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Advances in Polymer Science

Advances in Polymer Science

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Polymer Thermodynamics

Liquid Polymer-Containing Mixtures

Volume Editors: Sabine Enders
Bernhard A. Wolf

With contributions by

S.H. Anastasiadis · K. Binder · S.A.E. Boyer · S. Enders · J.-P.E. Grolier · S. Lammertz · G. Maurer · B. Mognetti · L. Ninni Schäfer · W. Paul · G. Sadowski · P. Virnau · B.A. Wolf · L. Yelash

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Editorial Board

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Aims and Scope

The series *Advances in Polymer Science* presents critical reviews of the present and future trends in polymer and biopolymer science including chemistry, physical chemistry, physics and material science. It is addressed to all scientists at universities and in industry who wish to keep abreast of advances in the topics covered

Review articles for the topical volumes are invited by the volume editors. As a rule, single contributions are also specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for *Advances in Polymer Science* in English.

In references *Advances in Polymer Sciences* is abbreviated as *Adv Polym Sci* and is cited as a journal.

Special volumes are edited by well known guest editors who invite reputed authors for the review articles in their volumes.

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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 indispensible 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: $2.8^{\circ}10^{8}$ 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.

Berlin
Mainz
Summer 2010

Sabine Enders
Bernhard Wolf

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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

Obituary

Prof. Dr. Ronald Koningsveld, for several decades leader in thermodynamics of polymer solutions and blends, was born on April 15, 1925 in Haarlem. In his teen years when he was living in Rotterdam, he was seized by science and music and he started studies of orchestral conducting, piano, and composition at Rotterdam Conservatory. Music remained his love for his whole life. However, following the advice of his father to do something more "practical", he entered the Technical University of Delft to study chemical engineering. After graduation in 1956, Ron joined the Central Research of Dutch State Mines (DSM) in Geleen and in his first years there he was engaged in polymer characterization. In parallel, he started his PhD studies at the University of Leiden under the guidance of A. J. Staverman in the area of phase equilibria in polydisperse polymer solutions with application to polymer fractionation. He obtained the title of Doctor of Mathematics and Natural Sciences in 1967. The papers based on these results rank among the most cited ones of Ron's almost 200 publications cited about 3,000 times (according to WoS). Ron continued working in DSM Research until his retirement in 1985 in various positions including Head of Department of Fundamental Polymer Research (1963–1980) and Managing Director of General Basic Research (1980–1985). In the latter position, Ron also managed external research funded by DSM. He stimulated significantly collaborative fundamental research on polymers in Europe and overseas. The collaboration extended to other countries including Belgium, Czechoslovakia, Germany, United Kingdom, and U.S.A.

Koningsveld is the name well known in the Academia – he was teaching polymer thermodynamics as a guest professor in the University of Essex, University of Massachusetts, Catholic University of Leuven, and ETH Zurich, and for 18 years he was a Professor of Polymer Science in the University of Antwerp.

He received honorary doctorates from the University of Bristol and Technical University of Dresden. Also, he was a consultant to Max-Planck Gesellschaft, Institute of Polymer Research in Mainz. In 2002, Ron's scientific achievements were appreciated by the Paul Flory Research Prize.

It would be difficult to enumerate all Ron's scientific achievements in the field of polymer thermodynamic. One can name the generalizations of the Flory–Huggins Gibbs energy leading to the prediction and experimental verification of coexistence of three phases in pseudobinary system with sufficiently broad distribution; or, the analysis of the functional form of the interaction term leading to the appearance of "off-zero critical concentration", at variance with zero critical concentration associated with theta-temperature. Thanks largely to Ron, polymer scientists realize that the cloud point curve is not the binodal and its maximum or minimum are not identical with the critical temperatures.

Ron had many good friends in the scientific society and some of them (Berghmans, Simha, Stockmayer) are coauthors of his last paper on correlation between two critical polymer concentrations – c^* for the coil overlap and c_s assigned to the maximum/minimum of the spinodal (*J. Phys. Chem. B* 2004, 108, 16168–16173). Unfortunately, Robert and Stocky are no longer with us as well. The scientific community can share Ron's knowledge in phase equilibria in the monograph *Polymer Phase Diagrams*, Oxford (2001) published with coauthors W. H. Stockmayer and E. Nies.

This reminiscence would not be complete without mentioning the second Ron's love – the music. Already in Delft as a student, Ron was engaged in Dutch College Swing Band as a pianist and arranger. During his work for DSM, Ron composed a number of pieces inspired by research of polymers: *Microsymposium Music* performed during Microsymposia on Polymers held every year in the Institute of Macromolecular Chemistry in Prague, *Polymer Music* in six movements for two pianos, *To Science* (inspired by Edgar Allan Poe, *Staudinger March* (commemorating Staudinger's 100th birthday), and *Short Communication*. Some of the readers may remember the "ouverture" to IUPAC Macro in Amherst in 1982, where polymer scientists (Stockmayer, MacKnight, Kennedy, Janeschitz-Kriegel and Ron as pianist) performed *Polymer Music*.

Ron passed away in Sittard on November 26, 2008. We grieve over a famous scientist known all over the world in the thermodynamic community, an outstanding academic teacher and a great personality.

Karel Dušek
Prague

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