

Introduction: Frontiers in Polymer Chemistry

The word polymer was introduced by Berzelius in 1833. About 100 years later, during the classic period of polymer science, Wallace Carothers reviewed the entire field of polymer chemistry including that of biological polymers and of polymer physics in a single article in *Chemical Reviews* (Carothers, W. H. Polymerization. *Chem. Rev.* **1931**, *8*, 353). Today, the field of synthetic and biological polymers is impacting extensively various areas of chemistry, biochemistry, molecular biology, nanotechnology, electronics, medicine, life sciences, materials, etc., and is reviewed in almost every individual and thematic issue of *Chemical Reviews*. The present thematic issue is focused only on a very selected series of subjects in an attempt to avoid overlap with very recent thematic issues such as "Nanostructures" (Vol. 99, No. 7, 1999), "Frontiers in Metal-Catalyzed Polymerization" (Vol. 100, No. 4, 2000), "Chemical Sensors" (Vol. 100, No. 7), and "Protein Design" (Vol. 101, No. 10, 2001).

Living polymerizations and iterative synthesis are the two most advanced synthetic methods in the field of polymer synthesis. Anionic, cationic, and metathesis living polymerizations are already well-established methods for the synthesis of well-defined and monodisperse polymers that have a narrow molecular weight distribution and complex topology and architecture. Their mechanisms have been relatively well elucidated both in the case of ring opening and of vinyl polymerization reactions and therefore will not be reviewed in this thematic issue. However, living radical polymerization and other methods to produce well-defined polymers by radical reactions are currently being developed and are investigated extensively in many laboratories, in spite of the fact that this is a topic of old concern (Otsu, T. Iniferter Concept and Living Radical Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121). This issue begins with an article by Fischer, who discusses the concept of the persistent radical effect and explains the mechanism via which this concept provides access both to selective radical organic reactions and to various methods used to accomplish living radical polymerization. Gridnev and Ittel follow with an analysis of the catalytic chain transfer in free-radical polymerization and its application to the design of various classes of well-defined polymers. Hawker, Bosman, and Harth review the synthesis of new poly-

mers by nitroxide-mediated living radical polymerization. The contribution by Kamigaito, Ando, and Sawamoto provides an extensive review of metal-catalyzed living radical polymerization. Today, the most versatile method for the synthesis of polymers with complex architecture is based on living anionic polymerization. A very comprehensive review on this topic is presented by Hadjichristidis, Pitsikalis, Pispas, and Iatrou.

Synthetic methods that are borrowing the tools of biology are being actively developed for the synthesis of nonbiological and biological macromolecules. Enzymatic polymerization is one of the most recent entries to this field and is reviewed by Kobayashi, Uyama, and Kimura.

Iterative synthesis is the only synthetic method available for the preparation of biological (peptides, nucleic acids, and polysaccharides) and nonbiological oligomers with well-defined sequences and molecular weight free of chain length distribution. One of the most powerful illustrations of the utility of this synthetic strategy is in the preparation of dendrimers. They represent a class of synthetic macromolecules that have impacted dramatically the field of organic and polymer chemistry in the past decade. A contribution by Grayson and Fréchet details the convergent iterative synthesis and the applications of dendrons and dendrimers. Another relevant example, the preparation of rod-coil block copolymers, relies on a combination of iterative synthesis and living polymerizations. The self-assembly of supramolecular structures from rod-coil block copolymers is analyzed by Lee, Cho, and Zin.

Folding and chirality (including its transfer and amplification) are two of the most important events that determine the correlation between the primary structure of biological macromolecules and their tertiary and quaternary structures that ultimately are responsible for their functions and properties. Biological macromolecules know how to fold in very specific secondary structures that determine their 3-dimensional architecture and their large diversity of functions. While the understanding of folding processes in biological macromolecules is still incomplete, it is believed that its complete elucidation relies on the ability to produce synthetic nonbiological macromolecules that will exhibit the same mecha-

nism of folding, formation of 3-dimensional structure, functions, and properties at the level of sophistication displayed by the natural compounds. Hill, Mio, Prince, Hughes, and Moore provide a very comprehensive review that discusses for the first time all classes of biological and nonbiological foldamers. On related topics, Nakano and Okamoto detail the synthesis and properties of helical polymers. This theme is further developed by Cornelissen, Rowan, Nolte, and Sommerdijk in their analysis of chiral architectures from macromolecular building blocks.

Both in biological and nonbiological macromolecules the intramolecular folding process is determined by a combination of primary structure and noncovalent directional and nondirectional interactions. Most recently, combinations of various noncovalent interactions were also used to self-assemble supramolecular polymers in which the repeat units are interconnected via noncovalent rather than covalent bonds. The field of supramolecular polymers is reviewed by Brunsveld, Folmer, Meijer, and Sijbesma.

Progress in the field of chemical and biological sciences is continually impacted by the development of novel methods of structural analysis. Sheiko and Möller review a field that started to develop only in the past several years, i.e., visualization of biological and synthetic macromolecules including individual macromolecules and their motion on surfaces with the aid of scanning force microscopy (SFM). Brown and Spiess analyze the most recent advances in solid-state NMR methods for the elucidation of the struc-

ture and dynamics of molecular, macromolecular, and supramolecular systems. Finally, Ungar and Zeng discuss the use of linear, branched, and cyclic model compounds prepared mostly by iterative methods in the elucidation of the polymer crystallization mechanism by using the most advanced X-ray diffraction methods.

Although I completely agree with the following statement made by one of the pioneers of the field of polymer science: "...*there is no substitute for reading every reference, cited-second-hand citations are incredibly unreliable...*" (Morawetz, H. *Polymers. The Origins and Growth of a Science*; Wiley: New York, 1985), I hope that our readers will find that the outstanding work done by the authors mentioned above will provide an excellent and state of the art report for the *Frontiers in Polymer Chemistry* at the beginning of the 21st century. The field of polymer chemistry was born at the interface between many disciplines and today is more interdisciplinary than ever.

Finally, I express my great appreciation for the cooperation on this thematic issue to all contributing authors and reviewers and to the Editorial Office of *Chemical Reviews*.

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