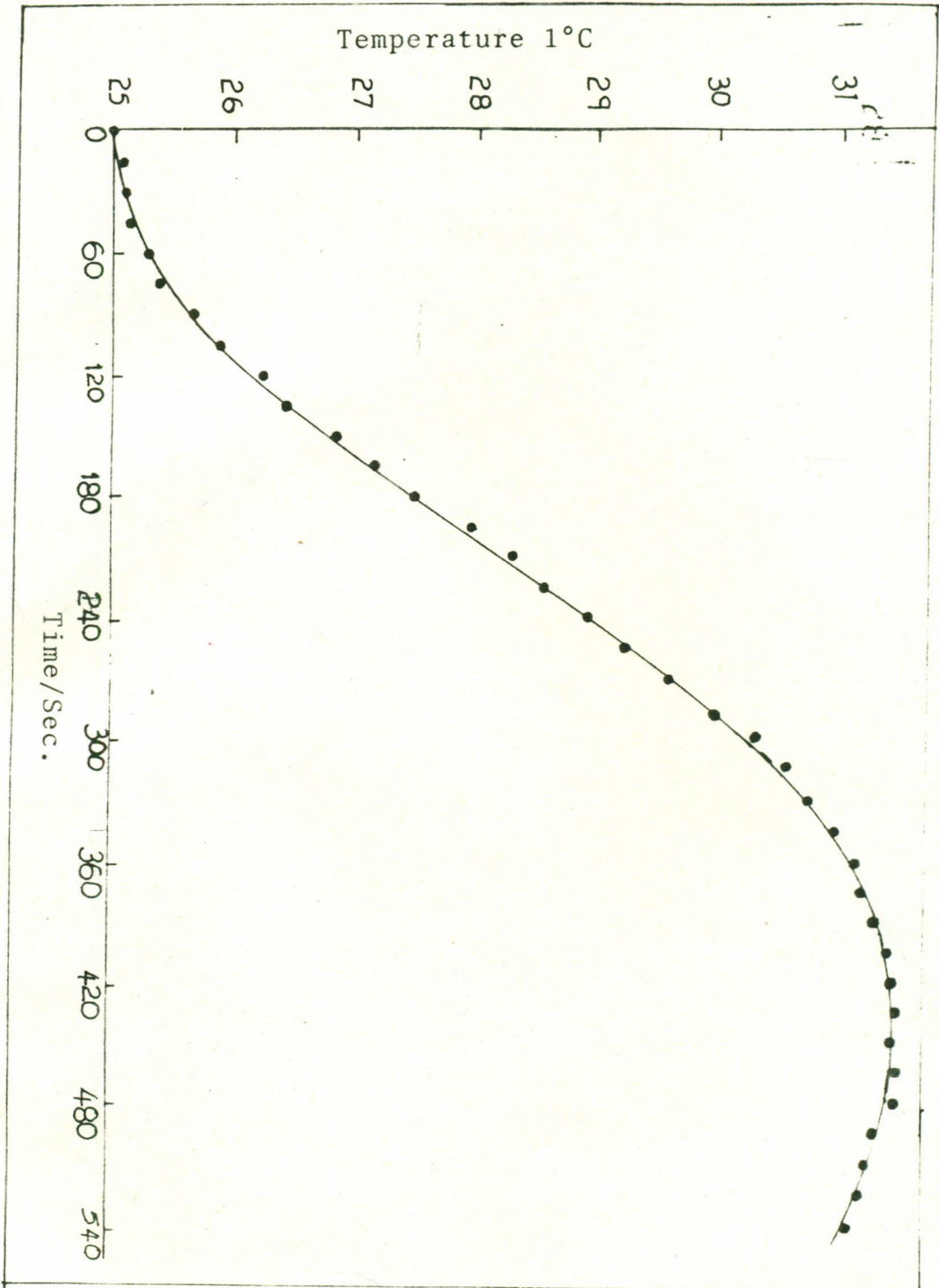


Fig. 21g : Variation of the back surface temperature with time, at 298K, for isotropic polystyrene sample, measurement in the perpendicular direction.

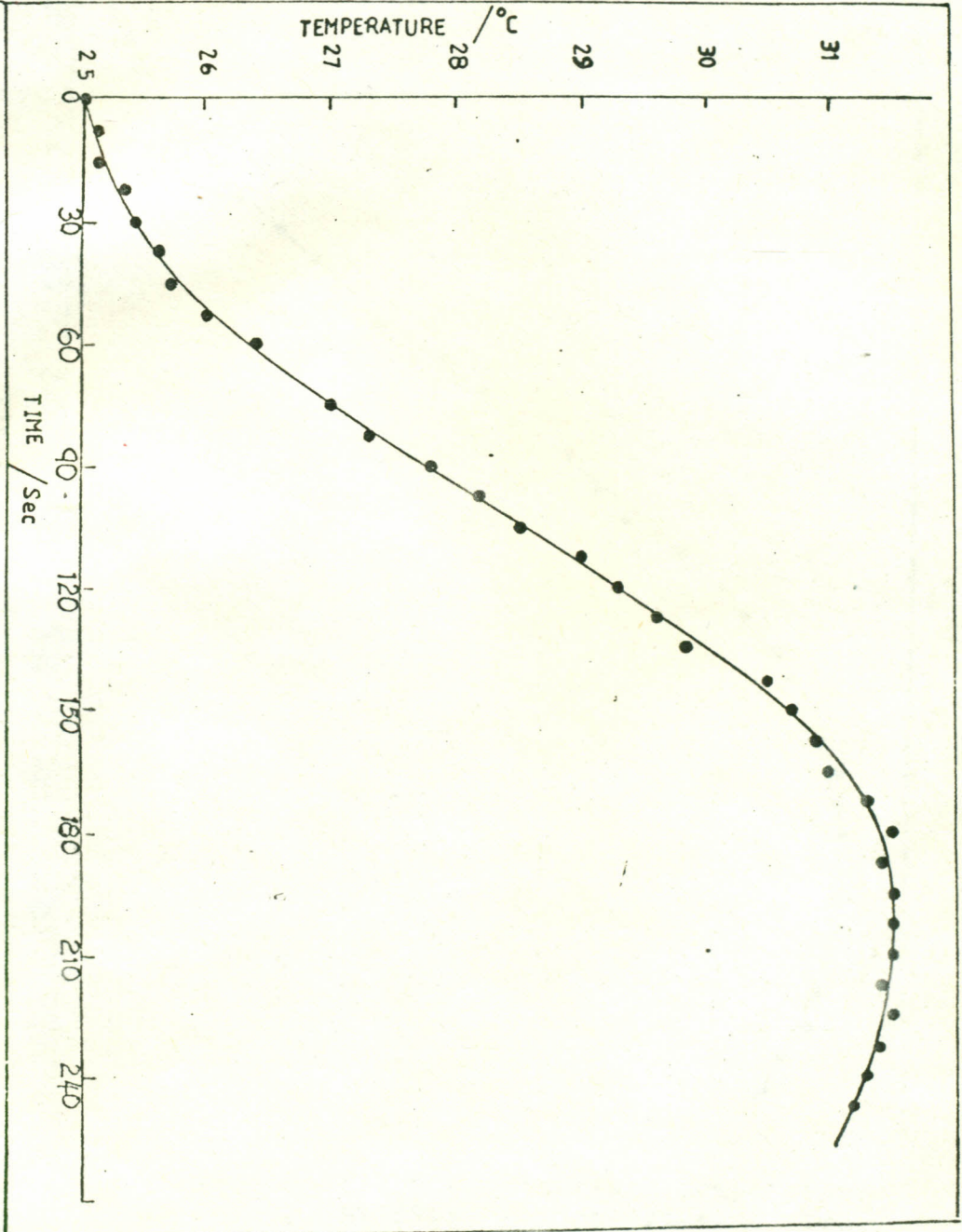


Fig. 21h : Variation of the back surface temperature with time, at 298K, for the polystyrene sample of draw ratio $\lambda=3$, for measurement along the direction of stretch.

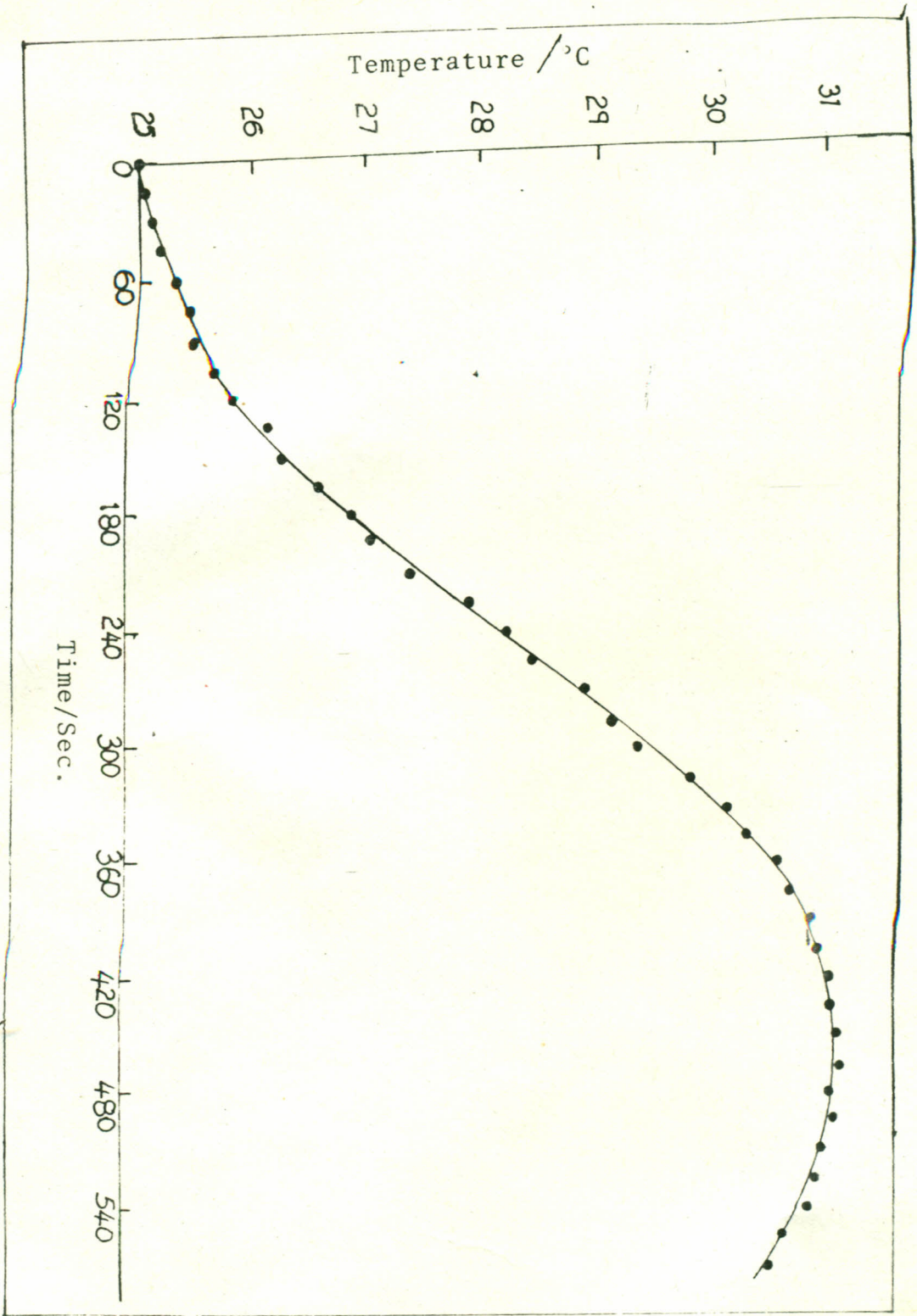


Fig. 211 : Variation of the back surface temperature with time, at 298K, for polystyrene sample of draw ratio $\lambda=3$, measurement in the perpendicular direction.