THE THERMAL PROPERTIES OF
MONOCHLORO-*para*-XYLYLENE

WARREN A. ALPAUGH

System Products Division, IBM Corporation, Endicott, N.Y. (U.S.A.)

DARRELL R. MORROW

Chairman Department of Packaging Science & Engineering, Rutgers University, New Brunswick, N. Y. (U.S.A.)

(Received 30 July 1973)

ABSTRACT

The three thermal properties that describe the heat transfer in a material were determined for a thin, tough, transparent, highly crystalline film of poly-monochloro-*para*-xylylene (PCPX). These three properties, viz. thermal conductivity (K), thermal diffusivity (α), and specific heat (C_p) were determined using a transient heating method.

The experimental method used involved the heating of a sample of stacked polymer sheets by an ultrathin heating foil. The heating foil, located in the center plane of the stack provided a source of constant heat flux when a current of known amperage was passed through it. By careful consideration of sample dimensions, the sample simulated an infinite solid. The thermal properties were calculated using standard solutions of the heat transfer equations of an infinite solid over a temperature range of -192 to $130\,^\circ$C. The experimental method was repeated to check the reproducibility of the results and compared with differential scanning calorimeter results.

A data acquisition system was developed to facilitate data handling for the transient experiments. The system included hardware capable of punching data on paper tape and a software package to analyze these data.

The conclusions drawn include: (1) the reproducibility of the experiments was well within the experimental errors; (2) the data acquisition system greatly facilitates acquisition of thermal data; (3) an incremental change occurs in C_p of PCPX in the vicinity of the γ relaxation reported by dynamical relaxation measurements and its occurrence indicates that this relaxation involves a cooperative motion of molecules; (4) owing to the significant magnitude of the C_p jump and the appreciable degree of crystallinity of PCPX, these internal motions occurring at the γ transition probably involve both amorphous and crystalline regions; (5) a direct relationship between thermal expansion and specific heat was indicated in PCPX as well as for polystyrene (PS) at relatively low temperatures $(-200$ to $-20\,^\circ$C); (6) the overall low values of thermal conductivity $(1.0$ to 2.5×10^{-4} cal sec^{-1} deg^{-1} cm$^{-1})$ and thermal diffusivity $(9.5$ to 5.3×10^{-4} cm^2 sec$^{-1})$ of PCPX indicate that it is ideally suited for insulation applications.

INTRODUCTION

(A) Scope

The three thermal properties that describe the heat transfer in a material are: thermal conductivity (K), specific heat (C_p), and thermal diffusivity (α). In this study these three thermal properties are determined for a thin, tough, transparent, highly crystalline polymer film of poly-monochloro-*para*-xylene (PCPX). A transient heating technique is used for simultaneous determination of these thermal properties. A data acquisition system using a paper tape punch was adapted to use with the transient heating equipment. Final results are calculated and plotted using a computer program.

(B) Specific heat of polymers

General description. The heat capacity is defined as the increase in heat content if the temperature of the sample is increased[1] by 1 °C. Most experimental heat capacities are measured under the condition of constant pressure (C_p). The parameter which is more amenable to theoretical interpretation is C_v, heat capacity at constant volume. These two quantities are related by a universal expression proposed by Nernst and Lindermann[2].

$$C_p - C_v = C_p^2 \left(\frac{T}{T_m}\right) A_0 \tag{1}$$

In this expression A_0 is a universal constant (0.0203 cal^{-1} deg mol) and T_m is the melting temperature. As can be seen from eqn. (1) at low temperatures, $T \ll T_m$, $C_p \simeq C_v$, and at higher temperatures where $T \geq T_m$, differences between C_p and C_v become important.

The units of heat capacities are generally represented by cal deg^{-1} g^{-1} or cal deg^{-1} mol^{-1}. For polymeric materials in this study one mole is considered as that number of grams equal to the gram molecular weight of one repeat unit of the polymer.

The heat capacity or the specific heat of a material closely reflect the internal structure and contribution arising from various sources such as lattice vibrations, lower frequency group vibrations, rotations of portions of the molecule and from the presence of defects such as holes, chain defects, and surface defects. It is generally thought that the heat capacity, since so many different contributions are involved, is not a strongly sensitive property. In fact, generally only major changes involving the entire polymer molecule such as the chain motion occurring at T_g or T_m can be observed using heat capacity measurements. Low temperature relaxations that are clearly observed by other techniques, such as torsional pendulum shear modulus measurements are generally not detected by specific heat measurements.

The theory of heat capacity in polymers must take into account all the various contributions of the molecular and atom mechanisms mentioned above and it is therefore very complicated. Wunderlich and Baur[1] have presented an excellent review on both the theory and experimental results of heat capacity work of high polymers.

Although it is difficult to predict the exact specific heat of a polymer over a wide temperature range, some characteristics common to all polymers are evidenced by experimental results. For example, consider the results of the specific heat of isotactic and atactic polypropylene (PP) reported by Wunderlich and Baur[1]. First consider the results of the atactic or amorphous PP. The specific heat of atactic PP increases with temperature with an anomaly at $\simeq 260$ K. This anomaly is shown as a jump in the C_p curve and reflects the secondary transition in the polymer known as the glass transition. All glassy materials show this anomaly at T_g. Since the T_g is a secondary transition, no maximum in the C_p curve is observed. After T_g the specific heat again increases with temperature. Next consider the specific heat of isotactic PP. The isotactic PP in this study[1] was 60% crystalline. The specific heat of atactic and isotactic PP is superimposable up to T_g. At T_g, because of the percent crystallinity of the isotactic PP, there is a smaller heat capacity jump and therefore the specific heat above T_g is less than the atactic sample. The melting range of the isotactic PP is between 370 and 450 K. The melting, being a first order transition, is shown as a fairly sharp maximum After the melting peak the specific heat increases until decomposition occurs. All other polymers reported by Wunderlich and Baur[1] exhibited similar behavior, i.e. a jump with no maximum at T_g and, if crystalline, a melting peak.

Methods of determining specific heat. Adiabatic calorimetry is the most widely used method for determining heat capacities. There are isothermal and non-isothermal measurements. Non-isothermal adiabatic calorimeters are most useful in the temperature range up to 600 K, which is the temperature range of most interest for high-polymer work. The basic design is given by Wunderlich and Baur[1] from work of Nernst. In principle, a metal calorimeter containing the sample, a heater, and a thermometer is supported in a jacket of large heat capacity of accurately measurable and controllable temperature. To reduce heat losses due to convection, jacket and calorimeter are contained in an insulated, evacuated container. Cooling can be done by liquid nitrogen or helium. The heating is done electrically. Routinely the order of magnitude of 0.1% accuracy is achieved. Accuracies as high as 0.01% have been claimed[3].

There are many more calorimeters described in the literature, all of similar design having heating rates of less than 1 °C min^{-1} with large equilibration intervals after 1 to 20 degree heating periods. These calorimeters, which are termed "precision calorimeters" by Wunderlich and Baur[1], all lead to the undesirable feature of long equilibration times. Many polymer samples are not thermodynamically stable enough to be measured by the classical precision calorimeters. Only a continuous and fast heating mode can, in many cases, prevent irreversible changes of the sample during measurements. These requirements led to the development of differential calorimeters; early workers in the field include Hoffman[4] (1952) and Wunderlich and Dole (1957)[5] More recently (1964) a dynamic differential calorimeter has been described by O'Neill[6]. The instrument is available commercially from the Perkin-Elmer Corporation, Norwalk, Conn. Wunderlich[7] describes a method for determining the specific heat of a polymer using the Perkin-Elmer instrument. A calibration curve is made

using a standard of Al_2O_3. The specific heat of polyethylene was determined with a standard deviation of $\pm 2\%$. The principle of operation of the dynamic differential calorimeter is that it keeps, at the same temperature, a thermodynamically stable reference material and a sample material which may undergo some thermal change. The zero temperature differential between reference and sample is achieved by supplying differential electrical power to small platinum heating wires located in the miniature sample holders. The differential heat input per second necessary to achieve this is monitored and recorded on a strip recorder. Endothermic or exothermic processes are directly measurable as a function of time.

In review, both adiabatic and dynamic calorimeters have been used to measure the heat capacities of polymers. The advantage of the adiabatic calorimeters is the high accuracy of $\pm 0.01\%$ while such factors as long equilibration times and relative expense of equipment detract from their use. The dynamic calorimeter on the other hand gives an accuracy of only $\pm 2\%$, but it has the advantages of high heating rates (0.62–80°C min^{-1}), which avoid changes in structure of the sample during heating, a small sample size (1 to 50 mg), and speed of measurement (minutes compared to hours).

(C) Thermal conductivity of polymers

General description. Thermal conductivity (K) of a homogeneous material is the time rate of heat flow, under steady-state conditions, through a unit area, per unit temperature gradient, perpendicular to an isothermal surface[8] or:

$$K = \frac{Qd}{(T_2 - T_1)\,at} = \frac{(\text{g-cal})\,(\text{cm})}{\text{deg}(\text{cm})^2\,\text{sec}} = \frac{\text{g-cal}}{\text{deg}(\text{cm})\,\text{sec}} \tag{2}$$

Like the heat capacity, the thermal conductivity is directly related to the chemical and physical composition of the polymer molecule. In polymers heat is conducted by the interaction of thermal vibrations of molecules and their component atoms. Variables such as temperature and pressure, molecular orientation and crystallinity are some of the factors which have been found[9] to affect the thermal conductivity of polymers. All these factors must therefore be considered if accurate and reproducible thermal measurements are to be produced.

Wunderlich and Baur[1] point out that polymer materials are often in a metastable state with a structure which is strongly thermal-history dependent. Figure 1 shows the work reported[10] on one polymer, polystyrene.

Attention is drawn to the wide discrepancy in results. These reflect the variations noted by different investigators for but one polymer, viz. polystyrene. However, the samples tested had variations in molecular weight[9], and various degrees of orientation[11] and crystallinity. These results point out the importance of having a well-characterized sample before meaningful thermal properties are reported.

Methods for determination of thermal conductivity. The guarded hot plate method, as described in American Society for Testing Materials C177[12], is the most accurate method for measuring equilibrium thermal conductivities. For this method
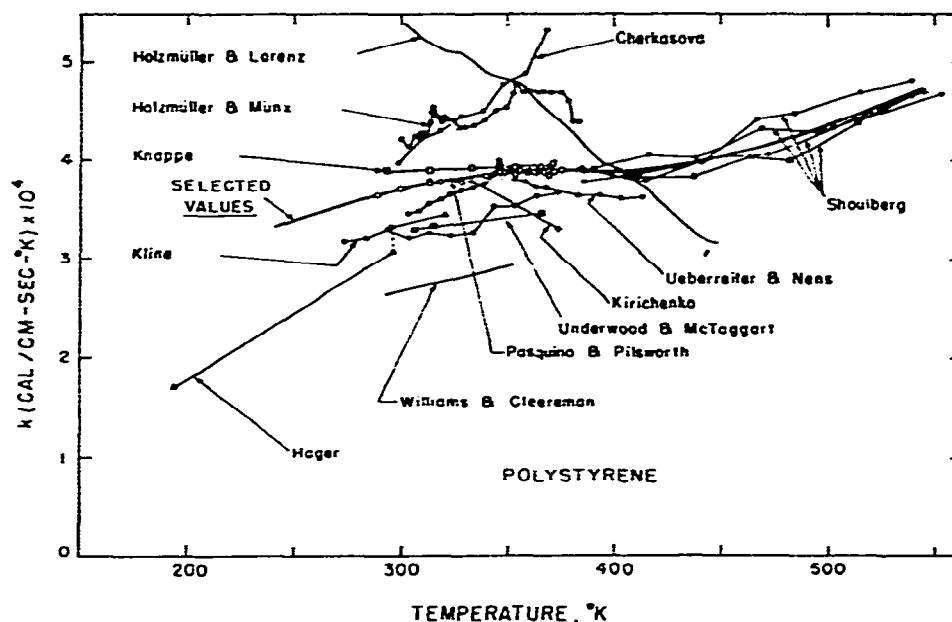
Fig. 1. Thermal conductivity of polystyrene showing wide variation of reported values (Carwile and Hoge[11]; for references in this figure see ref. 11).

sample thickness is, on the average, about 2 in. and the samples must have faces that are flat to within 0.003 in. ft.$^{-1}$. Two identical samples in both size and composition are needed for the test. The test consists of placing one sample on either side of a central heating section. The central heating section consists of a heater and surface plates. The heater is guarded against heat losses to the surrounding atmosphere by insulating guard plates. A hot junction of a differential thermocouple is placed between the heater and the sample. The cold junction of the differential thermocouple is placed on the outer side of the sample and a cooling unit is placed over the entire sample. A diagram of the apparatus is shown in Fig. 2.

At the beginning of the test, the temperature difference between the hot and cold plates is adjusted to not less than 10 or more than 40°F. The central heating unit and the cooling units are adjusted until the temperature drop through two sides does not differ by more than 1%. After equilibrium has been reached, temperatures at the hot (T_2) and cold (T_1) junction are noted along with the electrical power (Q) to the central heater and the sample dimensions of thickness (d) and area (a). Equation 2 can be used to calculate the thermal conductivity (K).

Kline[13] describes a method for the determination of thermal conductivity which uses a hollow rod sample. A heating wire is placed in the center of the rod and thermocouples are placed at the inside and outside of the rod. The whole configuration is placed in a thermal jacket. The jacket is cooled with liquid nitrogen and heated electrically. The accuracy of the method was not compared with that of the guarded hot plate, but the results obtained were in good agreement with those previously reported. The advantages are the less stringent test specimen requirements and speed
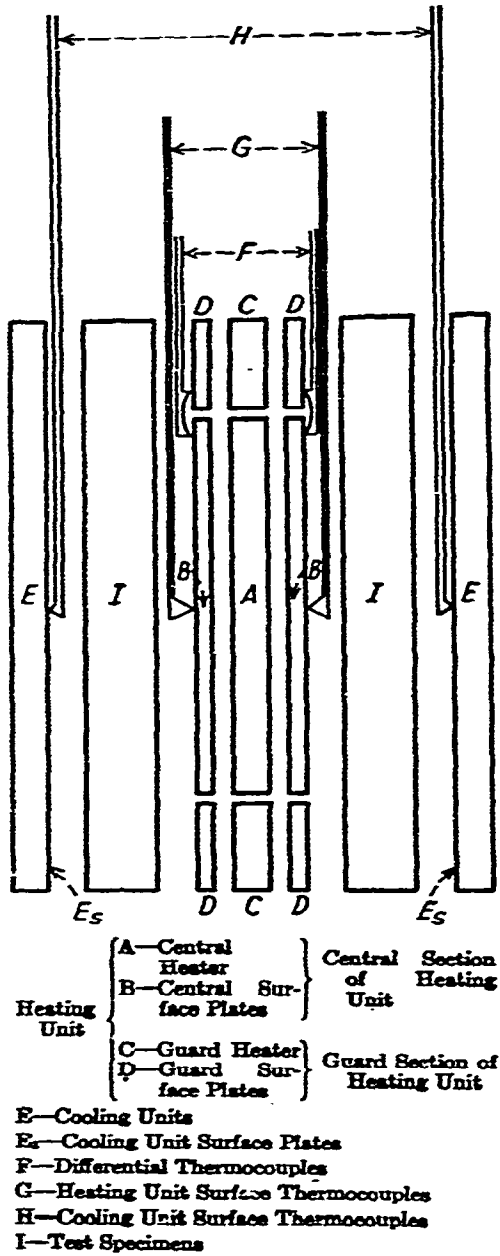
Fig. 2. Guarded hot plate. ASTM C177 [12].

of measurements. It is pointed out, however, that although any one measurement of the thermal conductivity is rapid, measurements of thermal conductivity over wide temperature ranges will take several hours.

Other methods for the determination of thermal conductivity are reviewed by Anderson[8]. In general any method that can accurately measure the temperature of a material at varying distances away from a heater with a known heat output can be

used to determine the thermal conductivity. Caution must be directed, however, to the loss of heat to the environment from the surface of the sample during a heat transfer measurement.

(D) Thermal diffusivity of polymers

In general terms the thermal conductivity parameter characterizes the ability of a material to conduct heat on a time-independent or steady-state basis; the thermal diffusivity parameter characterizes the ability of the material to transmit heat in a time-dependent manner. Thermal diffusivity is associated with heat transfer in the unsteady state. It is defined by Carslaw and Jaeger[14] as,

"... it measures the change of temperature which would be produced in unit volume of the substance by the quantity of heat which flows in unit time through unit area of a layer of the substance of unit thickness with unit difference of temperature between its faces."

The thermal diffusivity is an important engineering parameter. For example, to predict the heat transfer properties of a material during rapid heating or cooling, it is essential to know the thermal diffusivity.

The thermal diffusivity (α), thermal conductivity (K) and specific heat (C_p) are related by eqn (3).

$$\alpha = \frac{K}{\rho C_p} \tag{3}$$

where ρ is the density of the material.

The units for thermal diffusivity are $cm^2 \, sec^{-1}$. The interesting feature is that neither a heat unit nor a temperature unit appears in the expression.

Compared to the extensive work reported on thermal conductivity and specific heat, relatively little work has been reported on the thermal diffusivity of polymers. Frisch and Rogers[15] discuss the thermal diffusivity for a number of polymers. In this case, the thermal diffusivity was calculated by using eqn (3). Values for thermal conductivity (K), specific heat (C_p) and density (ρ) were taken from the literature. The obvious difficulty with this technique is that one can never be sure that the polymer samples used for the independent studies by various investigators were identical. Without using identical samples for the determination of K, C_p, and ρ, eqn (3) has little meaning.

(E) Experimental method of present study

General description. The experimental method of the present study for the determination of the thermal properties is the transient heating technique reported initially by Harmathy[16] and later by Steere[7]. Harmathy's paper was concerned with the thermal properties of building materials while Steere showed how Harmathy's experimental technique could be applied in the field of polymers.

The method[17] involves stacking polymer films on both sides of ultrathin (0.0001 in.) constantan foil. This foil acts as a heating foil when known current is passed over it and produces a constant thermal flux. A differential thermocouple with the hot junction placed in the stack of polymer film at a known distance from the heating foil monitors the rise in temperature as a function of time. The thermocouple signal is amplified and recorded on a strip chart recorder. From this plot the three thermal properties are determined simultaneously. The obvious advantage of this method is that only one sample need be used for the simultaneous determination of the three thermal properties; and unlike the methods described in the early sections, differences in sample thermal histories need not concern the investigator. The sample configuration of stacked sheets is also an advantage in that most polymers can be produced commercially in sheet form.

Equations and assumptions. The transient heating technique described by Harmathy[16] makes use of the fact that the initial temperature rise, due to a constant flux plane heat source, at points within a certain region of a finite solid is essentially the same as that in an infinite solid. The following equation given by Carslaw and Jaeger[14] represents the heat flow in an infinite solid with constant heat flux in the $x = 0$ plane and at zero initial temperature

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} \right) \qquad x > 0, \quad t > 0 \tag{4}$$

Noting that the flux $f = F_0$ where f is

$$f = -K \frac{\partial T}{\partial x} \tag{5}$$

and F_0 is constant flux per unit time per unit area.

The solution of eqn (4) with $f = F_0$, constant, $x = 0$, $t > 0$ is

$$f = F_0 \operatorname{erfc} \frac{x}{2(\alpha t)^{1/2}} \tag{6}$$

Further mathematical manipulation of eqn (6) as shown by Carslaw and Jaeger[14] gives:

$$T(t) = \frac{F}{K} \int_x^{\infty} \operatorname{erfc} \left[\frac{x}{2(\alpha t)^{1/2}} \right] dx \tag{7}$$

$$T_{(x,t)} = \frac{2Fx}{K} \left(\frac{\alpha t}{x^2} \right)^{1/2} \operatorname{ierfc} \left(\frac{x^2}{4\alpha t} \right)^{1/2} \tag{8}$$

Equation (8) has two unknowns, α and K. If t is replaced by $2t$, eqn (8) becomes

$$T_{(x,2t)} = \frac{2Fx}{K} \left(\frac{2\alpha t}{x^2} \right)^{1/2} \operatorname{ierfc} \left(\frac{x^2}{8\alpha t} \right)^{1/2} \tag{9}$$

Dividing eqn (9) by eqn (8) gives

$$\frac{T_{(x,2t)}}{T_{(x,t)}} = \frac{\sqrt{2}\ \mathrm{ierfc}\left(\dfrac{x^2}{8xt}\right)^{1/2}}{\mathrm{ierfc}\left(\dfrac{x^2}{4xt}\right)^{1/2}} \tag{10}$$

The value $T_{(x,2t)}/T_{(x,t)}$ can be determined experimentally by taking note from the recorder plot of the rise in temperature as the current is passed through the heating foil versus time. Equation (10) has only one unknown and solving it gives a value for the thermal diffusivity (α). Using the value now known for α, eqn (8) is used to calculate the thermal conductivity when the heat flux (F) is equal to

$$2F = \frac{I^2 r}{b_f^2 a_f} \tag{11}$$

where $b_f^2 a_f$ represents the width and thickness of the heating foil, r is the electric resistivity in Ω cm, and I is the current in A. The value of the specific heat (C_p) is then obtained from eqn (3) if the density (ρ) is known. The problem of the assignment of the average sample temperature to a transient thermal measurement is a common one. Harmathy[16] treated this problem and suggested one take the average temperature in space and time between the heater and the first thermocouple junction. This is given by

$$T_{av} = \left(\frac{2F}{Kx\tau}\right)\int_0^x \int_0^\tau (xt)^{1/2}\ \mathrm{ierfc}\left(\frac{x^2}{4xt}\right)^{1/2} dx\, dt \tag{12}$$

where x is the distance between heater and thermocouple junction and τ is the total heating time. This is how all temperatures of transient experiments were calculated in this study.

(F) Material used in present study—poly-monochloro-para-xylylene

PCPX is only one member of a family of polymers which have a generic name of Parylene. The parylenes are prepared by vapor phase deposition. The polymers are deposited on cold substrates as tough polymer films which are colorless and range from being transparent to milky. Development work on the parylenes has been carried out by the Union Carbide Corporation and they hold the pertinent patents*.

The parylenes have found wide application in the electronic field[18]. In general the parylenes exhibit good dielectric properties and very low permeability to moisture and other corrosive gases. These properties of parylene plus its good-to-excellent adhesion to a wide variety of substrates make it an excellent material for the coating of critical electronic assemblies. The film provides both insulation resistance and chemical and moisture resistance.

---

*For example, see British Patents 883,939; 883,940; 883,941 and German Patents 1,085,673: Chem. Abstr., 55 (1961) 22920 d.

180

Gorham[19,20] describes a synthetic method of producing parylenes which is termed pyrolytic polymerization. This method produces high yields (90% or higher) and polymers free of low molecular weight by-products. Gorham's method is illustrated below for PCPX.
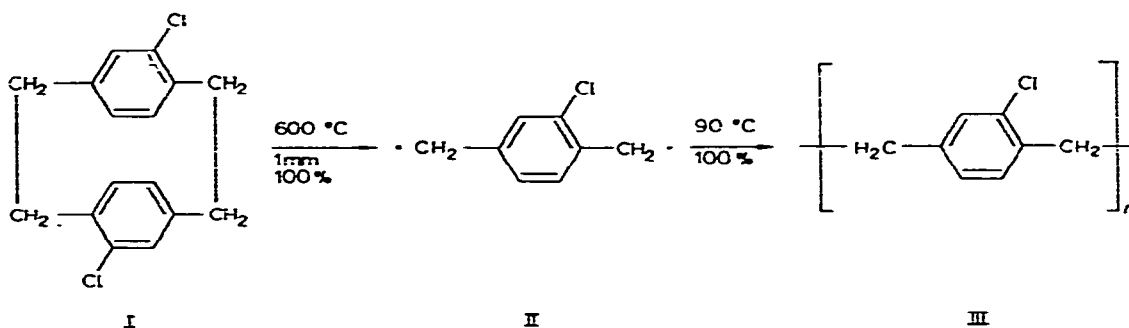

Fig. 3. Polymerization steps of poly-monochloro-*para*-xylylene.

The di-monochloro-*para*-xylylene (I) is quantitatively cleaved by vacuum vapor phase pyrolysis at $600^{\circ}C$ to form two molecules of monochloro-*para*-xylylene (II). In systems maintained at less than 1 mm, monochloro-*para*-xylylene spontaneously polymerizes on surfaces maintained below $90^{\circ}C$.

The samples for this study were supplied by Union Carbide Corp., Bound Brook, N.J. The method used for preparation of the films was the one described by Gorham.

Because of the very fact that the parylenes can only be produced as thin polymer films, the transient heating technique of Steere[17] was chosen as an ideal method to study their thermal properties. Previous thermal measurements over the wide temperature range of this study have not been made.

EXPERIMENTAL METHOD AND TECHNIQUES

(A) Description of transient heating equipment

The transient heating measurements were taken using equipment of the same basic design as described by Steere[17] and later by Schuler[21]. A diagram and photograph of the experimental equipment is shown in Figs. 4 and 5. The transient heating apparatus was designed using the following commercially available equipment:

1. Temperature chamber, MK 2300, Delta Design Inc.
2. Potentiometer, 8690, Leeds and Northrup Co.
3. Milliamperemeter, Model 911, Daystrom Inc.
4. D.C. power supply, Model DCR 40-10A, Sorenson.
5. Digital voltmeter, Digitest 500, Honeywell.
6. Single channel recorder, Mark 250, Brush, Inc.
7. Liquid nitrogen tank, 110 l, 50 psi

The only change in the equipment used in this study over that used by Schuler[21] was that of a digital voltmeter. The digital voltmeter was used to calibrate the single channel recorder and the automatic data acquisition system.

The data acquisition system which was designed for this study is also shown in Fig. 5. The diagram of the system is shown in Fig. 6. The system uses:

8. Voltage to frequency converter, Model 2210, Dymec, Hewlett-Packard Corp.
9. Electronic counter, Model 521CR, Hewlett-Packard Corp.
10. Coupler, Model 2540, Dymec, Hewlett-Packard Corp.
11. Paper tape punch, Sp2-M23, Friden.

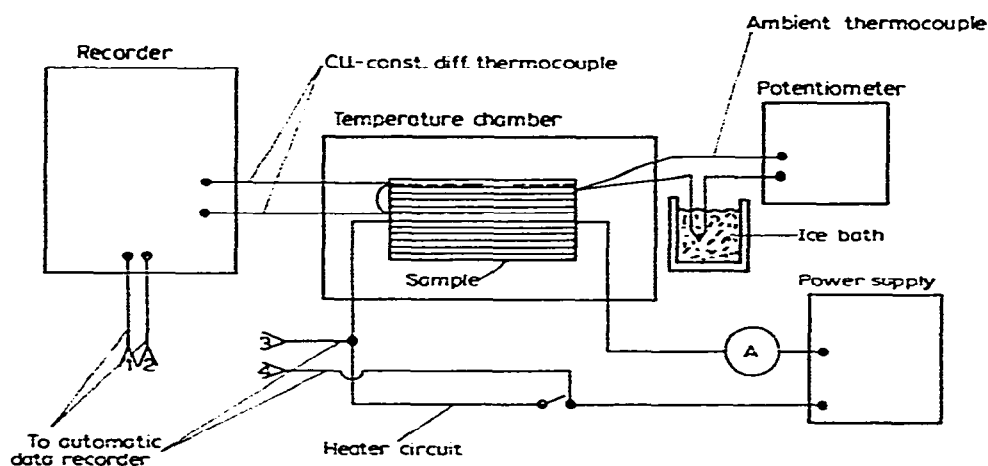The data acquisition system* was developed but not used in this study.
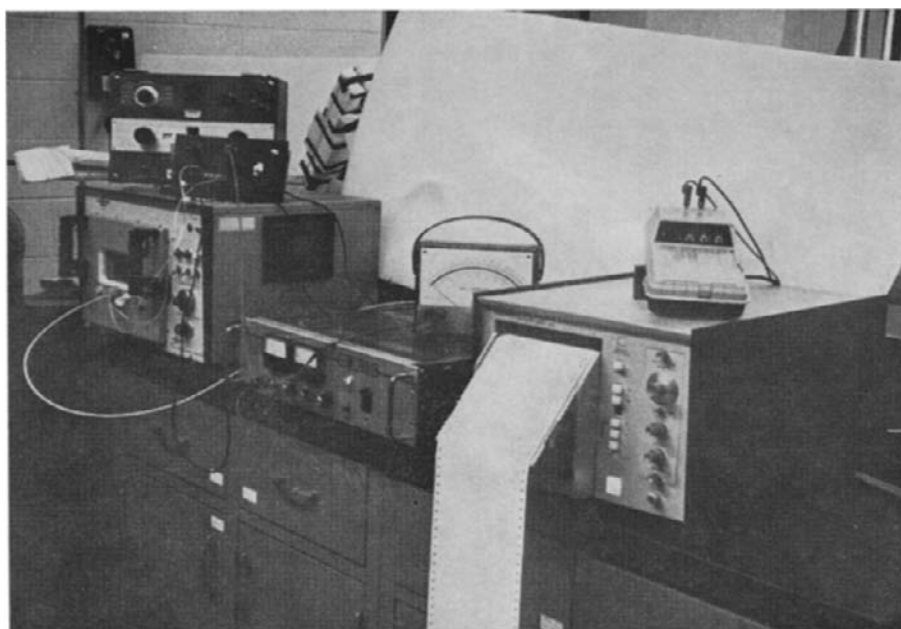

Fig. 4. Diagram of transient heating equipment.

(B) *Sample characteristics and preparation*

General description. Prior to making any transient heating experiments, the sample of PCPX was characterized to determine its density. An infrared spectrogram was made of the sample and compared to the reference spectra. Melting and glass transition temperatures were determined using a differential scanning calorimeter and a thermal mechanical analyzer. The highly crystalline nature of the film was confirmed with an X-ray diffraction pattern. All these techniques were deemed necessary in order to better understand the nature of the transient heating results. Results of both the preliminary investigation and the transient heating experiment will be discussed in detail in a later section.

Samples of PCPX were supplied by Union Carbide Corp., Bound Brook, N.J., in the form of 8-in. square films. The thickness of these films ranged between 1 and 2

---

*A detailed account of the system and a computer program which can analyze the data punched on the paper tape are available from the author.

mils. The sample to be tested was cut from these 8-in. squares using a standard paper cutter. After the pieces were cut to the desired size of $1\frac{1}{2} \times 3$ in., the film was washed in an ultrasonic cleaner and dried with a lint-free silk cloth to remove dust particles from the surface. Over 500 of these $1\frac{1}{2} \times 3$ in. films were then stacked on each side of an ultrathin (0.0001 in.) constantan heating foil that was soldered to copper foil

A
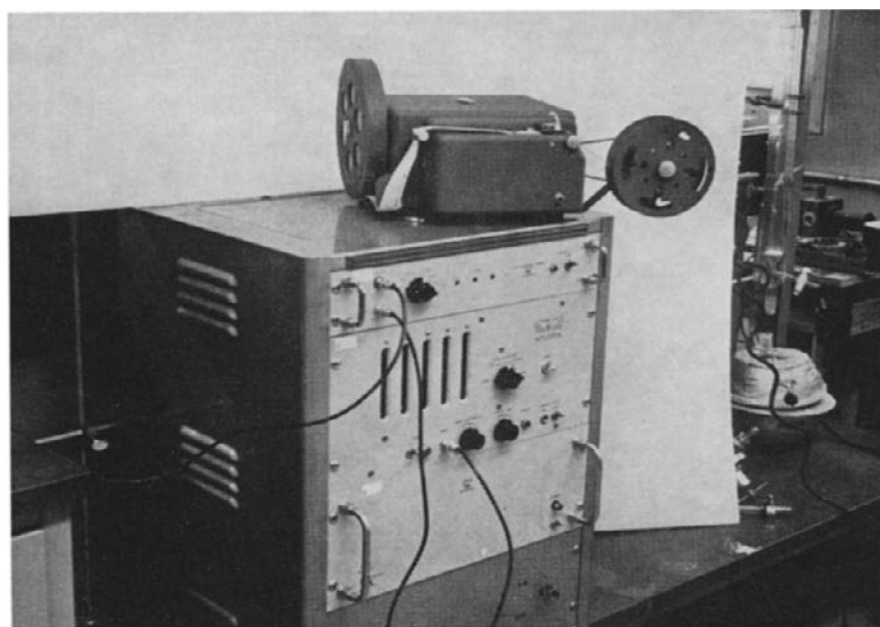
B

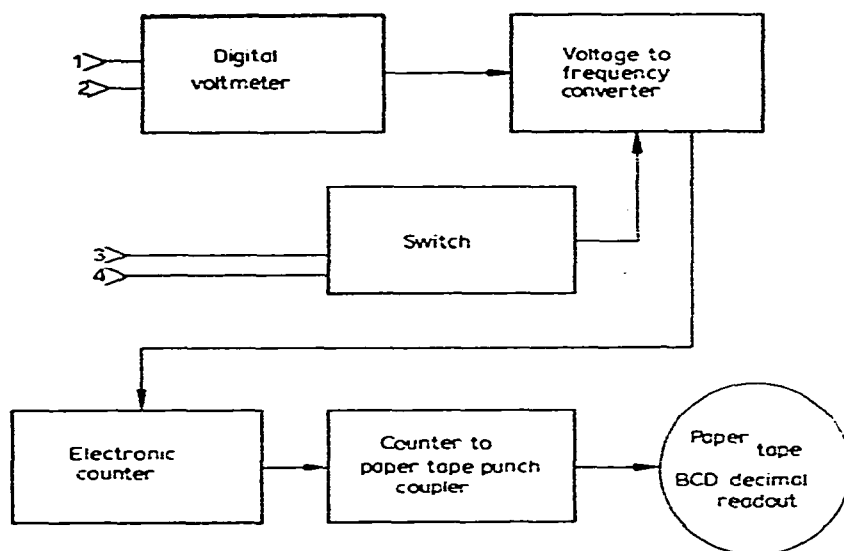Fig. 5. Photograph of transient heating equipment.

Fig. 6. Block diagram of data acquisition system.

contacts with a 25-W solder iron using standard electrical solders. A differential thermocouple made of edge welded copper–constantan foil, 0.002 in. thick, was then placed in the stack of film. The hot junction of the differential thermocouple was placed approximately 0.050 in. above the heating foil. The cold junction of the thermocouple was placed on top of the stack approximately 0.50 in. above the heating foil. The sample configuration is shown in Fig. 7.
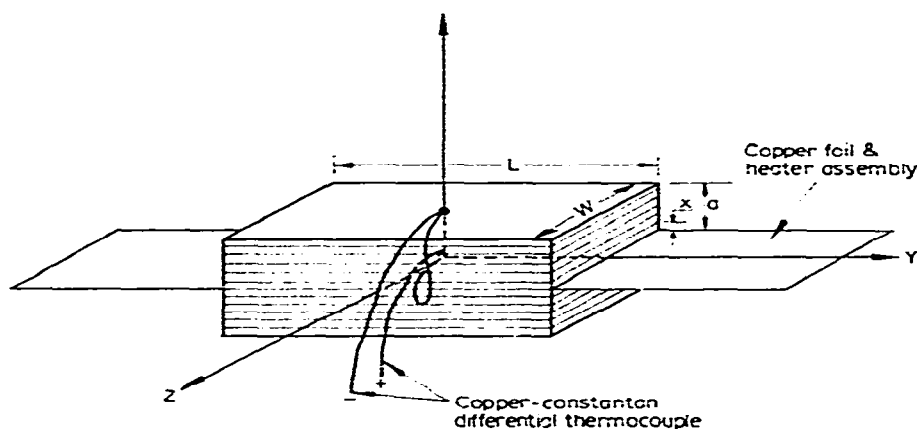

Fig. 7. Sample configuration.

Sample holder. In order to hold the sample in the temperature chamber and to provide a place to secure the delicate heating foil arrangement as well as to protect the thin, fragile thermocouples, Schuler[21] designed a sample holder. This sample holder, shown in Fig. 8, was used in this study without modification.
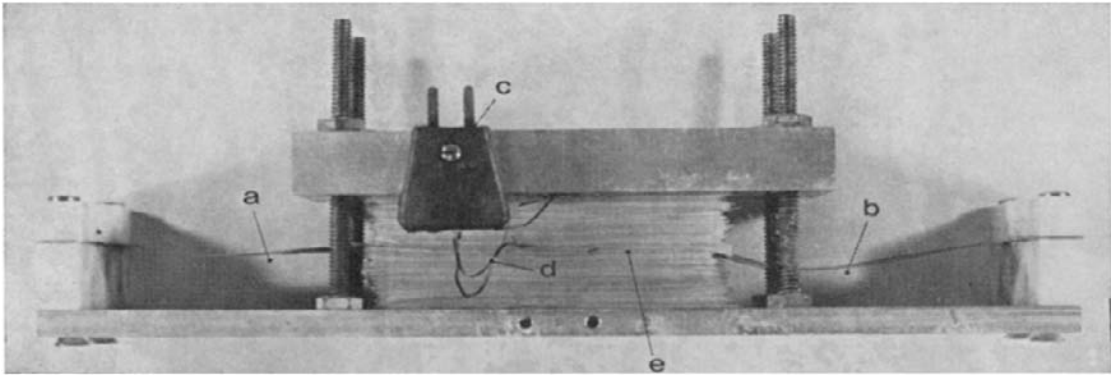
Fig. 8. Photograph of sample holder. (a, b) D.c. power leads; (c) Omega thermocouple plug; (d) thermocouples; (e) sample.

With this holder, the sample with heater and thermocouples attached may be assembled outside the temperature chamber. To ready the sample for a transient heating run, one need only place the sample holder in the temperature chamber and connect the heating foil to the d.c. power leads and clip the differential thermocouple to the recorder. The power leads are secured with screws on the sample holder and the differential thermocouple and cable are joined using an Omega plug-in type connector.

Sample dimensions. The sample dimensions were carefully considered. Equations (8) and (10) are the solutions to the differential heat transfer equations. The assumptions made in solving these equations were that a finite sample could be used to represent a semi-infinite solid. It is obvious therefore that since the sizes of an actual test specimen are finite, eqns (8) and (10) cannot be expected to hold for every point inside the specimen or for every length of time.

Starting with a total heating time (τ) of 20–40 sec, which was needed for the relative slow response of the data acquisition system, the following criteria were considered:

(1) Harmathy[16] analyzed eqns (8) and (10) and shows that it is necessary that $x\tau/x^2$ remains smaller than 1.6. Where x is the distance between the heating foil and the first junction of the differential thermocouple, the thermal diffusivity of a polymer can be taken generally to be 0.001 cm^2 sec^{-1}. In this study, $x = 0.05$ in. or 0.127 cm.

$$\frac{x\tau}{x^2} = \frac{0.001 \text{ cm}^2 \text{ sec}^{-1} \cdot 20 \text{ sec}}{(0.127 \text{ cm})^2} = 1.25 \tag{13}$$

(2) According to the argument presented by Harmathy, the height of the sample (a) above and below the heating foil should be

$$a \geq 4x \tag{14}$$

In the present case, a is 0.50 in., therefore:

$$0.50 \text{ in.} \geq 4 \cdot 0.05 \text{ in.}$$

(3) Using the argument of Steere[17] that the ratio of thickness (x) to width (W) of the sample should be 1/30, the width was then determined to be

$$W = 0.05 \text{ in.} \times 30 = 1.5 \text{ in.} \tag{15}$$

(4) The final consideration is that the length L of the sample be $\geq$ twice the width or

$$L \geq 2W \text{ or } L = 2W = 3 \text{ in.} = 2 \cdot 1.5 \text{ in.} \tag{16}$$

To minimize any heat losses at the surface of the polymer sample, the heating foil width was cut so that the sample material would extend 0.3 cm beyond each edge of the foil. The length of the heating foil was the same as the sample length with the solder joint just on the outside of the polymer stack.

(C) Method of transient heating experiment

Procedures. The sample was placed in the sample holder with the proper placement of the differential thermocouple and the entire sample holder was then placed in the temperature chamber. The two leads from the d.c. power supply were connected to the heating foil copper contacts. The plug for the differential thermocouple was cleaned with a fine sand paper and then connected to the recorder. Cleaning of the plug of the differential thermocouple was found to eliminate noise problems that were experienced in preliminary tests. The temperature of the chamber was then lowered to $-200°C$ by liquid nitrogen under a pressure of 50 psi. It took about 2 h for the sample to come to a thermal equilibrium.

While the sample was reaching thermal equilibrium, the recorder was calibrated. The calibration procedures followed were those outlined in the operator's manual of the recorder[22]. A differential voltmeter and the d.c. power supply (used to supply the heating foil current) were used for calibration. It was found that due to recorder drift, it was necessary to check the calibration before each experimental run. Since the differential voltmeter was connected to the recorder throughout the transient experiment, recorder calibration checks presented little problem.

The recorder amplified the signal of the differential thermocouple to values ranging between ± 2.50 V or a total voltage difference of 5.00 V. This voltage was shown on the recording chart by a full scale deflection. This means that if, at thermal equilibrium, the pen of the recorder was resting at any other place on the chart except at the extreme right division when a value of 2.500 V was being applied to the recorder, the calibration was off and recalibration procedures were undertaken. This quick check was made before each experimental run.

Thermal equilibrium was determined when the recorder showed a zero e.m.f. existing between the hot and cold junction of the differential thermocouple. When the sample reached thermal equilibrium, the temperature of the cabinet and sample was determined using a second copper–constantan differential thermocouple. One junction of this thermocouple was placed between the sample and the sample holder and the reference junction was placed in an ice-bath outside the temperature chamber. A Leeds and Northrup potentiometer was used to determine the ambient temperature.

The sample and equipment were now ready for the transient heating measurement. The experiment was initiated by passing a current of 3.50 A through the heating foil, producing a uniform planar heat flux. The current needed was previously determined by running some preliminary experiments at room temperature. A heating time of 20 sec was chosen as a desirable test period; the current was adjusted until this heating time was realized for ambient conditions. This current was kept constant throughout the entire temperature range of interest ($-200\,^\circ$C to $120\,^\circ$C). At the lower temperature ($-200\,^\circ$C) heating times decreased to $\simeq 14$ sec; and at the high temperatures ($100\,^\circ$C) the heating times increased to $\simeq 25$ sec. In all cases the heating was continued until the recorder showed full pen deflection.

Prior to closing the heating foil power supply switch, the recorder was set for a chart speed of 0.1 division per second and a sensitivity of 5 µV per division. This means that a full scale deflection of the pen during a transient heating run represents a temperature rise of 4–8 $^\circ$C corresponding to 250 µV.

One transient heating curve is represented by a recorder plot (see Fig. 9) of the rise in e.m.f. at the hot junction of the differential thermocouple with time. The data from this one plot were used to calculate C_p, K, and α. To determine the thermal
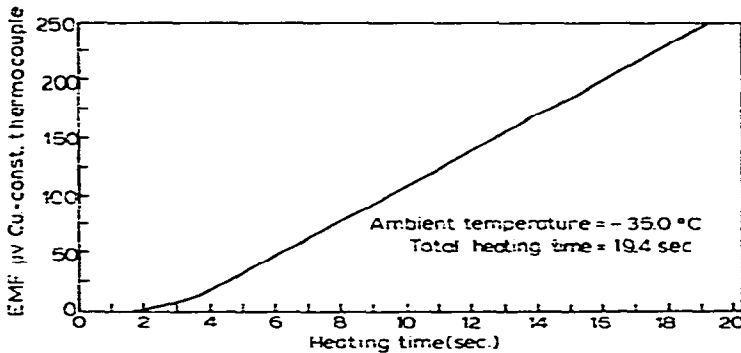
Fig. 9. Transient heating curve.

properties as a function of temperature, the temperature of the environmental chamber was raised by five degrees and the entire procedure repeated. The complete temperature range of -200 to $120\,^\circ$C was covered at 5-degree intervals in the manner just described. One experiment took approximately 78 h.

Calculations of the thermal properties. A typical recorder plot of e.m.f. versus time for one transient heating experiment is shown in Fig. 9. Table 1 gives the values of e.m.f. taken from this recorder plot.

In order to obtain the thermal properties from this plot, eqn (8) is used. It is rewritten here:

$$T_{(x,t)} = \frac{2Fx}{K}\left(\frac{\alpha t}{x^2}\right)^{1/2} \text{ierfc}\left(\frac{x^2}{4\alpha t}\right)^{1/2} \tag{8}$$

TABLE 1

VALUES OF e.m.f. (E) AND TIMES (t) TAKEN FROM TRANSIENT
HEATING CURVE SHOWN AS FIG. 9

Total heating time = 19.4 sec; ambient temperature = −35.0 °C.

$E(1)$ (μV)	$E(2)$ (μV)	t (sec)
8.0	44.0	3.0
13.0	55.0	3.6
18.0	73.0	4.0
24.5	88.5	4.5
30.0	104.0	5.0
37.5	120.0	5.5
44.0	135.0	6.0
51.0	152.3	6.5
58.0	167.5	7.0
65.5	183.5	7.5

The flux F is determined by the current passing through the heater (in A), by the area of the heater and by the electrical resistivity of the heating material. The flux is represented by eqn (11). Since the heating foil for both this study and the study of Steere[17] was obtained from the same source*, the value of the resistivity of the heating foil was taken to be that found by Steere[17]. He determined, experimentally, the resistivity-to-thickness ratio of the constantan foil to be 0.2207 to 0.2204 Ω in the temperature range of 24 to −185 °C.

Equation (10) is also used and is rewritten:

$$\frac{T_{(x,2t)}}{T_{(x,t)}} = \frac{\sqrt{2}\,\mathrm{ierfc}\left(\dfrac{x^2}{8\alpha t}\right)^{1/2}}{\mathrm{ierfc}\left(\dfrac{x^2}{4\alpha t}\right)^{1/2}} \tag{10}$$

By referring to the recorder plot shown in Fig. 9, the value of the temperature (T) rise at a certain time (t) at the first junction of the differential thermocouple located at a known distance (x) can be directly determined. Likewise, the value of the temperature (T) at twice that time ($2t$) is also easily determined. The only unknown then in eqn (10) is the thermal diffusivity (α). A total of 10 sets of points, thermal e.m.f. at time t, thermal e.m.f. at time $2t$ and the time t, were read from each recorder plot and eqn (10) solved for each set and the results averaged for that particular run.

Knowing α, eqn (8) was used to find the thermal conductivity K. The reported value is also the average of 10 calculations. Finally, specific heat was found by

$$C_p = \frac{K}{\alpha \rho} \tag{3}$$

where ρ is the density of the polymer film.

*Hamilton Watch Co., Lancaster, Pa.

Equations (3), (8), and (10) were solved for each set of points by a computer program originally written by Schuler[21]. This program employed the trial-and-error method of interval bisection in the calculation of the thermal diffusivity. An approximation for the integral of the complement of the error function ierfc(x) was used[23]. Modifications of this basic program were made in order that the results of thermal diffusivity (α), thermal conductivity (K), and specific heat (C_p) be plotted by the computer* as a function of temperature.

Experimental runs. Two experiments were performed using a sample of PCPX. The temperature range was -200 to $120\,^\circ$C. The first experiment consisted of 60 runs ranging in temperature from -170 to $120\,^\circ$C. The experiment was conducted over a four-day period, each day covering a specific temperature range. The first day the temperature range covered was -170 to $-50\,^\circ$C; second day, -50 to $25\,^\circ$C; third day, 25 to $90\,^\circ$C; and fourth day, 90 to $120\,^\circ$C. After each day of experimental runs, the sample was allowed to return to room temperature overnight and the experiment resumed the next day.

The second experiment consisted of testing the identical sample and sample configuration tested in the first experiment, the difference being that the experiment was continuous. The total time of this experiment was 68 h during which time the sample was always in a controlled temperature environment.

Preliminary runs were performed on the sample at room temperature to determine what current should be used to produce a heating time of 20 sec. The 20-sec heating time exceeded the heating times reported by Steere[17] and Schuler[21] who both used a heating time of 4–6 sec. It was therefore necessary to insure this increased heating time would not adversely affect the accuracy of the transient heating results. The first precaution taken was the careful consideration of sample size as discussed in *Sample dimensions* on p. 184.

Two additional experimental tests were performed to insure the increased heating time would not affect the transient results. The first was to vary the current supplied to the heating foil and thereby vary the heating time required to have full pen deflection. The current was varied between 3.5 and 4.5 A which produced heating times of 21.3 and 15.5 sec, respectively. The results of the thermal properties agreed within the accuracy of the experimental method. A second experiment consisted of monitoring the temperature at the differential thermocouple farthest from the heating foil. If the sample behaves as a semi-infinite solid, no temperature rise should be detected at this position in the sample. Indeed, no temperature rise was measured at the cold junction of the differential thermocouple even after 1-min heating time, which is far in excess of any heating time seen in an actual experimental run.

(D) Method of differential scanning calorimeter experiment

Procedure. A Perkin-Elmer (Norwalk, Conn.) differential scanning calorimeter (DSC) was used to determine the specific heat of PCPX for comparison with transient

---

*The computer program used is available from the author.

heating results. Wunderlich[7] describes in detail the method used. A sapphire (Al_2O_3) sample was used for calibration of the DSC. The specific heat values of the standard were taken as those of Ginnings and Furukawa[24]. The following procedure was followed: first, preliminary adjustment of all controls was made. The $4\times$ scale (about 13 mcal sec^{-1} for full scale deflection) and a heating rate of 10 °C min^{-1} was used. Step 2 consisted of placing a 0.13196-g sample of sapphire in an aluminum capsule and putting it into the sample holder of the DSC. An empty aluminum capsule was used as a reference and was placed into the reference holder of the DSC. Both the sapphire calibration standard and the reference sample holder were then covered with domed aluminum covers. A dewar flask was placed over the entire head assembly and then cooled with liquid nitrogen to -100 °C.

After establishing a baseline at a 10% chart reading, heating was started at a rate of 10 °C min^{-1} for 3 min. Heating was stopped and the pen was allowed to return to baseline without stopping the chart movement. If the pen did not return to within four divisions of baseline, the slope control was readjusted and the procedure described was repeated until the pen did return to baseline after a heating run.

Without changing any settings on the DSC the sapphire was replaced with 0.04484 g of polymer, making sure the same aluminum capsule and cover dome were used. The heating was started for the same time and rate used in the calibration run.

The final run involved removal of the polymer and running only the aluminum capsule and dome over the same temperature range and heating rate. This established a baseline value which was needed in the final calculation.

When these three different measurements (calibration standard, polymer sample, and blank) were run, the whole temperature range of -100 to 130 °C was covered in 30 °C steps.

Calculations of specific heat from DSC experiments. The amplitudes of the three measurements were read from the recording chart with a finely divided ruler. The blank run was subtracted from both polymer and standard amplitudes. The following calculation was made at 5 °C intervals over the entire temperature range.

$$C_p \text{ (polymer)} = \frac{A_{\text{(polymer)}}}{A_{\text{(sapphire)}}} \cdot \frac{\text{wt.}_{\text{(sapphire)}}}{\text{wt.}_{\text{(polymer)}}} \cdot C_p \text{ (sapphire)} \tag{17}$$

(E) Method of density measurements

The density of the thin polymer film was determined with the use of a density gradient column. The procedure followed was that described in Ref. 25. The method is based on observing the level to which a test specimen sinks in a liquid column exhibiting a density gradient, in comparison with standards of known density.

The density of the film was measured to ascertain if any physical changes occurred as a result of the transient heating experiment. The density was also needed for the calculation of the specific heat of the polymer film.

An ethanol–carbon tetrachloride density gradient column was prepared and

calibrated with glass floats purchased from Scientific Glass Apparatus Co. (Bloomfield, N.J.). The column had a density range of 0.79 to 1.59 g cm^{-3}. The sensitivity of the density gradient column was 0.08 g cm^{-3} mm^{-1}. Three samples were tested for each measurement. Measurements were taken at the start of the transient heating experiments, between the first and second transient heating experiments, and at the end of both experiments.

Graphical calculation was used. The glass float position versus float density was plotted which resulted in a straight line. The positions of the unknown specimens were plotted on the same chart and corresponding densities determined.

RESULTS

(A) Specific heat

The results of the specific heat studies are presented in Figs. 10–12. Figures 10 and 11 show the results of the first and second transient heating experiment, while Fig. 12 represents the results of the DSC study. Experiment 1 included 60 runs in a temperature range of -172 to $118°C$. Fifty runs were made during the second experiment during which a temperature range of -192 to $70°C$ was covered. The specific heat study made using the differential scanning calorimeter was made in the temperature range of $-100°C$ (the lower limit of the instrument) to $130°C$ and calculations were made at $5°C$ intervals.

(B) Thermal conductivity

The results of the thermal conductivity measurements of PCPX are shown in Figs. 13 and 14. The number of runs and temperature ranges for both the first and second set of experiments are the same as those described for the specific heat studies.
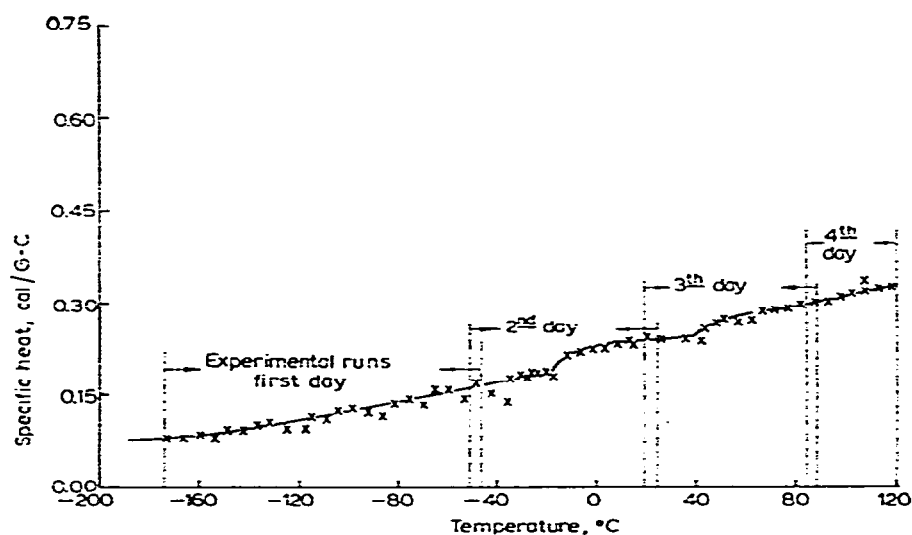
Fig. 10. Transient heating. Specific heat of PCPX. First set of experimental runs.
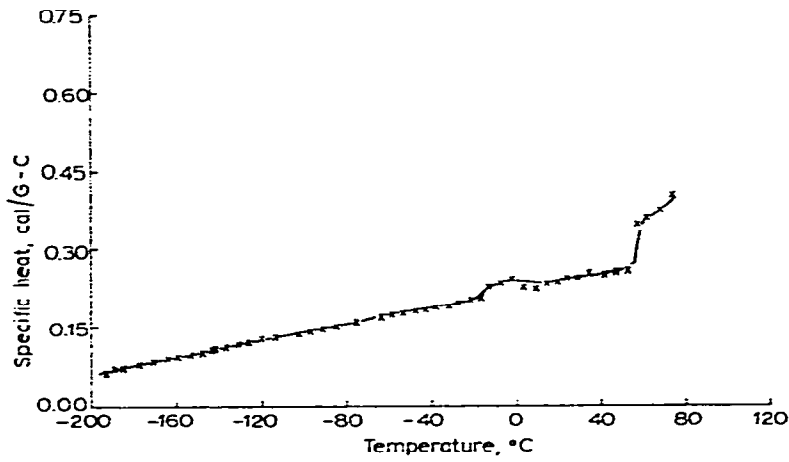
Fig. 11. Transient heating. Specific heat of PCPX. Second set of experimental runs.

Fig. 12. Differential scanning calorimeter. Specific heat of PCPX.

Fig. 13. Transient heating. Thermal conductivity of PCPX. First set of experimental runs.

Fig. 14. Transient heating. Thermal conductivity of PCPX. Second set of experimental runs.
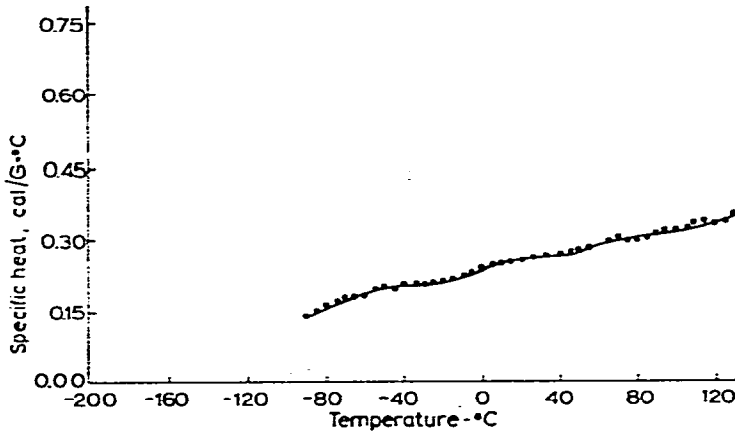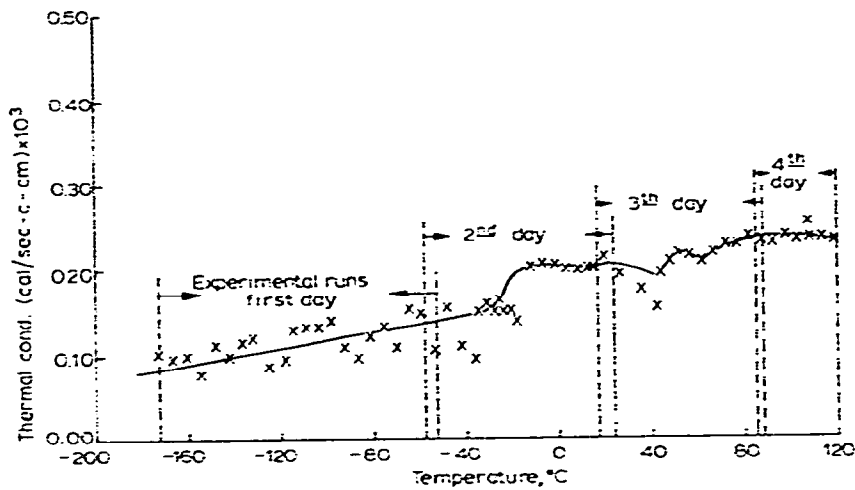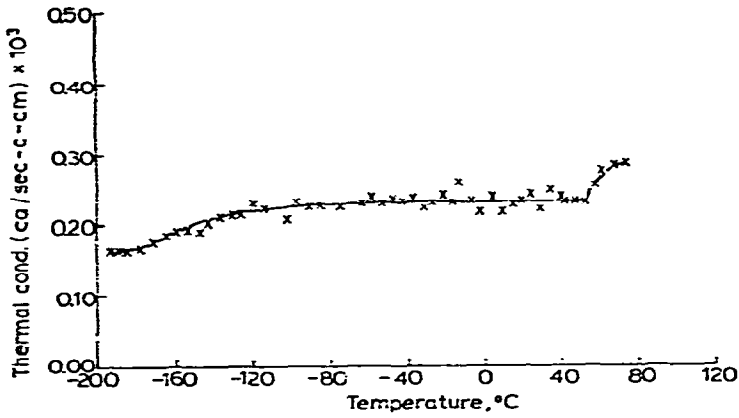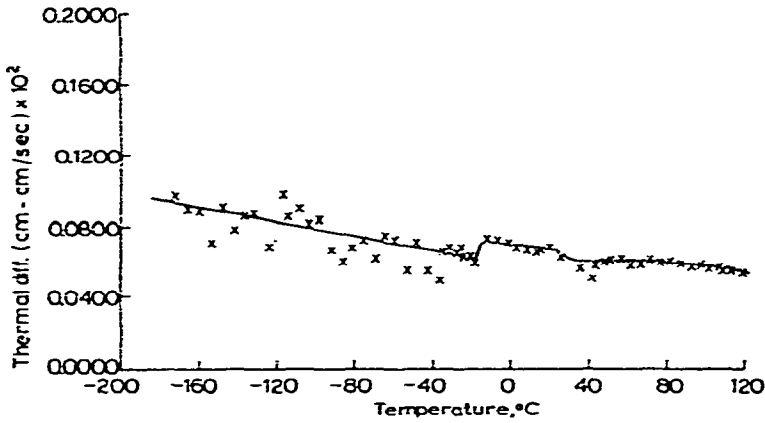

Fig. 15. Transient heating. Thermal diffusivity of PCPX. First set of experimental runs.
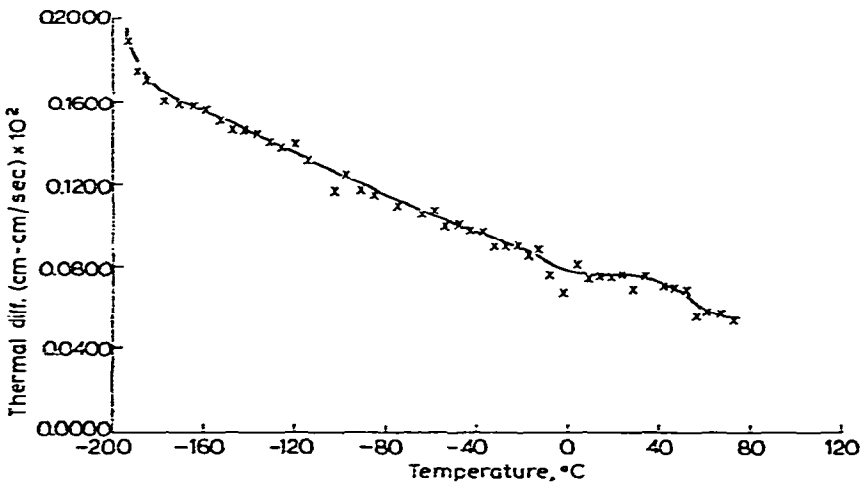

Fig. 16. Transient heating. Thermal diffusivity of PCPX. Second set of experimental runs.

TABLE 2

TRANSIENT HEATING RESULTS

First set of experimental runs.

THERMAL DIFF. (CM-CM/SEC)	THERMAL COND. (CAL/SEC-C-CM)	SPEC. HEAT (CAL/G-C)	INITIAL TEMP. (CENTIGRADE)	AVERAGE TEMP. (CENTIGRADE)	RUN
0.CC09587	C.0001023	0.0813	-180.C0	-172.67	1
0.CC08883	0.0000957	0.0812	-173.50	-166.10	2
0.CC08778	C.09CC989	0.0950	-167.20	-160.04	3
0.CC07C9R	C.0000780	0.0802	-161.40	-153.71	4
0.C009C52	C.0001112	0.0730	-155.C0	-148.37	5
0.C007781	C.0000982	0.0943	-148.60	-141.88	6
0.CC08559	C.0001156	0.1019	-142.50	-136.29	7
0.C008677	0.0001139	0.1050	-137.40	-131.43	8
0.CC067E6	C.0000872	0.0962	-131.40	-124.54	9
0.C009668	0.0000945	0.0963	-125.70	-117.21	10
0.C008464	C.0001277	0.1144	-119.40	-113.97	11
0.C008523	C.0001321	0.1124	-114.20	-108.60	12
0.CC08130	C.0001336	0.1243	-108.60	-103.40	13
0.CC083C2	0.0001396	0.1267	-103.20	-98.16	14
0.CC066C9	C.0001046	0.1272	-97.C0	-91.46	15
0.C005953	C.0000955	0.1161	-92.C0	-86.18	16
0.CC06727	C.0001201	0.1347	-86.20	-81.07	17
0.C0071E4	C.0001334	0.1409	-80.20	-75.37	18
0.C006125	C.0001088	0.1331	-74.40	-69.07	19
0.C00742A	0.0001532	0.1571	-68.70	-64.28	20
0.CCC718G	C.0001464	0.1571	-63.60	-59.12	21
0.CC05492	C.0001058	0.1427	-58.C0	-52.85	22
0.CC07C80	C.0001546	0.1662	-52.40	-48.11	23
0.CC05495	C.0001110	0.1498	-46.40	-41.46	24
0.CCC4896	0.0000947	0.1362	-41.C0	-35.69	25
0.CC06559	C.0001503	0.1741	-38.70	-34.43	26
0.C006746	C.0001600	0.1798	-34.30	-30.20	27
0.CC06467	C.0001514	0.1775	-31.40	-27.21	28
0.C006797	0.0001623	0.1824	-29.60	-25.54	29
0.C006254	C.0001499	0.1825	-27.50	-23.72	30
0.C00625P	C.0001522	0.1848	-24.50	-20.36	31
0.CC05886	C.0001382	0.1775	-22.C0	-17.62	32
0.CC07262	0.0002005	0.2103	-14.50	-11.28	33
0.CC07189	C.0002068	0.2170	-10.C0	-6.44	34
0.CC07C46	C.0002039	0.2205	-4.45	-0.92	35
0.C006749	C.0001986	0.2241	0.C0	3.54	36
0.C006583	0.0001784	0.2297	5.20	8.70	37
0.CC06513	C.0001999	0.2336	10.70	14.16	38
0.CC06631	C.0001914	0.2236	12.C0	15.49	39
0.C006749	C.0002126	0.2399	17.30	20.64	40
0.C006213	0.0001926	0.2362	21.C0	26.47	41
0.CC05618	C.0001757	0.2382	33.C0	36.58	42
0.CC04954	C.0001539	0.2340	39.C0	42.78	43
0.C005775	C.0001938	0.2555	41.C0	44.39	44
0.CC05975	C.0002077	0.2649	45.40	48.70	45
0.CC06C61	C.0002155	0.2707	48.70	51.89	46
0.C006128	C.0002144	0.2665	54.10	57.33	47
0.CC05803	C.0002070	0.2714	59.20	62.41	48
0.CC05758	C.0002164	0.2844	64.C0	67.15	49
0.CC06029	C.0002271	0.2870	69.40	72.46	50
0.CC05945	0.0002274	0.2913	74.30	77.34	51
0.CC06C13	C.0002342	0.2967	79.20	82.20	52
0.C005862	C.0002304	0.2993	85.20	88.19	53
0.C00574C	C.0002284	0.3029	90.30	93.27	54
0.CC057E5	C.0002357	0.3103	95.30	98.23	55
0.C005597	0.0002322	0.3160	99.70	102.64	56
0.C005687	0.0002530	0.3352	105.40	108.15	57
0.CC05534	C.0002325	0.3199	105.60	108.51	58
0.CC05512	C.0002342	0.3236	110.90	113.79	59
0.C00535R	0.0002299	0.3267	116.C0	118.89	60

TABLE 3

TRANSIENT HEATING RESULTS

Second set of experimental runs.

THERMAL DIFF. (CM-CM/SEC)	THERMAL COND. (CAL/SEC-C-CM)	SPEC. HEAT (CAL/G-C)	INITIAL TEMP. (CENTIGRADE)	AVERAGE TEMP. (CENTIGRADE)	RUN
0.0018925	0.0001630	0.0654	-200.00	-192.62	1
0.0017485	0.0001649	0.0716	-196.00	-189.09	2
0.0017052	0.0001646	0.0735	-192.00	-185.17	3
0.0016001	0.0001677	0.0798	-184.00	-177.55	4
0.0015833	0.0001765	0.0849	-177.00	-170.89	5
0.0015805	0.0001860	0.0896	-170.20	-164.41	6
0.0015611	0.0001910	0.0932	-165.00	-159.39	7
0.0015052	0.0001937	0.0979	-158.70	-153.26	8
0.0014581	0.0001967	0.0997	-152.60	-147.19	9
0.0014542	0.0002016	0.1057	-148.00	-142.87	10
0.0014556	0.0002022	0.1057	-147.20	-142.10	11
0.0014380	0.0002100	0.1111	-141.50	-136.57	12
0.0013995	0.0002115	0.1151	-135.10	-130.30	13
0.0013720	0.0002141	0.1188	-130.20	-125.51	14
0.0013871	0.0002203	0.1254	-124.00	-119.52	15
0.0013200	0.0002212	0.1275	-118.20	-113.73	16
0.0011722	0.0002069	0.1345	-106.40	-101.96	17
0.0012494	0.0002311	0.1408	-101.30	-97.11	18
0.0011746	0.0002235	0.1448	-94.80	-90.63	19
0.0011509	0.0002262	0.1497	-89.00	-84.93	20
0.0010994	0.0002247	0.1556	-79.00	-74.99	21
0.0010994	0.0002247	0.1556	-79.00	-74.99	22
0.0010604	0.0002298	0.1651	-67.40	-63.56	23
0.0010700	0.0002393	0.1702	-62.00	-58.27	24
0.0010009	0.0002293	0.1743	-57.10	-53.35	25
0.0010034	0.0002344	0.1779	-51.00	-47.31	26
0.0009766	0.0002321	0.1810	-46.00	-42.32	27
0.0009674	0.0002368	0.1863	-40.70	-37.11	28
0.0008948	0.0002224	0.1894	-35.00	-31.35	29
0.0009019	0.0002299	0.1942	-30.20	-26.61	30
0.0009047	0.0002412	0.2030	-24.60	-21.13	31
0.0008509	0.0002309	0.2065	-20.00	-16.45	32
0.0008859	0.0002604	0.2239	-16.00	-12.70	33
0.0007608	0.0002320	0.2321	-10.10	-6.66	34
0.0006772	0.0002156	0.2398	-4.70	-1.42	35
0.0008138	0.0002384	0.2232	1.00	4.32	36
0.0007448	0.0002156	0.2204	6.20	9.66	37
0.0007533	0.0002276	0.2302	11.30	14.64	38
0.0007536	0.0002317	0.2342	16.30	19.60	39
0.0007609	0.0002421	0.2424	20.90	24.10	40
0.0006877	0.0002195	0.2431	25.80	29.12	41
0.0007536	0.0002473	0.2498	31.40	34.52	42
0.0014531	0.0002381	0.2276	34.50	39.93	43
0.0007070	0.0002320	0.2500	39.40	42.57	44
0.0007013	0.0002332	0.2533	44.00	47.16	45
0.0006859	0.0002363	0.2558	49.70	52.85	46
0.0005584	0.0002536	0.3452	54.80	57.69	47
0.0005751	0.0002740	0.3592	59.00	61.73	48
0.0005729	0.0002816	0.3732	65.50	68.19	49
0.0005364	0.0002862	0.4054	71.30	73.93	50

TABLE 4

DENSITY OF PCPX (g cm^{-3})

Initial density	1.312
After first set of runs	1.312
After second set of runs	1.297

(C) *Thermal diffusivity*

The results of the thermal diffusivity studies of PCPX are shown in Figs. 15 and 16. The number of runs and the temperature ranges for both the first and second set of experimental runs are the same as those described for the specific heat and thermal conductivity studies.

(D) *Tables*

The results of both the transient heating experiments showing the three thermal properties, the run number, the initial and average temperature are shown in Tables 2 and 3.

The results of the density measurements are shown in Table 4.

DISCUSSION OF RESULTS

(A) *Specific heat measurements*

By referring to Figs. 10–12, it can be seen that the specific heat (C_p) curves exhibit the following characteristics: (1) specific heat increases monotonically in the temperature region of -200 to $-30°C$ between a value of 0.0810 to 0.1779 cal g^{-1} deg^{-1}; (2) in the vicinity of $-20°C$ there is a marked increase in C_p of 4.4 cal deg^{-1} mol^{-1}; (3) the C_p increases again in a linear fashion until approximately 50°C at which time another marked increase is observed; (4) the reproducibility of the results of the two transient heating curves is excellent until the 50°C transition is reached; (5) agreement of transient heating results and the differential scanning calorimeter are well within the reported accuracies[7,21] of the methods.

First let us consider the linear portion of the C_p curve at the lower temperature region (-200 to $-20°C$). It was found that the dependence of C_p with temperature in this lower temperature range can be represented by the following linear equation:

$$C_p = 0.0654 + \beta_s(200 + T) \tag{18}$$

where T is the temperature in this lower region and β_s is the slope of the C_p curve which for PCPX is 7.7×10^{-4} cal g^{-1} deg^{-2}. Using the data given by Wunderlich and Baur[1] of the heat capacity of PS, it can be seen that a similar equation could be used to represent the heat capacity of PS over this same temperature range and would have the form:

$$C_p = 0.083 + \beta_s(200 + T) \tag{19}$$

where β_s for PS is 9.8×10^{-4} cal g^{-1} deg^{-2}.

The increase in specific heat at low temperature reflects the thermal expansion of the material. As thermal energy is absorbed into the polymer network, molecular vibrations in both amorphous and to a lesser extent in crystalline regions increase causing an expansion of the network. As the network expands, more and more thermal energy is required. Therefore by comparing the values of β_s in eqns (18) and (19) one

could predict the expansion coefficient for PS to be greater than PCPX. This is indeed the case; the thermal expansion value for PS^{25} is 6.0–8.0 $\times 10^{-5}\,^\circ C^{-1}$, whereas the expansion value for PCPX as measured in this study with a DuPont thermomechanical analyzer was 3.5–5 $\times 10^{-5}\,^\circ C^{-1}$. It would seem, therefore, that the value of β_s (the slope of the C_p curve) and the thermal expansion are directly related in this lower temperature range.

It is now of interest to consider the relatively marked increase of C_p at $\simeq -20\,^\circ C$. Chung and Sauer[26] studied the mechanical relaxation of PCPX and their results are shown in Fig. 17. The data show a broad loss peak with a maximum at $-19\,^\circ C$ (0.4 cps) accompanied by a 40% decrease in modulus. Chung and Sauer
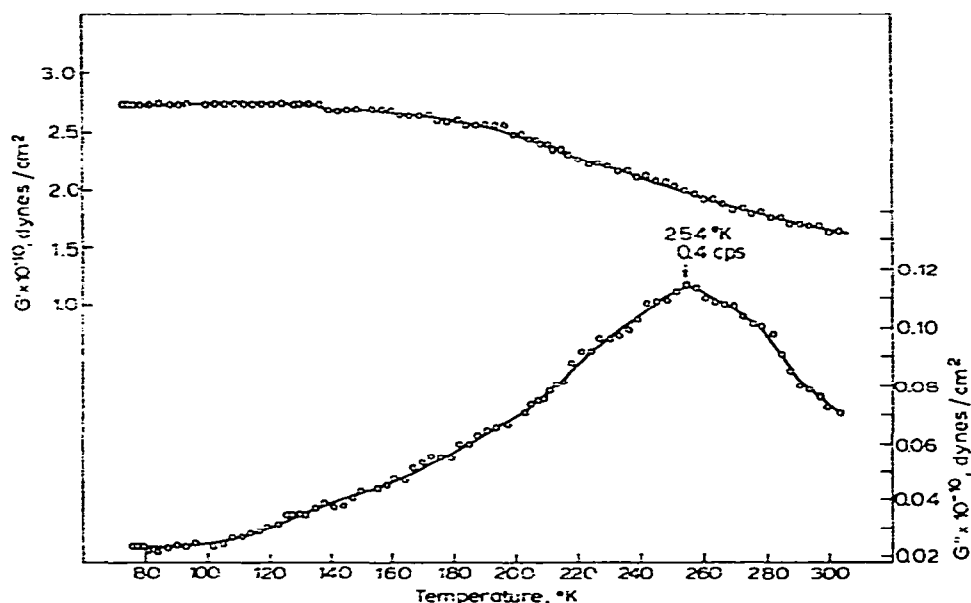

Fig. 17. Dynamical mechanical relaxation of PCPX (Chung and Sauer[26]).

attribute this γ loss peak to torsional motions of the monochlorophenyl groups and associated CH_2 groups in the main chain. This observation is further substantiated by Hiltner and Baer[27] who report both a lower temperature δ relaxation in poly-para-xylylene (PPX) at 50°K ($-223\,^\circ C$) which they attribute to just phenyl ring oscillation and a γ relaxation which is attributed to phenyl ring and associated CH_2 torsional motion. Hiltner and Baer[27] go on to show that the magnitude of the δ relaxation is affected by the degree of crystallinity in that the magnitude of the δ relaxation peak decreases with crystallinity and they therefore conclude that the phenyl ring oscillation causing this peak occurs mainly in the amorphous regions of the polymer network. The data comparing the magnitude of the γ peak as a function of crystallinity are not available and no such assignment can be made for the γ relaxation.

At first it was surprising that this γ relaxation could be detected with C_p measurements via the transient heating method in that for most low temperature

relaxations, although the molecular motions responsible for the relaxations contribute to C_p, the processes are not sufficiently cooperative to occur over a narrow temperature range. O'Reilly and Karasz[28] state in a review article which included the great majority of available data, "There are no abrupt changes in C_p from near 0 K to T_g similar to the mechanical or dielectric relaxations observed below T_g". In fact little work has been published to disclaim this observation. Work of Steere[29] and Schuler[21], however, both report the ability to measure polymer transitions other than T_g and T_m using C_p measurements. Both Steere and Schuler used the transient heating technique described earlier in this study. One of the materials studied by Steere was polytetrafluoroethylene (Teflon). His data show a sharp discontinuity at 19 °C and evidence of a small maximum near 30 °C. These peaks represent the two transitions in Teflon that are known[30] to exist in the region of room temperature. The first is first order and involves a rearrangement of the helical structure of the main chain. The transition at 30 °C is thought to be a minor change in the crystalline structure. Schuler[21] in his study of low and high density PE was able to discern β and γ relaxations at -30 and -125 °C. These internal friction peaks at comparable temperatures were reported earlier by Sauer and Woodward[31] using dynamic mechanical test methods.

Considering the above evidence it is concluded that C_p measurements can in some cases show temperature relaxations below T_g. Figure 18 is a thermomechanical
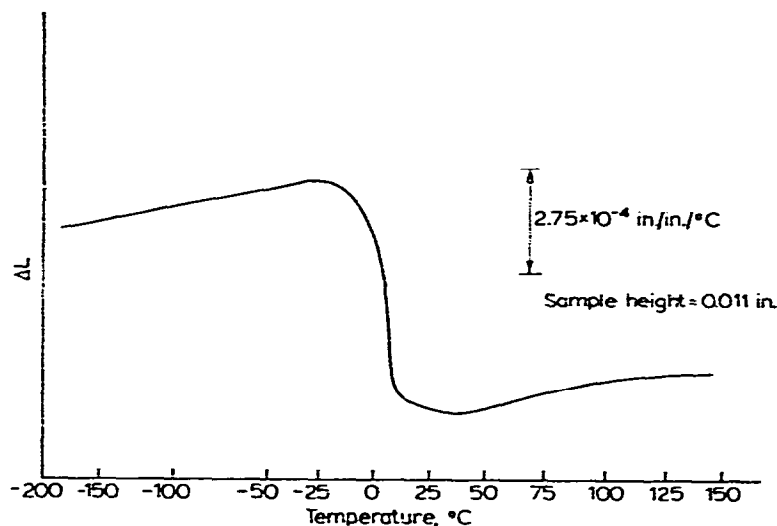

Fig. 18. TMA of PCPX showing expansion and softening.

analysis curve showing the expansion and softening of PCPX. The major softening point is shown at -20 °C which agrees with the loss peak in Chung and Sauer's[26] data and the abrupt jump in the C_p curve in this study. Since all three methods are able to show this relaxation, it would seem that the γ relaxation in PCPX, as described by Chung and Sauer[26] as torsional motions of the monochlorophenyl groups and

associated CH_2 groups, involves cooperative movements in the main chain of the molecule. And although conclusive evidence is not available, this cooperative movement, owing to the magnitude of the jump in the C_p curve, would most probably be occurring in both the amorphous and crystalline regions of the polymer network.

One more point must be mentioned concerning the jump in the C_p curve at $-20\,°C$. The results of the two experiments show a slight discrepancy in this temperature region. The first experiment results show the γ relaxation manifested as a jump in the C_p curve with no maximum, while the results of the second experiment show a similar jump in the C_p curve accompanied by a slight maximum. The presence of this maximum cannot be explained in that the transition is generally thought to be of the second order type and would therefore not show a maximum as would a first order transition.

To continue with the analysis of the C_p curve above the $-20\,°C$ jump, it can be seen that the C_p increases linearly again until it reaches $\simeq 50\,°C$. This jump of $6.5\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ is attributed to onset of the glass transition (T_g) of PCPX. The T_g transition appears some 10 to $30\,°C$ lower than the value reported in the literature[18]. The difference is attributed to the experimental methods used for T_g determination. Secant modulus data were used to determine the T_g in the earlier study[18]. These data were taken at 1 cps whereas the C_p measurements were clearly taken at a much lower rate. It is also of interest to note that in the TMA curve (Fig. 18), there is no apparent softening at $50\,°C$ or in the 80 to $100\,°C$ range. Therefore there is some confusion in the assignment of T_g.

The magnitude of the jump at T_g in Fig. 10 is $6.5\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ which is in good agreement with values reported for other polymers. Wunderlich and Baur[1] state that for many glasses, polymeric and non-polymeric, ΔC_p at T_g calculated per mol of "beads" is about $2.7\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$. These "beads" are the smallest sections of the solid that can move as a unit in internal rotation. For the case of PCPX there would be three "beads" per monomer unit and a ΔC_p at T_g of $2.25\ \mathrm{cal\ deg^{-1}}$ $\mathrm{mol^{-1}\ bead^{-1}}$. This lower value of 2.25 compared to $2.7\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ probably reflects the highly crystalline nature of PCPX. The magnitude at T_g in Fig. 11 is $12.6\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ or $4.2\ \mathrm{cal\ deg^{-1}\ mol^{-1}\ bead^{-1}}$ and represents a marked increase over the accepted value. It was found by both density measurements and visual inspection that sample degradation occurring in the T_g temperature region caused this greater than expected increase in C_p. A photograph (Fig. 19) shows the sample before and after the second experiment. Sample degradation is clearly shown in the upper portion of the photograph. Density measurements (Table 4) show a decrease in density after the second experiment which is also an indication of sample degradation. It is noted that after the first experiment no density changes were observed indicating no sample degradation during the first experiment. It is probable that some sample degradation occurred during the first experiment. It is felt, however, that by taking account of the reproducibility of the C_p data and the density data, the small degradation that might have occurred in the first experiment did not appreciably affect the results of the second experiment.

The region of the C_p curve above T_g is again linear up to 120°C which was the upper limit of the experiment. No comparison between the two transient heating results can be made above the 50°C range because sample degradation experienced during the second experiment forced its termination at 70°C.

The results of the DSC study and of the first transient heating experiment are in good agreement. The magnitude of the jumps in the C_p curve at the γ relaxation and at T_g is less but this is not surprising when one considers the fast heating rate and sample size of a DSC experiment.
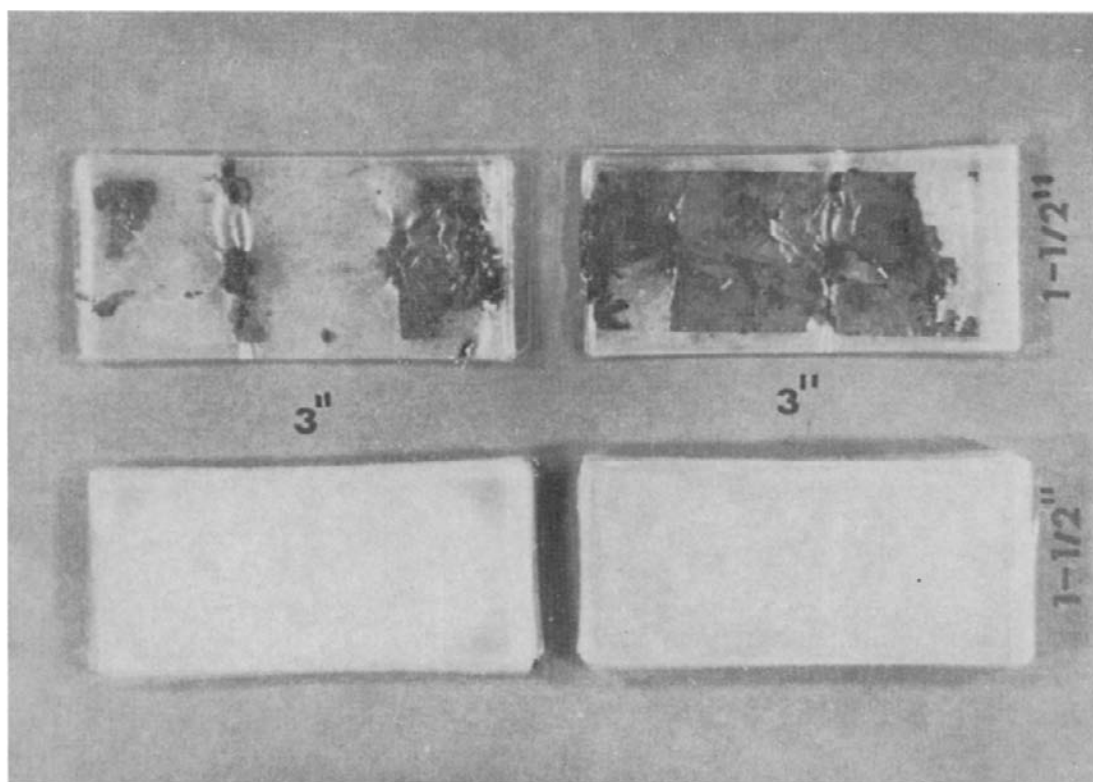

Fig. 19. Photograph of PCPX sample. Upper portion shows sample degradation that occurred during the second set of experimental runs.

(B) Thermal conductivity

The general features of the thermal conductivity curves are not as reproducible as the C_p curves; however, some general characteristics can be cited: (1) K increases slightly in a linear manner between −200 and 120°C with possible discontinuities seen at −20 and 50°C; (2) the values of K show considerable scatter particularly in the result of the first experiment (Fig. 13); (3) values of K shown as results of the second experiment show considerably less scatter; (4) the range of values of K falls between 0.9×10^{-4} and 2.5×10^{-4} cal sec^{-1} deg^{-1} cm^{-1} for the first experiment and 1.6 to 2.8×10^{-4} cal sec^{-1} deg^{-1} cm^{-1} for the second experiment.

The cause of the poor reproducibility and scatter (in the first experiment) is attributed to the manner in which the polymer films were held in the sample holder. When referring to the photograph (Fig. 8) it can be seen that the films were compressed between the top and bottom of the holder by tightening the bolts at the four corners of the holder. In the first experiment the sample configuration was constructed at room temperature and then placed in the temperature chamber and cooled to $-200\,°C$. It is therefore reasoned that thermal contraction lessened the surface contact of the polymer films thereby introducing air between the sheets of PCPX in the sample stack. The results of this thermal contraction resulted in lower than expected values of K and considerable scatter at the lower temperature regions. As the temperature of the chamber increased causing thermal expansion both the absolute value of K increased and scatter decreased.

The problem of thermal contraction and the resulting poor film contact was eliminated in the second experiment by retightening the four bolts after the sample was cooled to $-200\,°C$. This technique greatly decreased the scatter at the lower temperature range but created the problem of excessively high pressures in the upper temperature regions. This combination of high pressure and temperature could have been the cause of the sample degradation that was experienced during the second experiment. A modification of the sample holder is therefore recommended in that it be designed in such a manner that it keep a constant pressure on the stack of polymer throughout the temperature range of interest.

In considering the results of the second experiment (Fig. 14) the thermal conductivity increases from 0.9×10^{-5} cal sec^{-1} deg^{-1} cm^{-1} at $-170\,°C$ to 1.2×10^{-5} at $-120\,°C$. The curve is then linear with a low value of slope between -120 and $50\,°C$. At $\simeq 50\,°C$ there is a marked increase. There are some data points at $-20\,°C$ that could be considered as a discontinuity, but because of the scatter of the data it would be a presumptuous observation.

(C) Thermal diffusivity

The problem of thermal contraction as discussed in the section *Thermal conductivity* also adversely affected the results of the first transient experiment. Due to the scatter of data experienced during the first experiment, most of the discussion of the thermal diffusivity (α) will be taken from the data of the second experiment. The general features of the thermal diffusivity curve shown in Fig. 16 are: (1) there is over a 100% decrease in α within the temperature range of the experiment; (2) the values of α range between 1.9×10^{-3} cm^2 sec^{-1} at $-200\,°C$ to 0.5×10^{-3} cm^2 sec^{-1} at $70\,°C$; (3) anomalies in the α curve are shown at -20 and $50\,°C$; (4) by referring to Fig. 15 an almost constant diffusivity is shown between T_g and $120\,°C$.

The decrease in α with temperature curve of PCPX is in general agreement with the results of Steere[29] who studied polytetrafluoroethylene, poly(ethyleneterephalate) (Mylar), polypropylene, poly(vinyl chloride), and polycarbonate. All these polymers showed a decrease of α with temperature. The value of α closely agrees with those of PETP in that both PCPX and PETP show an increase of thermal diffusivity of about

100% between room temperature and near liquid nitrogen temperatures. Both show a change in slope at T_g and both have a region at high temperatures with almost constant diffusivity. The lower and upper value of α are also very close. The other polymers studied by Steere did not exhibit as steep a decrease or as low a value for α at the upper temperature regions.

(D) Practical application of data

Such properties as high dielectric strength, low permeability to moisture, and the method of application makes PCPX an ideal material to be used in the coating of critical electronic assemblies. While these properties are clearly important factors to consider in choosing a material for electronic assembly coating, it is of interest to also consider the thermal properties of PCPX and compare these properties to the thermal properties of other materials that might be considered. Epoxies, silicones, urethanes, and acrylics are some of the polymeric materials that have been widely used in the coating field and could be considered for use.

The thermal conductivity of PCPX at the operating temperature range of most electronic equipment in which circuit boards are used is much lower than the other polymeric materials mentioned above. The thermal conductivity of PCPX is $\simeq 2 \times 10^{-4}$ cal sec^{-1} deg^{-1} cm^{-1} whereas for epoxies, silicones, urethanes, and acrylics, the thermal conductivities[32] are 4.5, 3.5–7.5, 5, and 4–6 cal sec^{-1} deg^{-1} cm^{-1}, respectively.

α is the important thermal property to consider when the circuit is under non-steady-state or transient conditions. The circuit would of course experience transient conditions during the initial warm-up period. To provide a good insulation material in this transient case, a material with low α is desired. PCPX exhibits the lowest value of α of any polymeric material mentioned above. Although accurate measurements of α for epoxies, silicones, urethanes, and acrylics have not been made, a calculation using values of K, C_p, and ρ given in the Modern Plastics Encyclopedia[32] gives values of 1.6×10^{-3} for epoxies, 0.9×10^{-3} for silicones. 0.9×10^{-3} for urethanes, and 1.2×10^{-3} cm sec^{-1} for acrylics. PCPX had a value of 0.5 to 0.6×10^{-3} cm^2 sec^{-1}.

CONCLUSIONS AND RECOMMENDATIONS

(A) Experimental apparatus

The transient heating apparatus used in this study is highly recommended for future research on the thermal properties of polymer films. The computer software package developed for the interpretation of transient results can easily be used with transient data of any polymer. The automatic data acquisition system developed during this study will greatly decrease the burden of data handling in future studies. The data acquisition system could also be used for other types of research projects with only a slight modification of software package.

The reproducibility of the apparatus has been demonstrated. To improve reproducibility to an even greater degree, it is recommended that the sample holder

be redesigned so that a constant pressure can be applied on the sample throughout a heating run. One design that is suggested is a second class lever arrangement; with this design a known amount of pressure could be applied to the sample by simply hanging a weight on the end of the lever arm. The whole configuration could then be placed in the temperature chamber eliminating pressure change caused by thermal expansion and contraction.

Re-emphasis is made to the importance of maintaining accurate calibration of the recorder and data acquisition equipment throughout the experiment. Calibration checks using an accurate digital voltmeter should be made before each transient heating run.

The accuracy of the method depends greatly upon the expertise of the experimenter and the electronic test equipment available. For example, the heat flux is determined by measuring the current passing through the heating foil of a determined area. It is therefore important that great care be taken in cutting and measuring the heating foil and in measuring of the current. The sample thickness between the heating foil and thermocouples is also a critical measurement. If a micrometer is used, however, the thermal expansion and compression during the experiment will cause some variations in thickness. Density changes with temperature are another possible source of error. Even with all these possible sources of error, it can be noted that the transient results agree well with the differential scanning calorimeter results which have the reported[7] accuracies of 2%.

(B) Poly-monochloro-para-xylylene

Conclusions drawn from the thermal data of PCPX are as follows:

(1) One can detect a significant change in the specific heat of PCPX in the vicinity of the γ relaxation at $-20°C$, indicating that this relaxation involves a cooperative motion of molecules. This supports the observation of Chung and Sauer[26] who attribute this relaxation to torsional motion of the monochlorophenyl groups and associated CH_2 groups in the main chain. Further evidence points to the fact that these motions are manifested in both amorphous and crystalline regions of the network.

(2) The glass transition was shown at $50°C$ as (a) a jump in the C_p curve of 6.5 cal deg^{-1} mol^{-1}; (b) a discontinuity in the thermal conductivity curve; and (c) a marked decrease in the thermal diffusivity curve.

(3) A direct relation between thermal expansion and specific heat increase was indicated in PCPX as well as PS at relatively low temperatures.

(4) The overall values of the thermal conductivity and thermal diffusivity of PCPX as compared to other polymer films indicate that this material is ideally suited for insulation applications.

(C) Future studies

In future thermal work it would be of interest to examine other polymers in the parylene family. Gorham[20] reported the synthetic method of the preparation of seven

different parylenes and Chow et al.[33] discussed another parylene. Chung[34] describes the mechanical relaxation of three parylenes, viz. PCPX, PDCPX, and PPX, and shows γ relaxations at -20, -117, and $-114\,°C$, respectively. It would be of interest if these relaxations could be detected with transient heat measurement.

Although a ΔC_p was seen at the γ relaxation of PCPX, there is some question as to the capability of C_p measurements to detect lower temperature γ transitions in PDCPX and PPX. The reason is that the decrease in modulus at the γ relaxation is only about 25% in PDCPX and PPX as compared to some 40% in PCPX.

To substantiate the assignment of phenyl motion and associated CH_2 motion occurring in both amorphous and crystalline regions, both n.m.r. data and additional d.m.r. data would be very helpful.

Niegisch[35] shows the existence of an alpha and beta modification of the crystal structure of PPX. Under most polymerization conditions, the alpha form is the preferred state and upon heating above $220\,°C$, transformation to the beta form takes place. It would be of interest to see the effect of this polymorphic phase change on the thermal properties. It is possible that due to the high crystallinity of the film (80% in some cases) the polymorphic phase change could be detected.

Effects of orientation on the thermal properties of PCPX need to be investigated. During this study it is very possible that during the second experiment, when the material experienced both temperatures above T_g and relatively high pressures, a small increase in orientation of the polymer chains may have occurred. It is thought, however, that the small amount of orientation caused by the pressure due to thermal expansion would not appreciably affect the thermal properties. It would be of interest, however, to see what effect would be caused by stretching or pressing the film under high pressures.

REFERENCES

1 B. Wunderlich and H. Baur, *Adv. Polymer Sci.*, 7, 2 (1970).
2 W. Nernst and F. A. Lindermann, *Z. Elektrochem.*, 17 (1911) 817.
3 J. M. Sturtevant, in A. Weissberger (Ed.), *Technique of Organic Chemistry*, Vol. 1, Part 1, Interscience, New York, 3rd edn., 1959, Ch. X.
4 J. D. Hoffman, *J. Amer. Chem. Soc.*, 74 (1952) 1969.
5 B. Wunderlich and M. Dole, *J. Polymer Sci.*, 24 (1957) 201.
6 M. J. O'Neill, *Anal. Chem.*, 36 (1964) 1238.
7 B. Wunderlich, *J. Phys. Chem.*, 69 (1965) 2078.
8 D. R. Anderson, *Chem. Rev.*, 66 (1966) 677.
9 D. Hansen, R. C. Kantayya and C. C. Ho, *Polymer Eng. Sci.*, 6 (1966) 260.
10 L. C. K. Carwile and H. J. Hoge, *Tech. Rep. 66-27-PR, U.S. Army Natick Laboratories, Natick, Mass.*, April 1966.
11 K. H. Hellwege, J. Hennig and W. Knappe, *Kolloid Z.*, 188 (1963) 121.
12 American Society for Testing Materials, *ASTM Standards C177-63, Part 14, 15*, 1965.
13 D. E. Kline, *J. Polymer Sci.*, 50 (1961) 441.
14 H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, London, 2nd edn., 1959, Ch. II.
15 H. L. Frisch and C. E. Rogers, *J. Polymer Sci.*, Part C, 12 (1966) 297.
16 T. Z. Harmathy, *J. Appl. Phys.*, 35, 4 (1964) 1190.
17 R. C. Steere, *J. Appl. Phys.*, 37, 9 (1966) 3338.
18 Union Carbide Corp., *Parylene Product Data, Publication J-2891*, Plastics Div., New York.

19 W. F. Gorham, *J. Polymer Sci.*, A-1, 4 (1966) 3027.
20 W. F. Gorham, *Polymer Preprints*, 6, 1 (1965) 73.
21 R. A. Schuler, *M.S. Thesis*, Department of Mechanics and Materials Science, Rutgers University, 1969.
22 *Mark 250 Recorder Manual, No. 15-806317-00*, Clevite Corp., Brush Instrument Div., Cleveland, Ohio, 5.1–5.2, 1966.
23 M. Abramowitz and I. Stegum, *Handbook of Mathematical Functions*, Dover, New York, 1965.
24 D. C. Ginnings and G. T. Furukawa, *J. Amer. Chem. Soc.*, 75 (1953) 522.
25 American Society for Testing Materials, *ASTM Standards D1505-63T, Part 27, 500*, 1965.
26 C. I. Chung and J. A. Sauer, *J. Polymer Sci.*, Part A-2, 9 (1971) 1087.
27 A. Hiltner and E. Baer, *Relaxation Processes at Cryogenic Temperatures*, to be published.
28 J. M. O'Reilly and F. E. Karasz, *J. Polymer Sci.*, Part C, 14 (1966) 49.
29 R. C. Steere, *J. Appl. Polymer Sci.*, 10 (1966) 1673.
30 F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Interscience, New York, 1962.
31 J. A. Sauer and A. E. Woodward, *Rev. Mod. Phys.*, 32 (1) (1960).
32 *Modern Plastics Encyclopedia*, Vol. 46, No. 10A, 983, 1969–70.
33 S. W. Chow, W. E. Loeb and C. E. White, *J. Appl. Polymer Sci.*, 13 (1969) 2325.
34 C. I. Chung, *Ph. D. Dissertation*, Department of Mechanics and Materials Science, Rutgers University, 1969.
35 W. D. Niegisch, *J. Appl. Phys.*, 37, 11 (1966) 4041.