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ANALYSIS BY CALORIMETRY*

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ABSTRACT

The last years have seen the development of differential calorimetry into a scanning technique for routine analysis. In order of ease of determination heats of fusion, heats of reaction, phase diagrams, purity analysis, heat capacity and similar heat effects are added to the list of quickly measurable quantities. Accuracies of the order of 1–5% of heats of fusion and heat capacity are obtainable under favorable conditions. Special topics which have been discussed are instrumentation, transition temperatures, heat capacities, glass transitions, heats of transitions, and phase diagrams.

INTRODUCTION

Any physical or chemical process can be followed directly by continuous monitoring of the thermal functions of state. The theory of thermodynamics has been worked out for over 100 years, and in most cases, a detailed connection to the microscopic process description has been established. Despite this understanding of the basis of thermal analysis, its use has been restricted in the past because of experimental difficulties. Since there is no perfect insulator for heat and every heat conductor absorbs large amounts of heat, measuring techniques are beset by "loss" determinations and empirical calibrations. In adiabatic calorimetry one tries to reduce losses by surrounding the sample with an enclosure at equal temperature; a technique which has been successfully developed, but proved cumbersome, slow, and expensive. Another path was followed in twin calorimetry. In this case losses in a reference system are kept at closely the same level as in the measuring system. With the development of automatic recording and electronic amplification, a comparison measurement became faster and more precise. The modern version of the twin calorimeter became known as a scanning calorimeter. This instrument is a hybrid between the twin calorimeter and the differential thermal analyzer[1].

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INSTRUMENTATION

Scanning calorimetry is based either on the measurement of temperature difference between reference and sample, both in identical heat flux environments: or on the recording of the electronically governed heat flux differential, proportional to the temperature difference between reference and sample. The first principle is close to that of the common DTA. For quantitative measurement the temperature gradient is kept negligibly small, so that the heat flow into the sample can be approximated by

$$dQ/dt = K(T_b - T) \tag{1}$$

where K is the geometry and construction material dependent thermal conductivity of the thermal resistance layer around the sample. T_b is the block, and T the sample temperature. An analogous equation holds for the reference. Between both, T_b can be eliminated, and under special conditions $Q_{\text{sample}} - Q_{\text{reference}}$ can be evaluated. In the second principle the heat flux is similarly

$$dQ/dt = K\Delta T \tag{2}$$

where K is determined by the gain of the differential amplifier and ΔT is the unrecorded temperature difference between sample and reference. The detailed performance comparison between the two systems lies in the sensitivity of ΔT detection, and even more so on the reduction of thermal lags between the sample and thermocouple in the first case, and between sample, temperature sensor, and heater in the second case[1].

TEMPERATURES OF TRANSITION

Transition temperatures and phase diagrams can be evaluated from the baseline deflection of the DSC-trace as shown in Fig. 1. Advantages over plain thermometry are in the quantitative evaluation of the percentage completion of the transition and the measurement as a function of heating rate. By using fast heating rates (up to 1000°C/min), it is possible to evaluate metastable transitions and hysteresis phenomena[2] (see Figs. 2 and 3). Pyrosynthesis is a technique where unknown starting materials are reacted with known chemicals and analyzed in the calorimeter. Both, from the reaction temperature (and heats) and the crystallization temperatures on cooling, and changed melting and evaporation temperatures on reheating, chemical analysis can be performed as is shown in Fig. 4. The accuracy in temperature measurement over the range of 100 to 700°K of commercially available instruments is for sufficiently well-defined transitions in the range of 0.1–0.8°C standard deviation.

HEAT CAPACITIES

Heat capacity measurements have in the past been the domain of adiabatic calorimetry. With increased accuracy of scanning calorimeters, it is now possible to

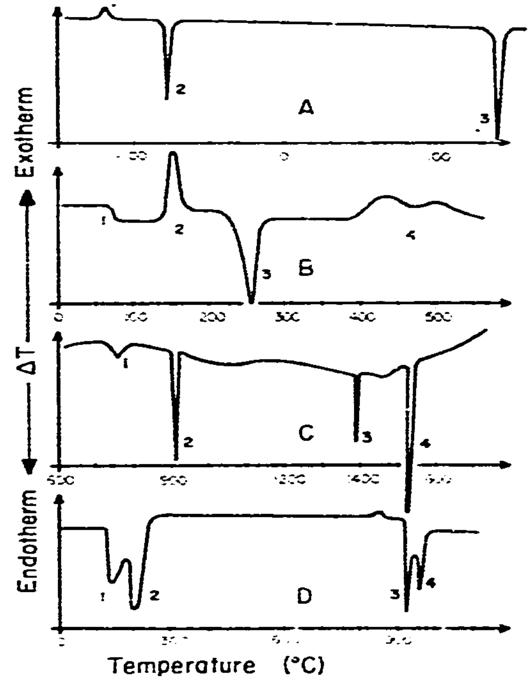

Fig. 1. Transition temperatures by thermal analysis. Four thermal analysis curves of pure substances: A. Amyl alcohol (1) Some crystallization at −119 °C due to fast cooling before heating, the sample was crystallized only incomplete; (2) melting at −79 °C; (3) boiling at 139 °C. B. Poly(ethylene terephthalate) (1) glass transition at about 75 °C, the sample was quenched to the amorphous glassy state before measurement; (2) crystallization at 145 °C; (3) melting at 253 °C; (4) decomposition. C. Iron (1) α to β transition; (2) β to γ transition; (3) γ to δ transition; (4) melting at 1533 °C. D. Barium chloride, $BaCl_2 \cdot 2H_2O$ (1 and 2) loss of water; (3) orthorhombic to cubic phase transition; (4) melting at 950 °C.

obtain routinely 1–5% accuracy (versus 0.1–1% of adiabatic calorimetry)[4]. The great advantage of the scanning calorimeter is its potential to make a complete run from 100 to 700°K within an hour, so that with computer coupling of data generation and handling at least one, but possibly several samples can be measured per day. A typical recording of heat capacity runs on heating and cooling is shown in Fig. 5. For many samples limitations such as purity and thermal stability determine the level of accuracy of heat capacity rather than the thermal measurements, so that DSC data are not necessarily limited by instrument factors. Heat capacities are the basis of other thermodynamic functions of state: *H*, *G*, and *S*. With wide range heat capacities known, these can be evaluated and equilibria calculated. As an example of particular value, the heat capacities of linear macromolecules can be cited[5]. Many of these polymers have similar back-bone chains, and as a result, additive heat capacities. Considerable information on these heat capacities and their corresponding vibrational spectra has been assembled.

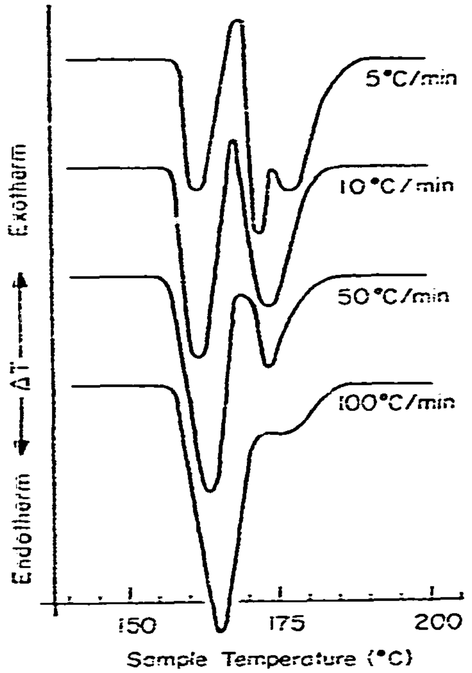

Fig. 2. Evaluation of the melting point of metastable polyoxymethylene hedrites[3]. At low heating rates reorganization of the metastable crystals causes multiple melting points, at fast heating rates the transition temperature from metastable crystals to metastable melt can be observed directly (~165 °C). The equilibrium melting point is about 185 °C.

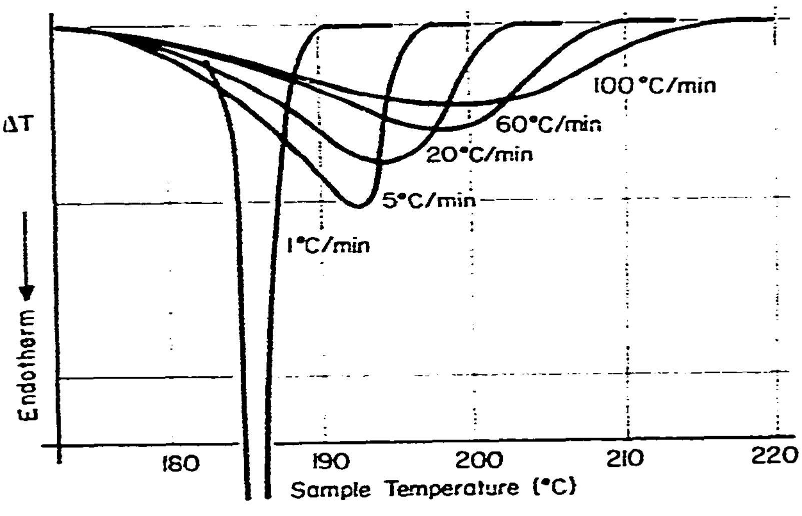

Fig. 3. Melting peaks of slow melting extended chain polyoxymethylene crystals. At low rates of heating these melt close to the equilibrium melting temperature (about 185 °C) at fast rates the crystals superheat[3].

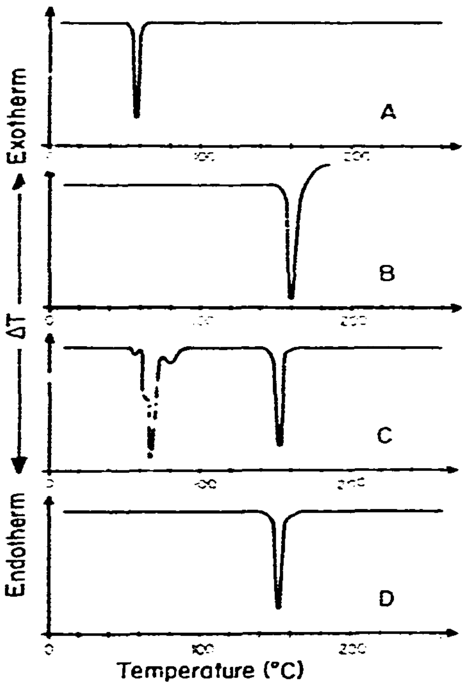

Fig. 4. Pyrosynthesis of *p*-nitrophenylhydrazone. A and B: Boiling of pure acetone and melting followed by decomposition of pure *p*-nitrophenylhydrazine; C: Pyrosynthesis of the two components with excess in acetone; D: Rerun of sample formed in reaction C shows only the melting point of *p*-nitrophenylhydrazone.

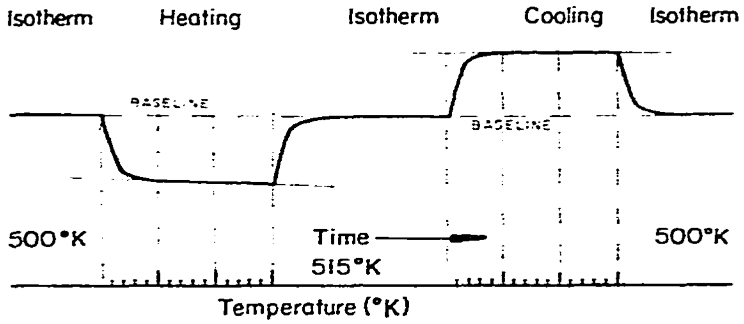

Fig. 5. Copy of DSC trace of aluminum oxide (sapphire) to measure heat capacity. Sample weight 74.23 mg, heating rate 5 °C/min. Program mode: constant temperature 500 °K, heating by 15 °C, constant temperature 515 °C, cooling by 15 °C, constant temperature 500 °K.

GLASS TRANSITIONS

The glass transition is uniquely determined by quantitative heat capacity measurement. All presently known glasses show a ΔC_p of about 2.7 cal/deg mole of mobile unit (bead)^6. In addition to the mere determination of the glass transition,

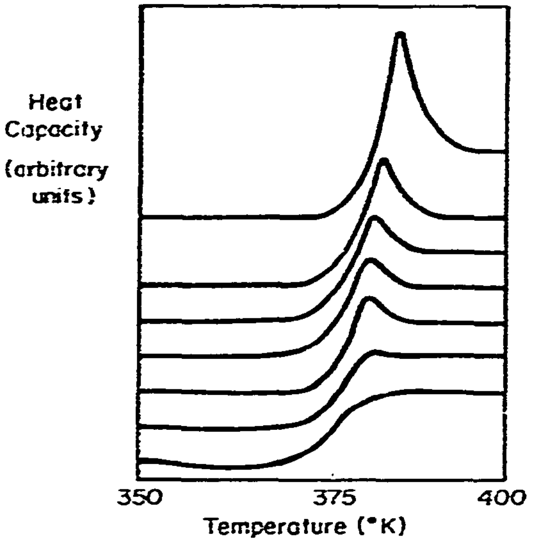

Fig. 6. Apparent heat capacity of polystyrene in the glass transition region[7]. Measured by DSC on heating at 5 °C/min after cooling at (from top to bottom): 0.5 °C/h, 0.2 °C/min, 0.5 °C/min, 1 °C/min, 2.5 °C/min, 5 °C/min, and 30 °C/min. Successive curves are displaced vertically.

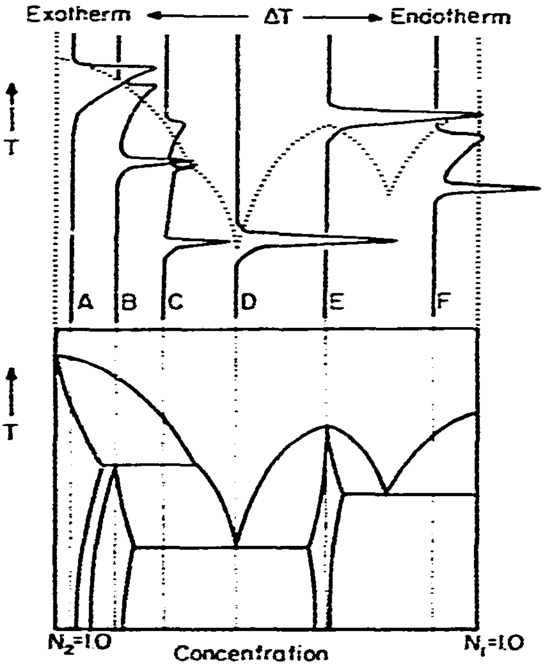

Fig. 7. DSC traces taken on heating as a function of composition. Hypothetical two-component system of the phase diagram illustrated in the bottom half of the figure. A: Solid solution. B: Peritecticum. C: Composition between peritecticum and eutecticum. D: Eutecticum. E: Compound. F: Composition between eutecticum and pure component.

time dependent measurements allow the determination of the thermal history of the sample via its hysteresis behavior. Figure 6 shows changes in the apparent heat capacity as found for polystyrene. Slowly cooled glasses heated fast, show a maximum in heat capacity; fast cooled glasses heated slowly, show a minimum[8].

HEATS OF TRANSITION AND PHASE DIAGRAMS

A straightforward application of DSC to the study of phase transitions is the measurement of the transition temperature, the heat of fusion, and for multiple component systems, the phase diagram for characterization and analysis of materials. The appearances of DTA-traces of different composition materials for a hypothetical phase diagram are illustrated in Fig. 7. Of increasing use has been in addition the application of the fast heating capability of DSC to phase transition study. In this case metastable states can be analyzed. The technique has become of utility in the characterization of linear macromolecules which frequently show a broad melting range of up to 100°C or more. With scanning calorimetry at sufficiently high rate of heating the broad melting range can be analyzed under zero entropy production conditions. The resulting data are useful in interpretation of crystal morphology and

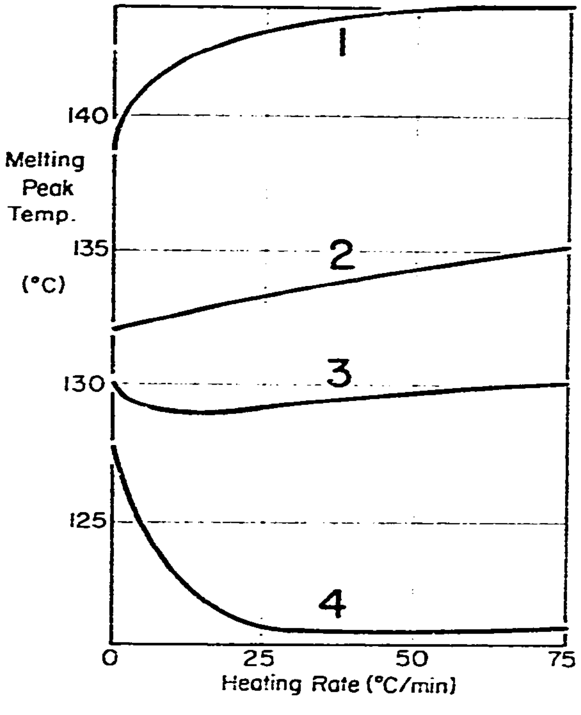

Fig. 8. Melting peak temperatures by thermal analysis of polyethylene at different heating rates[2]. Curve 1: Extended chain crystals of polyethylene showing superheating. Curves 2 and 3: Spherulitic polyethylene showing almost zero entropy production melting (some superheating in curve 2 and some reorganization in curve 3). Curve 4: Solution grown lamellae of polyethylene showing strong rearrangement.

defect structure as is illustrated by Fig. 8. Kinetic data on crystallization and melting have been derived[9].

HEATS OF REACTION

Heats of reaction are the most obvious changes accompanying chemical changes. they are easily followed quantitatively. Since best results are achieved on continuous heating, nonisothermal kinetics needs to be used for the interpretation of the data.

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