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PRECISION SPECIFIC-HEAT MEASUREMENTS ON POLYMERS BY AUTOMATED DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The automation of a differential scanning calorimeter (DSC-II) with a computer and an interface is described. Specific-heat and enthalpy measurements on polymer standards of polystyrene (NBS-706 and NBS-705) and polyethylene (NBS-1475) are presented. Under favorable conditions the accuracy compared to published measurements is within 1%, but some differences are as large as 3%. An auto-annealing program for studying enthalpy relaxation in polymers is discussed. Other applications of automated DSC are reviewed.

INTRODUCTION

The widespread application of the methods of thermal analysis (differential scanning calorimetry, DSC, and differential thermal analysis, DTA) to the solution of chemical problems [1] has grown in the past ten years. Adaptation of computers and microprocessors to thermal analysis [2,3] has improved the precision of the measurements and has facilitated the data acquisition and analysis. This paper describes the interfacing of a digital voltmeter (HP3497A) and an HP85 computer with a Perkin-Elmer DSC-II scanning calorimeter. The purpose of the automated system was to provide precise digital measurement of power and temperature, on-line data analysis to provide specific-heat and enthalpy measurements, and computer control of annealing and other experiments.

The types of problems that can be investigated by precision scanning calorimetry are legion. Examples are glass transition and enthalpy relaxation [4], melting phenomena [5], degree of crystallinity [6], kinetics of crystallization [7], heats of reaction [8], reaction kinetics and even photochemically induced reactions [9,10]. Temperature and energy calibrations with indium and alumina are discussed here. Comparisons with standard polymers NBS-705 and NBS-706 (polystyrene) and NBS-1475 (polyethylene) show that the precision of the C_p measurements is 1–3%. A program for automatically running annealing and enthalpy relaxation experiments is presented.

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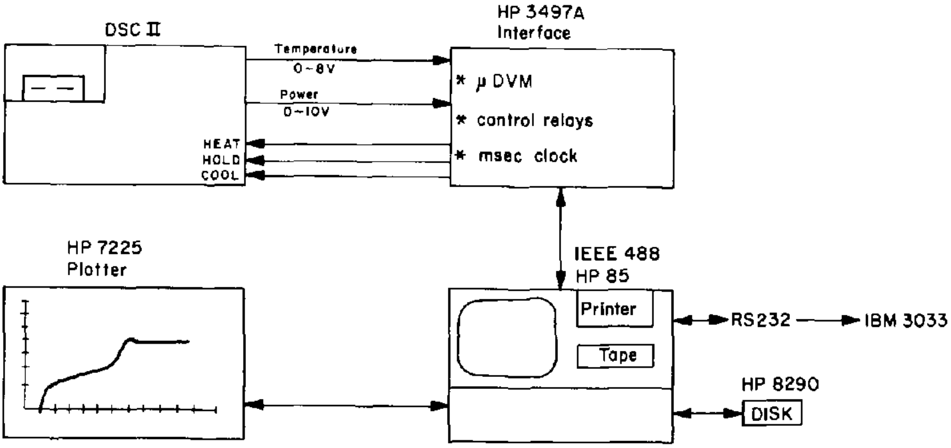

Fig. 1. Schematic diagram of DSC-II, HP3497A interface, HP85 computer and HP7225 plotter.

EXPERIMENTAL

Automation and programs

A Perkin-Elmer DSC-II was interfaced through an HP3497A interface to a Hewlett-Packard HP85 computer (Fig. 1). The DSC-II was reconditioned by replacement of the sample head, the controller board and the power supply. A custom analogue filter to the 10-V power signal and the necessary interface wiring were installed. The HP85 computer, which has as standard equipment 16K of memory, graphics CRT, printer and tape storage device, was purchased with an additional 16K of memory and the printer, plotter, mass storage, matrix, input/output and advanced programming ROMs. The 3497A interface had the optional built-in 5.5-place digital voltmeter (HP3255) and 20-channel scanner card. An HP7220 plotter and an HP82901M two-drive floppy-disk system completed the computer system. The IEEE488 interface was used to interconnect the Hewlett-Packard equipment.

The wiring between the DSC and the 3497A interface consists of three control lines and two data lines. The control lines are connected to the COOL, HOLD and HEAT buttons on the DSC and activate switches. A relay wired from the scanner card in parallel with each of the three switches allows these functions to be controlled from the computer by toggling the appropriate relay. The first data line is connected to a 0–8-V signal, which is output by the DSC temperature programmer corresponding to a sample temperature of 0–1000 K. The second data line monitors a 10-V signal representing the power being supplied to the sample chamber. The operator loads the sample, sets heating and cooling rates, and sets the calorimeter to the correct starting temperature.

A computer program allows the HP85 to control the DSC-II. Two main objectives were followed during the design and writing of this program: the data collection process should be as accurate as possible, and the program should be convenient to use.

Several things were done to ensure the accuracy of the data to be collected. The data collection routine is paced by a very accurately timed pulse originating from the 3497A interface. This pulse triggers the appropriate relay to start and stop a run and paces the data-taking routine at 0.300-s intervals in relation to the starting time. At the end of a run, the actual temperature is compared with the temperature calculated from heating rate and time. If a discrepancy of more than 0.1°C is found, the operator is notified. This procedure was satisfactory for runs as long as 30 min (20°C min^{-1} to 600°C).

The isothermal values of power and temperature at the beginning and the end of a run, which are very important to the accurate measurement of heat capacity, are given special attention. The DSC is given time to stabilize for 1 min before these values are read, and then, to remove the effects of noise, the values are taken as averages of 16 readings.

According to standard calorimetry practices, the temperature of the system is calibrated from the melting points of lead and indium, and the power signal is calibrated against the heat capacity of alumina or the heat of melting of indium.

During data-collection routines there is a real-time display of the incoming data and a tone function to keep the operator informed of the process taking place. This feature allows the operator to follow the progress of an experiment while being free to do other work in the lab.

Another convenient feature has been for the computer to check to see if the DSC was set to the same conditions that were specified in the program's initialization process. At the start of a run the starting temperature and the heating rate are checked in the first 1.5 s of the experiment. If a discrepancy is found, the DSC is reset and an appropriate message is displayed. Not only is the operator saved the rerun time, but the DSC will restabilize fairly rapidly after such a short run time.

Figure 2 is a schematic representation of how heat capacity is determined. Because this is a differential measurement, it is necessary to determine the difference between the voltage readings of the sample and of the baseline. The isothermal voltage readings, shown as dashes before and after the trace in Fig. 2, are used to normalize the two traces to each other and correct for any slope in the baseline. The difference is then determined by subtracting baseline trace from sample trace.

Once the difference in voltage between sample and baseline is recorded, the voltage is converted to Joule-seconds through a power calibration factor K. As mentioned earlier, the power is calibrated by measuring the heat capacity of alumina or the heat of fusion of indium and taking the ratio of these values to the published values. The calibration constant is fitted by a

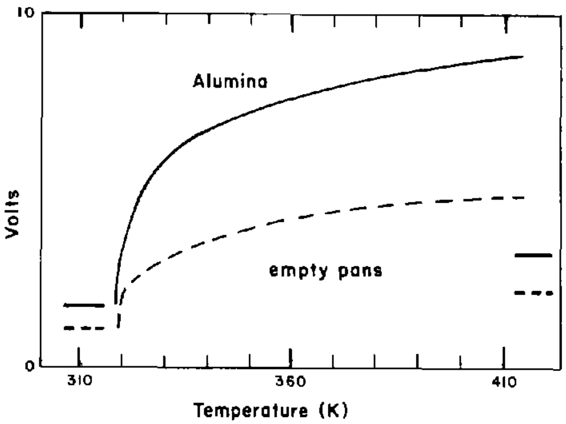

Fig. 2. Heat capacity determination of alumina standard. Voltages for alumina and empty pans (baseline) are shown for initial, dynamic heating and final conditions.

linear function of temperature for each heating rate and stored in the program. When a heating rate is specified during the initialization process, the corresponding calibration curve is chosen automatically.

Besides the calibration curve, a number of other constants and conditions are automatically keyed into the program when the heating rate is specified. These deal with limiting values and timing considerations. The program allows the use of heating rates from 0.3125 to 80°C min^{-1}.

The sampling rate is always 0.3 s per reading. Over the range of possible heating rates, the change in temperature between readings varies by a factor of 256, from 0.00156°C at 0.3125°C min^{-1} to 0.4°C at 80°C min^{-1}. A potential problem exists with such a scheme. The slow heating rates use up the limited amount of computer memory (1800 points maximum) over a short temperature range. To alleviate the situation, the operator has been given the option to extend this range by skipping some number of points between each recorded reading.

A powerful feature of this system is the ability to run an auto-anneal program. It measures the change in heat capacity of a sample that results from annealing the sample for a specified time and temperature. The program will measure the heat capacity of the unannealed sample, go to the anneal temperature and hold isothermally for the specified time, return to the starting temperature and again measure the heat capacity. Typical results (discussed later) are shown in Fig. 10. The program will run completely unattended for up to 15 anneal cycles (100°C range). This amount of data will fill a disk (248 Kbytes).

Energy calibration

Alumina

The specific heat of Al_2O_3 [11] was measured from 320 to 420 K at three

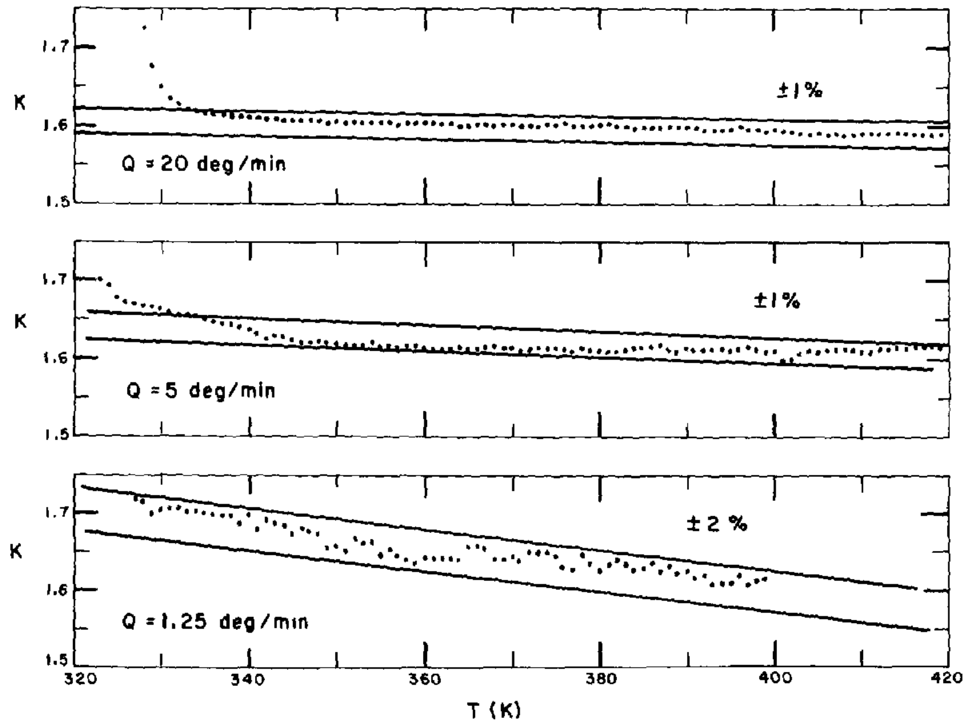

Fig. 3. Calibration constant determined from alumina sample at three heating rates.

heating rates. A calibration constant K is defined as

$$K(T)=\frac{C_p(T)mq}{\Delta V_{S-B}}=\mathrm{mJ\ s^{-1}\ V^{-1}} \tag{1}$$

where $C_p(T)$ = specific heat (mJ mg^{-1} °C^{-1}), m = mass of sample (mg), q = heating rate (°C s^{-1}), ΔV_{S-B} = difference in voltage (sample minus baseline) (V).

Figure 3 shows $K(T)$ as a function of temperature at three heating rates. The precision of the specific-heat measurements decreases with heating rate because the voltage decreases directly with power input required to maintain the heating rate. A larger variation in K is observed at lower heating rates.

Indium

The heat of fusion of indium or any other pure material is used as a calorimetric standard. Integration of the area under the melting curve was done by using Simpson's rule; Fig. 4 shows calibration constants at different heating rates. A value of 28.40 J g^{-1} for the heat of fusion from National Physical Laboratory [12] yields good agreement with the alumina data, since the energy calibration constant should be independent of the material used. These results are in contrast to the results of Richardson and Savill [13],

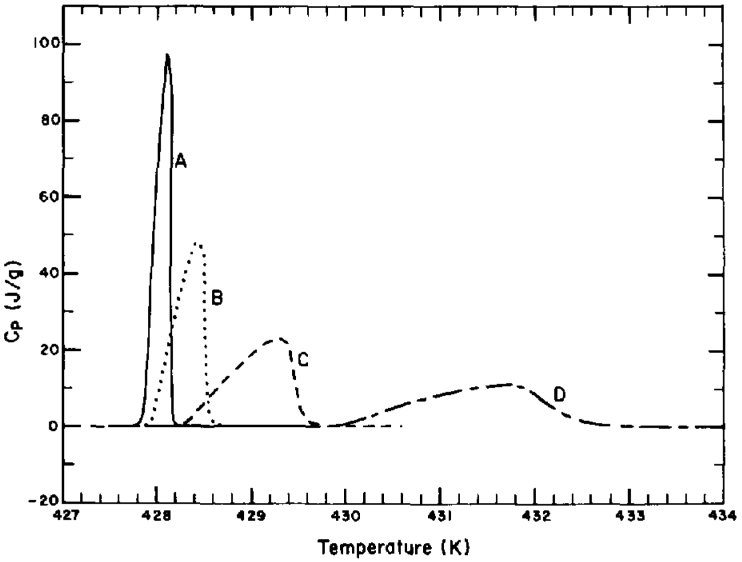

Fig. 4. Calibration constant determined from heat of fusion of indium at four heating rates. (A) 0.3125°C min^{-1}, $K = 1.583 \pm 0.002$; (B) 1.25°C min^{-1}, $K = 1.600 \pm 0.002$; (C) 5°C min^{-1}, $K = 1.608 \pm 0.002$; (D) 20°C min^{-1}, $K = 1.612 \pm 0.004$.

which were several percent lower, and support the current value of $\Delta H_f = 28.40$ J g^{-1} for indium. The measured value of K is more precise from indium because of the larger voltages, particularly at low heating rates. Clearly, the calibration constant applies only at the temperature of measurement. Since the calibration constant from alumina applies over a range of temperatures, it will be applied for all of the polymer samples reported here. Alumina is more representative of a polymer sample than indium in its specific heat and thermal conductivity.

Temperature calibration

The temperature reading is determined from the voltage reading from a platinum resistance thermometer. A linear equation (2) defines the temperature within ±0.05 K. A temperature calibration program determines V at 10°C intervals over a temperature range of 300–600 K. The constants A and B are determined by a least-squares program. The change in temperature calibration with heating rate is adjusted through the contant A, and B is effectively independent of heating rate.

$$T = A + BV \qquad (2)$$

Polystyrene

Styrene polymers are available from the National Bureau of Standards as standards for molecular-weight measurements. NBS-706 was prepared by

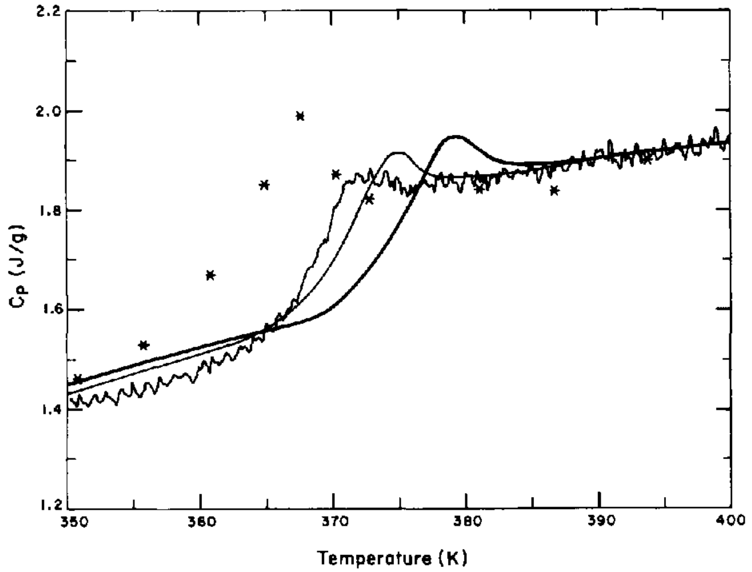

Fig. 5. Change in C_p at T_g of NBS-706 polystyrene as a function of heating rate: 1.25, 5 and 20°C min^{-1}; (*) adiabatic calorimetry (ref. 14).

free-radical polymerization, with $M_W = 257{,}800$ and $M_N = 136{,}500$. NBS-705 was prepared by anionic polymerization, with $M_W = 179{,}300$ and $M_N = 170{,}900$. Moreover, precision adiabatic calorimeter measurements are available for these samples and qualify them as secondary standards, since their thermal properties are representative of those of other amorphous polymers.

NBS-706

The specific heat of NBS-706 was measured from 300 to 400 K, encompassing the glass and liquid ranges at several heating rates (1.25–20°C min^{-1}). In Fig. 5 the change in T_g with heating rate is ~ 4°C/decade, which is typical for polymers. Specific-heat data at 20°C min^{-1} in the glass and liquid regions (outside the transition region) agree with the adiabatic calorimeter results (Fig. 6) [14]. It is apparent that the transition region occurs at a much lower temperature in the adiabatic calorimeter because of the lower heating rate. However, the transition is much lower than expected. A shift of T_g of 8–10°C would correspond to 2–3 decades of heating rate or 0.002°C min^{-1}. The actual rate in the adiabatic calorimeter is 0.1–0.2°C min^{-1}. A possible reason for these differences may be a large (2–5 K) gradient in the DSC sample, which was not corrected for by the heating rate dependence of the melting point of indium.

The specific heat of the glass is lower than the adiabatic calorimeter results by 1%, and the results compare within 0.5% in the liquid. The slope of C_p in the glass is 5×10^{-3} J g^{-} K^{-2} and 3.3×10^{-3} J g^{-1} K^{-2} in the liquid,

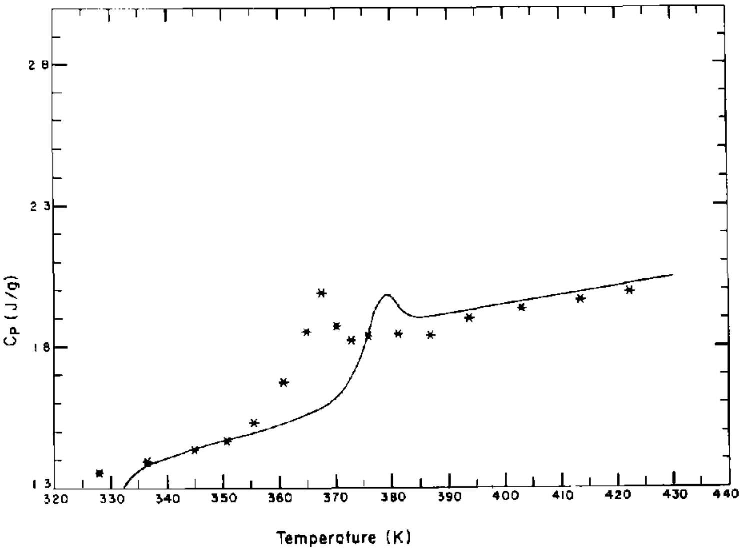

Fig. 6. Comparison of C_p from adiabatic calorimetry (ref. 14) with DSC-II results.

which compares favorably with the adiabatic calorimeter results of 4.3×10^{-3} and 3.2×10^{-3} J g^{-1} K^{-2}, respectively.

NBS-705

Chang and Bestul [15] measured C_p of NBS-705 with an adiabatic calorimeter from 4 to 350 K for a quenched and an annealed sample. Our measurements are shown in Fig. 7. The results are typical for a narrow-distribution polystyrene sample. The measured C_p is 2% high from 300 to 350 K, which is at the limit of the experimental accuracy. We examined other pellets

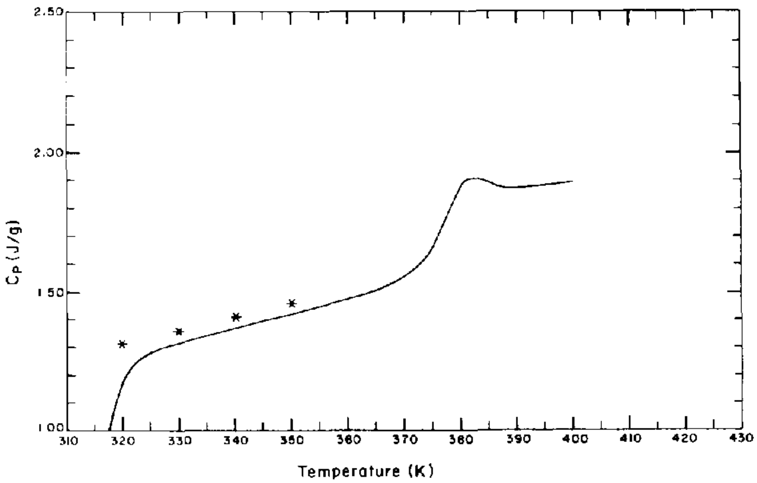

Fig. 7. C_p of NBS-705 polystyrene. (*) Data of Chang and Bestul [15].

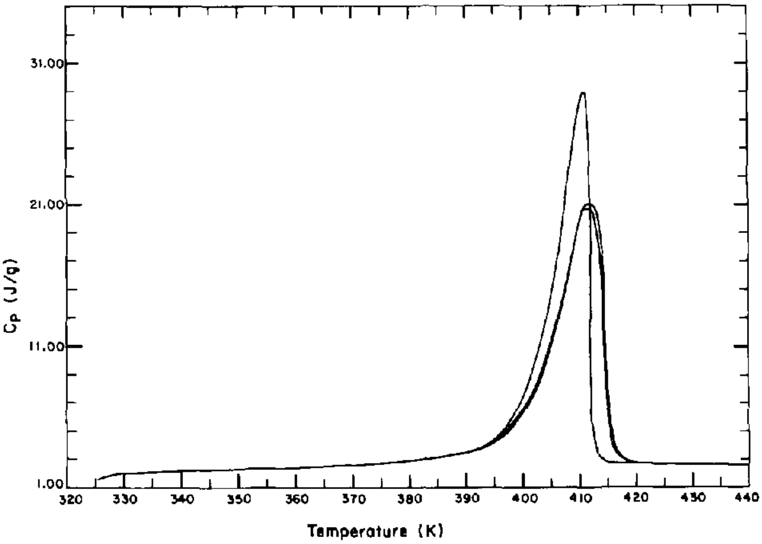

Fig. 8. C_p of NBS-1475 polyethylene showing melting endotherm. Larger peak as cooled sample, smaller peak cooled at 20°C min^{-1} (duplicate runs).

from the sample and found similar results. One possible reason for the high results is that in operating near ambient, the temperature control is not as good because of the small gradient between the sample and the environment. At higher temperatures (350–360 K) better agreement between our results and Chang's is found.

Polyethylene 1475

Polyethylene is an important polymer to study by DSC because of its high and variable crystallinity. Chang [16] has reported specific-heat data from 10 to 350 K on samples of PE-1475 with different thermal histories. The important melting behavior of polyethylene (high density) 1475 can be measured by DSC, and the dependence of C_p on level of crystallinity can be checked. These results can qualify PE-1475 as a secondary specific-heat standard for calibration of the DSC for polymer studies. Figure 8 shows results on PE-1475 from 330 to 440 K for the sample as received and the same sample cooled from the melt at 20°C min^{-1} to 310 K. Melting begins at 390 K and is complete at 410 and 418 K. The heat of melting of the two samples is 208 and 212 J g^{-1}, respectively. If the heat of fusion of 100% pure polyethylene is 293 J g^{-1}, then the samples have degrees of crystallinity of 71 and 73%, respectively. Different thermal histories can lead to slightly larger percent crystallinity and to multiple-peaked melting behavior [6].

The specific heats are lower than Chang's results by 2–3% (Fig. 9). This may be due to a difference in the thermal lag between polymers and indium and alumina. Differences in the observed C_p are less at the 5 K min^{-1} heating rate, where the thermal lag would be smaller. Gaur [17] has compiled

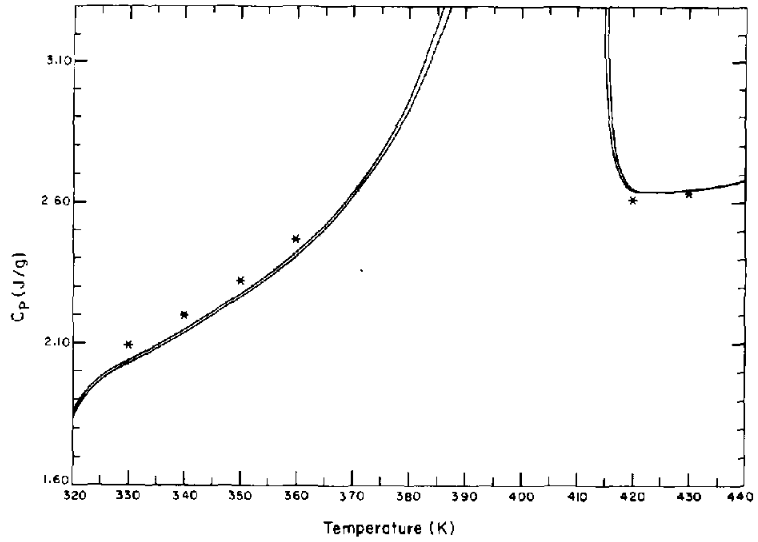

Fig. 9. C_p of NBS-1475 polyethylene. Data points from 330 to 360 K, Chang [16], and data points 420–430 K, Gaur [17].

data on polyethylene as a function of temperature and crystallinity, and our results are compared with his preferred data for liquid PE in Fig. 9. For the liquid state, the agreement is within the experimental error of either result (~ ±1%). This agreement puts the specific-heat data for polyethylene on a firm foundation and qualifies PE-1475 as a secondary standard for polymer calorimetry.

Annealing of NBS-706

Polymers change their physical properties upon annealing at temperatures from T_g to 50°C below T_g. Calorimetry is a sensitive and easy method to characterize the annealing or aging process. In this paper, the experimental methods and programs have been described, and the analysis and interpretation of enthalpy relaxation will be described in future papers. The basic programs for determining C_p of a polymer are used in the anneal program to determine the effect of annealing on C_p. An initial run on the sample is made to remove the thermal history and to provide a reference thermal history (20°C min^{-1} is the reference cooling and heating rate for these studies). Other cooling and heating rates can be used, ranging from 0.31 to 80°C min^{-1}. After cooling at 20°C min^{-1} to the anneal temperature T_A, the sample is held at T_A for annealing times ranging from 10 min to days. Longer anneals are more effectively done outside the DSC. Typical anneal schedules are at 5, 10, 15, 20, 25 and 30°C below T_g for 10, 30, 100, 300 and 1000 min, respectively. These schedules produce marked changes in C_p and the relaxation behavior. After each run, a baseline run on the sample is done

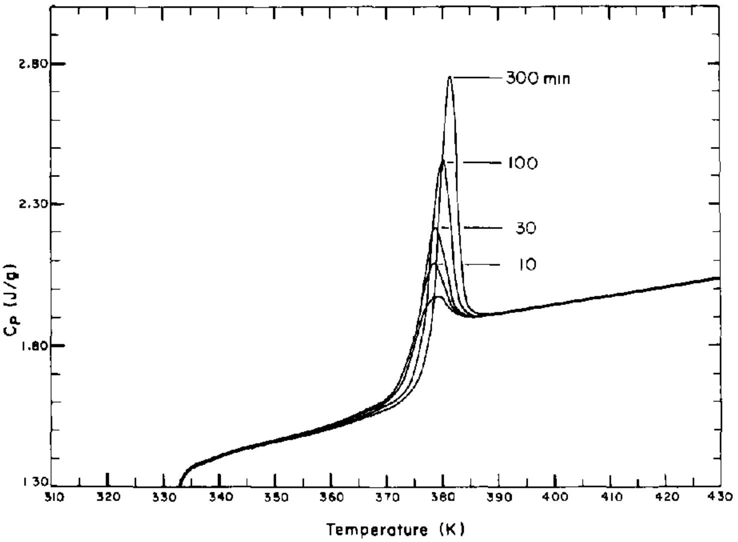

Fig. 10. Automatic annealing experiments for NBS-706 at 355 K for 10–300 min.

to ensure that all changes in C_p during an anneal are due to annealing and not to instrumental or other changes in the sample. Figure 10 shows a typical overnight annealing run on NBS-706 annealed at 355 K for the times indicated. The peak in C_p is due to the loss of enthalpy upon annealing, which is recovered as the sample is heated through T_g. Below T_g there are small but significant changes in C_p associated with annealing. At temperatures several degrees above the maximum in C_p (T-max) the liquid C_p agrees for all samples (better than 0.5%) as would be expected. The excellent reproducibility in the melt is the criterion for reproducibility and precision of these measurements. Enthalpy relaxation is discussed in detail in a review article [18] and will be the subject of future papers.

CONCLUSIONS

We have demonstrated that the Perkin-Elmer DSC-II can be readily automated with commercial computer and interface hardware (Hewlett-Packard). Programs that utilize the precision of the DSC-II and add versatility to its use have been produced. Temperature and power are readily calibrated with standard samples (indium and alumina) and programs.

Specific-heat data on NBS-706 polystyrene agree with literature data within ±1%. Results with NBS-705 polystyrene and NBS-1475 polyethylene are within 1–3% of literature results [16,17], and differences are larger than for other samples. The degree of crystallinity in NBS-1475 is 71% as received and 73% after cooling at 20°C min^{-1}. Enthalpy relaxation in NBS-706 has been demonstrated with an automatic annealing program.

The automated DSC-II promises to provide a sensitive quantitative tool to investigate (a) changes in amorphous and crystalline polymers as a function of thermal history, (b) polymer blends, (c) the effect of stress on thermal response of polymers, and (d) polymer reactions and kinetics.

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