

Macromolecules Containing Metal and Metal-Like Elements, Volume 5: Metal-Coordination Polymers.

Edited by Alaa S. Abd-El-Aziz (The University of Winnipeg), Charles E. Carraher, Jr. (Florida Atlantic University), Charles U. Pittman, Jr. (Mississippi State University), and Martel Zeldin (Hobart and William Smith Colleges). Wiley & Sons: Hoboken, NJ. 2005. xvi + 408 pp. \$150.00. ISBN 0-471-68237-3.

Volume 5 of this series concentrates on metal-coordination polymers. Polymers of this nature have a long history that includes an explosion of research ignited by the Advanced Materials Program of the Air Force in the 1950s, which focused on main-chain structures with increased thermal properties. This area of research has continued to evolve, with new momentum spurred by the needs of modern nanobiotechnology, which makes use of the advanced properties enabled by these unique materials.

The book contains 14 chapters written by authors from research laboratories around the globe. The first chapter, written by three of the editors, provides an excellent background for those not intimately familiar with the field. This introductory chapter connects the remaining chapters of the book, which is particularly useful since the other chapters focus mostly on results from the laboratories of the individual authors. Although every chapter contains an introduction to the specific area, the first chapter provides a nice global picture of the field. Some of the topics covered in the book include expected examples of magnetism, conjugated main-chain structures, stimuli-responsive materials, polymers for solar energy conversion, and redox active systems, as well as some “unexpected” subjects, such as catalytically active metal-containing polymers and coordination networks. The field, and thus the book, is dominated by main-chain structures; however, the book does include several examples of other architectures, including side-chain metal-containing polymers, which hold much promise for future research efforts.

This book is a nice addition to the field, providing entry for new researchers interested in these fascinating materials while at the same time illustrating some of its most recent advances.

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Crystallization of Polymers, 2nd ed., Volume 2: Kinetics and Mechanisms. By Leo Mandelkern (Florida State University). Cambridge University Press: Cambridge, U.K. 2004. x + 468 pp. \$160.00. ISBN 0-521-81682-3.

This volume, the second of three in the current edition of Mandelkern’s treatise on the crystallization of flexible chain synthetic polymers, is true to its title, “Kinetics and Mechanisms”. Each of the five chapters is introduced by a few well-

chosen examples of the effect of one or more parameters (temperature, molecular weight, pressure, etc.) on the rate of overall crystallization or on the growth rate of crystalline structures, typically spherulites. A systematic presentation of further examples of kinetic effects organized into appropriate sections follows. Polyethylene and isotactic polystyrene are the most cited materials, but are by no means the only ones, and experimental methods are generally calorimetry and optical microscopy. The “mechanism” part of the volume title is developed in the context of the theory of nucleation.

Crystallization of homopolymers from the melt state is addressed in the first chapter, which occupies nearly half the volume. Here we become aware that Mandelkern has a number of points to make, some quite directly and others in a more insinuating manner. The author argues convincingly that the conventional Avrami analysis of the rates of isothermal crystallization is inadequate because the nature of uncrystallized polymer segments is altered by the transformation process itself. With the simpler “free growth” method that emphasizes the early stages of crystallization, Mandelkern obtains the robust systematic behavior of the Avrami exponent n (integral and decreasing with increasing crystallization temperature). Inexperienced readers may be puzzled by the treatment of what is conventionally called Hoffman–Lauritzen theory, by far the dominant approach for analyzing the temperature dependence of the growth rate of lamellar (folded chain) polymer crystals. Mandelkern never mentions “Hoffman–Lauritzen,” but uses terms such as “Gibbs coherent nucleus” for the secondary nucleus, “Turnbull–Fisher relation” for the kinetic analysis of crystal thickness, and “Frank theory” for establishing regimes where the temperature dependencies of the rate of growth are different. The author properly emphasizes that nuclei may differ in structure from mature crystals and that regular folding with adjacent reentry is not confirmed (or refuted) by kinetic analyses. The purpose of his lengthy discussion of the sharpness of “regime” transitions eluded this reader, but the demonstration that apparent transitions of regimes are sensitive to the choice of transport parameters was welcome. Mandelkern further shows that temperature dependencies of overall kinetics and growth rate can be accounted for with equal accuracy by three-dimensional or two-dimensional nucleation theory, a fact that is often overlooked. The effects of molecular weights are described and documented well, but the interpretation is limited.

The second chapter considers the crystallization of copolymers from the melt. Most of this space is devoted to random copolymers in which dilute comonomer units are excluded from the crystal, an effect that both limits crystalline fraction and reduces the rate of crystallization. In such materials, the melting point of a crystal and hence the driving force for crystallization depend on the amount of comonomer in the melt. Mandelkern modifies both Avrami and nucleation expressions and predicts behavior in qualitative accord with experiment. Block copoly

mers are considered as well; these materials crystallize by what appears to be homogeneous nucleation in microphase-separated domains.

Various mixtures of polymers are surveyed in the third chapter, in which different combinations of blend miscibility and crystallizability are considered. Nucleation theory is modified to account for the free energy change that accompanies demixing in a miscible blend when only one component crystallizes. This theory appears to work in some cases, but not in others for reasons that are not understood. The final chapter treats crystallization of polymers from solutions with low-molecular-weight solvents. The first 12 pages present a debate of sorts with the Bristol school about the reason for a minimum rate of crystallization of normal alkanes some 10 degrees below the melting (dissolution) temperature; this effect is not seen with polymer solutes. The remainder of the chapter is a comprehensive survey of the effects of concentration, temperature, and molecular weight, most of which can be understood in a qualitative sense.

The penultimate chapter on "Crystallization under applied force" is curiously placed between those on blends and solutions. This chapter starts with the accelerating effect of hydrostatic pressure on overall crystallization rate, with considerable space devoted to linear polyethylene and the effects of polymorphism. Uniaxial deformation of networks (mainly *cis*-polyisoprene) likewise increases the rate of crystallization mainly by increased melting temperature and undercooling. There is a short section on biaxial deformation and shear.

This book is a comprehensive summary of the effects of temperature, molecular weight, composition, etc. on the rates of nucleation and growth of polymer crystals. As such, it is a valuable resource for those wanting to learn about what has been done in the field. Theoretical developments are better suited for readers with at least some background, as most derivations are not developed in detail. The subject index is sketchy. This reader would have liked the overall tone of the volume to be more positive about the current state of our knowledge. There are many instances where Mandelkern writes "Serious questions can be raised regarding ... [some aspect of a theory or model]". While the author is correct, he demonstrates repeatedly that the important effects are adequately—if not perfectly—accounted for by classical concepts of nucleation and growth combined with established concepts of mass transport in polymers.

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Macromolecular Nanostructured Materials. Springer Series in Materials Science, 78. Edited by Norikazu Ueyama and Akira Harada (Osaka University). Springer: Berlin, Heidelberg, New York, and Kodansha, Tokyo. 2004. xvi + 336 pp. \$149.00. ISBN 3-540-22327-4.

The chemistry of nanomaterials intersects with many scientific fields, and supramolecular chemistry is one field of research that has been particularly affected by the recent boom in interest in nanomaterials. This volume, edited by two experts in the field of supramolecular chemistry, covers recent work on the synthesis and characterization of organic and organometallic supramo-

lecular nanostructures. There are 19 research accounts, all written by experts in the field of self-assembling macromolecules. The coverage is tilted toward research conducted by Japanese groups (14 of the 19 chapters). Nevertheless, the book gives a good impression of state-of-the-art research on complex, self-assembling macromolecules.

The book is divided into four sections of multiple chapters. Section 1, "Precise Synthesis of Supramolecules", primarily focuses on the assembly and properties of rotaxanes and catenanes. Stoddart and co-workers describe their work on redox-switchable supramolecules and their integration into micro- and nanofabricated crossbar switches. The authors do a great job of illustrating the challenge of device stability and catalog both the molecules that work well in the context of devices as well as those that work poorly. In the next two chapters, Harada and Steinke et al. review the assembly of polymeric rotaxanes using cyclodextrin and cucurbituril, respectively. The focus of these chapters is on supramolecular synthesis and characterization, although Harada also describes his group's demonstration of physical nanomanipulation of threaded cyclodextrin rings with an STM tip.

Section 2, "Macromolecular Organic Assemblies", focuses on supramolecular work with more specific goals in mind. Michunobu and Nishide open the section with an account on the characterization of individual molecular polyradicals—organic polymers in which each monomer has one or more unpaired spins—by magnetic force microscopy. The authors' correlated AFM and MFM images of discrete polymer molecules clearly show the unique magnetic features of these macromolecules and point to future research on integrating organic radicals into magnetic storage and imaging. Liaw then describes the synthesis and properties of many polyimides; it is not clear how this relates to nanomaterials, but the relationship between the structures of monomers and the properties of polymers derived from them is thoroughly characterized. The next three chapters are descriptions of different characteristics of self-assembling gelators. Gronwald and Shinkai outline the use of organogelators as templates for sol–gel synthesis and calcination of silica nanotubules. Hanabusa reviews his group's exploration of the motifs of molecular design in organogelator assemblies. Finally, Aoshima reviews the synthesis and behavior of polymeric hydrogels formed from polyvinyl ethers. In all of the chapters in Section 2, the main theme is the relationship between the structures of the organic building blocks and the nanostructure and properties of the final assembled materials. This part of the book truly illustrates the unique degree of structural control achievable when assembling nanostructures from organic macromolecules.

The synthesis and structures of organometallic polymers and polymer-coated clusters are addressed in Section 3, "Macromolecular Inorganic Assemblies". This section contains chapters on a number of subjects in this area, including assembly of metal-containing amphiphiles (Fuhrhop et al.), electroactive, metal-containing polymers (Hirao; Nishihara and Murata), polymerization of silsesquioxane-containing monomers (Kim and Chujo), metal-complexed oligopeptides (Okamura and Ueyama), and polymer-coated cluster catalysts (Toshima). Little of this section is devoted to the explicit nanostructure of the materials, and most of the chapters could have contained more information about the characterization of nanomaterials.

In the final section, "Biological Macromolecular Complexes", a variety of topics on biomacromolecular nanostructures are covered. This section includes chapters on biomolecule–metal complexes (Reedijk), biomolecular AFM (Yamaguchi and Harada), and nucleic acid–polysaccharide hybrids (Shinkai et al.), as well as two chapters on naturally occurring nanostructured biomaterials (Yamamoto and Ueyama on nacre, and Osaki on spider silk). This section is more focused on nanostructure and the properties of materials than the previous one, and the authors of each chapter do a good job of connecting macromolecular conformation and composition to useful properties.

Overall, this book would have benefited from a general introduction to the goals and challenges of applying supramo-

lecular chemistry to nanomaterials research. Readers may want to know whether the editors consider supramolecular structures and nanomaterials synonymous, or to what extent new techniques for designing and characterizing nanomaterials have uniquely impacted supramolecular chemistry. Nevertheless, the text covers a broad range of modern topics in organic nanomaterials, and readers will learn a great deal about current research in this field.

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