

Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

TEACHING THERMAL ANALYSIS OF POLYMERIC MATERIALS

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Abstract

Thermal analysis and polymers are two subjects in the field of chemistry and materials sciences that have not developed to the level commensurate with their importance. In this paper the reasons for this deficiency are traced to the history of the development of these subjects which led to only limited availability of courses of instruction. A first remedy to this problem is suggested, teaching via the internet. The attempt by the author to generate such a course is described in this paper. The course contains an up-to-date store of basic information. It is divided into 36 'lectures' and displayed in about 3000 computer screens filled with graphs, text, and hypertext. All lectures are downloadable. ** Including presentation software, each lecture requires only 1–3 Mbyte of computer memory. The inclusion of color, movies, and sound would exceed the capacity of most presently available personal computers, but might point the way to future of teaching the ever increasing number of subjects.

Keywords: computer aided teaching, materials, polymer

Introduction: The history of materials and thermal analysis

In the early thinking of the Greek philosophers the connection of the structure of materials and the nature of heat was basic to the understanding of the world around us. Plato (428–348 BC) and Aristotle (384–322 BC) suggested that there exists only one primeval matter and two contrasting qualities: hot-cold and wet-dry. As these qualities are impressed on the primeval matter, the four basic elements are produced in the form of fire (hot & dry), air (hot & wet), earth (cold & dry), and water (cold & wet). All material things are then assumed to be different combinations of these four elements. *** Today it is not difficult to extract the roots of this theory, namely that heat, Q , is equated to 'fire,' and the other three elements are the traditional, macroscopic phases, gas, solid, and liquid, respectively. A self-consistent theory of matter was

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** The course 'Thermal Analysis of Materials' discussed in this paper is available by downloading from the internet at the address: <http://web.utk.edu/~athas/courses/tham99.html>

*** In the Chinese Taoist cosmogony the five basic components of the physical universe were earth, wood, metal, water, and fire (Lao-tzu, 6th century BC). It is of interest to note that these five elements have a similar link to materials science and thermal analysis.

thus created long ago, based exclusively on what we would call now the macroscopic experience.*

Thermal analysis is today's macroscopic tool to analyze materials. From its ancient roots, thermal analysis has developed into four basic branches: thermo-mechanical analysis (TMA), dilatometry, thermogravimetry (TGA), and calorimetry. The corresponding variables of state addressed by these techniques are pressure (or stress), p , and length (or strain), l , volume, V , mass, m , and changes in heat content, ΔH (at constant pressure and without exchange of work $\Delta H = Q$). All of these techniques are usually carried out as a function of time, t . At the beginning of this century these four experimental techniques had reached a modern level of perfection. The main theory that combines the variables needed to describe the state of matter in a state of equilibrium became known as thermodynamics, one of the central parts of any physical chemistry and physics texts. The changes with time were up to this time less frequently considered. They gained more interest in the first half of the 20th century when the detailed structures of reactants and products became known and could be traced as a function of time through chemical and physical processes. The study of the time-dependence became known as the field of kinetics which was later also called 'dynamics'.

Why is it then that today with the many improvements in instrumentation, the field of thermal analysis has major difficulties in finding the needed scientists and technicians to rise to its potential high level of service to science and technology? The effort to remedy this problem is spearheaded by dr. Edith Turi who chairs the ICTAC education committee and to whom this article is dedicated. A general summary of the status of education in thermal analysis is given in the references [1]. To find an answer to this problem let us briefly follow the development of the two fundamental branches of the science of materials: structure and energetics. Both of them started out as macroscopic descriptions, but are now also well understood in terms of the microscopic atomic and molecular properties.

We know today from research in the early 20th century that the microscopic length scale of these atoms is the ångstrom (0.1 nm). This unit of length is about 10^{-4} times the smallest macroscopically recognizable lengths, and much of the teaching of chemistry and polymer science has been concentrating on presenting the structure of matter based on these enormously small fundamental particles.

Quantitative experiments in the other branch of science, the energetics, began with the macroscopic evaluation of heat, Q . First, a reliable thermometer was invented in Venice during the 17th century, the closed-capillary, liquid-in-glass thermometer. Next, Richmann established in 1747 the calorimetric mixing formula that expresses how bodies at different temperatures, T , come to thermal equilibrium at an intermediate temperature. Following discrepancies between experiment and results

* Macroscopic systems are recognizable directly on a human scale. Particles of micrometer size can be 'seen,' for example, by the light they diffract (dust particles in strong sunlight) or by imaging with an optical microscope. The microscopic systems, in turn, are of molecular size and need special analyses, such as electron microscopy or X-ray diffraction.

expected from Richmann's formula led to the concepts of latent heat and heat capacity. Latent heat, L , is absorbed without change in temperature, and heat capacity, C , is the heat needed to increase temperature by one unit (kelvin) $[\partial(H/\partial T)_{p,n} = C_p]$, at constant pressure, p , and number of moles, n . Then, it took about 100 years until one could eliminate the erroneous assumption that there is a material basis to heat which had been called the caloric. A mathematical theory of the caloric by Carnot (1824) was based on the efficiency of a reversible heat engine and suggested that heat is conserved. Thompson (Count Rumford), however, had inferred earlier (1798) that heat can be created by friction and is not conserved, a conclusion reached by observing seemingly unlimited amounts of heat on boring cannon barrels with blunt drills. This controversy was resolved by the quantitative experiments of Joule in the 1840s who proved that the energy of an electric current can produce either heat or mechanical work with a constant conversion factor. From these experiments he inferred properly that heat was a state of motion, not a material. In the early 1850s Thomson (Lord Kelvin) and Clausius recognized independently that two distinct principles had been misconstrued, namely, Joule had correctly asserted that heat could be created and destroyed proportional to the exchanged amount of mechanical, electrical, or chemical energy, w (first law of thermodynamics, the total energy, U , of a system is conserved: $dU = \delta Q + \delta w$, where w represent the exchanged energy in form of work). But Carnot's result also holds, it rests not on conservation of heat in general, but of entropy, S , under equilibrium conditions and is expressed by the second law of thermodynamics (the change in entropy during a reversible process is zero: $\Delta S = Q_{\text{reversible}}/T = 0$, or better, the entropy production during a reversible process is zero $\Delta_i S = 0$).

With basic molecular structure and macroscopic energetics well understood for the last 100 years, we might rephrase the above question: Why is it that today, with a clear understanding of the field of thermal analysis, there are only few well-trained scientists and technicians who can raise the profession of thermal analysis to the high level in science and technology it is capable of [1]?

The link structure and energetics on a microscopic level, it is easiest to represent the atomic motion by molecular-dynamics simulations using supercomputers, a technique which is only emerging presently [2]. The vibrational motion of atoms was linked already by Einstein and Debye early in the 20th century to the basic quantity of calorimetry, the heat capacity $[C_v = (\partial U/\partial T)_{v,n}]$ at constant volume, V , and number of moles, n . The total energy, which is $U = \int_0^T C_v dT + \sum L_i$ (where L_i are the various latent heats that are exchanged between 0 and T), is represented by the Hamiltonian of the crystal, and the temperature can be extracted from the kinetic energy $(3kT/2 = \Sigma mv^2/2)$ where the sum goes over the kinetic energy of all atoms of the system; m is the atomic mass, v , the atomic velocity, and k , Boltzmann's constant). The time scale of atomic motion, however, is the picosecond (10^{-12} s), by a factor of 10^9 larger than the macroscopic, human time scale.

Perhaps this difference of five orders of magnitude in distance from human level of experience between the microscopic description of energetics and molecular structure is at the root of the slower development of the understanding of energetics or calorimetry [3] and the lack of experts in the field. Furthermore, detailed molecular motion can only be visualized now, after sufficient computing power for simulation of large assembly of atoms and molecules is possible [2].

The development of teaching of the science of the materials

If one looks into the first edition of the Encyclopædia Britannica of 1771 [4], one finds, for example, under 'Chemistry' a discourse of 166 pages of descriptions of the various important compounds and practices of chemistry based on the ancient theory of 'fire, air, earth and water.' Under physics, on the other hand, only the definition is listed in the Encyclopædia: 'A denomination sometimes given to natural philosophy.' Information about physics had to be obtained from its constituent fields such as mechanics, optics, acoustics, magnetism, heat, and physical properties of matter, all of which fused only into modern physics in the 19th century.

In the beginning of the 20th century, the teaching of chemistry and physics as two separate disciplines, as we know it today, was well established, and this historical separation is at the root of problems of teaching of thermal analysis and polymer science.

Thermodynamics, being part of physics and chemistry, was developed when molecular structure was not well known. With the knowledge about molecular structure to assess motion and interaction, a new field was created, statistical thermodynamics. Similarly, the broadening of thermodynamics from equilibrium to non-equilibrium systems lead to the new field of irreversible thermodynamics. Both of these new fields that should be integral parts of thermodynamics were classified as advanced topics, and as such not taught in the basic studies of thermal analysis. In fact, instead of combining equilibrium, statistical, and irreversible thermodynamics, with molecular physics and kinetics, the practitioners of thermodynamics were often taking pride in its generality and the possibility of understanding the basic principles without reference to molecular structure. The unique combination of these fields that should make the basics of thermal analysis [5] was not made. The teaching of thermal analysis was thus largely based on equilibrium thermodynamics.

Perhaps in this light it is not surprising that one has observed a drastic decline in interest in thermodynamics and calorimetry. An ICTAC 1990/91 survey [6] of 443 university and college professors involved in teaching of thermal analysis or thermodynamics in the U.S. revealed what was argued for many years in the Education Committee of the ICTAC: *too little is done in teaching of thermal analysis*. The startling result from this survey was that when taking the 10,400 students that were taught by the professors surveyed as a data base, only 6% took a course in thermal analysis and only 21% heard about thermal analysis in courses like Analytical Instrumentation, Polymers, Physical Chemistry, or Materials. This is clearly not a good base for the future of thermal analysis, and is particularly perplexing since 51% of

these same departments polled had one or more pieces (up to 20 in one case) of modern thermal analysis equipment and more than 1000 students and their faculty were involved with this equipment in their research.

Turning now to the second basic element, the knowledge of structure of materials, a similar historical problem developed as in the energetics. Macromolecules, the object of polymer science, were not known at the beginning of the 20th century. After their definitive description by Staudinger in 1922 polymers, or more precisely flexible, linear macromolecules, were not included into the subjects taught in most chemistry and physics departments of the leading universities. The research with this newest class of molecules was not considered to be sufficiently precise. The early knowledge about the synthesis and properties of macromolecules was largely developed in industrial research laboratories.

Being concerned in this article with teaching of the science of materials,* a science which deals with the study of properties and applications of substances such as ceramics, metals, polymers, glasses, and composites as they are used in construction and manufacture, one can see that this field needed to evolve because the teaching of chemistry or physics was not sufficiently updated as new knowledge developed.

The course 'Thermal Analysis of Materials', to be summarized next, was thus developed over the years to bridge instruction in the various topics that developed historically in different disciplines or were designated as special advanced subjects. The goal of this effort that can be traced back to my first teaching efforts in this field [7]. It is to generate basic teaching and learning material for the thermal analyst. Going through the various basic texts of chemistry, physical chemistry, and physics, the topics were collected that are important to the understanding of materials, but are usually excluded in present-day teaching of this subject and are available only in specialized literature. These topics are presented in this course together with a short review of the better treated subjects and directions to the advanced fields of materials science. Using the internet as publication medium gives a broader, world-wide distribution and supplies teaching and learning material without financial limitations. Although thermal analysis and flexible macromolecules are the central topics, an effort is to outline also the overall integration with other methods of measurement and other classes of molecules. By presenting large numbers of direct research results, often from our laboratory, the material presented should give some feel of the excitement of the field.

The computer-course 'Thermal Analysis of Materials'

About the course

This computer-assisted course grew out of the two three-credit courses 'Physical Chemistry of Polymers' and 'Thermal Analysis' at the University of Tennessee, Knoxville (UT). First, the lectures were illustrated with overhead foils, generated by

* The term materials science was entered into Merriam Webster's Dictionary only in 1961.

computer, so that printouts could be provided as study material. In 1990 these overheads were changed to computer-projected slides and the textbook 'Thermal Analysis' was published [3]. In 1994, a condensed text was added to the slides in the form of lecture notes. The present, computer-assisted course was first offered in 1998.

The course is designed for seniors or beginning graduate students interested in study of 'Thermal Analysis of Materials.' Anyone with some background in physical chemistry and polymers may benefit from the course. Typical prior knowledge in physical chemistry may have been gained from a standard undergraduate physical chemistry course, or even a good course in 'Freshman Chemistry' or 'Introduction to Materials Science.' The knowledge in polymer science may have come from some introductory course, or been developed by working with polymers. Since the course can be taken at one's individual pace, missing prerequisites can, and should be, filled-in at the appropriate time using the given general reference texts. Since the thermal analysis of materials science covers many specialized topics, it will also be necessary to occasionally consult the advanced treatises cited in the first screen of each lecture. Taken under the indicated conditions, anyone who needs a more basic understanding about macromolecules and thermal analysis would benefit from the course. The field of flexible macromolecules is emphasized. The fields of small molecules and rigid macromolecules (see Lect. 01), as well as mechanical properties, are treated on a more elementary level to serve as a tie to the widely available, general engineering courses.

For self-study, one should read the text and alternate to the figures. Additional information is available through hypertext as illustrated below in Fig. 1. A list of general references is pointed-to in the title screen, specific references, in all lecture titles. Occasionally specific references are also contained on figure screens. Printouts can be made of any screen. The text and figures are based on bitmap graphics (630×470 pixels) in the compressed WPG format (WordPerfect™). After the initial study, the suggested problems should be solved. The final learning and review can then be based on the succession of figure screens only.

The course can also be used as resource material for the instructor. The picture screens are then the base of the discussion in the lecture. For projection, one can employ a LC-display projector or normal overlays (after printing from the picture files).

Seven examples of topics that are different for polymeric materials

(A) The structure of macromolecules is characterized by a diversity of shapes and sizes, as is discussed in Chapter I of the Course. These are items unimportant for small molecules. Small molecules can easily be prepared with high chemical purity (*i.e.*, are of constant size) and they are often rigid (*i.e.*, are of fixed shape).

(B) Classically one treats solutions of two components as ideal, regular, or real; and concentrates for the non-ideal case only on solutions of salts by discussing the Debye–Hückel theory. Polymer science, in turn, adds the effect of different molecular sizes with the Flory–Huggins equation (Chapter VII). Considerable differences in

size may, however, also occur in small molecules and their effects are hidden falsely in activity coefficients.

(C) The comparison of the entropy of rubber contraction to that of the gas expansion, on one hand, and to energy elasticity of solids, on the other, helps the general understanding of entropy (see Chapter V). Certainly, there must be a basic difference if one class of condensed materials can be deformed elastically to only less than 1% and the other by up to 1000%.

(D) The kinetics of chain reactions of small molecules is much harder to follow (and prove) than chain-reaction polymerization. Once the reaction is over, the structure of the produced macromolecule can be studied as a permanent documentation of the reaction path (Chapters I and III).

(E) The notoriously poor polymer crystals described in Chapter V and their typical microphase and nanophase separations in polymer systems have forced a rethinking of the application of thermodynamics of phases. Equilibrium thermodynamics remains important for the description of the limiting (but for polymers often not attainable) equilibrium states. This fusion of thermodynamics, irreversible thermodynamics, and kinetics is introduced in Chapter II as the basis of thermal analysis, and used as an important tool in the documentation of Chapters VI and VII.

(F) The solid state, finally, has gained by the understanding of macromolecular crystals with helical molecules, their defect properties, mesophases, small crystal size, and glass transitions (Chapter V).

Thermal Analysis of Materials, table of contents

CHAPTER I (ATOMS, SMALL AND LARGE MOLECULES)

Lecture 1 (Microscopic Description of Matter and History of Polymer Science)

Lecture 2 (Nomenclature)

Lecture 3 (Chain Statistics of Macromolecules, I)

Lecture 4 (Chain Statistics of Macromolecules, II)

Lecture 5 (Size and Shape Measurement)

CHAPTER II (BASICS OF THERMAL ANALYSIS)

Lecture 6 (Heat, Temperature, and Thermal Analysis)

Lecture 7 (The Laws of Thermodynamics)

Lecture 8 (Heat Capacity I)

Lecture 9 (Heat Capacity II, ATHAS)

Lecture 10 (Non-Equilibrium Thermodynamics)

Lecture 11 (Phases)

CHAPTER III (DYNAMICS OF CHEMICAL AND PHASE CHANGES)

Lecture 12 (Stepwise and Step Reactions)

Lecture 13 (Chain and Matrix Reactions)

Lecture 14 (Molecular Mass Distributions)

Lecture 15 (Copolymerization and Reactions of Polymers)

Lecture 16 (Crystal and Molecular Nucleation Kinetics)

Lecture 17 (Crystallization and Melting Kinetics)

CHAPTER IV (THERMAL ANALYSIS TOOLS)

Lecture 18 (Thermometry and Dilatometry)

Lecture 19 (Calorimetry)

Lecture 20 (Differential Scanning Calorimetry)

Lecture 21 (Temperature-Modulated DSC)

Lecture 22 (Thermomechanical Analysis, DMA and DETA)

Lecture 23 (Thermogravimetry)

CHAPTER V (STRUCTURE AND PROPERTIES OF MATERIALS)

Lecture 24 (Crystal Structure I)

Lecture 25 (Crystal Structure II)

Lecture 26 (Crystal Morphology)

Lecture 27 (Defects in Polymer Crystals)

Lecture 28 (Equilibrium Transitions and Prediction of Melting)

Lecture 29 (Mesophases and Their Transitions)

Lecture 30 (Melts and Glasses)

CHAPTER VI (SINGLE COMPONENT MATERIALS)

Lecture 31 (The Order of Transitions)

Lecture 32 (Size, Extension, and Time Effects on Fusion)

Lecture 33 (Analysis of the Sample History Through Analysis of the Glass Transition)

CHAPTER VII (MULTIPLE COMPONENT MATERIALS)

Lecture 34 (Macromolecular Phase Diagrams)

Lecture 35 (Glass Transitions of Copolymers, Solutions, Blends)

Lecture 36 (Melting Transitions of Copolymer, Solutions, Blends)

Examples of figure screens

The file-names of the illustrated figures are listed in the bottom frame in the figures, which also shows the most frequent codes to continue with the course. Figures 1 to 6 are typical examples, briefly summarized next.

Figure 1 illustrates the operation of the course using figures, text, and hypertext. One may page through the figures on the computer screen, or as in the live lecture offered at UT as Chem-690 which is illustrated by projecting the figures in sequence. For self-study one would read the text pages and jump to the figures by pressing the bolded figure numbers. Should the need arise, one can jump to the additional material stored in the hypertext. Typically, a single lecture contains 30 to 80 figures, 8 to 20 text pages, and 20 to 50 hypertext pages.

Figure 2 presents one of the about 20 mini-biographies available in the hypertext, highlighting the major scientist contributing to the early development of the subject under discussion. Figure 3 shows the ultimate connection between structure and energetics on the example of melting of dendrites and lamellae of polyethylene and the superposition of crystal perfection on slower heating rates. Figure 4 illustrates a recently developed nonequilibrium phase diagram which is used as the base for extrapolation to equilibrium. A similarly new research is summarized in Fig. 5. The Lissajous figure of temperature-modulated differential scanning calorimetry (TMDSC) indicates the ampli-

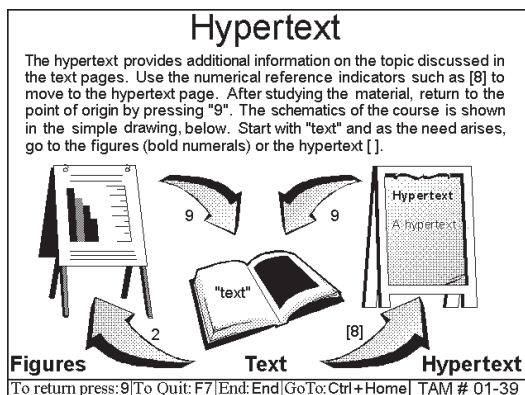



Fig. 1 Mode of operation of the computer course including figures, text, and hypertext

Werner Kuhn, 1899–1963

Kuhn was born in Switzerland, near Zürich. He began his studies at the ETH in Zürich in 1917, ending with a doctorate in Chem. Engineering. After 1930 he turned to the study of macromolecules. He was then a professor at the Technical College in the German town of Karlsruhe.

In 1934 Kuhn (*Kolloid Z.*, 68, 2) analyzed for the first time the behavior of a flexible macromolecule, permitting rotation about bonds and replacing the real chain with a chain of "statistical chain segments." Kuhn also worked out an early model of rubber elasticity [*Kolloid Z.*, 76, 258 (1936)] based on the coiled molecules. In 1939 he assumed a position at the Physical Chemistry Institute of the University of Basel.



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Fig. 2 Example of a mini-biography

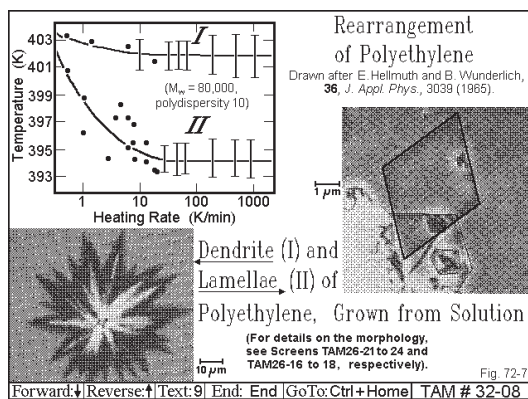


Fig. 3 Example of the connection between structure and energetics

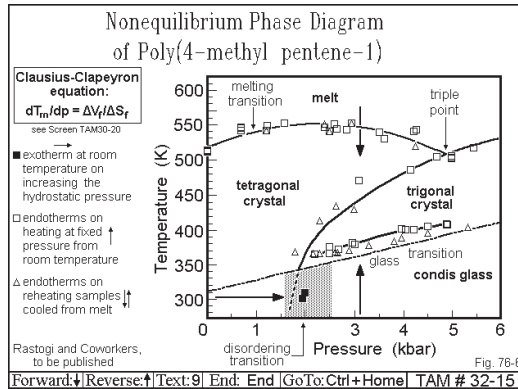


Fig. 4 Example of a non-equilibrium phase diagram

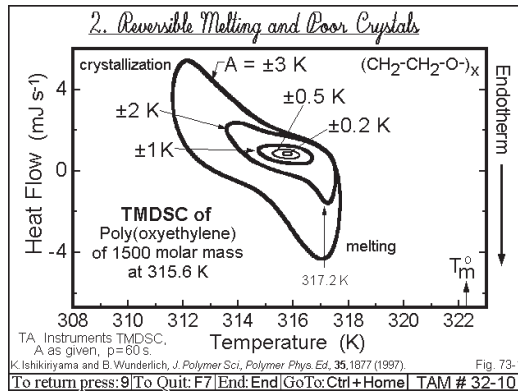


Fig. 5 New information available through temperature-modulated differential scanning calorimetry

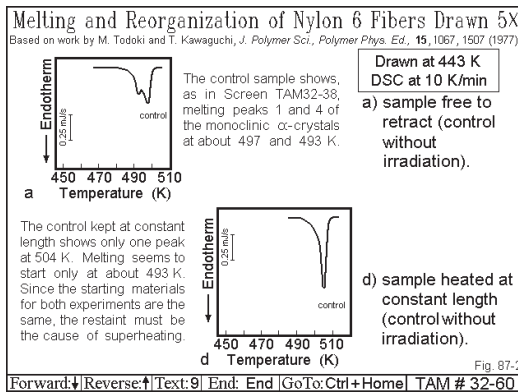


Fig. 6a An example of a pseudo-animation to clarify complex literature data

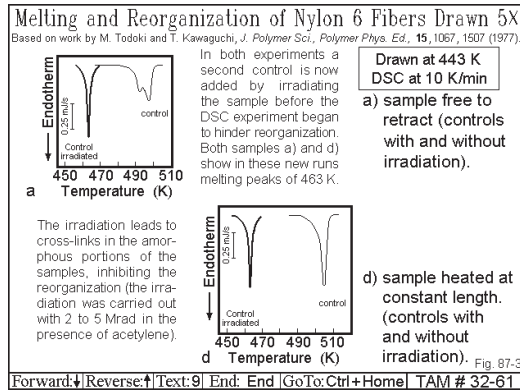


Fig. 6b An example of a pseudo-animation to clarify complex literature data

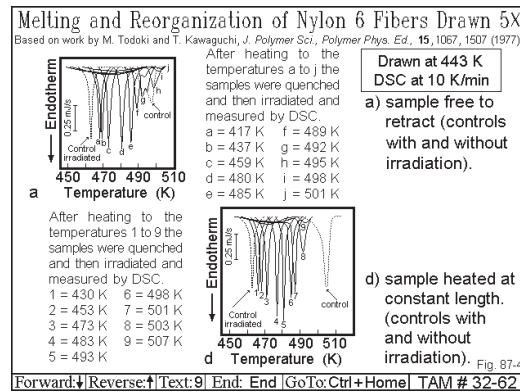


Fig. 6c An example of a pseudo-animation to clarify complex literature data

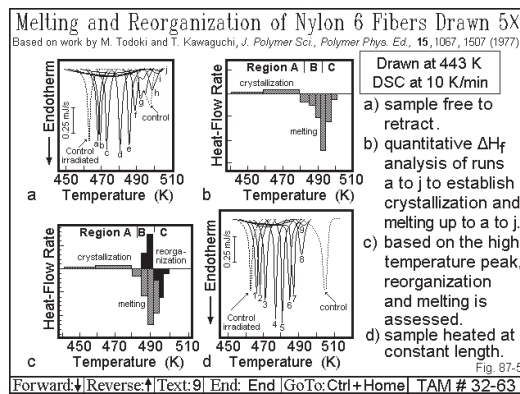


Fig. 6d An example of a pseudo-animation to clarify complex literature data

tude-dependence of melting and crystallization. These experiments can be used to elucidate growth and perfection of defect crystals and give quantitative information of the irreversibility of crystallization and melting (supercooling).

Figure 6, finally shows how by sequential build-up of graphs the topic of melting and reorganization of fibers can be easily displayed. The sequence of screens TAM32-60 to 63 clarifies the actual steps of the experiment with the explanatory text located on screen TAM32-87. When reading the cited literature, only the curves in screen TAM32-63 are available. It is much harder to distinguish the important results gained from this pioneering work in thermal analysis of fibers. This type of pseudo-animation is used also frequently to show the changes of distribution curves with defining parameters, as well as processes observed on phase transition. More examples can easily be checked from our web page listed in the footnote to the title of the paper.

Conclusions

The computer-assisted course 'Thermal Analysis of Materials' is a first example in the generation of a modern curriculum for professional thermal analysts. The education would start with undergraduate materials, chemistry, or physics training. As soon as specific interests develop, courses of specialization should be included as electives. The number of special courses is almost unlimited. A few suggestions are introductions to polymer science, analytical chemistry, metallurgy, geology, rheology, solid state physics or chemistry, fiber science, pharmaceutical, medical, biological, or food-science subjects. At the appropriate time, at the senior year or the beginning of the graduate study 'Thermal Analysis of Materials' should be taken. To round-out the education, the chosen field of interest should be continued with specialization in depth into the appropriate thermal analysis techniques, preferably coupled with study of one or more of the modern analysis techniques for the study of microscopic structure and motion, such as X-ray, neutron, infrared, Raman, and light scattering and spectroscopy, solid state NMR, AFM and STM techniques, and computer simulation. The course can also serve as a base for continuing-education in thermal analysis for researchers who have joined the field after their formal training was completed.

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