Bernhard Wunderlich

Thermal Analysis of Polymeric Materials

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With 974 Figures

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Preface

Thermal analysis is an old technique. It has been neglected to some degree because developments of convenient methods of measurement have been slow and teaching of the understanding of the basics of thermal analysis is often wanting. *Flexible, linear macromolecules*, also not as accurately simply called *polymers,* make up the final, third, class of molecules which only was identified in 1920. Polymers have never been fully integrated into the disciplines of science and engineering. This book is designed to teach thermal analysis and the understanding of all materials, flexible macromolecules, as well as those of the small molecules and rigid macromolecules. The macroscopic tool of inquiry is thermal analysis, and the results are linked to microscopic molecular structure and motion.

Measurements of *heat* and *mass* are the two roots of quantitative science. The macroscopic heat is connected to the microscopic *atomic motion*, while the macroscopic mass is linked to the microscopic *atomic structure*. The macroscopic units of measurement of heat and mass are the joule and the gram, chosen to be easily discernable by the human senses. The microscopic units of motion and structure are the picosecond (10^{-12} seconds) and the ångstrom (10^{-10} meters), chosen to fit the atomic scales. One notes a factor of 10,000 between the two atomic units when expressed in "human" units, second and gram—with one gram being equal to one cubic centimeter when considering water. Perhaps this is the reason for the much better understanding and greater interest in the structure of materials, being closer to human experience when compared to molecular motion.

In the 19th century the description of materials could be based for the first time on an experiment-based atomic theory. This permitted an easy recognition of the differences between *phases* and *molecules*. Phases are macroscopic, homogeneous volumes of matter, separated from other phases by well-defined boundaries, and molecules are the constituent smallest particles that make up the phases. As research progressed, microphases were discovered, initially in the form of colloidal dispersions. More recently, it was recognized that phase-areas may be of nanometer dimensions (nanophases). On the other hand, flexible macromolecules have micrometer lengths or larger. Particularly the nanophases may then have structures with interfaces that frequently intersect macromolecules, giving the materials unique properties.

Finally, the classical phases, gases, liquids, and solids, were found to be in need of expansion to include mesophases and plasmas. The discussion of history in the first lecture shows the tortuous path scientific discovery takes to reach the present-day knowledge. Easier ways can be suggested in hindsight and it is vital to find such simpler approaches so to help the novice in learning. In this book on "Thermal Analysis of Polymeric Materials" an effort is made to discover such an easy road to understand the large, flexible molecules and the small phases, and to connect them to the small molecules and macroscopic phases which are known for much longer.

Since the goal of this book is to connect the new knowledge about materials to the classical topics, but its size should be restricted to two to three semesters' worth of learning, several of the standard classical texts were surveyed by the author. Only when a topic needed special treatment for the inclusion of thermal analysis or macromolecules, was this topic selected for a more detailed discussion in this book. The knowledge in polymer science, in turn, often improves the understanding of the other types of molecules. A typical example is discussed in the first lecture when describing the classification-scheme of molecules. With this approach, the learning of materials science, as a whole, may be less confusing. A series of six additional examples of such improvement of the understanding is given on pg. VII.

The study of "Thermal Analysis of Polymeric Materials" is designed to accomplish two goals: First, the learning of the new subject matter, and second, to stimulate a review of the classical topics. Naturally, one hopes that in the future all topics are included in the main educational track. This joining of the physics, chemistry, and engineering of small and large molecules with thermal analysis is of urgency since most students must in their career handle polymeric materials and deal with the application of some type of thermal analysis. A list of short summaries of the seven chapters of the book is given below for a general orientation and to allow for reading, starting at different entry points:

Chapter 1 Atoms, Small, and Large Molecules is designed to enhance the understanding and history of the development of knowledge about small and large molecules. Furthermore, the nomenclature, description, and characterization of linear macromolecules by basic theory and experiment are summarized.

Chapter 2 Basics of Thermal Analysis contains definitions of systems, flux, and production and the following thermodynamic functions of state which are needed for the description of thermal analysis results: heat capacity, enthalpy, entropy, and free enthalpy.

Chapter 3 Dynamics of Chemical and Phase Changes is a summary of the syntheses by matrix, stepwise, step, and chain reactions. It also contains information on emulsion polymerizations, cross-linking, gelation, copolymerization, and decomposition. Kinetics of nucleation, crystallization, and melting, as well as glass transitions are chosen as representative of the dynamics of phase changes.

Chapter 4 Thermal Analysis Tools contains a detailed description of thermometry, calorimetry, temperature-modulated calorimetry (TMC), dilatometry, thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), and thermogravimetry (TGA).

Chapter 5 Structure and Properties of Materials covers the solid states (glasses and crystals), mesophases (liquid, plastic, and condis crystals), and liquids. Also treated are multiphase materials, macroconformations, morphologies, defects and the prediction of mechanical and thermal properties.

Chapter 6 Single Component Materials provides detailed descriptions of phase diagrams with melting, disordering, and glass transitions. In addition, the effects of size, defects, strain on transitions and properties of rigid amorphous and other intermediate phases are treated in the light of thermal and mechanical histories.

Chapter 7 Multiple Component Materials, finally covers our limited knowledge of chemical potentials of blends, solutions, and copolymers. The Flory-Huggins equation, phase diagrams, solvent, solute, and copolymer effects on the glass, melting, and mesophase transitions are the major topics.

This book grew out of the two three-credit courses "Physical Chemistry of Polymers" and "Thermal Analysis" at The University of Tennessee, Knoxville (UTK). First, the lectures were illustrated with overhead foils, generated by 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 (Academic Press, Boston). In 1994, a condensed text was added to the slides as lecture notes. A much expanded computer-assisted course "Thermal Analysis of Materials" was then first offered in 1998 and is a further development, enabling self-study. The computer-assisted course is still available via the internet from our ATHAS website (*web.utk.edu/~athas*) and sees periodic updates. It is the basis for the present book. A short version of the ATHAS Data Bank, a collection of thermal data, is included as Appendix 1. A treatise of the theory of "Thermophysics of Polymers" was written by Prof. Dr. Herbert Baur in 1999 (Springer, Berlin) and can serve as a companion book for the theoretical basis of the experimental results of "Thermal Analysis of Polymeric Materials."

The book contains, as shown above, a critically selected, limited series of topics. The field of flexible macromolecules is emphasized, and the topics dealing with small molecules and rigid macromolecules, as well as the treatment of mechanical properties, are handled on a more elementary level to serve as a tie to the widely available, general science and engineering texts.

Topics that are Different for Polymers and Small Molecules

The structure of a macromolecular substance is characterized by a diversity of molecular shapes and sizes, as is discussed in Chap. 1. These are items unimportant for small molecules. Chemically pure, small molecules can be easily obtained, are of constant size and often are rigid (i.e., they also are of constant shape).

Classically, one treats phases of two components as ideal, regular, or real solutions. Usually, however, one 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 as of basic importance (Chap. 7). Considerable differences in size may, however, also occur in small molecules and their effects are hidden falsely in the activity coefficients of the general description.

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 Chap. 5). Certainly, there must be a basic difference if one class of condensed materials can be deformed elastically only to less than 1% and the other by up to 1,000%.

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 permanent documentation of the reaction (see Chaps. 1 and 3).

The notoriously poor polymer crystals described in Chap. 5 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. Thermal analysis, with its methods described in Chap. 4, is quite often neglected in physical chemistry, but unites thermodynamics with irreversible thermodynamics and kinetics as introduced in Chap. 2, and used as an important tool in description of polymeric materials in Chaps. 6 and 7.

The solid state, finally, has gained by the understanding of macromolecular crystals with helical molecules, their defect properties, mesophases, small crystal size, glass transitions, and rigid-amorphous fractions (Chaps. 5 and 6).

General References

The general references should be used for consultation throughout your study of *Thermal Analysis of Polymeric Materials*. You may want to have the textbooks at hand which you own, and locate the other reference books in the library for quick access. Frequent excursions to the literature are a basis for success in learning the material of this course.

Typical books on polymer science are (chemistry, physics, or engineering):

1. Rodriguez F, Cohen C, Ober CK, Archer L (2003) Principles of Polymer Systems, 5^{th} ed. Taylor & Francis, New York.
2. Stevens MP (1989) Polymer Chemistry, 2^{nd} ed. Oxford University Press, New York.
3. Billmeyer, Jr. FW (1989) Textbook of Polymer Science, 3^{rd} ed. Wiley & Sons, New York.

Typical physical chemistry texts are:

4. Atkins PW (1998) Physical Chemistry, 6^{th} ed. Oxford University Press, Oxford.
5. Mortimer RG (1993) Physical Chemistry. Benjamin/Cummings, Redwood City, CA.
6. Moore WG (1972) Physical Chemistry, 4^{th} ed. Prentice Hall, Englewood Cliffs, NJ.

As mentioned above, the companion book treating the theory of the subject is:

7. Baur H (1999) Thermophysics of Polymers. Springer, Berlin.

Reference books for numerical data on polymers and general materials are:

8. Brandrup J, Immergut EH, Grulke EA, eds (1999) Polymer Handbook. Wiley, New York, 4^{th} edn.
9. Lide DR, ed (2002/3) Handbook of Chemistry and Physics, 83^{rd} ed. CRC Press, Boca Raton, FL. (Annual new edns.)

For detailed background information on any type of polymer look up:

10. Mark HF, Gaylord NG, Bikales NM (1985–89) Encyclopedia of Polymer Science and Engineering, 2^{nd} ed; Kroschwitz JI ed (2004) 3^{rd} ed. Wiley, New York. Also available with continuous updates via the internet: www.mrw.interscience.wiley.com/epst

For more advanced treatises on physical chemistry, you may want to explore:

11. Eyring H, Henderson D, Jost W (1971–75) Physical Chemistry, An Advanced Treatise. Academic Press, New York.
12. Partington JR (1949–54) An Advanced Treatise on Physical Chemistry. Longmans, London.

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