

Preface

More than half a century has passed since the pioneering books by Flory [1] and by Huggins [2] dealing with some of the most important features concerning the thermodynamics of polymer containing systems. This volume of “*Advances in Polymer Science*” has been composed to update our knowledge in this field. Although most of the experimental observations referring to macromolecular systems could already be rationalized on the basis of the well-known Flory–Huggins theory, quantitative agreement between experiment and theory is normally lacking. The reason for this deficiency lies in several inevitable simplifying assumptions that had to be made during this ground-breaking period of research.

In the meantime, valuable progress could be achieved, thanks to modern computers, improvements of experimental methods, and data handling. This situation has among others provoked a new textbook [3] focusing on polymer phase diagrams. It is the central purpose of this volume to present some further examples for recent developments that were made possible by the above-described improvements. The individual contributions to this issue of the *Advances in Polymer Science* are grouped according to the degree they are connected with the previous text books.

The first part (*B.A. Wolf*) deals with a straightforward extension of the Flory–Huggins theory to account for some aspects of chain connectivity and for the fact that chain molecules may react on changes in their molecular environment by conformational rearrangements. In this manner, several hitherto unconceivable experimental observations (like pronounced composition dependencies of interaction parameters or their variation with chain length) can be understood and modeled quantitatively. This contribution is followed by a chapter devoted to progress in the field of polyelectrolyte solutions (*G. Maurer et al.*); it focuses on the calculation of vapor/liquid equilibria and some related properties (e.g. osmotic pressures) using sophisticated models for the Gibbs energy. Such thermodynamic knowledge is particularly needed for different industrial application of polyelectrolytes, for instance in textile, paper, food, and pharmaceutical industries.

An interesting example for the development and advancement of experimental methods is presented in the third chapter (*J.-P. E. Grolier et al.*), dedicated to the

measurement of interactions between gases and polymers based on gas sorption, gravimetric methods, calorimetry, and a “coupled vibrating wire-*pVT*” technique. Information in this field is of particular interest for polymer foaming and for the self-assembling of nanoscale structures. The fourth section (*S. H. Anastasiadis*) is concerned with interfacial phenomena in the case of polymer blends and reports the current state of the art on measuring and modifying interfacial tensions as well as different possibilities for its modeling. Such information is indispensable for the development and optimization of tailor-made materials based on two-phase polymer blends. The fifth contribution (*S. Enders*) formulates a theory for the simulation of copolymer fractionation in columns with respect to molecular weight and chemical composition. Narrowly distributed polymers are often required for basic research and the removal of harmful components is sometimes essential for special applications.

All previously discussed methods are primarily based on phenomenological considerations, in contrast to chapter six (*K. Binder et al.*), which starts from statistical thermodynamics. This section reviews the state of the art in fields of Monte-Carlo and Molecular Dynamics simulations. These methods are powerful tools for the prediction of macroscopic properties of matter from suitable models for effective interactions between atoms and molecules. The final chapter (*G. Sadowski*) makes use of the results obtained with simulation tools for the establishment of molecular-based equations of state for engineering applications. This approach enables the description and in some cases even the prediction of the phase behavior as a function of pressure, temperature, molecular weight distribution and for copolymers also as a function of chemical composition.

The Editors are well aware of the fact that the above selection is not only far from being complete, but also to some extent subjective. However, in view of the importance of polymer science (worldwide annual production [4] in 2008: $2.8 \cdot 10^8$ t with a growth rate of approximately 12% per year) and accounting for the significance of thermodynamics in this area, further volumes of the “Advances in Polymer Science” covering missing thermodynamic aspects and presenting further progress in this field are expected.

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References

- 1 P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y. 1953
- 2 M. L. Huggins, Physical Chemistry of High Polymers, Wiley, N.Y. 1958
- 3 R. Koningsveld, W. H. Stockmayer, E. Nies, Polymer Phase Diagrams, Oxford University Press, Oxford 2001
- 4 Statistisches Bundesamt, Fachserie 4, Reihe 3.1, Jahr 2007

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