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TRENDS IN THERMAL ANALYSIS

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ABSTRACT

The state of art and trends of the major thermal analysis technique, differential scanning calorimetry, DSC, are discussed in this paper. Instrumentation goals should be extension of measurement to 10 K, precision DSC to 0.1%, direct recording of heat capacity, and fast calorimetry to heating rates of 10,000 K/min. The development of data treatment involve the generation and assembly of tables of data on reversible and irreversible processes for the identification of materials and their thermal history, empirical and theoretical prediction schemes, and computer methods for data comparison. In the area of theory, irreversible thermodynamics and nonisothermal kinetics, the influence of anharmonicity on thermal properties, and the thermodynamics of liquids, glasses and mesophases are in various stages of development. Finally, the most basic trend is the use of modern teaching techniques involving, besides classical means, audio, video and computer methods. The trend is to give the field a new direction which ultimately should lead to the development of the professional "THERMAL ANALYST".

INTRODUCTION

Thermal analysis in the form of calorimetry is based on two functions of state, temperature T and heat Q.[1]

$$T = (dU/dS)_{n,V} \tag{1}$$

$$Q = U - w \tag{2}$$

The symbols U, S, n, V, and w have the usual meaning: total energy, entropy, number of moles, volume, and work, respectively. It is convenient to replace the total energy U with the enthalpy H to avoid correction of the measured data for volume and extension work occurring during measurement. The slightly modified definition of H is:

$$H = U + pV - fl \tag{3}$$

where p is the pressure, f, the tensile force and l, the length of the sample. To these thermodynamic functions one adds the variable time, t. This addition of time to the well established functions of equilibrium thermodynamics is at the center of most present developments in thermal analysis. Only now is the precision of time dependent, scanning techniques high enough to develop an understanding of thermal history effects and metastable states. This understanding is needed particularly in the field of linear macromolecules where crystals are always far from equilibrium.

In the paper I will try to trace some trends in differential scanning calorimetry from the past into the future. Papers like this should not be read after, let us say, five years because predictions and extrapolations of trends are always influenced by the authors interests and have the tendency of changing with time due to unforeseen developments. These unexpected changes are, however, what makes a developing field exciting.

HISTORY

To understand the future of thermal analysis, it is necessary to understand its history. The scientific development of thermal analysis is the story of increasingly better methods of measurement. One must start with 17th Century Florence to look for the first tool needed for scientific thermal analysis, the thermometer.[2] Only with the invention of the sealed liquid-in-glass thermometer it became possible to set up repeatable temperature scales. Fahrenheit, Reaumur, and Celsius are the best known names attached to early, empirical temperature scales. Also, the first theory of heat, the theory of the "caloric", had its origin in the 18th Century as the differences between temperature and heat became clearer. The outstanding thermal analyst of that time was J. Black to whom the first calorimetry research can be traced. A typical early calorimeter is that of de la Place, shown in Fig. 1.[3] Based on the experiments of the 18th Century one finds in the 19th Century as major progress the development of thermodynamics as a key theory for understanding of nature.[4] It is based on the three laws of thermodynamics of which the first, the conservation of energy, provides the basis of calorimetry and gives the parallel to the earlier discovered conservation of mass.

$$aA + bB = cC + dD + \Delta H \tag{4}$$

$$\Delta H{:}\ H_{(\text{products})} - H_{(\text{reactants})}$$

Even phase transitions and simple changes in the variables of state can be expressed by eq. 1.

The 20th Century started with the invention of automatic, multiple thermocouple thermometry which permitted differential thermal analysis (DTA).[5] This technique saw in its first 50 years about 1000 publications, most of qualitative nature with respect to calorimetric information.[6] A major increase in application and quality of DTA occurred by application of electronics to measurement precision and computer techniques to data acquisition and treatment. By 1972 the rate of production of research publications had reached 1000 reports each year, and by now DTA and DSC (differential scanning calorimetry) are part

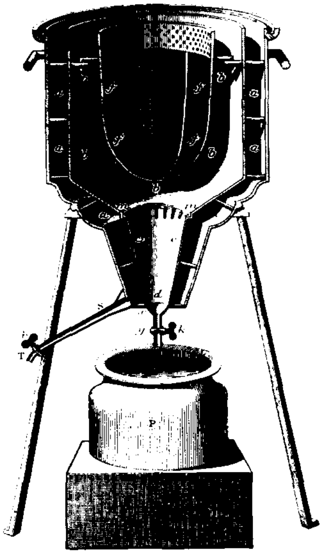


Fig. 1. Typical ice calorimeter of the 18th Century.[3] The measuring cavity for the sample is f, b is the space for the ice used for calorimetry, a is the ice-water container for insulation. The amount of water produced in b on introduction of the sample is weighed and gives the calorimetric information.

of many research publications, not listed separately in the title.[7] As the name of DSC indicates, there has been a shift from measuring only transition temperatures quantitatively, to full calorimetry.

In the following sections, the present problems and goals for the future of differential scanning calorimetry are discussed under the headings: Instrumentation, Data Treatment, Theory, and Instruction.

INSTRUMENTATION

Differential calorimetry has developed into a viable alternative to adiabatic calorimetry. Adiabatic calorimetry is the classical, high precision method of choice for measurement of heat capacities and heats of transition in the temperature range of 10 to 300 K.[8] Routine precision is 0.1% and reports of precision as high as 0.01% have been made. The technique is, however, even with modern electronics and computers quite tedious, expensive, and difficult to handle. Only in few research laboratories is adiabatic calorimetry available. The limited access to thermal data has lead to many of the problems to be discussed below.

The development of DSC became possible by reduction in sample mass to milligram size and by fast, continuous temperature measurement.[9] The computerization has permitted, in addition, a large increase in sampling rate. These changes lead to a new approach to the heat loss problem that is central to calorimetry. The fast measurement and the differential technique minimize the heat loss. To date, the best DSC techniques approach 0.1% precision and can compete with adiabatic calorimetry in the 200 to 400 K temperature range.[10] From 400 to 1000 K, DSC is already the preferred instrumentation.

Present problems which must be addressed for further progress are the basic non-proportionality of the recorded temperature differences in both, the heat conduction and the electrical compensation type DSC. A simplified treatment of heat flux from the block heater (at Tb) into sample (at Ts) and reference (at Tr) can be written as:[11]

$$dT_s/dt = [K/(W + C_p)] (T_b - T_s) \tag{5}$$

$$dT_r/dt = [K/W] (T_b - T_r] \quad (= q) \tag{6}$$

$$T = [W + C_p/K)/KJ (dT_s/dt) - Wq/K \tag{7}$$

$$C_p = K\ T(dt/dT_s) - W[1 - (dT_r/dT_s)] \tag{8}$$

where K is the geometry proportional thermal conductivity term, independent of sample properties as long as the temperature gradient within the sample is negligible and assumed to be identical for reference and sample; W is the "watervalue", the heat capacity of the empty sample calorimeter, assumed to be identical to the reference calorimeter water value; C_p, finally is the sample heat capacity. Equation 8 shows the C_p is only proportional to the amplitude of the DSC-trace if the base line is horizontal (naturally without electronic compensation). Fortunately, the error is small if the baseline deviates from the horizontal, but highest precision requires extensive calibration.

In Fig. 2 a plot of temperatures vs. differential heat input (D) of an electrical compensation DSC is shown. The left curve shows that during the transition the heating rate of the reference increases. As a result, there must be a partial compensation of the heat of transition by the average heater. Its output is, however, not recorded, and thus there will be a distortion of the actual melting peak. In the recovery period after the transition, the lost heat is recovered, so that the integral heat is not affected, but careful calibration is needed to get to precision calorimetry.

Besides these intrinsic problems that must be solved (if possible more direct than by calibration only), one would like to see a direct recording DSC, i.e. a DSC which has built-in references and can instantaneously evaluate heat capacities. Only a small beginning has been made in this direction.[12]

A final goal should be the development of a faster DSC. Typical heat conduction calculations suggest that a microgram calorimeter could be designed for

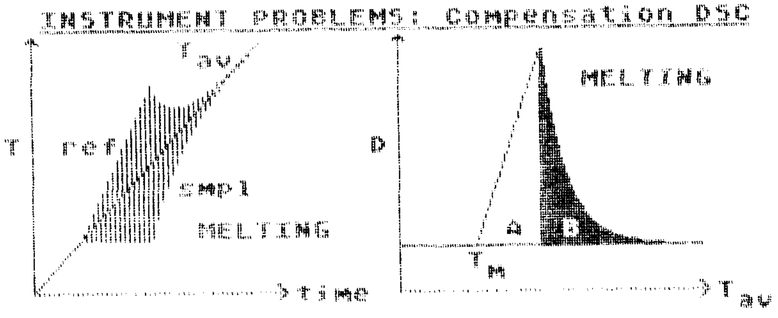


Fig. 2. Temperature changes and differential power input (D) for an electrical compensation DSC during a sharp fist order transition. (Assuming only negligible temperature gradients between heaters and calorimeters.)

up to 10,000 K/min heating rate. Instruments like this would be of interest for the study of unstable materials and intermediates that are particularly often observed in the study of macromolecules. Such superfast DSC could also be used to simulate many industrial processes, opening a new application for thermal analysis.

To summarize: Instrument trends should include:

Low temperature DSC to 10 K
Precision DSC to 0.1%
Direct Cp recording DSC
Low mass, fast DSC to 10,000 K/min.

DATA TREATMENT

The literature on DSC developes, as in most scientific fields, exponentially, with no limit in sight. At the turn of the Century it was perhaps still possible to master the literature by reading all papers. Since the rate of publication of thermal analysis reports is presently in excess of 1000 papers per year, it is impossible to keep up to date.[7] Literature study is thus usually restricted to rather narrow fields of interest and the abstraction of the complete literature in terms of data tables gains increasing importance. Large-volume data tables are available in the standard works such as Landolt-Boernstein,[13] the TPRC Data Series,[14] and the Selected Values of Properties of Chemical Compounds.[15] These collections have, however, two major shortcomings which need to be corrected through the combined effort of all thermoanalysts and their professional organizations. First, these collections are still not fully automated, i.e. many are not computer searchable and most are not computer updated. Data search through tables is thus still tedious and the result may still be outdated. Second, the area of linear macromolecules is almost completely absent in the above mentioned data collections. The main reasons are the frequent elimination of irreversible data from such collections and the relative newness of the field. Research on macromolecules has started only at about 1920 and large scale, quality data were developed only after about 1960.[16]

The trends are to develop larger, automatically searchable and continously updatable, critically reviewed data banks. Figure 3 illustrates an outline of the ATHAS Data Bank under construction in our laboratory.[17]

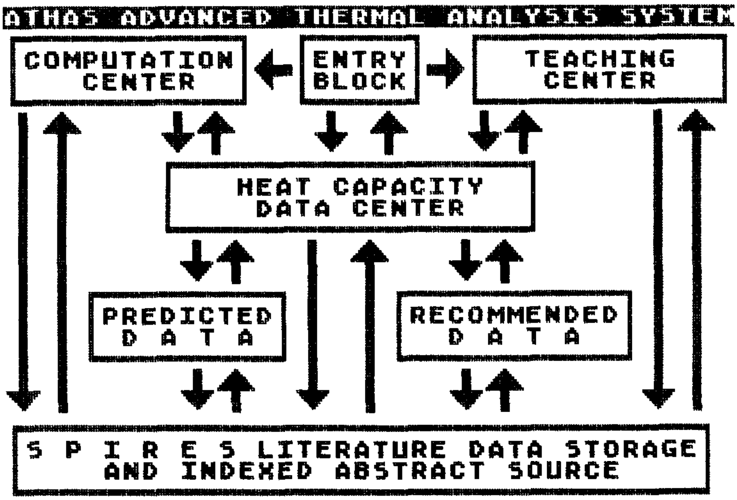


Fig. 3. Block diagram of the proposed ATHAS Thermal Analysis Center for Computation, Teaching, Data Collection and Retrieval.[17]

This data bank encompasses presently only heat capacity data.[18] One example of its use is the evaluation of the heat capacity of polyethylene. It is not a difficult task to find through computer search of Chemical Abstracts that there are about 100 published measurements on the heat capacity of polyethylene. In reading all these papers, we found, however, that not one of the authors was aware of all the prior literature when reporting their new data.

Having found all literature is for the user still not the answer to the question: what is C_p? A review of the many papers must now be made to find the best set of data. The ATHAS data bank attempts to do all this simultaneously. A first answer displays a set of recommended data in standarized format (plot or table). Next, if more information is needed, the detailed choices among the many publications are described and reasons given for exclusion of some and averaging of other measurements (standards of acceptable data). The final information available from the data bank is a complete uncritical listing of all published heat capacities in tabular, standardized form. All data are expected to be available at the computer terminal in proper form to go into the Computation Center for calculations of derived quantities, comparisons, integrations etc. Furthermore, knowledge about predictions of unknown heat capacities based on all prior measured data can be called for. Finally, instruction is possible, as shown in the upper right hand corner of the schematic. At present, work is in progress on all of the blocks, but the overall computer system must still be assembled. We hope to accomplish this demonstration project of modern data treatment during the next 3-5 years.

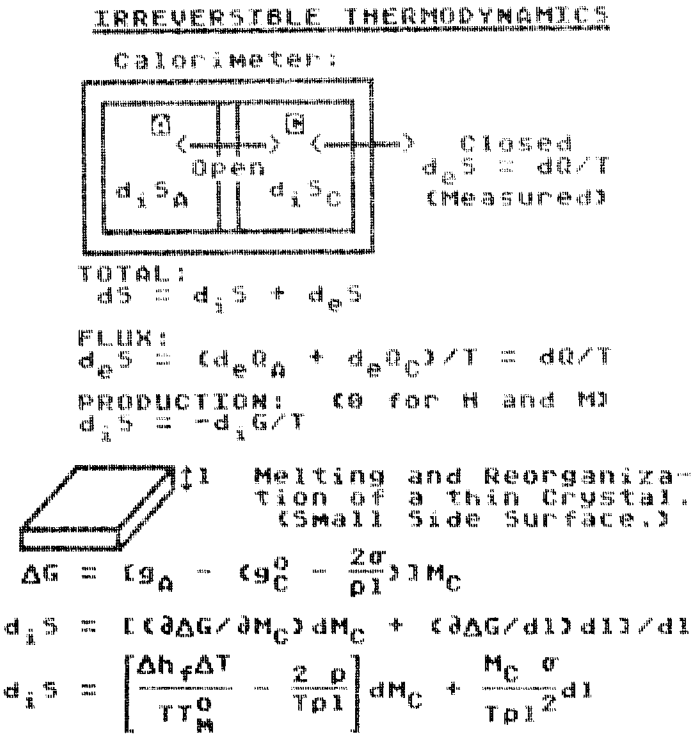
To summarize: Data treatment trends should include:

Data tables of reversible and irreversible processes
Empirical and theoretical data prediction schemes
Data comparison.

THEORY

The theory of thermal analysis in general, and calorimetry in particular, is quite far developed. Present problems are perhaps more the lack of application of already developed theory rather than the development of new theories. One example of this missing application of well established theory is the application of irreversible thermodynamics to DSC.[1] As is shown in Fig. 4, the calorimeter is an ideal open system in irreversible thermodynamics nomenclature. There seems to be little effort in the thermal analysis literature to use this powerful technique. To a larger degree there is an application of equilibrium thermodynamics to DSC. Frequently its use must, however, be questioned because of the influence of time in DSC.

A topic which has seen recent development is that of the non-isothermal kinetics.[19] The constant rate heating (and cooling) mode of most thermal analysis lends itself to experimentation in this area. The major problem seems not to be the development of needed kinetics formalism, but to understand the microscopic path or, as is more often the case, the interactions between several paths of a given process.[20]



IRREVERSIBLE THERMODYNAMICS

Calorimeter:

Closed
$d_eS = dQ/T$
(Measured)

TOTAL:
$dS = d_iS + d_eS$

FLUX:
$d_eS = (d_eQ_A + d_eQ_C)/T = dQ/T$

PRODUCTION: (0 for H and M)
$d_iS = -d_iG/T$

Melting and Reorganization of a thin Crystal. (Small Side Surface.)

$$\Delta G = [g_A - (g_C^0 - \frac{2\sigma}{\rho l})]M_C$$

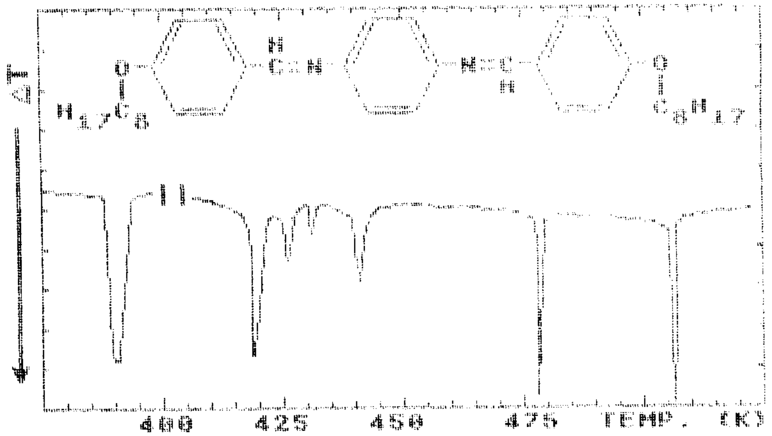
$$d_iS = [(\partial\Delta G/\partial M_C)dM_C + (\partial\Delta G/dl)dl]/dl$$

$$d_iS = \left[\frac{\Delta h_f\Delta T}{TT_M^0} - \frac{2\ \rho}{T\rho l}\right]dM_C + \frac{M_C\ \sigma}{T\rho l^2}dl$$

Fig. 4. Schematic and equations for the treatment of DSC in the framework of irreversible thermodynamics. Examples: Melting and reorganization of a thin, metastable lamella.

In the discussion of heat capacities,[21] it became apparent that present measurement and theory are in agreement over most of the temperature range for solids. The reamining problem in the inversion of vibrational frequency spectra to heat capacities is the effect of anharmonicity. Some problems exist also at temperatures below 10 K. Greater difficulties can be found in the interpretations of liquid thermal properties and the interpretation of the glass transition and the residual entropy of glasses at absolute zero.

A new research area is the study of mesophases and their transitions, a topic ideally suited for DSC methods.[22] Quantitative calorimetry is necessary to interpret the degree of disorder introduced into a given crystal. With increasing quantitative information on thermal properties, it becomes possible to predict the behavior of new materials. Figure 5 illustrates the DSC trace of bis-(n-octyloxybenzal)-phenylene diamine (BOOBPDA).[23]



'ATHAS' laboratory for ADvanced THermal AnalysiS

Fig. 5. Thermal analysis trace of BOOBPDA.[23] The transitions are interpreted as follows (from low T to high): 1) 388 K, 17.6 kJ/mol; rigid crystal to condis crystal (conformational disorder). 2) 415 K, 6.7 kJ/mol; condis crystal to smectic liquid crystal (?). 3) 422 K, 2.1 kJ/mol; smectic polymorphism (? → B). 4) 428 K, 0.4 kJ/mol; smectic polymorphism (B → C). 5) 437 K, 3.2 kJ/mol; smectic polymorphism (C → A). 6) 476 K, 3.6 kJ/mol; smectic to nematic liquid crystal. 7) 504 K, 2.3 kJ/mol; final disordering to isotropic melt.

Only through information on the entropy of disordering was it possible to suggest the different mesophases and initiate more detailed studies of molecular motion in mesophases.

To summarize: Trends in the development of the theory should include:

Development of irreversible thermodynamics and non-isothermal kinetics

Study of the influence of anharmonicity on thermal properties

The thermodynamics of liquids, glasses, and mesophases.

INSTRUCTION

The teaching of thermal analysis presents a special problem. Until recently the number of researchers involved in the performance of thermal analysis has been small. The study of thermodynamics is considered, in addition, part of everyone's basic education. The perhaps 100 times increase in number of practitioners of thermal analysis over the last 20 years has lead thus to a lack of broad based graduate training in the field. Such training is self-understood in other fields, such as X-ray crystallography or NMR spectroscopy. Few users of DSC-equipment are trained to answer or discuss questions like:

What is the magnitude of the heat capacity of a given material? Why does a glass transition or a melting transition occur at a particular temperature? What are the magnitudes of the enthalpies and entropies of various crystals, melts or glasses? What are the effects of deviation from equilibrium? How can one study thermal history?

Improvement can only be achieved through instruction at a continuing education level and at the initial undergraduate and graduate level. Problems arise from a shortage of qualified instructors and small numbers of students at any one time and place. Modern self-instruction techniques are being developed making use of audio and video courses,[24] and more recently also interactive microcomputers.[25] Teaching of this type has the potential to fill the need to upgrade the education in thermal analysis. It might also carry the seed to revolutionize the teaching of scientific subjects in general.[26]

To summarize: Instruction trends should include:

Modern techniques such as audio, video and computer instruction
New directions in general education in thermal analysis
The evolution of the professional "THERMAL ANALYST"

CONCLUSIONS

The conclusion to be drawn from the observed and hoped for trends in thermal analysis is the emergence of a professional thermal analyst. The speeding up of this process should be the goal of the often rather recently established national and international thermal analysis societies.

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REFERENCES

1 B. Wunderlich, The Basis of Thermal Analysis, in Thermal Characterization of Polymeric Materials, E. Turi, ed., Academic Press, New York, 1981.
2 W. E. Middleton Knowles, A History of the Thermometer, Johns Hopkins Press, Baltimore, 1966.
3. A. Lavoisier, Elements of Chemistry, Paris 1789, Part III, Chapter III. Translation by R. Kerr, Edinburgh, 1790; Reprinted, Dover New York, 1965.
4. see for example: The Scientific Papers of J. W. Gibbs, Vol. 1,

Thermodynamics, Dover Publ. New York, 1961. Reprint of the 1906 edition by Longmans, Green and Co.

5 see for example: H. LeChatelier, Z. phys. Chem. 1 (1887) 396 and N.S. Kurnakov, Z. anorg. Chem. 42 (1904) 184.

6 W.J. Smothers and Y. Chiang, Handbook of Differential Thermal Analysis, Chem. Publ., New York, 1966.

7 J. H. Sharp, ed. Thermal Analysis Abstracts, Heyden and Son, Ltd. London and Chemical Abstract Service, Selects on Thermal Analysis (#03B) Am. Chem. Soc. Washington.

8 J.M. Sturtevant, Calorimetry, in A. Weissberger and B.W. Rossiter, Physical Methods of Chemistry, Vol. 1, Part V, Chapter 7, J. Wiley, New York, 1971.

9 B. Wunderlich, Differential Thermal Analysis, in A. Weissberger and B.W. Rossiter, Physical Methods of Chemistry, Vol. 1, Part V, Chapter 8, J. Wiley, New York, 1971.

10 H. Suzuki and B. Wunderlich, J. Thermal Anal., to be published.

11 F. H. Müller et al., Kolloid Z.Z. Polymere, 172 (1960) 97; 192 (1963), 1, 29.

12 see for example Mettler FP85 DSC from -20 to +400°C.

13 Landolt-Boernstein, Zahlenwerte und Functionen, Springer, Berlin, 6th ed. Vol. II Parts 1-5, 1956-71; continued as "New Series" Group IV, Macroscopic and Technical Properties, K.H. Hellwege, ed.

14 Y.S. Touloukian and C. Y. Ho, eds. Thermophysical Properties of Matter, The TRP Data Series. IFI/Plenum New York, 1970-1979 (Vol. 4-6, Specific Heat).

15 Selected Values of Chemical Thermodynamic Properties. Natl. Bur. Stand. Technical Notes 270-3 to 270-7. Inst. for Basic Standards NBS, Washington, 1968-1973.

16 E. Turi, ed., Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981.

17 U. Gaur and B. Wunderlich, ACS Symp. Series, T. Proder, ed., Vol. 197, Washington, 1982, p. 355.

18 U. Gaur, B. Wunderlich et al., J. Phys. Chem. Ref. Data, 10 (1981) 89, 119, 1001, 1051; 11 (1982) 313, 1065; 12 (1983) 29, 65, 91.

19 see for example T. Ozawa, Polymer, 12 (1971) 150 or K. Harnisch and H. Muschik, Colloid and Polymer Sci., 261 (1983) 908.

20 P.D. Garn, CRC Crit. Rev. Anal. Chem. 3 (1972) 65.
M.C. Ball and M.J. Casson, Thermochim. Acta, 27 (1978) 387.

21 Yu. V. Cheban, S.-F. Lau, and B. Wunderlich, Colloid Polymer Sci., 260 (1982) 9.

S.-F. Lau and B. Wunderlich, J. Thermal Anal., 28 (1983) 59.

22 J. Grebowicz and B. Wunderlich, Adv. Polymer Sci., 60/61, 1 (1984).

23 H. G. Wiedemann, J. Grebowicz, J. Wesson, and B. Wunderlich, Proc. 12th Natas Conf. J. C. Buck ed. (1983) p. 295.

24. B. Wunderlich, Thermal Analysis, a 3 credit audio course, available through Rensselaer Polytechnic Institute, Cont. Ed. Div., Troy, NY 12181 USA.

25 B. Wunderlich, Introduction to Differential Scanning Calorimetry, a 2 credit computer course, available through Rensselaer Polytechnic Institute, Cont. Ed. Div., Troy, NY 12181, USA.

26 B. Wunderlich, Am. Laboratory, 14(6) (1982) 28.