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Book Review

Calorimetry and Thermal Analysis of Polymers, edited by Vincent B. F. Mathot. *Hanser Publishers*, Munich, Vienna, New York. 1994 ISBN 1-56990-126-0 Price $ 88.00, 369 pages

This book is based on a Transitional Training Project in Polymer Science and Technology organized in 1989. It is intended as an aid in the training of thermal analysts in the fields of calorimetry and thermal analysis of polymers. Ten of the contributors of the project authored the 13 chapters covering: thermodynamics (A. Schuijff), calorimetric methods (W. Hemminger), fundamentals of DSC and DTA (G. W. H. Höhne), DSC on Polymers (M. J. Richardson), thermal characterization of states of matter (V. B. F. Mathot), the glass transition region (M. J. Richardson), curing of thermosets (M. J. Richardson), thermal transitions and gelation in polymer solutions (H. J. Berghmans), the crystallization and melting region (V. B. F. Mathot), microcalorimetry (L. Benoist), reaction calorimetry for polymerization studies (R. Riesen), coupled techniques – TGA-DTA-MS (M. Wingfield), and evolved gas analysis of polymers by coupled GC, FTIR and MS (J. A. J. Jansen). Each chapter of the well-produced book has a collection of references to the literature (varying from 4 to 386) and a summary of acronyms and symbols. All is tied together with a 17 page index. Missing topics are films and fibers and the "Thermal Analysis" is limited to DTA, DSC, and the three last chapters on coupled techniques. Dominating the book are the two chapters by V. B. F. Mathot (64 and 70 pages, respectively).

After a brief introduction of thermodynamics in the first chapter (15 pages) by Schuijff in which the basic definitions and laws are covered, Hemminger and Höhne give in the next two chapters (74 pages) an authoritative description of instrumentation and its theory. These chapters are at a level any thermal analyst should be able to handle, but may not. Anyone in the field can gauge his or her accomplishment by going through these chapters and making sure the large amount of information is applied to everyday thermal analysis. The new development of modulation, oscillation, alternation, and dynamics in DSC was unfortunately entering the scene of thermal analysis too late to be included.

Next, there are three masterfully written chapters by Richardson (total 52 pages). They start with the statement "DSC is one of the easiest modern analytical techniques to use." This certainly only applies to the few experts that reach Richardson's level of accomplishments. But, reading the three chapters it looks easy, indeed. Many remarks are close to everyday experience and help the interpretation of the experiments, steer around the pitfalls of the glass transition, and permit the interpretation of curing. The latter is done by measurement of heat of reaction, changes in glass transition, and attempts at elucidation of kinetics.

The chapter by Berghmans is an expert review of gelation of 24 pages. After a competent description of thermal analysis of the solvent-crystallization phase diagrams and liquid-liquid phase separation, the various gelation processes are discussed: The chapter is

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kept largely qualitative, but with many references to the nonequilibrium nature of polymer crystallization. The special thermodynamic effects of the size of the macromolecule relative to the small solvent are unfortunatley omitted, although the asymmetry that is introduced by this size difference is mentioned.
This brings us to the two key chapters by Mathot on "Thermal Characterization" and "Crystallization and Melting." The first part stresses the importance of heat capacity. Details of measurement, calibration, and instrumentation are given with many hints of how to avoid the common errors. The reader is guided carefully through the confusing effects of amorphous and semicrystalline states on the various examples of polyethylene as well as polypropylene and polystyrene. Single phase, two-phase, and three-phase equilibrium and nonequilibrium situations are considered. For the first time the implications of a "rigid amorphous" phase are carefully traced by measurement of heat capacity. Crystallization and melting is mainly illustrated on the various linear, branched, and copolymerized polyethylenes. Correlation of crystallization and melting with branching, molar mass and thermal history is authoritatively presented and linked to crystal structure parameters. Multiple melting peaks are discussed and related to crystal size, structure, and composition. Overall, these two chapters present thermal analysis as its best. A quantitative analysis is connected to the phase structure of the polymer. A better description of calorimetry of the broad range of polyethylenes does not exist.

The book is completed with four shorter chapters. One on Microcalorimetry (15 pages), one on Reaction Calorimetry (14 pages), one on coupled TGA, DTA and MS (7 pages), and one on Evolved Gas Analysis by Coupled Techniques (18 pages). A large number of applications are briefly described in the light of the specialized instrumentation. Included are glass transitions, ice formation in pores, wax crystallization in mineral oils, mixing and dissolution, adsorption, evaporation, thermal conductivity, heats of polymerization, curing of composites, combustion, thermal desorption, pyrolysis and life-time prediction, Curie-point pyrolysis of polymers. The results range from quantitative to qualitative information, illustrating the enormous breadth of applicability of thermal analysis.

If the training project was able to transfer anything close to the broad coverage and in-depth information to the participants, it must have been a full success. In printed form, it allows all of us to learn much, starting from a simple level and going to the frontier of present day research. This is a book that should not be absent from the bookshelf of any thermal analyst.

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