THERMALLY STIMULATED CONDUCTIVITY IN POLY(VINYL-FLUORIDE)

A Thesis

presented by

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to the

University of St. Andrews

in application for the Degree

of Master of Science

DECLARATION

I hereby certify that this thesis has been composed by me, and is a record of work done by me, and has not previously been presented for a Higher Degree.

This research was carried out in Inveresk Research International, Inveresk Gate, Musselburgh under the supervision of Dr. A. Sharples of Inveresk Research International and of Mr. J.W. Allen of the School of Physical Sciences, University of St. Andrews.

Edward J. Stanley

CERTIFICATE

We certify that Edward J. Stanley, B.Sc., has spent six terms at research work at Inveresk Research International, Inveresk Gate, Musselburgh under our direction, that he has fulfilled the conditions of Ordinance No 51 (St. Andrews) and that he is qualified to submit the accompanying thesis in application for the Degree of Master of Science.

Research Supervisors

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Abstract

This thesis is concerned with the technique of thermally stimulated conductivity applied to a simple vinyl polymer, poly(vinyl fluoride). The thermally stimulated conductivity spectra obtained show peaks due to different phenomena and the separation of these effects is described.

By using novel experimental methods one of the peaks is shown for the first time to be unequivocally associated with the release of previously injected trapped charge, and the location of this trapped charge is discussed.

Two other important thermal effects are also described, one of which is the presence of dipole orientation peaks in the thermally stimulated conductivity spectrum. These peaks are shown to correspond with peaks observed by other workers using different techniques. The other important phenomenon observed in poly(vinyl fluoride) is the presence of a hitherto unreported thermoelectric effect and the origin of the effect is discussed.

By using the techniques described in this work further advantageous investigations in other polymers could be made and previously published data reinterpreted.

CONTENTS

CHAPTER I

INTRODUCTION

Over the last few years evidence has accumulated to indicate that the currents which can be detected in most polymers (including those such poly(ethylene), poly(styrene), and poly(ethylene terephthalate) normally considered as insulators) can be ascribed to movement of electronic charges rather than ions.[1-3] More recently it has been shown that simple vinyl polymers can show quite high dark currents, to an extent that they can no longer be considered as insulators.[4] Viton (the copolymer of perfluoropropylene and vinylidene fluoride), for example, shows a dark steady state current seven orders greater than poly(ethylene); and poly(vinyl fluoride) shows photocurrents of up to 10^{-6} amp.

The existence of such a large difference in current between, say poly(ethylene) and poly(vinyl fluoride) leads to the question as to why this should be so. In particular it is of interest to know whether the bulk physical or chemical structure is responsible, or whether impurity centres or defects are involved which could act as donors or traps. If the latter is the case then it is possible, in theory, to vary the conductivity of such materials by manipulating the impurity concentration.

It is the purpose of this thesis to report the investigations carried out into the existence of such impurities in poly(vinyl fluoride) and other novel effects observed in this polymer using the technique of thermally stimulated conductivity.

1.1 Outline of the Method of Thermally Stimulated Conductivity

The technique of thermally stimulated conductivity (TSC) has been used extensively in the past for obtaining trapping parameters in organic and inorganic solids and is usually carried in the following way.

A sample of the material furnished with electrodes is cooled down

to a low temperature. A source of energising radiation (UV light) is then used to excite the charge carriers from their donor sites in the material, if they exist, and an external field applied. Under the influence of this field the charge carriers drift to the trapping centres where they are localised by the low temperature. The radiation is then removed and the sample heated at a preselected rate. On reaching the temperature at which sufficient thermal energy is given to the charge carriers to excite them from their traps they escape and a current is observed as they move towards their recombination centres. This current increases as the thermal energy reaches a sufficient level to excite the carriers from their traps and then decreases as the traps become empty, and a peak will be observed in the current-time plot. The temperature at which the peaks occur will depend on, among other parameters, the trap depth and the heating rate.

However current peaks depending on release of intrinsically generated charge from trapping sites are not thought to occur in poly(vinyl fluoride) and the methods of analysis must be chosen with care. In the work to be reported the amended technique chosen for obtaining thermally stimulated currents is more akin to that used recently by von Turnhout.[5] This is sometimes called thermally stimulated depolarisation.

Using this method the sample is heated to a temperature T, and an external field applied. This applied field causes rapid alignment of dipoles and migration of mobile charges. After a time t, the sample is cooled down so that the dipoles are frozen in and the charge immobilised. The resulting frozen polarisation can arise from a total of three effects and these are:

(1) immobilised space charge (previously injected from the electrodes under the influence of the electric field).

(2) an asymmetric distribution of charge immobilised in defect traps.

(3) orientation of polar groups within the sample.

Clearly it is of major interest to know how these various factors contribute to the thermal currents.

It is possible to do this from isothermal experiments but the decay of some of the charges proceeds too slowly at a low temperature for convenience and in order to increase the speed of the discharging process the sample is heated at a preselected rate under short circuit conditions. Peaks will then appear on the current-temperature graph as the thermal energy increases to the point at which the thermal relaxation of the process involved is reached.

1.2 Background of Thermally Stimulated Conductivity

The use of thermally stimulated conductivity as a method for discharging previously polarised samples (often called electrets) originated with Frei and Groetzinger[6]. Later it was used by Gross[7] and Gubkin[8] and others[9] who varied the temperature arbitrarily while discharging the sample since they were only interested in the total amount of charge released. Von Altheim[10] was the first worker to realise that the charge release process was controlled by molecular motion and depended strongly on temperature and for this reason a linear heating rate was used by Bucci et al[11,12] and others. This linear heating rate is now used almost universally since it makes the analysis of the thermal spectra easier.

Further work on polymers using this method of the technique of thermally stimulated conductivity is scarce though Lilly et al[13] have reported work on poly(ethylene terephthlate). They came to the conclusion that the polarised state in this polymer is due to either long relaxation time dipoles or an immobilised ionic space charge.

More recently von Turnhout[5] has studied the discharge of electrets formed in poly(methyl methacrylate) and poly(ethyl methacrylate) in some

detail. He explained his results in terms of dipole orientation and previously injected space charge. (He also developed the theory of thermally stimulated depolarisation initially put forward by Gross to include space charge effects).

Kryszewski et al[14,15] are the only workers to have reported results on poly(vinyl fluoride) using the technique of thermally stimulated conductivity. However the thermal spectra that they obtained were complex and suffered from irreproducibilities. In spite of this they came to the conclusion that the most likely explanation for their results was injection of electrons from the metal electrodes with subsequent trapping.

The work on poly(vinyl fluoride) presented in this thesis is based on the method of thermally stimulated conductivity and it is shown that using this method it is possible to obtain reproducible results and distinguish between various effects that arise during the course of the experiments by choosing different conditions. In previous investigations of discharging mechanisms in other polymers the different possible effects have not usually been distinguished. As a result, some apparent thermally stimulated current peaks have been incorrectly attributed to trapping. The techniques described here could be used to advantage in the investigations of other polymers and the reinterpretation of published data.

CHAPTER II

EXPERIMENTAL APPARATUS

Figure 1 shows the equipment used for thermally stimulated conductivity (TSC) experiments in diagrammatic form. The sample SA, was placed in the vacuum chamber between two metal electrodes and connected to the ammeter which consisted of a sensitive voltmeter, V, measuring the voltage drop across a known resistance R. The temperature of the sample was controlled by the heating element TC, and measured by the thermocouple T. Both the current and the temperature of the sample were measured simultaneously by the recorder REC. An electric field was applied to the sample by a battery E which had a switch, S, in series so that short circuit measurements could be made. This equipment is described in more detail in the following sections.

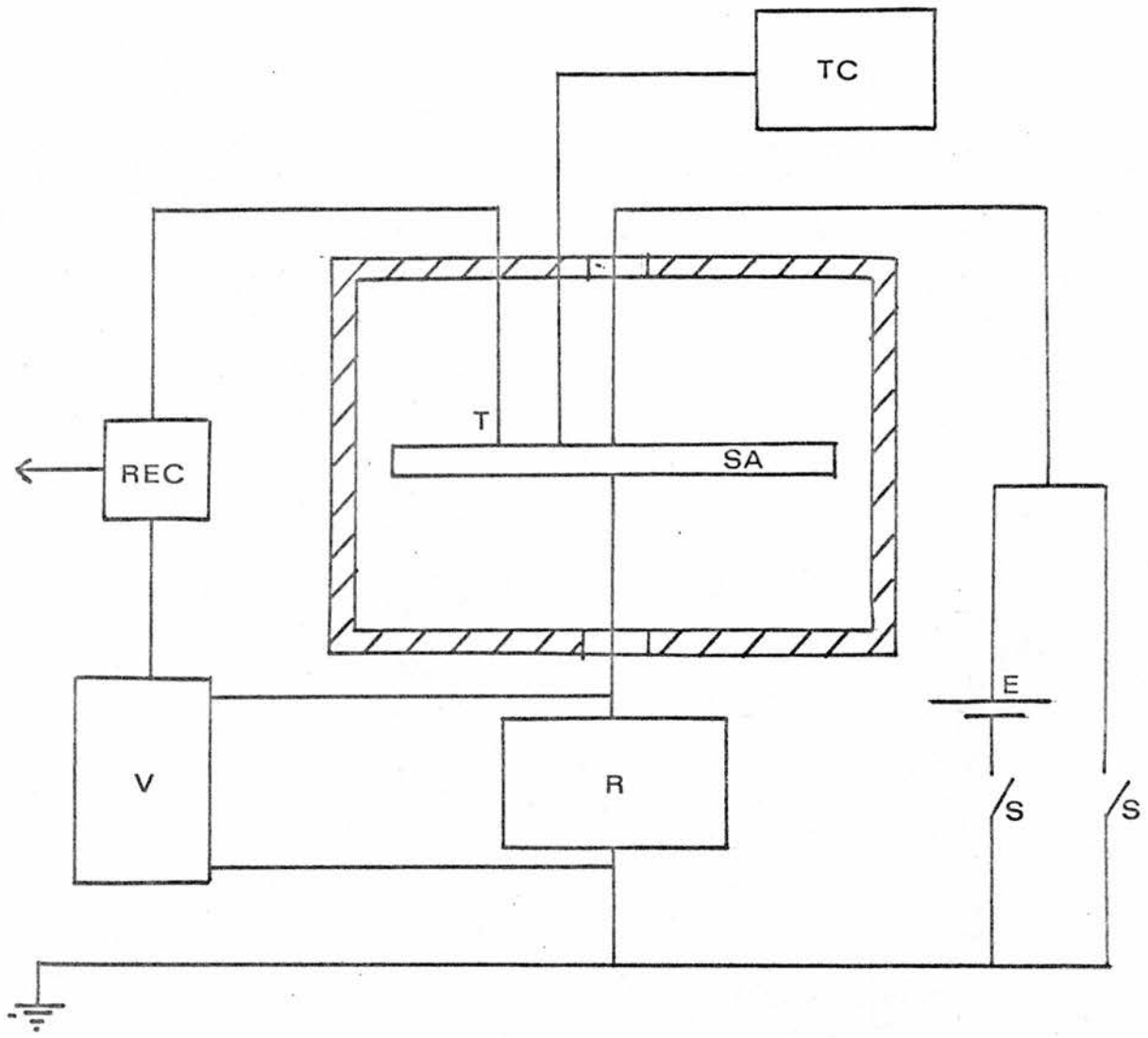
2.1 Materials

The poly(vinyl fluoride) (PVF) samples used in the experiments to be described were commercial films obtained from Du Pont De Nemours, designated as 200SG40TR Tedlar. They were fifty micrometres (μm) thick, transparent but containing a small amount of UV stabilising additives.

Prior to application of the electrodes the films were washed in ethanol to neutralise any surface charge and then dried in a stream of warm air. In general the electrodes were applied by evaporating silver onto each side of the polymer to form discs 2 cm in diameter. Electrical leads of silver wire were attached to the electrodes by means of silver dag (a silver dispersion in MIBK manufactured by Acheson Colloids Company).

In some of the experiments it was necessary to use a highly insulating layer to prevent short circuiting and also as a material for blocking electrodes. The most satisfactory film was found to be one comprising a mixture of poly(tetrafluoroethylene) and fluorethylene propylene. The material was 12.5 μm thick and was again supplied by Du Pont under the trade name of Teflon fep.

Figure 1



Block diagram of T.S.C. equipment

2.2 Apparatus

The TSC apparatus is shown in figure 2. The instrument basically consisted of a brass vacuum chamber placed on an insulating base held above bench height by four aluminium legs. The top of the vacuum chamber was made of stainless steel to which was attached a hollow stainless steel finger projecting into the chamber. Three mounting bolts for supporting the film were also attached to the underside of the top. The chamber itself was insulated from the top by two annuli of Tufnol and two 'O' rings. The polymer sample to be studied was clamped between two brass rings and held in contact with the base of the stainless steel finger by the three mounting bolts and three corresponding nuts. In this position the sample was placed about 3 mm above a silica window so that it could be illuminated if required. The leads from the sample electrodes were taken out through the vacuum chamber wall via two rubber bungs.

The temperature of the sample was measured by means of a chromel-alumel thermocouple seated in a groove in the base of the finger so that it was in direct contact with the top side of the polymer sample.

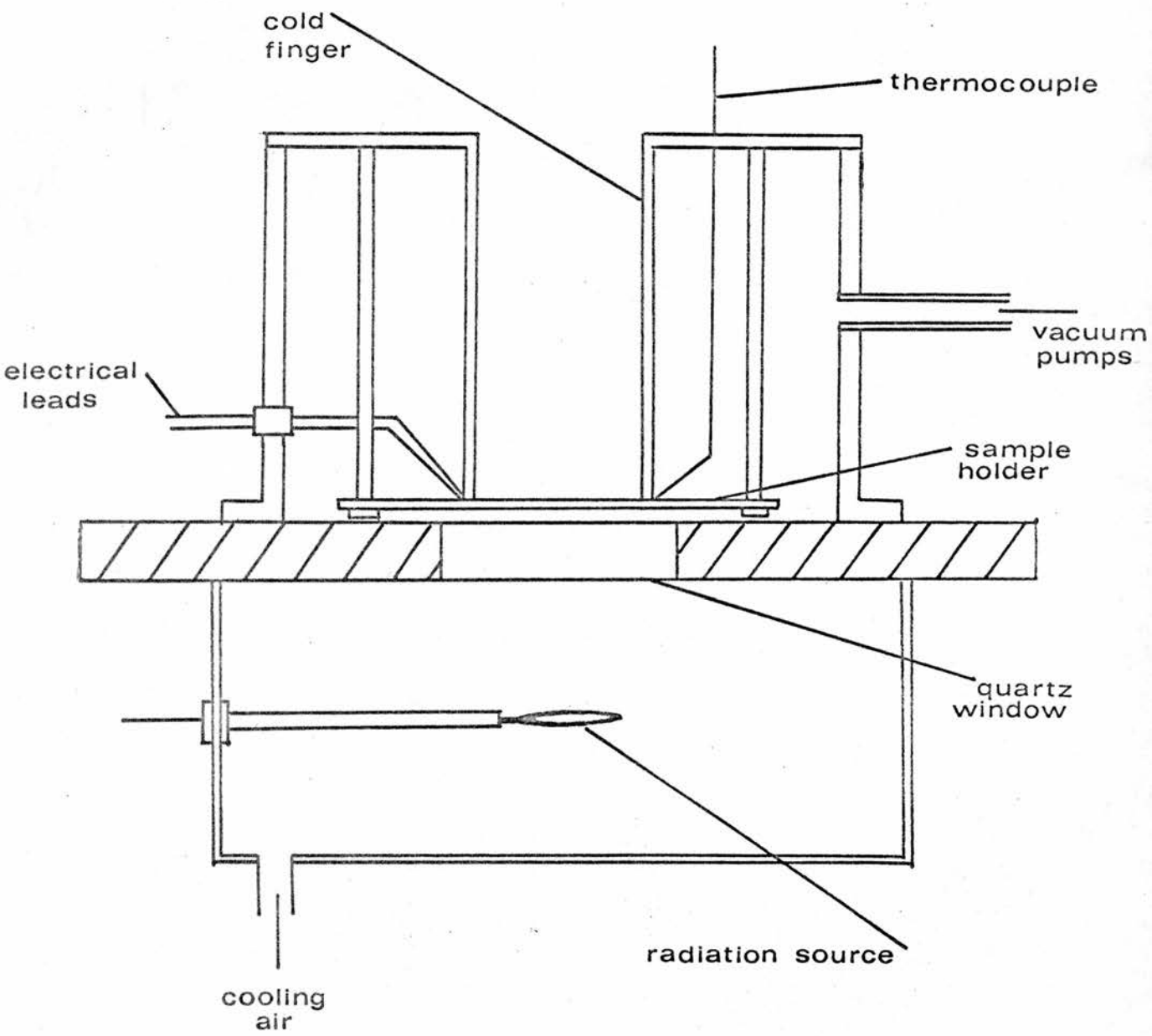
The electric field was applied to the sample by means of a dry cell which was enclosed in a metal container to eliminate any stray capacitance effects. Situated on the side of this enclosure was an off/on switch for the field and also a polarity reversing switch for the voltage output from the thermocouple.

A vacuum was created inside the chamber by means of a mercury diffusion pump and a rotary backing pump and could be maintained at less than 10^{-3} torr over the temperature range used in the experiments.

2.3 Heating System

The temperature range over which the sample could be taken was from $-196^{\circ}C$ to $200^{\circ}C$. The low temperature was obtained by the addition of

Figure 2



T.S.C. apparatus

liquid nitrogen to the finger and subsequent heating was effected by means of a Variac controlled, resistance wound heating element. Near linearity in the heating rate over the whole temperature range was obtained by observing the thermocouple output and making adjustments to the Variac where necessary. The heating rate could be varied between $0.5^{o}C$/min and $15^{o}C$/min.

2.4 Current Measuring System

The current was measured with a Vibron 33B2 vibrating capacitor electrometer, manufactured by Electronic Instruments, used in conjunction with a B33B current measuring unit. By this means the voltage drop across measuring resistors of values 10^{6}, 10^{8}, 10^{10} ohms could be measured and easily converted to current. These measured currents were accurate as long as the effective resistance of the sample was greater than that of the measuring resistance.

Difficulties were experienced under short circuit conditions at about $130^{o}C$ since at this temperature the effective resistance of the sample fell below that of the measuring resistor of 10^{6} ohms. However up to this temperature it was possible to check the accuracy of the readings since there was some overlap on the ranges used and consistency could be checked by switching from one measuring resistor to another.

Voltage could also be measured by the Vibron instrument though not for values higher than 1 volt. Unfortunately the use of the Lindemann electrometer described later in connection with the measurement of higher steady state voltages was not possible for dynamic experiments.

The output from the Vibron was recorded by an Ether 6 channel recorder, one of the channels being used to measure the output from the thermocouple.

CHAPTER III

EXPERIMENTAL METHODS

3.1 Opposed Electrodes

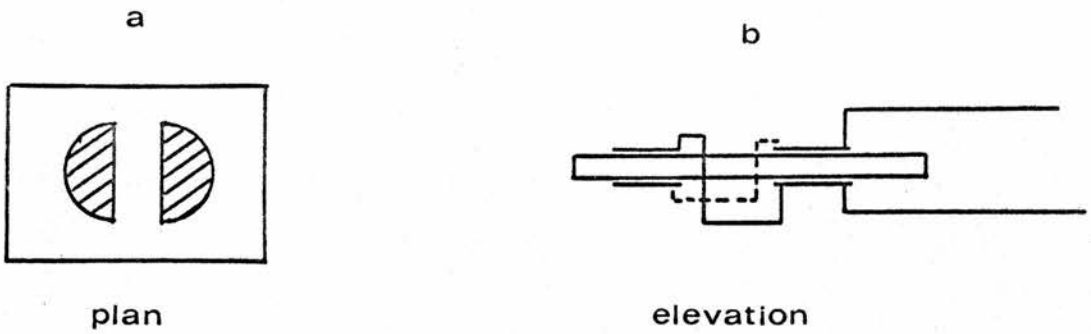
Generally the electrodes were circular in shape and 2 cm in diameter but since the polymer was heated from only one side during the TSC experiments it was clear that a thermal gradient must be built up during the heating process. This thermal gradient was thought to be the cause of a thermoelectric effect which was observed and which obscured the high temperature parts of the TSC plots. In order to overcome this problem a method using split-opposed electrodes was devised.

These electrodes consisted of two silver semi-circular discs evaporated symmetrically on either side of the sample and were separated on each side by about 5 mm with the same total area as the discs used in the other experiments. The diagonally opposite electrodes on either side were connected to each other so that any current arising from an asymmetric temperature gradient was counterbalanced. These electrodes are shown schematically in figure 3a,b.

Using this set up it was necessary to prevent the two top electrodes from short circuiting while being in contact with the base of the finger and this was effected by the interposition of an insulating layer of Teflon fep, 12.5 μm thick, between the finger and the sample.

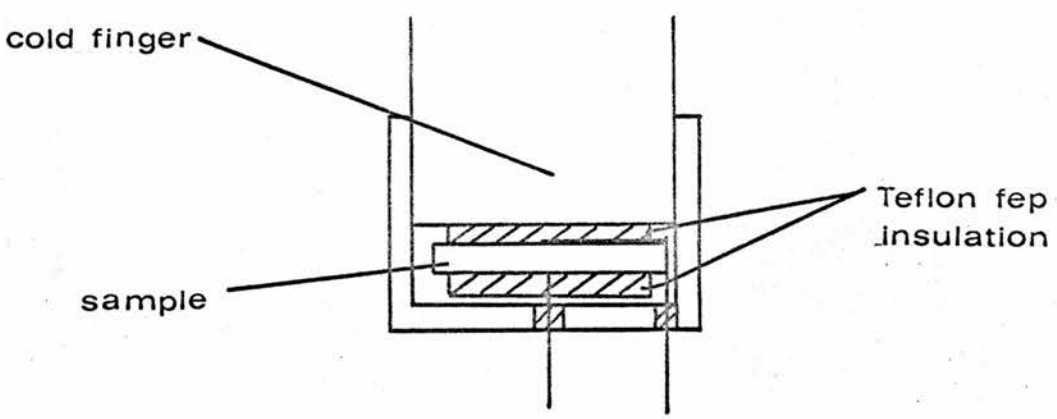
Owing to the poor thermal conductivity of the insulating layer a substantial temperature lag was apparent between the temperature of the sample and that measured by the thermocouple and as set up this could be only overcome in a vacuum by the use of a very slow heating rate (about $0.5^{o}C$/min). To try and reduce this temperature lag the brass clamps used as a sample holder were discarded and a stainless steel jacket was fitted over the end of the finger. This is shown in figure 4. The sample,sandwiched between two insulating layers of Teflon fep, was

Figure 3



Schematic representation of opposed electrodes

Figure 4



Experimental set up using stainless steel jacket

thus enclosed by stainless steel and this helped to obtain a more even temperature distribution. In this case the electrical leads were taken out via two poly(tetrafluoroethylene) plugs in the base of the jacket.

In order to improve the heat transfer properties further an atmosphere of nitrogen was used in some of the experiments.

3.2 Pressed Electrodes

The experiments show that evaporated silver on PVF creates injecting electrodes but in attempting to distinguish between some of the peaks in the TSC spectrum it was necessary to have non-injecting electrodes. This was attempted by evaporating silver onto one side of samples of Teflon fep and pressing the silver into contact with the PVF. However this method was found to give very noisy peaks below room temperature and, more importantly, was found to be injecting at higher temperatures. This system was substituted by one using blocking electrodes with more successful results.

3.3 Blocking Electrodes

The success of experiments using blocking electrodes depends on the criterion that the material used for the electrodes must be of greater resistivity than the material to be studied, which, in this case, is PVF. One material that obeys this criterion is Teflon fep and a system using this polymer was devised. However this system suffers from the same defects as that with opposed electrodes and again there was an unwanted temperature lag.

To try and improve the heat conduction across the system intimate thermal contact was obtained between the relevant layers by subjecting the sandwich to a large pressure prior to the evaporation of the electrodes.

Thus a PVF sample was sandwiched between two layers of 12.5 μm thick Teflon fep and subjected to a pressure of 3,000 lb/sq.in. at a

temperature of 60°C for thirty minutes. Silver electrodes were then evaporated onto the sandwich arrangement and the system enclosed in the stainless steel jacket described previously.

This set-up was found to give satisfactory and reproducible results.

CHAPTER IV

EFFECT OF THE HEATING RATE ON THE THERMALLY STIMULATED CONDUCTIVITY CURVES

Since the position of any peak on the temperature scale of the TSC plots is dependent on the rate of heating of the material, initial experiments were carried out in which the heating rate was varied between $1^{o}C$/min and $10^{o}C$/min.

On varying the rate over this range it was found that the positions of the peaks in PVF below room temperature were displaced towards a higher temperature with increased heating rate and on average the peaks were shifted by $10^{o}C$ for a fivefold increase in rate. However the amount of charge released calculated from the area under the current-time plots remained constant and was not dependent on the heating rate.

At heating rates greater than $5^{o}C$/min it was found difficult to obtain a high temperature peak observed in PVF unequivocally without experiencing difficulties in current measurements. These difficulties have been mentioned earlier and stem from the effective resistance of the sample decreasing to less than 10^{6} ohms at about $130^{o}C$.

With the above problem and the inaccuracies that arose in the temperature measurements in the opposed and blocking electrode experiments due to the presence of the insulating layer interposed between the thermocouple and the sample, it was decided, in general, to use a heating rate of about $3^{o}C$/min.

CHAPTER V

RESULTS AND DISCUSSION

Both the usual method of thermally stimulated conductivity and the method used in this work have been described briefly in the introduction. On PVF the usual method of TSC gave no results as can be seen from the following experiments:

A 50 μm thick sample of PVF with unopposed electrodes, one being semitransparent, was subjected to a field of 24 kV/cm (120 volts applied) at -196°C for five minutes. The field was then removed and the sample warmed up under short circuit conditions. No detectable current was observed up to room temperature. A similar experiment was also carried out in which the sample of PVF was subjected to UV irradiation for the same period of time as the field, before being warmed up under the same conditions. This gave a similar result in that no TSC peak was observed.

These results can be explained if PVF does not contain intrinsic charge carriers, (or the trapping levels are very deep) and this argument has been supported by other workers.[3,4] In other words the currents that are observed in this polymer arise from charge injection from the electrodes or from reversible charge absorption processes.

With this in mind modifications to the above experimental sequences were devised which did give rise to thermally stimulated currents. These sequences are listed below for ease of reference and are designated sequence A and sequence B.

Sequence A

(a) Cool the sample to -196°C .

(b) Apply -120 volts.

(c) Heat at a linear rate with the field still applied.

Sequence B

(a) Apply -120 volts to the sample at room temperature.

(b) Cool rapidly to -196°C with the field still applied.

(c) Short circuit and heat at a linear rate.

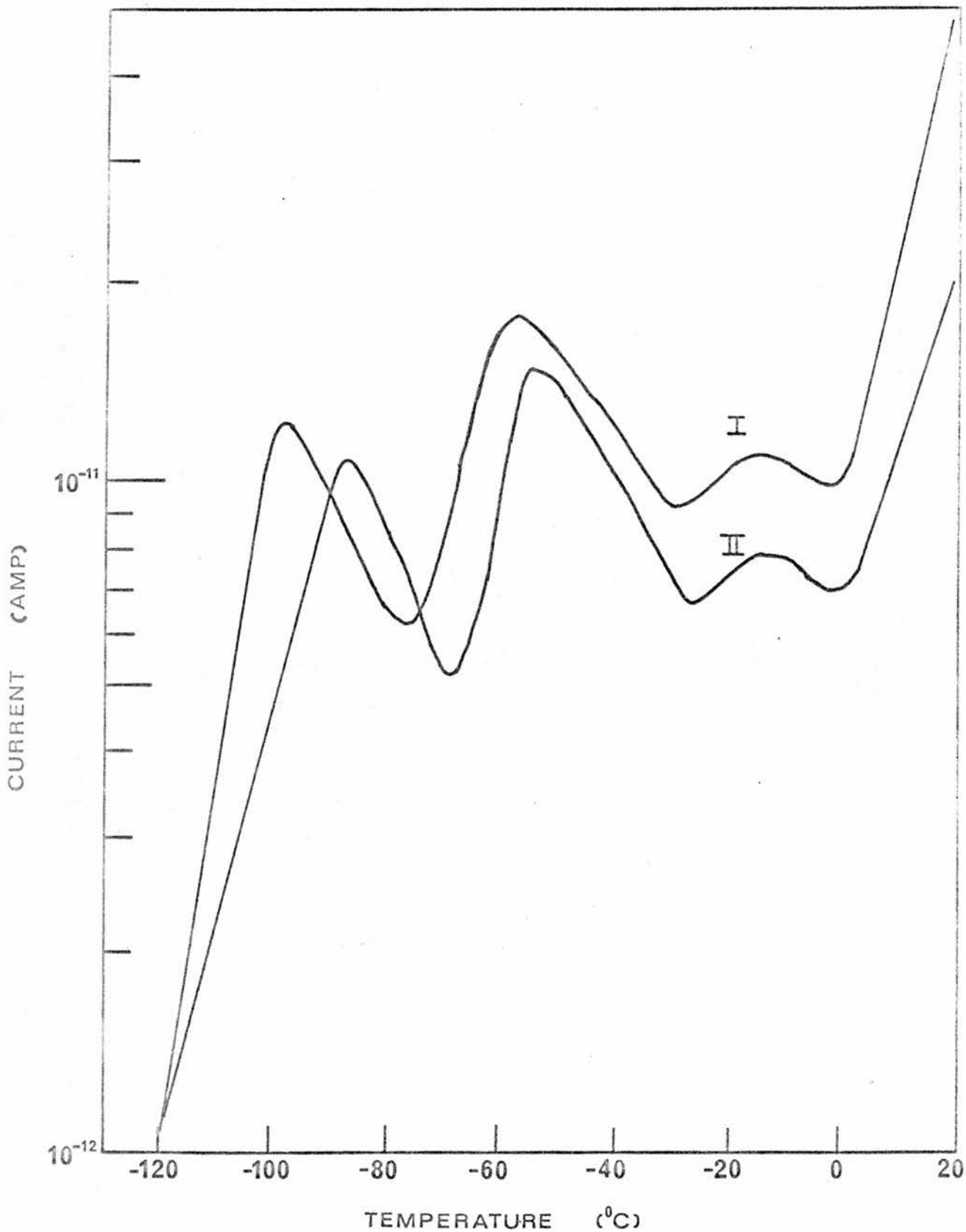
Since the results in PVF are least complicated below room temperature the work in this region is discussed first.

5.1 Thermally Stimulated Currents Below Room Temperature

As is shown later the application of a field to a sample of PVF with evaporated electrodes gives rise to a detectable steady state current which results from injection of charge carriers from the electrodes. The charge carriers may subsequently be trapped as they migrate across the sample under the effect of the field. If the temperature of the sample is then lowered the charge carriers will be immobilised and remain so even when the electrodes are short circuited. As explained previously, warming the sample under these conditions will give rise to peaks in the current, if the traps are not too deep, as the charges move back under the reverse field.

Using this argument the following experiment was carried out in which a sample of PVF, furnished with evaporated silver electrodes, was subjected to a field of 24 kV/cm at room temperature for 10^4 seconds and then cooled to -196°C following sequence B. On warming the sample at the 'standard' heating rate of 3°C/min the current-temperature (time) plot shown in figure 5 was obtained. The observed current was in the correct direction (namely opposite to that observed during the application of the field at room temperature) and is designated II in the figure. From the discussion at the beginning of this section it would seem natural to deduce that the peaks observed in the current-time plot are due to release of charge from traps but if this hypothesis were correct the current time plot for the experiment in which sequence A was used would be different. In this case the application of a field at a low

Figure 5



I 120 volts applied
II S/C conditions

T.S.C. peaks below room temperature

temperature with subsequent warming would give a stepwise increase in the current with no peaks apparent. These steps would occur as the thermal energy becomes sufficient to empty the associated trap and the current thus would become less trap dominated. The stepwise increase will occur at each successive trap giving a continual increase in current.

However when the experiment using sequence A was carried out a near identical plot, but of opposite sign, to that using sequence B was obtained. This is shown in figure 5 and is designated I. The temperatures at which the peaks occurred were $-95^{o}C$, $-60^{o}C$, $-15^{o}C$, and the area under the current-time plot was measured and found to be constant at 3.2×10^{-8} coulombs.

Since the second graph obtained was not consistent with the concept of traps an alternative explanation was sought and one which is consistent with the above results is that the application of a field displaces charge to a limited extent at room temperature which returns to its original position on short circuiting. Such limited displacement of charge is typified by dipole orientation.

The following calculation shows that the value of the amount of charge displaced is consistent with this idea.

Dielectric displacement is given by

$$D = \varepsilon E = \varepsilon_{o} E + P \qquad (1)$$

where E is the field strength, P the polarisation of the sample, ε the dielectric constant and ε_{o} the dielectric constant of free space.

Multiplying (1) by the area of the electrodes, A, and using the capacitor relation

$$Q = CV = \varepsilon AV/d$$

the total amount of charge displaced during the polarisation is

$$Q = AV\varepsilon_{o}/d + AP \qquad (2)$$

The first term of the equation relates to the charging current of a vacuum capacitor and the second to the polarisation of the dielectric material, which in this case is PVF. Clearly the TSC experiments will not show the component due to the instantaneous charging of the capacitor and the only important term is the second. Thus it is possible to calculate the maximum possible charge obtained if all the dipoles were aligned by the field and this is given by,

$$Q_{max} = AP = AN\mu$$

where μ is the dipole moment of a C-F bond, N is the dipole density and A is the area of the electrodes.

The density of PVF is 1.4 gm/cc and assuming that there is one C_2H_3F group per dipole, then using Avogadro's number,

$$N \simeq 10^{22} \text{ dipoles/cc.}$$

The dipole moment of a C-F group is approximately 2 debyes, or 6.7×10^{-28} coul. cm, and in the above experiments the area of the electrodes, A, was 3.1 cm^2 so that

$$Q_{max} = AN\mu$$
$$= 2 \times 10^{-5} \text{ coul}$$

This is a factor of 10^3 greater than the charge displaced in the above experiments (3.2×10^{-8} coul) which means that only one in 10^3 dipoles has been oriented.

In order to test the hypothesis that the low temperature peaks were due to dipole orientation, experiments using blocking electrodes from which there is no injection of charge were carried out.

5.1.1 Blocking Electrodes

The experimental set up for using blocking electrodes has already been described in the experimental section but before carrying out the experiments it was necessary to obtain the value for the voltage drop across the PVF when a field is applied across the entire sandwich structure.

This voltage drop can be calculated by considering a field applied across two dielectrics (1 and 2) in contact.

The voltage drop across each dielectric is proportional to the thickness d, and inversely proportional to the dielectric constant so that

$$\frac{V_1}{V_2} = \frac{d_1}{d_2}\frac{\varepsilon_2}{\varepsilon_1} \qquad (3)$$

where V_1 is the voltage drop across dielectric, 1, d is the thickness of 1, and ε_1 is the dielectric constant of 1.

Also $V_1 + V_2 = V$ = total voltage applied across the system.

This equation was checked by evaporating silver electrodes onto PVF and connecting these to a Lindemann electrometer. The sample of PVF was then sandwiched between two layers of Teflon onto which were already evaporated silver electrodes and these connected to a battery.

Voltages of varying magnitude were then applied to the sandwich structure and the voltage drop across the PVF measured. The voltage drop across the PVF was then plotted against the voltage applied to the sandwich and is shown in figure 6. Also shown is the theoretical line which was calculated by putting numerical values in equation 3.

Thus d_1 = 2 x thickness of Teflon = 500 μm

d_2 = thickness of PVF = 50 μm

ε_1 = dielectric constant of Teflon = 2.1

ε_2 = dielectric constant of PVF = 7

Equation (3) thus yields

$$V_1 = 33V_2$$

which gives the total voltage across the sandwich V to be $V = 34V_2$.

From the graph it can be seen that the measured drop across the PVF is low compared to the theoretical line and gives $V = 46V_2$.

The difference between the two equations can be explained by the large experimental error involved and the results were considered

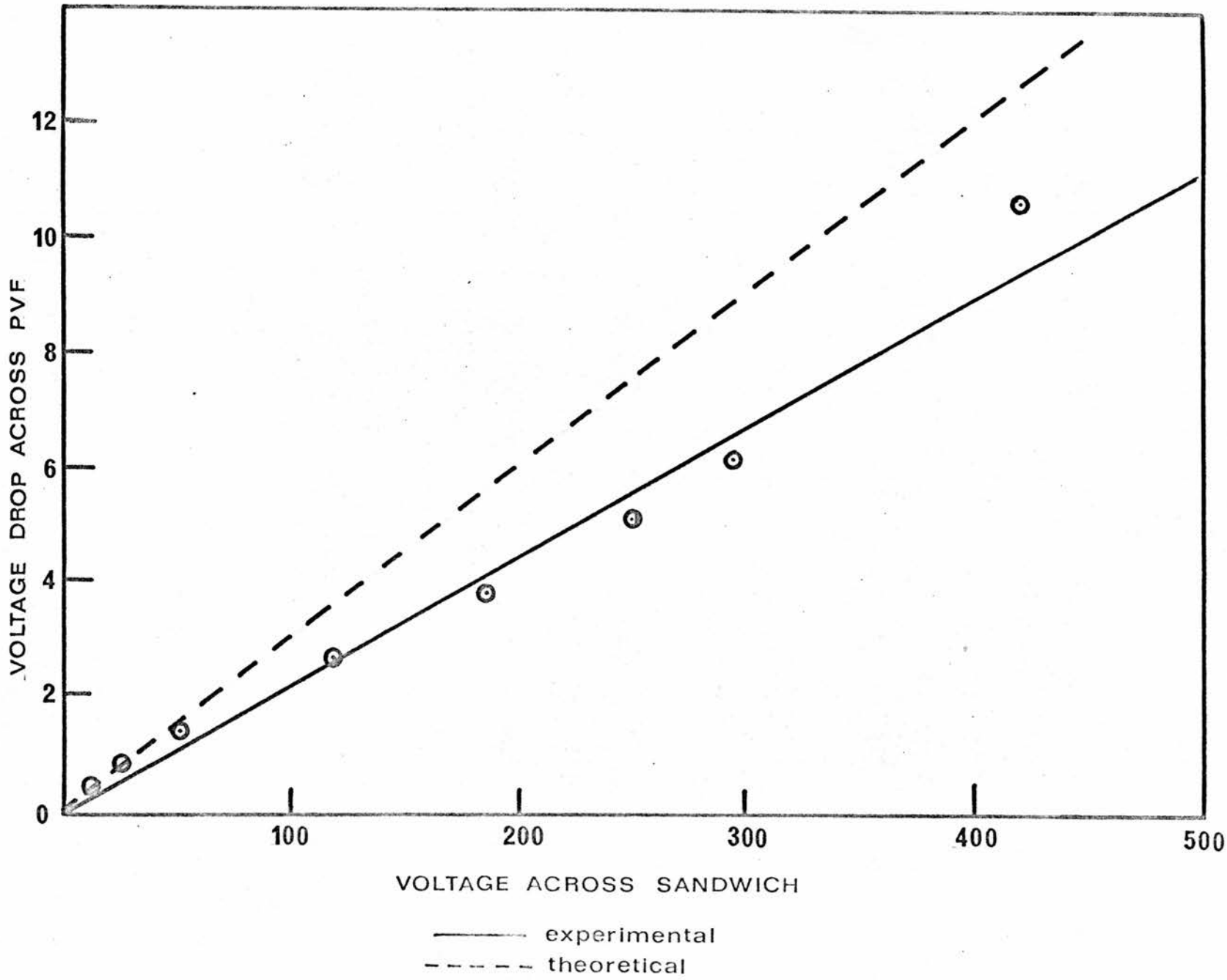


Figure 6

Voltage drop across P.V.F. against voltage applied across PTFE/PVF/PTFE sandwich

to be verification of equation 3.

In the experiments to be described the blocking electrodes were made of Teflon fep whose thickness was 12.5 μm. Putting a new value for the thickness in equation 3 yields;

$$V_2 = 0.6\ V_1$$

In order to compare the results with other TSC plots the voltage drop across the PVF must be 120 volts which makes the voltage across the Teflon fep 200 volts and the total applied voltage 320 volts.

The blocking electrodes system was then set up as described in the experimental section and a TSC plot using 320 volts in sequence A obtained. The plot gave 3 peaks that were noisy, probably due to the difference in the thermal expansion between the two materials, but the area under them could be measured and was found to be 9×10^{-9} coul. Using sequence B an identical plot was obtained with the same amount of charge displaced and this compared well with the figure obtained using evaporated electrodes, which was 3.2×10^{-8} coul.

The knowledge that the amount of charge displaced in experiments using 'blocking' electrodes and evaporated electrodes is similar coupled with the fact that blocking electrodes are non-injecting indicates that the three peaks observed are due to a limited reversible displacement of charge. This sort of displacement is typified by dipole orientation and it is thought that the existence of three separate peaks in the TSC plots is likely to be associated with the second order transition in the polymer when radicals or short side chains become mobile.

Various workers have reported transitions in PVF in the past, all of them using dielectric relaxation methods. The results of these are given in Table 1

TABLE 1

Method	Peak Temperature, °C			
Present work	-95	-65	-20	
Dielectric loss[16]			-20	75
Mechanical loss[17]			-25	75
Viscoelastic[18]			-20	41
Dielectric loss[19]		-75		45
Dielectric loss[20]		-60		
Dielectric loss[21]		-60		

From this table it can be seen that the temperatures at which peaks have been observed in the TSC work correspond to temperatures at which transitions have been reported by other workers. The exception is the -95°C peak but this is explained by no workers having reported dielectric experiments carried out at such a low temperature. Although there is a good correlation between the results it is important to remember that conventional methods for measuring loss peaks are carried out either isothermally or isochronously whereas in TSC experiments both the temperature and time are varied simultaneously. This means that in the latter case the results are dependent on the heating rate and are thus not strictly comparable with other methods, though von Turnhout has developed a theory for comparing the results.

On studying the table the other important point that emerges is that a further TSC peak may be expected above room temperature. However before reporting the investigations at higher temperatures the application of a field at room temperature will be discussed.

5.2 Currents at Room Temperature

The application of a field of 24 kV/cm, across a 50 μm thick sample of PVF with evaporated electrodes gives a current-time relation as shown in figure 7. The relevant curve is designated I. From this it can be

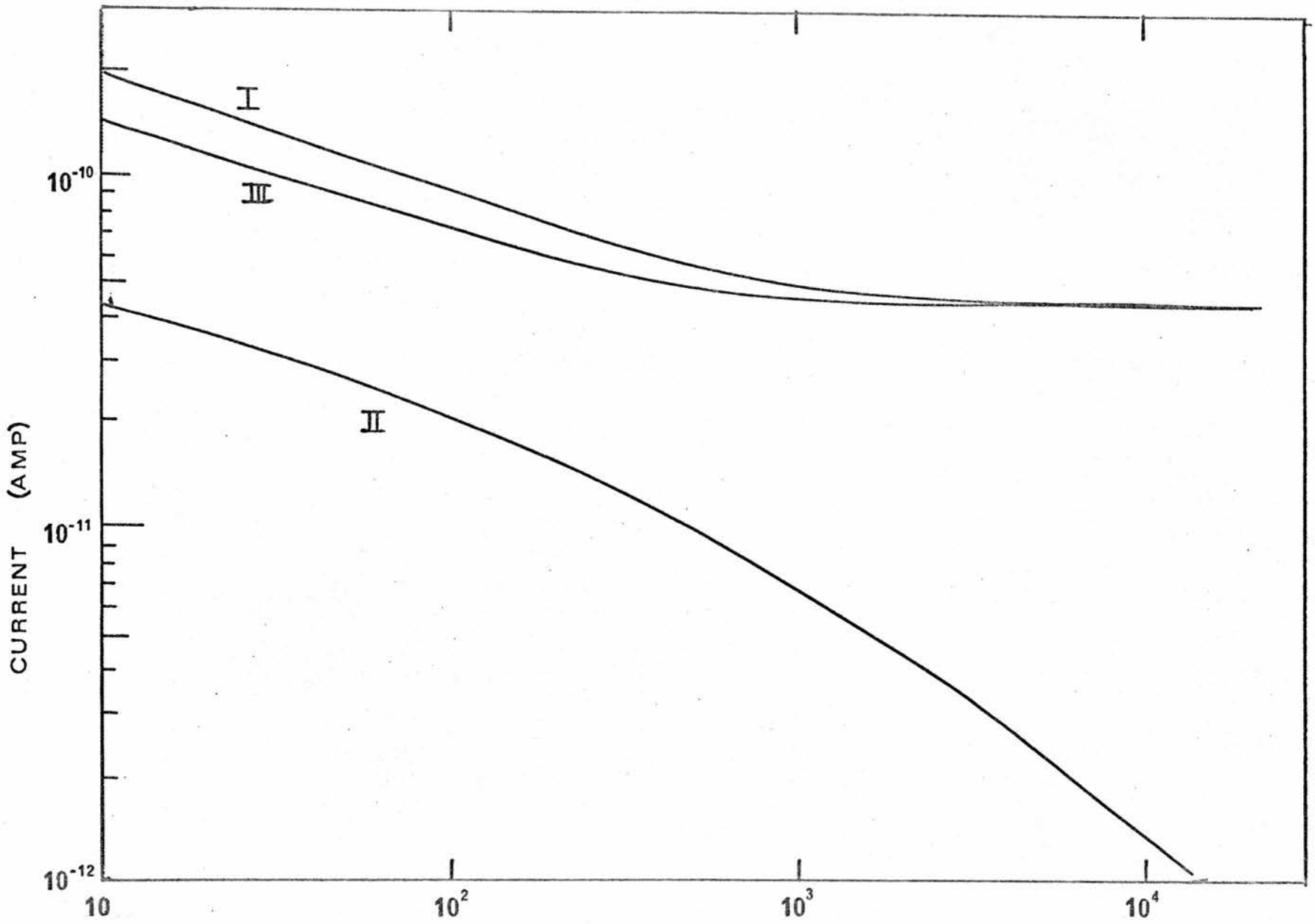


Figure 7

Room temperature currents

I evap. electrodes 120 volts
II pressed electrodes 120 volts
III = I − II

seen that a steady state is reached after 4×10^{3} seconds at a level of about 4×10^{-11} amp. The existence of a steady state current suggests that there is injection of charge carriers from the electrode with subsequent transport across the sample.

If however pressed electrodes are used, in which silver is evaporated onto quartz and pressed into contact with the film, a different result is obtained.[22] A continually decreasing current is observed, figure 7 II, which can be associated with the orientation of dipoles. This current terminates when all the dipoles have taken up their positions. The area under the curve is 2.5×10^{-8} coul which corresponds quite closely with the amount of charge released in the TSC runs below room temperature. The two processes can thus be equated.

Short circuiting the sample both with pressed and with evaporated electrodes gives a current time curve which is identical to II but opposite in sign which shows that the dipoles relax in both cases as expected. However the important point is that the trapped charge, if present, is not released to any detectable extent at room temperature.

The amount of charge injected can be obtained by subtracting II from I to give III. This is also plotted in figure 7 and can be seen to be time dependent and shows that a detectable amount of charge is injected and absorbed by the film. Since this charge is probably located at the injecting electrode its effect in the external circuit will only be registered in proportion to the distance moved. Consequently the area under curve III less the steady state current measured as 1×10^{-8} coul represents only a lower limit for the amount of charge injected.

Nevertheless the important point is that charge can be injected and retained by the polymer at room temperature and may be expected to be released at higher temperature.

5.3 Thermally Stimulated Conductivity above Room Temperature

Up to now there are two indications that a peak might be observed above room temperature in the TSC spectrum. One is the injection of charge just mentioned and the other is the existence of a high temperature dielectric loss peak reported by other workers (see Table 1).

In order to study the TSC plots above room temperature the previous sequences A and B mentioned earlier were used but extended to include higher temperatures. As noted this gives;

Sequence A^1

(a) Cool the sample to $-196^{o}C$

(b) Apply - 120 volts

(c) Heat at a linear rate with the field still applied to about $130^{o}C$.

Sequence B^1

(a) Apply -120 volts at room temperature and heat to about $100^{o}C$

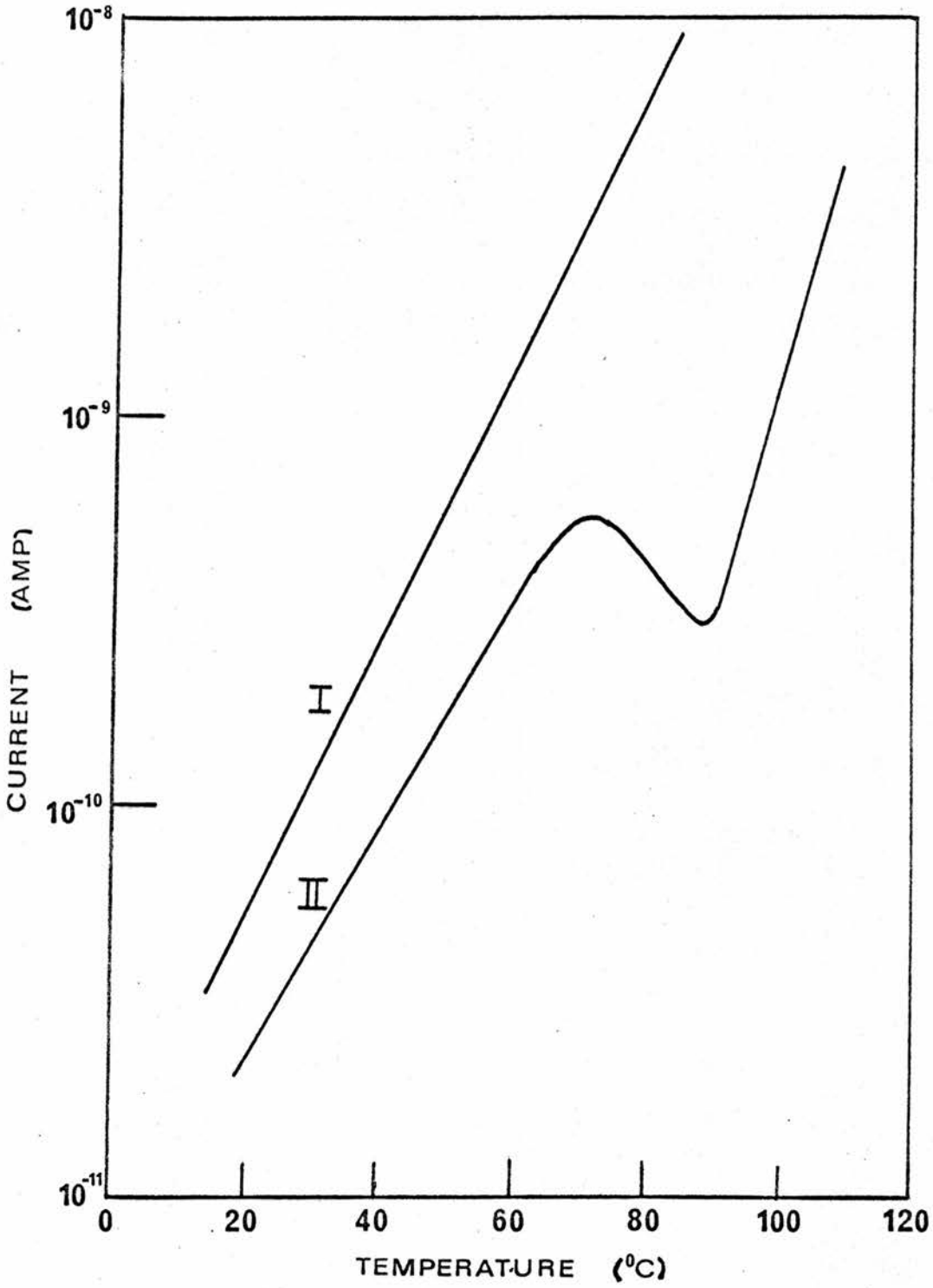
(b) Cool down to $-196^{o}C$

(c) Short circuit and heat at a linear rate.

Figure 8,I shows that on applying sequence A^1 to a sample of PVF the low temperature peaks were observed as before but above room temperature there was a continually increasing current ascribable to conduction across the sample.

Sequence B^1, however, gave some new features which are shown in figure 8,II. From this figure it can be seen that there is a peak at $75^{o}C$ which is in the region of the glass-rubber transition temperature and is clearly of some importance. Also, above room temperature there is a further increase in current which tends to overlay the $75^{o}C$ peak. The appearance of this current was mysterious since it increased to a level of 10^{-8} amp at a temperature of $130^{o}C$ and showed no sign of decreasing. It was not possible to obtain any results above this

Figure 8



T.S.C. peaks above room temperature

I 120 volts applied II S/C conditions

temperature since at this temperature the effective resistance of the sample decreased to such an extent that current measurements were meaningless. Since the magnitude of the charge displaced, calculated from the area under the current time curve was in excess of 10^{-3} coul it was considered that this current might be an artefact of the experimental set-up. Further experiments were then carried out to see if this was so and investigate the effect.

5.3.1 The Thermoelectric Effect

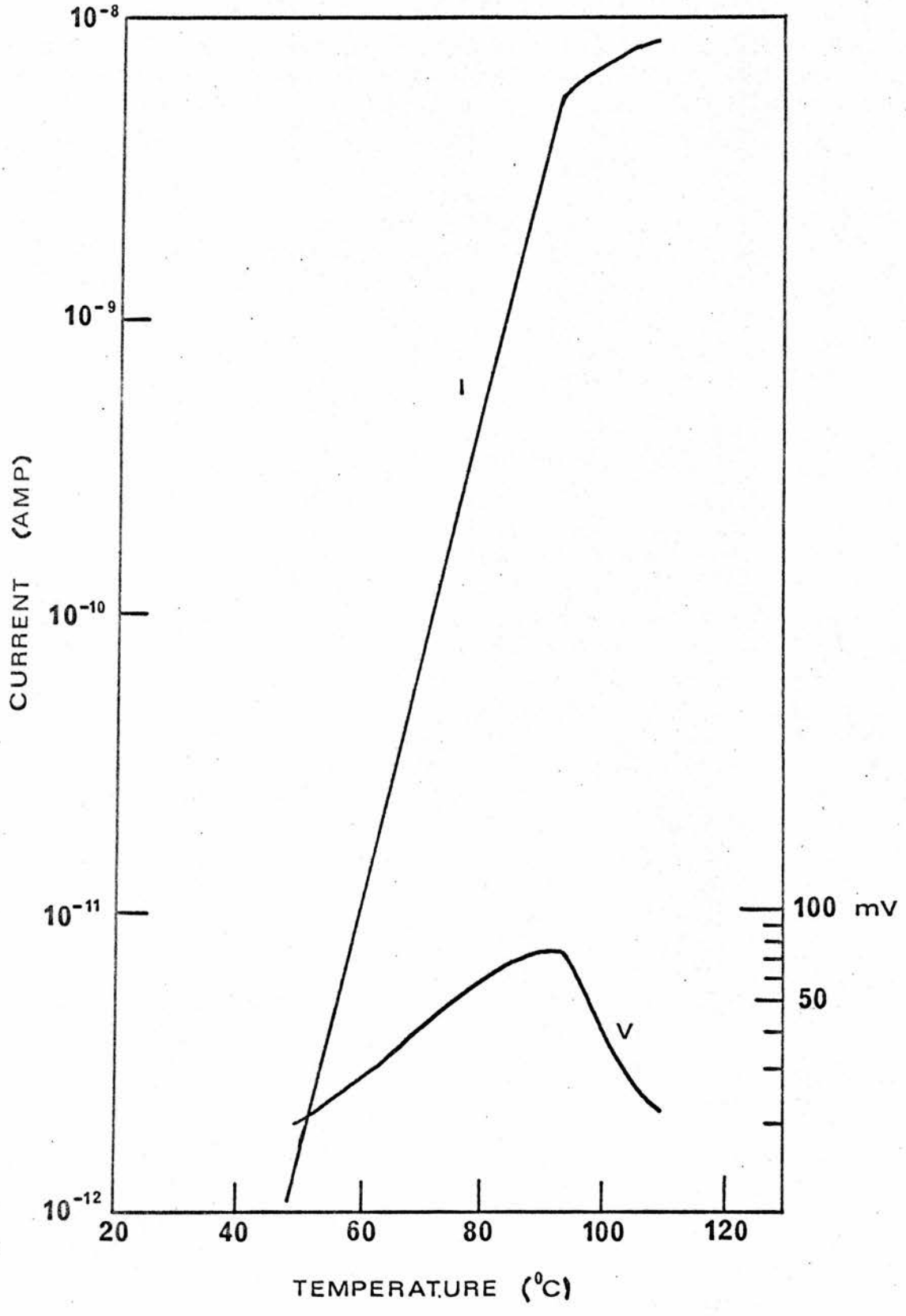
During the investigations carried out into the cause of the high temperature short circuit current it was found that when a fresh sample of PVF with evaporated electrodes was heated under short circuit conditions a current was observed.[23] This current took the form of that shown in figure 9 and it can be seen that the current increased to 10^{-8} amp at $120^{o}C$.

As mentioned before the sample was only heated from one side. It is therefore clear that there must be a temperature gradient across the sample and it was thought that this gradient might be the cause of the short circuit current. If this was so then heating the sample from the other side would reverse the temperature gradient and thus reverse the direction of current flow.

The reversal in the temperature gradient was effected by heating the lower electrode by a source of radiant heat. The source of heat used was a 125 W UV lamp situated directly underneath the sample and although the heating rate was not as great as that obtained in all other cases the current was observed to be in the reverse direction and reached a level of 10^{-10} amp.

A further feature of the effect which indicated its thermoelectric origin was the voltage associated with the effect. This was measured by

Figure 9



Short circuit current and voltage arising from heating a fresh sample of PVF

removing the current measuring unit of the electrometer and measuring the voltage directly. As can be seen from figure 9 the voltage associated with the short circuit currents was of the order of 100 mV which is consistent with a thermoelectric effect. On the other hand the voltage associated with the dipole orientation peaks in the other experiments was greater than 1 volt (the limit of the instrument) and was consistent with the high voltages (120 volts) used to orient the dipoles.

From the above evidence it seems probable that the effect was caused by a thermal gradient which allows charge carriers to move from the hotter electrode towards the cooler and thus set up a reverse voltage. However the existence of the current over a long period of time indicates that the charges are moving out of the sample which in turn means that the reverse voltage measured is not the voltage associated directly with the thermoelectric effect. It will, nevertheless, be proportional to it. The existence of such a thermoelectric effect in polymers of this type has been observed by Ranicar and Fleming who measured the Seebeck coefficient in poly(vinyl chloride) and came to the conclusion that the charge carriers were electrons. The direction of the current in the above experiments in PVF also gives the important result that the charge carriers in PVF are electrons.

The short circuit current has now been explained adequately but it was of some inconvenience since it tended to swamp the 75°C peak using sequence B^1 thus making it difficult to decide if this peak was due to a high temperature dipole orientation process or to the release of previously injected charge.

In order to overcome this effect two different approaches were used. One was the use of non-injecting electrodes and the other the use of opposed electrodes in which any asymmetric temperature gradient was counterbalanced.

The use of non-injecting blocking electrodes is described first.

5.3.2 Blocking Electrodes

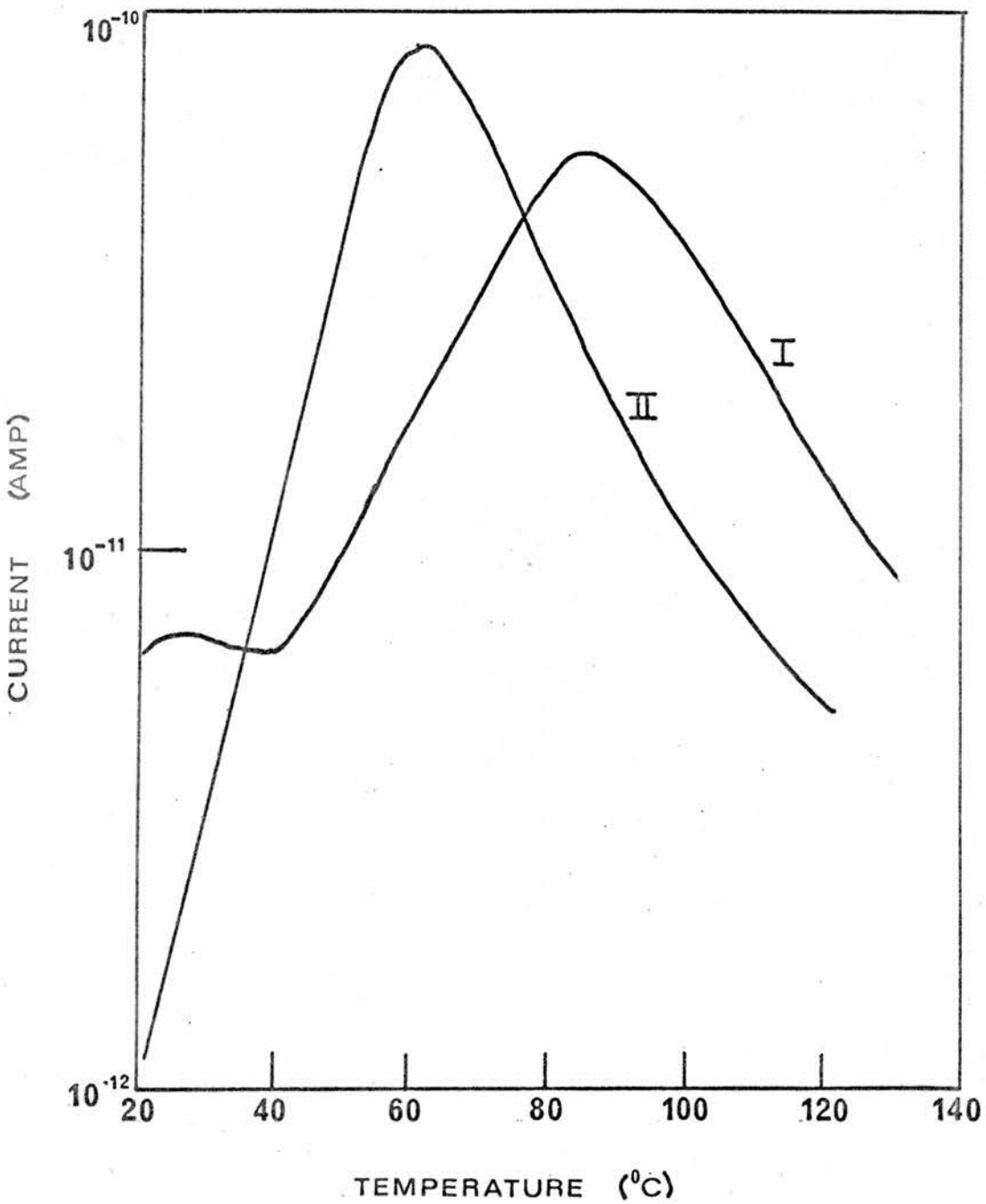
Since charge injection and subsequent transport across the film takes place when a field is applied to a sample it follows that the thermoelectric current also depends on the injection of charge. (This, of course, is different to a thermovoltage which depends on a build up of charges at the electrode). The simplest way to prevent injection of charge is the use of blocking contacts and these have been described in some detail earlier.

This system was then again set up and using sequence A^1 and applying 320 volts a TSC curve was obtained which showed a single peak above room temperature at 95°C (see figure 10) with an associated charge of 7.2×10^{-8} coul. The peak position was displaced from that previously observed due to the temperature lag set up by the Teflon fep insulating layer and the non-appearance of a current above this temperature showed that there was no injection of charge carriers into the sample.

Sequence B^1 on the same sample showed an almost identical plot to that using sequence A^1 and thus confirmed that the peak was due to dipole orientation. The temperature of this peak, is near the glass-rubber transition temperature where the polymer backbone becomes mobile and since the charge associated with the peak is of the same order as that associated with the low temperature peaks it seems reasonable to ascribe the peak to the onset of dipole movement at the glass-rubber transition. This kind of peak has been observed by other workers who have compared a.c. bridge measurements with TSC results.[5,25]

The activation energy of the dipole relaxation process associated with the 75°C peak can be measured by using the initial rise in current with temperature as used by Bucci et al.[12] From the slope of the

Figure 10



T.S.C. above room temperature using blocking electrodes I. 120 volts applied
II S/C conditions

ℓn i versus 1/T line plotted out from figure 10 the activation energy of the dipole relaxation peak was measured to be 0.75 eV.

5.3.3 Charge Release Peak

The preceding experiments have now confirmed that there are four peaks in the TSC spectrum that are ascribable to dipole orientation. Three of them are visible below room temperature and one above at 75°C. However the existence of a high temperature peak due to the release of trapped charge remains undetermined.

In order to try and detect this peak it was necessary to allow charge to be injected from the electrodes which ruled out the use of blocking electrodes. Thus the method chosen to minimise the current due to the thermoelectric effect was the use of opposed electrodes. These electrodes were set up in such a way that the thermal gradient across the sample was counterbalanced by two sets of semicircular electrodes connected in opposition. The experimental method using these electrodes has been already described in the experimental section. Using opposed electrodes on a fresh sample of PVF a control TSC run was obtained during which the sample was heated from room temperature under short circuit conditions. The current was not found to have been entirely eliminated but it was reduced to a level of 10^{-11} amp at 100°C. This was a factor of 10^3 down and was considered small enough to proceed with the search for a trapped charge peak.

A control run was first carried out on PVF using sequence A^1 during which the three low temperature peaks below room temperature were observed and also a continually increasing current above room temperature, resulting from conduction of charges across the sample. The plot obtained was identical to that observed using unopposed electrodes.

On applying 120 volts across a sample of PVF for 2400 sec at room temperature, cooling down to -196°C, short circuiting, and heating,

the three low temperature peaks were again evident and also a peak at $75^{o}C$. No further peak was, however, detectable up to a temperature of $120^{o}C$ owing to the small residual current due to the thermoelectric effect which had not been completely eliminated.

In order to increase the amount of charge injected into the polymer, 120 volts was applied at $80^{o}C$. Integrating the area obtained by subtracting the steady state current from the observed current decay, it was deduced that 7.0×10^{-5} coul had been injected into the sample. This is considerably greater than that introduced at room temperature and it is interesting to note that it was possible to do this. The explanation for this apparent anomaly is difficult though one possibility is that since the voltage was applied at $80^{o}C$, which is above the glass-rubber transition temperature, the phase change which occurs at this temperature could possibly create a position whereby new trapping sites could be formed so that more charge can be trapped. The other possibility for increased charge injection at higher temperatures is that at room temperature the steady state current observed may only be a 'quasi' steady state where all the low temperature dipoles have been oriented but the charge injection process is not complete. This process could be so slow that the time taken for the traps to fill completely is much longer than the 4×10^{3} sec observed, and in this case the current decay would be so slow that any change in current could be ascribed to the change in the temperature of the sample. This possibility is substantiated by the knowledge that other workers[26] have used the photoconducting properties of PVF and found the charge carrier mobility in the presence of light to be in the range $10^{-11} - 10^{-12}$ cm^{2}/volt sec. This gives a transit time of about $10^{3} - 10^{4}$ sec in the presence of light which is clearly much greater than that for the dark since the photocurrents in PVF are a factor of

10^3 up on the dark current.

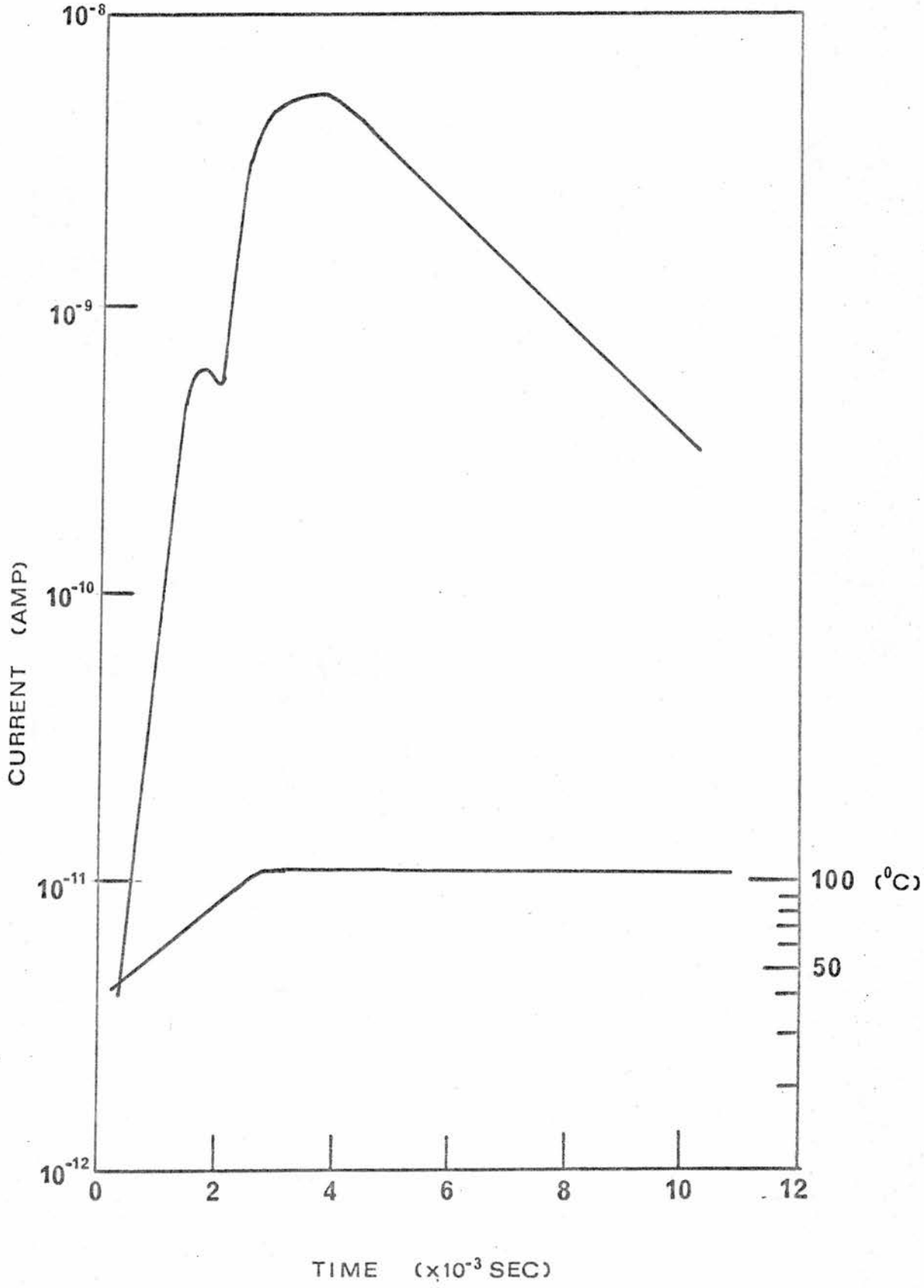
In the above discussion no account has been taken of the dipole orientation process which takes place at 75°C. Since the amount of displaced charge involved in this case is a factor of 10^3 down on the injected charge it can safely be ignored in these experiments though clearly the faster decay in the current-time plot at 80°C means that the dipole orientation takes place faster at this temperature. This, of course, is to be expected.

The sample of PVF which had been subjected to an electric field at a temperature of 80°C was then cooled down to room temperature and short circuited. On warming the sample a peak at 75°C was observed. However this was almost obscured by an increasing current above this temperature. On reaching a temperature of 100°C the current had risen to a level of 3×10^{-9} amp and showed no sign of decreasing.

Unfortunately at this temperature a further difficulty arose since it was known that at 130°C the effective resistance of the sample became less than that of the measuring resistance of the electrometer. To overcome this difficulty the temperature was held constant at 110°C and after 600 sec at this temperature the current started to decay and this is shown in figure 11. Since this decay started not long after the temperature reached 110°C and was held constant, it was estimated that the peak would have occurred at 120°C had the same rate of heating been continued throughout the experiment. This estimate of the temperature is obtained by extrapolating the temperature curve in figure 11 to a higher value.

From the area under the peak it was calculated that 3×10^{-5} coul of charge was released. Since this was near the value for the amount of charge injected, and since this peak is known from the blocking electrode experiments not to be associated with dipole orientation,

Figure 11



T.S.C. above room temperature showing charge release peak

then the 120°C peak can be ascribed to the release of previously injected and immobilised charge. The existence of other peaks at higher temperatures associated with the same process has not, however, been ruled out since the temperature in these experiments was limited to 120°C.

There are several methods for obtaining the activation energy from the TSC curve, of which Garlick and Gibson's[27] has the widest validity. In their analysis they assumed that the trap was initially full so that there was no immediate retrapping and they derived an equation from which the activation energy can be obtained directly from the initial rise of the current. The expression for the current is given by,

$$i = A\exp(-E_T/kT)$$

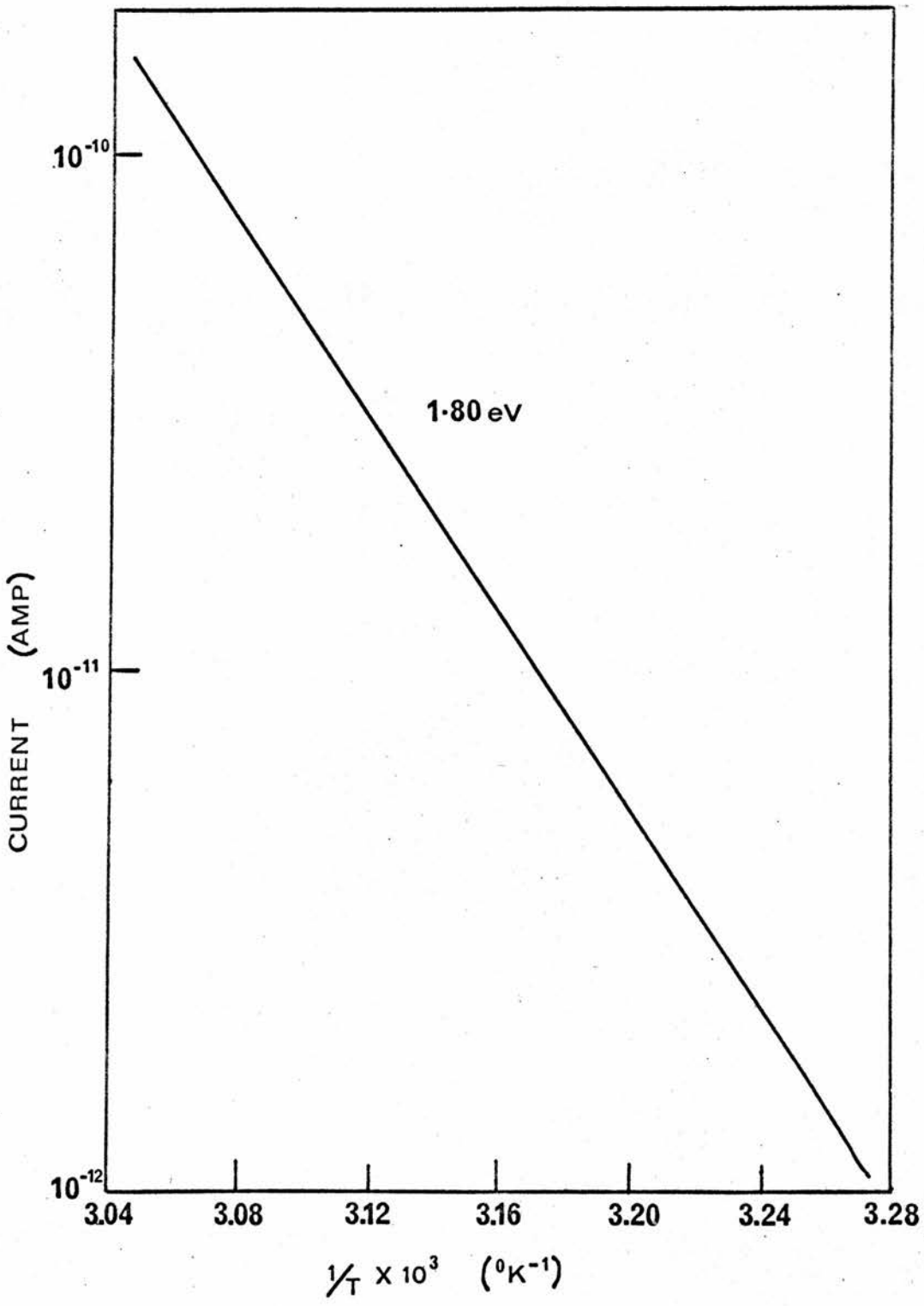
where i is the current, E_T the trap depth, and A a constant. From this it can be seen that plotting ℓn i versus 1/T a straight line should be obtained whose gradient is given by -E/k. Plotting out the initial rise in current in this fashion from figure 11 a straight line was obtained (figure 12) and from this an activation energy of 1.80 eV was obtained.

Thus summarising this section, experiments have shown that charge carriers can be injected into PVF, immobilised, and subsequently released at a higher temperature by heating the polymer under short circuit conditions. This indicates that traps of some kind do exist in PVF. However the origin of them is difficult to ascertain since there are two general types which will give the same kind of current peak. These two possibilities for the trapping sites are either a defect trap caused by chemical or physical defects or a localised trap intrinsic to the polymer. The experiments described here cannot distinguish between these two possibilities.

5.4 Steady State Current Temperature Relationship

The TSC experiments have shown that two processes occur when a

Figure 12



Activation energy plot obtained from the initial rise in current in figure 11

field is applied across a sample of PVF. There is a reversible displacement of charge, ascribed to dipole orientation and also an injection current which involves injection of charge carriers from the electrodes. In studying the steady state current it is clearly desirable to separate these two processes and this was done in the following manner.

A sample of PVF was heated to a high temperature, the field applied and the steady state current determined at a series of decreasing temperature. Using this sequence of events it was assumed that the dipoles would be oriented at high temperatures even though the thermal energy tends to oppose this, and would remain so on going through the glass-rubber transition temperature.[29] The results of the experiments are shown in figure 13 and it can be seen that there is a single value for the activation energy over the temperature range $150^{o}C$ - $20^{o}C$ and has a value of 1.05 eV.

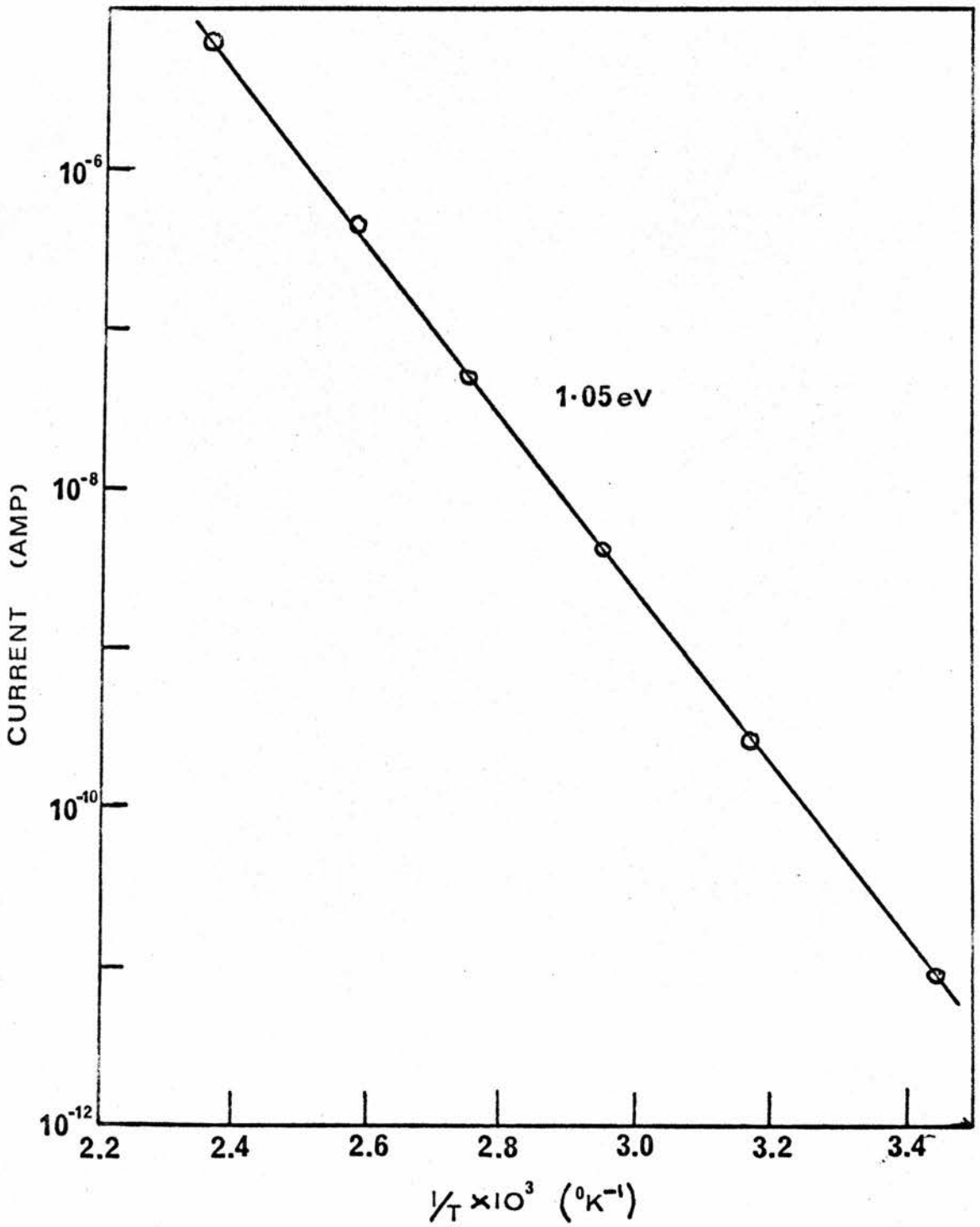
The current observed in the external circuit which results from dipole orientation will be superimposed on the current due to the charged moving towards the electrodes. However the values of the activation energies obtained from the current-temperature graphs in both the steady state and the charge release process cases are larger than the activation energy of the dipole orientation process. Hence it follows that the dipole orientation current component can be ignored in the experimental conditions used.

5.5 Discussion

The TSC experiments yield an activation energy of 1.80 eV, while the steady state current experiments yield an activation energy of 1.05 eV. In both cases the charge carriers are supplied initially by the electrodes.

Since the mobility in these materials is so low it is probable that conduction occurs by the hopping of electrons between localised

Figure 13



Steady state activation energy plot for PVF

states. It is possible for the hopping to occur by thermal activation over the barriers between adjacent sites : a typical barrier height is 0.5 eV.[28] In addition, electrons can be trapped at defect sites and then thermally released. This process also leads to a thermally activated conduction process. It appears from the observed activation energies that, under the rather different conditions of the two experiments, one is seeing the effects of a deeper trap in the TSC experiment than in the steady state experiment.

CHAPTER VI

CONCLUSIONS

Results from the TSC experiments on PVF are consistent with the picture that the charge carriers in this polymer are not intrinsically generated but are injected from the electrodes. Thus the application of an electric field across a sample of PVF with evaporated electrodes injects charge into the polymer which is immobilised on cooling the sample down. Subsequent heating under short circuit conditions with a linear heating rate gives the charge carriers sufficient energy for them to escape from their trapping sites and as they move under the influence of the reverse electric field an increasing current is observed. As the trap is depleted the current decays and so a peak is observed the position of which is associated with the trap depth.

In the case of PVF a peak of this type occurs at a temperature of about $120^{\circ}C$ which typically has a height of 5×10^{-9} amp and an associated charge of about 3×10^{-5} coul. If the charge is uniformly distributed across the sample this is equivalent to a trap density of $\sim 10^{16}$ traps/cc.

From the present work it has not been possible to distinguish between the various mechanisms contributing to the thermal activation energy. However, it is thought that the measured activation energy is rather high for a hopping mechanism, so one concludes that trapping and subsequent ionisation of electrons occurs. The observed trap density, $\sim 10^{16}$ cm^{-3}, is consistent with defect rather than intrinsic traps.

Two other important thermal effects have been observed in PVF which can be distinguished from the charge release peak by the use of blocking and opposed electrodes. The use of blocking electrodes made it possible to show that four of the peaks observed in the TSC experiments are associated with reversible displacement of charge.

The most likely explanation for this type of displacement is orientation of dipoles which takes place at various second order transition temperatures, at which temperatures the thermal energy becomes sufficient to allow displacement of side groups of the polymer chain. Three of these peaks at -60^{o}, -75^{o}, $+75^{o}$C have been correlated with peaks observed in dielectric loss experiments by other workers, but the fourth peak at -95^{o}C has not been previously observed.

Previous workers have come to the conclusion that the low temperature peaks observed in PVF are due to release of charge from traps but this possibility has been eliminated by using blocking electrodes and this method is clearly a powerful means for distinguishing between the two effects.

The second important thermal effect observed was the existence of a thermoelectric effect in PVF which was thought to be due to the temperature gradient set up across the sample during the heating process. These currents can rise as high as 10^{-8} amp across a 50 μm sample and the direction of the current flow indicated that the charge carriers in PVF were electrons. Clearly, this effect will exist in any experimental system where the sample is heated from only one side and can give rise to misleading results.

Thus TSC has proved a useful and valuable tool for investigating the electric properties of PVF and by using this technique with different electrode systems reproducible results can be obtained. These methods are simple to use and provide a powerful means for investigating effects in other polymers.

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