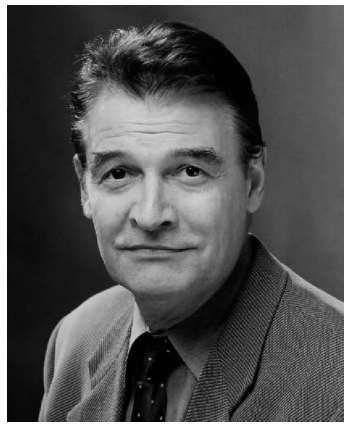
Introduction to Frontiers in Polymer Synthesis



Virgil Percec was born and educated in Romania (Ph.D. 1976). He defected from his native country in 1981 and after short postdoctoral appointments at the University of Freiberg, Germany, and the University of Akron, U.S.A., he joined the Department of Macromolecular Science at Case Western Reserve University in Cleveland (1982) as an Assistant Professor. He was promoted to Associate Professor in 1984, to Professor in 1986, and to Leonard Case Jr. Chair in 1993. In 1999 he moved to the University of Pennsylvania as P. Roy Vagelos Professor of Chemistry. Percec's research interest lies at the interface between organic, bioorganic, supramolecular, polymer chemistry, and liquid crystals, where he contributed over 620 refereed publications, 50 patents, and over 1000 endowed and invited lectures. His list of awards includes Honorary Foreign Member to the Romanian Academy (1993), Humboldt Award for Senior American Scientists (1997), NSF Research Award for Creativity in Research (1990, 1995, 2000), PTN Polymer Award from The Netherlands (2002), the ACS Award in Polymer Chemistry (2004), the Staudinger−Durrer Medal from ETH (2005), the International Award of the Society of Polymer Science from Japan (2007), and the H. F. Mark Medal from the Austrian Research Institute for Chemistry and Technology (2008). He is a Fellow of IUPAC (2001), PMSE Division of ACS (2003), AAAS (2004), and RSC (2008). He holds Doctor Honoris Causa Degrees from the Polytechnic University, Jassy, Romania, and from the University of Athens, Greece (both from 2007). He is the editor of the *Journal of Polymer Science, Part A: Polymer Chemistry* (since 1996) and of the book series *Liquid Crystals* and serves on the Editorial Boards of 20 international journals.

One of the pioneers of the field of Polymer Science made the following statement in the Preface to his book on the history of polymers: "*I found out quickly that there is no substitute for reading every reference cited—second-hand citations are incredibly unreliable*."[1] In spite of the fact that I agree with this statement, in an interval of less than ten years I accepted for the second time[2] the invitation of Josef Michl to edit a Thematic Issue of Chemical Reviews on Polymer Synthesis. The first reason was that the Editors of this journal and the members of their Editorial Board and Editorial Office provide an example of dedication and leadership for the other editors in the field of chemistry, and therefore, it was impossible to turn them down. The second reason is that some of the current electronic sources of information are no more reliable than secondhand citations, and therefore, I feel that comprehensive reviews written by premier practitioners are needed more than ever before. The third reason was that, at this time, the field of polymer synthesis is already accepted as a traditional discipline of chemistry and currently is assuming the leading role of bridging between organic, organometallic, and supramolecular chemistry, catalysis, biology, medicine, and nanotechnology. Therefore, it is very important to read the most recent developments at the Frontiers in Polymer Synthesis described by the inventors of this interdisciplinary field. Since the previous thematic issue was published,[1] several landmark discoveries produced by the field of polymer synthesis were recognized as providers of unprecedented impacts in novel functional materials through conducting organic polymers[3] and in synthetic methods for organic, medicinal, polymer, and supramolecular chemistry through metathesis reactions.[4] These topics were extensively reviewed and will not be discussed again in this thematic issue.

The ultimate goal of polymer synthesis is to design, through a complementary and synergistic combination of covalent and supramolecular methods, synthetic polymers that approach the structural complexity and fidelity of biological macromolecules. These synthetic polymers would have to ultimately provide functions on demand with the aid of their precise primary structure. While these synthetic methods are in their early stages of development, traditional but more efficient synthetic methods for polymer synthesis continue to be elaborated. The goal of this Thematic Issue is to highlight with a group of 27 reviews the most recent advances in the development of new synthetic methods and strategies of polymer synthesis and discuss their use in the design of polymers with complex topology and architecture and the self-assembly of complex systems.

The current state of the art in polymer synthesis relies on living polymerization methods that were discovered for carbanionic species in 1956.[5a,b] They were followed by living polymerizations proceeding by carbocations,[5c] metathesis[4] and free radicals.[5d,e] In the first four reviews, Sawamoto and co-workers, Yamago, Rosen and Percec, and Satoh and Kamigaito discuss advances in novel methodologies for living radical polymerization of olefins, for the elaboration of complex polymer topology and the control of tacticity. Chen and Nozaki and co-workers review the developments of coordination polymerization of polar vinyl monomers by single-site metal catalysts. Aoshima and Kanaoka highlight living cationic polymerization of functional monomers. Kobayashi and Makino present the latest developments in enzymatic polymerization, while Akagi discusses the synthesis of helical polyacetylene by asymmetric polymerization in a chiral liquid crystal field. The use of living radical polymerization to develop various bioapplications, mostly by RAFT, is reviewed by Davis, Perrier, and co-workers, while Klok and co-workers discuss the synthesis of polymer brushes by living radical polymerization. Hadjichristidis and co-workers survey the living ring-opening polymerization of *N*-carboxyanhydrides of α-aminoacids for the synthesis of well-defined peptides, while Kricheldorf teaches us how to synthesize biodegradable and biocompatible polymers by ring-opening polymerization of various heterocyclic compounds. One of the most recent developments in polymer synthesis involves the transformation of step condensation polymerization reactions[6] into chain polymerization reactions and their use in the generation of living condensation polymerization. This topic is reviewed by Yokozawa and Yokoyama.

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Wooley, Hawker, and co-workers expand the click chemistry concept of Sharpless,[7a] to a diversity of organic reactions, and develop orthogonal polymer synthesis methods based on new click reactions. For over one century, covalent polymerization reactions were the main tool of polymer synthesis. In the past 20 years, the merging of supramolecular synthesis[7b] with covalent synthesis led to supramolecular polymerization, a topic discussed mechanistically by Meijer and co-workers. Chemists usually start reactions with heat, light, or electricity. A far less common option is to use mechanical stress.[7c] In their review, Moore and co-workers demonstrate that stress not only triggers reactions in polymers but can also direct their course and provide new functions. Design of acetylenic polymers for various functions is reviewed by Tang and co-workers, while Hsu and co-workers review the synthesis of conjugated polymers for organic solar cell applications.

Combinations of synthetic methods were used for the synthesis of polymers with complex topologies such as for the case of hyperbranched polymers discussed by Voit and Lederer, rotaxanes discussed by Harada and co-workers, and polycatenanes discussed by Niu and Gibson. Even more complex topologies and architectures are highlighted by Li and Aida in a review on dendrimer porphyrins and phthalocyanines. Complex polysaccharide derivatives, widely used in chromatographic separation of enantiomers, are discussed by Ikai and Okamoto, while Yashima and co-workers review the synthesis, structure, and functions of helical polymers. Biohybrid complex polymer capsules and their design, synthesis, and fascinating applications are reviewed by van Hest and co-workers. A comprehensive review by Percec and co-workers on dendron-mediated self-assembly, disassembly, and self-organization of complex systems brings the field of polymer synthesis close to the complexity, precision, and functions of biological systems. At this time, the combination of covalent and supramolecular synthesis is approaching the size, precision, and complexity of biological macromolecules. Progress in this field requires the development of efficient iterative methods,[7d] novel nonstatistical[7e,f] synthetic methods, analytical and structural analysis methods, and novel strategies to discovery and prediction,[7g] as well as the transplant and adaptation of structural analysis methods from structural biology to synthetic systems.

Finally, I would like to express my greatest 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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1. References

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