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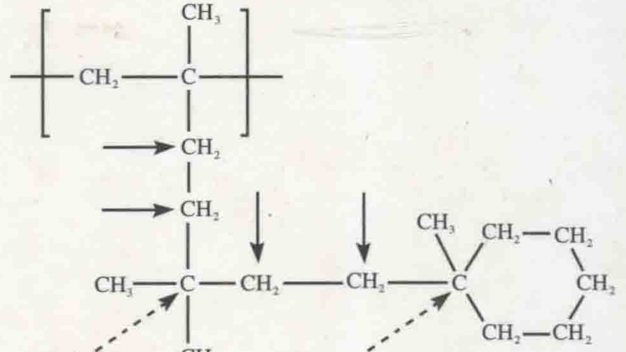
Third Edition, Revised and Expanded



Jozef Bicerano

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Third Edition, Revised and Expanded

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The Dow Chemical Company
Midland, Michigan, U.S.A.

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To my wife, Cynthia, whose patience, support and companionship have facilitated my work and made my life enjoyable; to the memory of my father, Salamon, who would have enjoyed seeing the publication of this book; to my mother Riketa; and to my daughter Holly.

PREFACE

The efficient design of new polymers for many technological applications requires the prediction of the properties of candidate polymers and the use of these predictions to evaluate, screen, and help prioritize the synthesis of these candidates. The solution of these problems often requires significant extensions of existing quantitative structure-property relationships. In particular, the candidate polymers for advanced "high-tech" applications requiring outstanding performance characteristics often contain exotic structural units for which the simple additive (group contribution) techniques cannot be applied. Some of the required group contributions to the physical properties are often not available, and there are no experimental data to use in estimating these missing group contributions. This limitation is inherent to group contribution methods and unavoidable in applying such methods to truly novel types of structures.

This difficulty was overcome in 1989 by developing a method in which many properties are expressed in terms of topological variables (connectivity indices) combined with geometrical variables and/or other structural descriptors used to obtain refined correlations. The remaining properties are calculated from relationships that express them in terms of the properties being calculated by using the topological variables. This method enabled the prediction of the properties of all polymers of interest, without being limited by the absence of the group contributions for the structural fragments from which a polymeric repeat unit is built. It was equivalent to the prediction of the properties by the summation of additive contributions mainly over atoms and bonds instead of groups. The values of these atom and bond contributions were dependent on the environment of each atom and bond in a particularly simple relationship.

The relationships developed in this work therefore enabled their users to transcend the limitations of traditional group contribution techniques in predicting the properties of polymers. Our work owed much, however, to the solid foundation of earlier quantitative structure-property relationships in polymers, developed over many decades by the meticulous efforts of many researchers. In particular, much of the information provided in D. W. van Krevelen's classic textbook, *Properties of Polymers* (whose third and last edition was published by Elsevier, Amsterdam, in 1990), was extremely valuable in our work.

The new methodology was tested extensively in practical work at The Dow Chemical Company. It was found to be able to predict the properties of novel polymers as accurately and reliably as can be reasonably expected from any scheme based on simple quantitative structure-property relationships. The only computational hardware required to perform these calculations is a good hand calculator. The method was, nonetheless, automated by implementation in a simple interactive computer program (SYNTHIA). This software implementation has enabled its much easier use, especially by non-specialists. It has thus resulted in much greater efficiency as well as significantly reducing the possibility of human error.

The use of this computer program involves simply drawing the structure(s) of the repeat unit(s), specifying the calculation temperature (and also the mole fractions or weight fractions of the repeat units for copolymers), and asking the program for the predicted values of the properties. In addition, this program allows the user to obtain graphs of many of the predicted properties as a function of the temperature; and, for copolymers, also as a function of the composition. This computer program is available from Accelrys, Inc., in San Diego, California, USA, to which it has been licensed for commercialization by Dow.

At the core of this book is the new scheme of quantitative structure-property relationships developed in the course of the author's work, as summarized above. However, as described below, the book has evolved significantly since its first edition was published a decade ago.

The first edition (1993) was essentially a research monograph describing the new method. It was written mainly to help scientists and engineers working on applied problems in polymer science and technology in the chemical and plastics industries. Secondary objectives included providing detailed information that could serve as starting points for fundamental research on polymer properties, as well as serving as an auxiliary textbook to help teach students at both the undergraduate and graduate levels how to calculate the industrially important properties of polymers. A highly empirical approach was used throughout the first edition. Fundamental considerations were often deliberately not addressed in detail, to avoid lengthy digressions from the main theme and the very practical focus of the research monograph.

The commercial successes of both the book and the SYNTHIA software program, as well as the positive feedback which the author received directly from many readers of the book and many users of the software, provided the encouragement needed to develop first the revised and expanded second edition of the book (1996), and now this completely revised third edition.

Some of the revisions in each new edition are direct improvements and/or extensions of the methods developed earlier to predict the physical properties of polymers. Other revisions consist of more detailed background information and discussion on the topics covered by the book, including extensive tabulations of additional experimental data and literature references. Some revisions involve mainly the reorganization of the material discussed in a given chapter in a manner which may facilitate comprehension. Revisions and extensions were made to increase the utility of the book as a research monograph presenting a new method to calculate polymer properties, while also making it much more self-contained to encourage its extensive use as both a general reference and a textbook. The third edition takes a major step forward in the expansion of the breadth of the scope of the book. While still keeping simple quantitative structure-property relationships for amorphous polymers at its core, it now also covers a broad range of topics at the frontiers of polymer modeling. These "frontier" areas include multiscale modeling, and methods for predicting the morphologies and the properties of interfaces and of multiphase materials. It is hoped that, especially with its significant expansion in scientific scope to cover state-of-the-art methods based on fundamental physics, readers will find this third edition useful in their work as a far more comprehensive resource for the predictive modeling of polymers than the previous two editions.

Jozef Bicerano

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Mike Winkelman prepared a patent application covering the methodology.

Eric Eidsmoe wrote a computer program which implemented the relationships presented in this book. This computer program and many of the relationships incorporated in it were improved and their usefulness in solving practical problems was demonstrated as a result of extensive use by many researchers at Dow. Steve Mumby, Steve Harris, Fiona Case and David Klipstein (all from Biosym Technologies, Inc.; now named Accelrys, Inc.) made various contributions which resulted in the successful commercialization of the software package.

Cathy Wedelstaedt, Andy Ahn, Laura Beecroft, Chuck Broomall, Jim Curphy, Eric Fouch, Kurt Kuhlmann, Jean McPeak, Pam Percha, Tom Tomczak and Tanisha Sangster ran a series of experiments to obtain data which supplemented the experimental data found in the literature, and thus helped in the development of the quantitative structure-property relationships.

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