

QUANTITATIVE THERMAL ANALYSIS OF MACROMOLECULAR CLASSES AND CRYSTALS

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ABSTRACT

Quantitative thermal analysis means scanning calorimetry. Today a precision of $\pm 1\%$ or better can be achieved over the enormous temperature range from 100 K to 1000 K. Since scanning calorimetry is fast, it is also possible to study metastable systems as are encountered in macromolecules. Most macromolecular systems are only partially or not at all crystallized, i.e., they are partially or fully glassy. By establishing the fully crystalline and fully glassy limiting thermal properties, a detailed discussion of the common intermediate states is possible. A series of 10 polyoxides and polyolefins will be discussed for which all thermal properties are known from 0 K to beginning decomposition in the melt. Special attention will be paid to the glass transition of semicrystalline polymers which indicate a wide variety of structure sensitive effects.

INTRODUCTION¹⁻³

Mr. Chairman, Ladies and Gentlemen,

It is a pleasure to come to the 8th ICTA and report on the progress of our Advanced Thermal Analysis System¹⁻¹⁰, which is based not only on our work, but much more so on the collective work of all thermal analysts. First, I would like to thank the Organizing Committee for the invitation for this planary lecture. Next, let us get to work. Schematically ATHAS¹ is shown in Fig. 1. Its main three parts are the Computation Center⁴, the Heat Capacity Data Center² and the Teaching Center. Some examples of the latter were demonstrated at the 7th ICTA in Kingston. It consists of audio and computer courses as well as of publications directed to continuing education in and review of thermal analysis. This lecture may be taken as a part of this effort. The data center is the center block of ATHAS, it enables us to combine the work of all thermal analysts into a solid experimental basis on which the theory⁵ can be tested and expanded. Critically evaluated heat capacity data on over 100 macromolecules are collected in the data bank.² Its first plans were announced at the 4th ICTA in Budapest and a progress report was given at the 7th ICTA in Kingston. The computation center is at present in the last stages of development⁴, as will be illustrated below. One of its important results is the development and theoretical backing of various addition schemes of heat capacities¹⁰ which were detailed at the 6th ICTA in Bayreuth. Other efforts of ATHAS involve the evaluation and improvement of instrumentation³ and research on the thermal properties of macromolecules.⁷⁻⁹

Some examples, concerning fast thermal analysis and measurement under elevated pressure, were discussed at the 1st, 2nd, 3rd and 4th ICTA, the research on mesophases was summarized at the 7th ICTA in Kingston.

HEAT CAPACITY DESCRIPTION⁴⁻⁵

The heat capacity of linear macromolecules is best subdivided into four temperature regions. Heat capacities below 5-10 K, though interesting from a theoretical point of view, will not be treated here since they contribute negligibly to the integral thermal properties at higher temperature. They are strongly dependent on the physical state (crystalline, amorphous, or semicryst.).

In the 10 to 100 K temperature range heat capacity measurements are completely dominated by adiabatic calorimetry. The theory of heat capacity is well understood. Since practically all macromolecules are solids below 100 K, i.e. glassy, crystalline, or partially crystalline and partially glassy, the heat capacity is exclusively of vibrational origin and well described by the harmonic oscillator approximation. It proved useful to separate the vibrations into skeletal and group vibrations. The former are of relatively low frequency, strongly coupled, and represent the intra- and inter-molecular vibrations of the chain molecules as a whole. They can be modelled making the assumption that the atoms are attached rigidly to the backbone chain. The skeletal vibrations dominate the heat capacity in this 10 to 100 K temperature range. All efforts to calculate the intermolecular, skeletal vibrations from crystal-structure and force-constant data alone have badly failed in the past. Heat capacity measurements provide the best means for evaluation of the low frequency integral vibrational spectrum. The intramolecular skeletal vibrations are somewhat higher in frequency and are accessible in their upper frequency range through isolated-chain, normal-mode calculations. Such calculations permit also the evaluation of the usually numerous group vibrations. Once the vibrational spectrum is established, the heat capacity (at constant volume) can be calculated up to high temperatures. Figure 2 shows a typical example of the cumulative frequency spectrum and Fig. 3 illustrates the heat capacity contributions of the skeletal and group vibrations for polytetrafluoroethylene.

The Einstein function inverts the frequency spectrum to the heat capacity and vice versa:

$$C_v = \frac{Nk(\theta/T)^2 \exp(\theta/T)}{[\exp(\theta/T) - 1]^2} \quad (1)$$

where T is the temperature and θ is the frequency, both expressed in kelvin ($\theta = hv/k$ with ν representing the frequency in Hz, h and k are Planck's and Boltzmann's constant, respectively; $1 \text{ Hz} = 4.7994 \cdot 10^{-11} \text{ K}$, $1 \text{ cm}^{-1} = 1.4388 \text{ K}$). To

connect C_v with the measured C_p , one can use the thermal expansivity α and the isothermal compressibility κ .

$$C_p - C_v = \alpha^2 VT / \kappa \quad (2)$$

Since α and κ are usually, at best, available at one temperature, one makes often use of the semiempirical Lindemann expression:

$$C_p - C_v = C_p^2 (T/T_m^0) A_0 \quad (3)$$

where T_m^0 is the equilibrium melting temperature and A_0 is a constant which has for most polymers a value close to $5.11 \cdot 10^{-3}$ K mol/J (per mole of heavy atom). In the lower portion of this temperature range (below about 50 K) the heat capacities of less crystalline materials are usually higher, because of lower intermolecular vibrational frequencies.

The next temperature region is from about 100 K to the glass or melting transition. Solid heat capacities are practically independent of crystallinity in this temperature range. Most measurements are made by differential scanning calorimetry (DSC). In many cases it is possible, after computation of the group vibrations, to evaluate the intramolecular skeletal vibrations. The intermolecular vibrations are commonly already excited at these temperatures and contribute thus a constant amount to the heat capacity. Of special problem are the semicrystalline macromolecules between the glass and melting transitions. They have a microphase-separated, two-phase structure with most molecules bridging both phases. This special influence of phase boundaries on molecular mobility gives rise to positive and negative C_p -deviations from the values computed under the assumption of a macroscopic, two-phase system (crystallinity model). The heat capacity deviations permit to analyze structure-sensitive properties.

The last temperature range is that of the liquid state, it starts at the glass transition or the melting temperature. Very little theoretical knowledge exists about its heat capacity, except that the group vibrations change little on fusion. The change of the skeletal vibrations in frequency due to the volume expansion is also of little influence on heat capacity, since, once excited, the heat capacity contribution of a vibrational degree of freedom remains unchanged on lowering of the frequency. The change in volume-expansion makes itself felt through a sizeable increase in C_p at the glass transition caused by potential energy increase (hole formation). Overall, liquid heat capacities are often changing linearly with temperature and have a smaller increase with temperature than solids. In case of no group vibrations, as in Se- or O- group contributions, the heat capacity decreases with temperature. This occurs most

likely because of increasing changes of vibrational modes of motion to internal rotations which have lower heat capacity contributions (the classical limit changes from R to $R/2$).

HEAT CAPACITY ANALYSIS⁶

The heat capacity analysis is described on the well studied example of polyethylene and the aliphatic polyoxides.^{6b} The analyses of a number of other polymers are in various stages of completion.⁶ With the presently available data we hope to prepare ultimately a list of 30 fully characterized polymers. First, C_p of all liquid polymers of the chemically related group are compared, as is illustrated in Fig. 4. The heavy line portions represent the actual measurements. From the figure it is clear that the equation listed represents polyoxide heat capacities. All measured data have an average deviation of + 0.5% and a standard deviation of \pm 3%, which is about the same as the overall experimental accuracy of the data bank data. The equation of Fig. 4 can be used down to the glass transition temperature of the respective polymers, and heat capacities of not listed polyoxides, as well as copolymers and blends, may be estimated from their O - and CH_2 - concentration.

The next step in the analysis is the evaluation of the group vibrations from either normal mode calculations of isolated chains, or attributed infrared and Raman spectra. If neither of these are available, it is often sufficient to substitute the vibrational spectrum of chemically identical groups of other macromolecules (or small molecules). For example, all polyoxide group vibrations are adequately described by the appropriate group vibrations of polyoxymethylene and polyethylene, and for the fluorinated polyethylenes of those of polytetrafluoroethylene and polyethylene. After computation of C_v from the experimental C_p -data, using eqs. 2 or 3, the group vibration contributions to the heat capacity are subtracted, making use of eq. 1. This results in the experimental heat capacities due to the skeletal vibrations. The inversion to an approximate skeletal frequency spectrum is accomplished with a two-parameter Tarasov function.⁴ Table 1 illustrates the two limiting frequencies Θ_3 and Θ_1 for several macromolecules. Θ_3 is the upper limit of an intermolecular, 3-dimensional vibrational distribution-function (quadratic in frequency dependence, as suggested by Debye); Θ_1 is the upper limit of an intramolecular, 1-dimensional vibrational distribution function. Regularities based on masses and intermolecular forces can be derived from these values, and it is possible to plot available Θ -values for extrapolation to unknown polymers.

With plots of Θ -temperatures and lists of group vibrations, it is possible to calculate heat capacities of solid macromolecules over a wide temperature

TABLE 1

Macromolecule	Theta Temperatures in Kelvin		N
	θ_3	θ_1	
Selenium, crvstalline	98	350	3
Selenium, amorphous	54	343	3
Polyethylene, crystalline	158	519	2
Polyethylene, amorphous	80	520	2
Polypropylene, crystalline	91	714	7
Polypropylene, amorphous	78	633	7
Polyoxytrimethylene, crystalline	101	433	6
Polyoxytrimethylene, amorphous	72	411	6
Polyoxymethylene, crystalline	122	211	2
Polyoxyethylene, crystalline	114	352	4
Polyoxytetramethylene, semicryst.	91	436	8
Polytetrafluoroethylene, crystalline	54	250	2
Polytrifluoroethylene, semicryst.	56	315	4
Poly(vinylidene fluoride), semicryst.	66	346	4
Poly(vinyl fluoride), semicryst.	105	440	4

range as shown in Fig. 5. If needed, corrections to the heat capacity at constant pressure are possible with eqs. 2 or 3.

Knowing the crystalline, glassy and liquid heat capacities for many macromolecules permits now the discussion of a series of additional thermodynamic functions. Enthalpy, Entropy, and the Gibbs Function (free enthalpy) are available by integration of C_p and C_p/T . With data on equilibrium melting⁷ and the glass transition², it is also possible to get to the absolute entropies of glasses listed in Table 2, and establish full thermodynamic characterization.

TABLE 2

Entropies of Some Glasses at 0 K in J/(K mol).

Macromolecule	S_0^a
Selenium	3.56
Polyethylene	2.59
Polyoxymethylene	5.78
Polyoxyethylene	7.73
Polyoxytrimethylene	3.91
Polytetrafluoroethylene	3.38
Polypropylene	1.87

The values of the glassy entropy close to absolute zero are unexpectedly small, and must await full interpretation.

The next step of the thermal analysis concerns the heat capacity of semicrystalline macromolecules. With the prior established solid and liquid heat capacities it is possible to check on the 2-phase model of semicrystalline macromolecules. Surprisingly, a wide variety of behavior seems to exist. More or less close to the fusion endotherm a positive heat capacity deviation is observed for all polymers. This has been linked to premelting and defect

formation. For polyethylene and polytetrafluoroethylene these positive deviations close to the melting temperature seem to be the only limits to additivity. The results on polyoxymethylene are shown in Fig. 6. Here a negative deviation is obvious which is interpreted as a 0.13 fraction of "rigid amorphous" polymer. In the polyoxymethylene this rigid amorphous does not participate in a glass transition up to melting. Similar observations in polypropylene show that the rigid amorphous fraction is gradually unfreezing. This explains the occasionally observed "double glass transitions."

With this broad-based analysis of heat capacities, a significant progress was possible in the understanding of macromolecules. Further progress is, however, also possible in the description of equilibrium and non-equilibrium transitions. Their interpretation after measurement by DSC is often hampered by discarding of the heat capacity information as the subtracted "baseline".

ANALYSIS OF TRANSITIONS^{7,8}

The basic transition analysis is that of a transition with enthalpy and entropy change (first order transition) and that of a transition with an abrupt change in heat capacity only (glass transition). Figure 7 shows the typical transition behavior on thermal analysis. A detailed analysis of many first order transitions has led us to a classification scheme of the condensed phases which is listed in Fig. 8. Central are the three doubly outlined, classical phases, the isotropic melt and the two solids: the amorphous glass and the fully ordered crystal. In-between the crystal and melt are the increasingly more liquid condis, plastic and liquid crystals. All these states are connected, as indicated by the arrows on the right, by first-order-like transitions. Very typically the transition to the isotropic melt shows only small entropy changes for the liquid crystals (indicative of only a few per cent of orientational order, in accord with high mobility); the plastic crystals show a quite constant transition entropy of about 7-14 J/(K mol) (indicative of the retention of a high degree of positional crystal order without orientational alignment); while the condis crystals show a wide variation in transition entropy (indicative of the different degrees of conformational freedom achieved in the crystal). These classifications⁸ help greatly in the thermal analysis of mesophase macromolecules which have recently achieved industrial importance.

Turning to the left side of Fig. 8, it is indicated that all partially ordered mesophases may have the possibility to also freeze their motion without increase in order by going to the corresponding glass. The glass transition gives a second means of identification of a new polymer. Empirical analysis of large lists of macromolecules have shown that the change in heat capacity at the

glass transition is often $11 \text{ J}/(\text{K mol})$ per mobile group (bead) of the molecule. With this rule it is possible to make a first, semi-quantitative judgment of how much mobility is gained in a new material.

Glass transitions and first order transitions do, however, not only permit a quantitative assessment of mobility and order through their caloric functions, they can also be characterized by their time-dependent, non-equilibrium characteristics. For example, the glass transition reveals through its broadening over a larger temperature range phase-structure information, and through its hysteresis behavior, activation energy parameters. The quantitative interpretation of such data and the theoretical description is only in its beginning. Similarly, kinetics of melting as well as crystallization can reveal special materials characteristics. For example, the special molecular nucleation barrier to crystallization becomes obvious on plotting melting-crystallization rate data through the equilibrium melting temperature. Because of lack of space (and time in the lecture) it is only possible at this point to conclude with a series of example slides (not reproduced) for illustration. Most are taken from the references listed below as examples of the ATHAS activities over the last few years.

CONCLUSIONS^{9,10}

Starting from a detailed analysis of heat capacity of linear macromolecules, I hope to have shown that considerable advance in thermal analysis is possible. Not only can the equilibrium thermodynamic properties be established and linked to fundamental, atomic-scale properties, such as the vibrational frequency spectrum; but it is also possible to discuss non-equilibrium states such as are found in glassy, mesophase, partially crystalline, and microphase-separated polymers. The various states can be characterized quantitatively through their heat capacity baseline and their transition behavior. Addition schemes can be developed to increase the discussion base, and various tests of sample history are possible based on non-equilibrium transitions. Overall, the potential of thermal analysis has only begun to be applied to materials study.

Acknowledgments

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LEGENDS TO FIGURES

- Fig. 1. Schematic Representation of ATHAS.
- Fig. 2. Cumulative Frequency Spectrum of Polytetrafluoroethylene.
- Fig. 3. Computed and Experimental Heat Capacities of Polytetrafluoroethylene (I: experimental C_p , II: computed C_v , III: group vibration contribution to C_p , IV: skeletal contribution to C_v).
- Fig. 4. Heat Capacities of Liquid Polyoxides. The heavy lines represent measurements, the thin lines the equation. N_C = mole fraction of carbon atoms, N_O = mole fraction of oxygen atoms. M = methylene, E = ethylene.
- Fig. 5. Calculated Heat Capacities at Constant Volume for Solid Polyoxides.
- Fig. 6. Heat Capacity of Semicrystalline Polyoxymethylene Showing Negative Deviations. Based on data by F. S. Dainton et al. [Polymer 3, 271 (1972)] and data bank information.
- Fig. 7. First Order and Glass Transition.
- Fig. 8. Schematic of the 9 Condensed Phases.

Figure 1

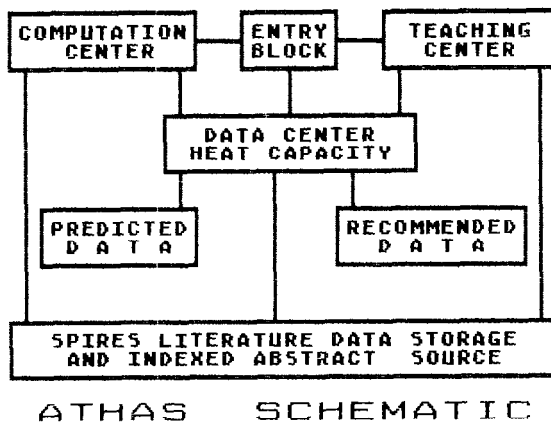


Figure 2

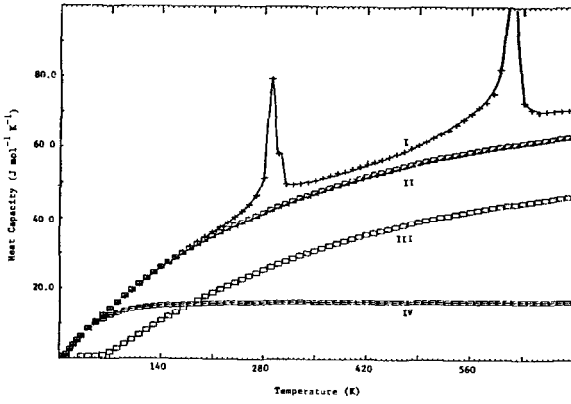
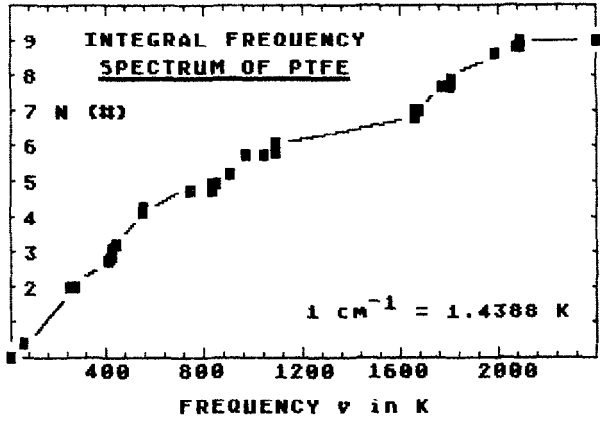
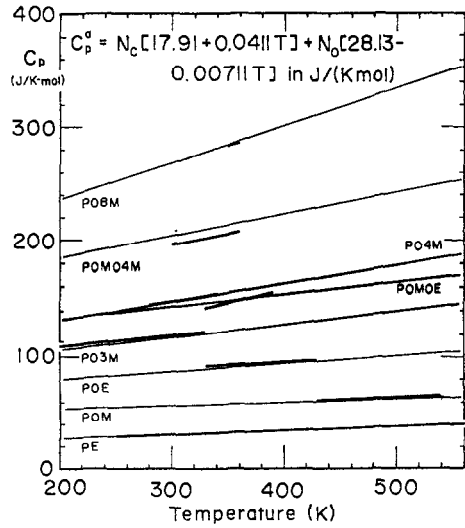


Figure 3

Figure 4



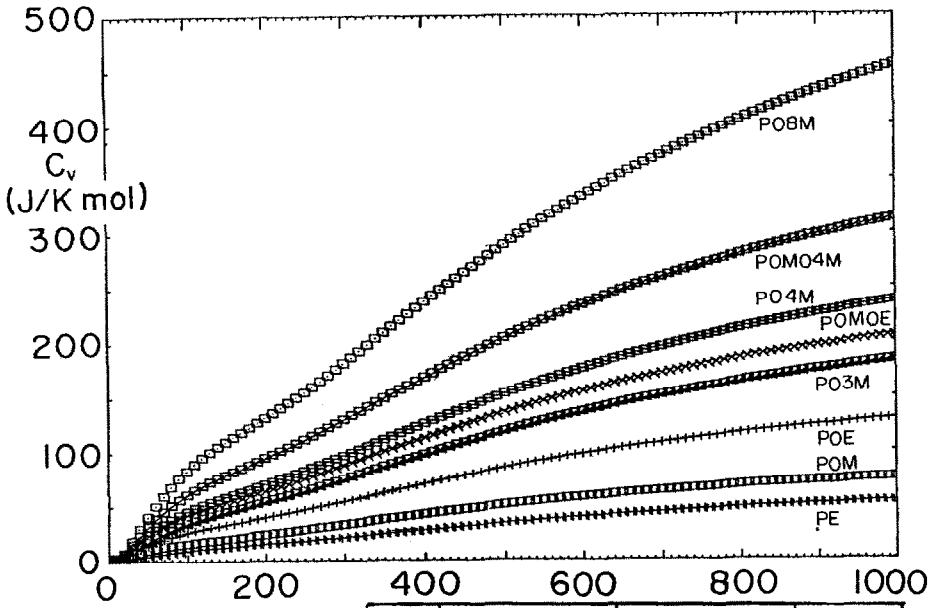


Figure 5
(Temperature in K)

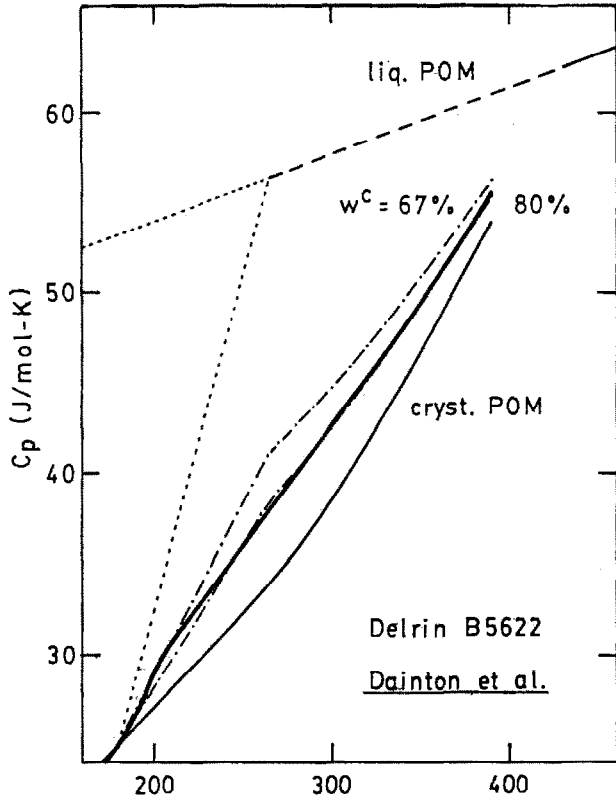


Figure 6
(Temperature in K)

Figure 7

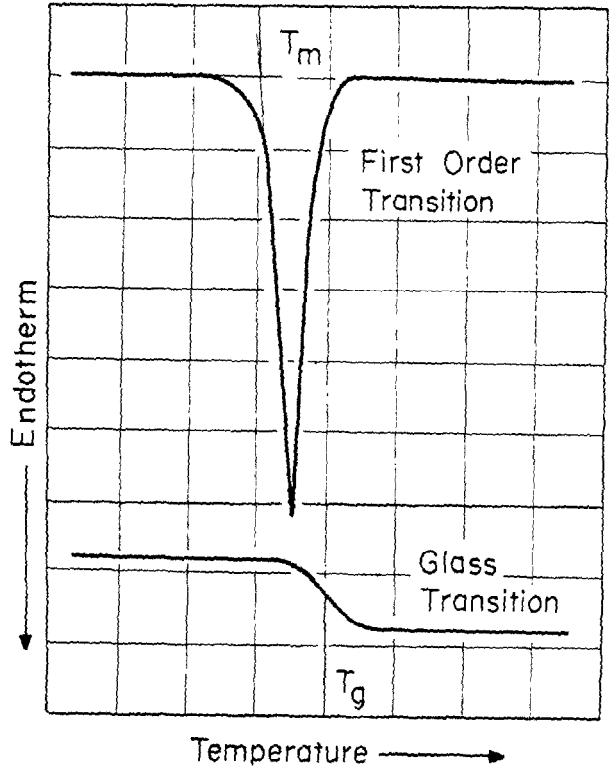


Figure 8

