

# MATERIALS-CHIRALITY

Mark M. Green

R. J. M. Nolte

E. W. Meijer

EDITORS

VOLUME 24 IN TOPICS IN STEREOCHEMISTRY

SCOTT E. DENMARK AND JAY SIEGEL, SERIES EDITORS

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# MATERIALS-CHIRALITY

EDITED BY

MARK M. GREEN  
R. J. M. NOLTE  
E. W. MEIJER

VOLUME 24  
TOPICS IN  
STEREOCHEMISTRY

Series Editor

SCOTT E. DENMARK  
JAY SIEGEL

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# **MATERIALS-CHIRALITY**

**VOLUME 24**

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## INTRODUCTION TO THE SERIES

Since its first appearance in 1967, the *Topics in Stereochemistry* series has stood as the standard-bearer for advances in the broad field of stereochemistry. The visionary founders of the series anticipated, with remarkable foresight, the extraordinary growth and impact that stereochemistry has had on all reaches of the chemical enterprise. Fortunately, there is no cease of interest in the importance of stereochemistry as the discipline of chemistry evolves and its borders expand and diffuse into the related fields of biology, medicine, physics, materials science, chemical engineering, and environmental science.

The field of stereochemistry serves as a unifying theme for the expanded definition and diversification of chemistry. The consequences of molecular and macromolecular shape and topology are central to issues of chemical reactivity, physical properties, and biological function. With that view, the importance of stereochemistry had never been greater, and it is hoped that this series will provide a forum for documentation of significant advances in all of these subdisciplines of chemistry.

The *Topics in Stereochemistry* series has set itself apart by maintaining a remarkable balance of chapters that are both definitive, standing the test of time, and current, addressing the impact of stereochemistry at the most exciting frontiers. As a student and researcher, I have often turned to chapters in *Topics in Stereochemistry* for the foundations and the state of the art in new areas of interest. It is my hope that the series continue to enjoy that level of confidence in the chemistry community and that it retain, in this second incarnation, the esteem that the founders have worked so hard to establish.

I am fortunate in having been able to enlist the help and guidance of an international board of editorial advisors who have provided great assistance by suggesting chapter topics and suitable authors for articles both here and in future volumes. While I am grateful for the assistance of this editorial advisory board, it is the editor and the authors who are solely responsible for any shortcomings of *Topics in Stereochemistry*.

S. E. DENMARK

## FOREWORD

This volume, dedicated entirely to the field of materials science, signals the scientific, conceptual as well as editorial evolution of this series. In my introduction to the 1999 relaunch of this series, I noted that, more than ever, stereochemistry serves as a unifying theme for the expanded influence of chemistry on the "... related fields of biology, medicine, physics, materials science, chemical engineering and environmental science." Volumes 22 and 23 have been consciously composed to represent a range of areas in which chirality plays a central role in the understanding and practice of the enterprise. However, the importance of molecular and macromolecular stereochemistry is perhaps most evident in the general field of materials science. Indeed, two earlier chapters in this series by Goodman (Volume 2) and Farina (Volume 17) have treated individual aspects of polymer stereochemistry.

When Professor Mark Green joined the editorial board, he suggested that a single volume dedicated to Materials-Chirality would be both timely and of broad interest to the chemistry community. Better still, he volunteered to serve as volume editor along with Bert Meijer and Roeland Nolte after he and Dave Walba had organized an ACS Symposium dedicated to Mario Farina a few years before under the title Materials-Chirality. This idea intrigued me as there had been only one thematic volume in this series, the one in 1981 dedicated to inorganic stereochemistry edited by Professor Gregory Geoffroy.

After reading the chapters in this volume, it is clear that the editors have not only done a spectacular job but have also chosen authors whose expertise and writing skill are certain to capture the imagination of practitioners in the field and generalists alike. The regular readers of this series, whose focus may reside primarily in small-molecule stereochemistry, will find a fascinating world wherein chirality takes on even greater significance in the relationship of structure with physical and chemical properties. This volume is destined to become the definitive resource of the state of the art in Materials-Chirality

SCOTT E. DENMARK

*June 2003*



## PREFACE

Materials take us beyond the small molecule into a world characterized by very large molecules and by arrangements among molecules, a world from which the concept of chirality found its origin. There is no better example of this connection between materials and chirality than the famous experiment of Pasteur in which his hands, on dissolving the separate tartrate crystals, took us from the observation of chirality as a material characteristic to chirality directly derived from a molecular property. This volume demonstrates that the continuing evolution of the ideas of chirality is returning us to the world of materials, to a domain beyond the chiral properties of individual molecules, and in doing so is providing us with new ideas that were not previously accessible. Let's take a quick overview of the origins of chiral ideas before we find out how chiral materials, while obeying the familiar rules, are offering a stereochemistry not previously imagined.

The best source we know for the historical development of the chirality concept is in T. M. Lowry's text, *Optical Rotatory Power*, published originally in 1935 and republished by Dover Press in 1964. This classic treatment of the subject informs us of the roles of Jean Baptiste Biot (1774–1862) and Augustin Fresnel (1788–1827), who investigated the nature of rotatory polarization of light, and how Biot reported in 1815 that the light phenomenon investigated in quartz crystals could be reproduced in organic substances, "oils of turpentine [sic], laurel, and lemon, and in alcoholic solutions of camphor." Biot's interest in exploring the rotatory phenomenon across the spectrum of the states of matter was shown in early experiments, which ran the gamut from the glassy states formed by sugars to the gaseous state formed by turpentine. The latter led to a famous accident. In 1817, in trying to understand the effect of dilution on the rotatory power of turpentine, he convinced the peers of an ancient church to allow him to conduct an experiment in their cloister. Biot needed the space to construct an apparatus in which he would fill a long tube with turpentine vaporized from the liquid using the heat from a boiler. He set the church on fire when the boiler exploded, but not before he recorded the fact that the vapor had rotatory power, the first demonstration of this effect in the gas state.

By 1815 Biot had extended his observations to tartaric acid, the molecule later to be the subject of Pasteur's critical investigations. As described by Lowry, by 1832 Biot's studies of tartaric acid allowed him to report "that an aqueous solution of tartaric acid, containing approximately 50 per cent by



weight of the acid, gave a rotation of  $+8.5^\circ$  (for white light with its optical center of gravity in the yellow), but that its rotation was 'stronger for the less refrangible rays.'"

Pasteur was twenty-six years old in 1848 when he carried out the experiment that introduced the concept of "molecular dissymmetry." The experiment is best described in Pasteur's own words, given to us in translation by Lowry: "I hastened therefore to reinvestigate the crystalline form of Mistscherlich's two salts. I found, as a matter of fact, that the tartrate was hemihedral, like all the other tartrates which I had previously studied, but, strange to say, the paratartrate was hemihedral also. Only the hemihedral faces, which in the tartrate were all turned the same way, were inclined in the paratartrate sometimes to the right and sometimes to the left. I carefully separated the crystals which were hemihedral to the right from those hemihedral to the left, and examined their solutions separately in the polarizing apparatus. I then saw with no less surprise than pleasure that the crystals hemihedral to the right deviated the plane of polarization to the right, and that those hemihedral to the left deviated to the left."

Molecular theory in 1848 could not yield understanding of the relationships among the solid salts, the solutions they formed, and the optical activity. But Pasteur was able to ask a question that pointed everyone in the correct direction. Again taking Pasteur in translation by Lowry: "Are the atoms of the dextro-acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron, or disposed according to some particular dissymmetric grouping or other?"

Just as Pasteur was a child when Biot reported the detailed nature of the rotatory power of tartaric acid in 1832, Joseph Achille Le Bel (1847–1930) and Hemricus Jacobus van't Hoff (1852–1911) were children when Pasteur asked the question quoted above. But both gave detailed answers to Pasteur's question when they were both about the same age as Pasteur was when he separated the hemihedral crystals of sodium ammonium tartrate. In 1874 Le Bel published a memoir in French in which he stated two general principles introducing the structural basis of optical activity arising from tetrahedral carbon while in the same year van't Hoff independently published a pamphlet in Dutch introducing these concepts in more detail. How influential van't Hoff's pamphlet was at the time is attested to by its rapid translation into both French and German. The latter translation subjected van't Hoff to severe criticism from Kolbe, who occupied a distinguished position in chemistry at the time, but in fact the last word on van't Hoff's work is best given to Lowry writing in 1935: "In spite of the criticisms with which the German translation was assailed by Kolbe, the space-chemistry of carbon compounds, as set out in van't Hoff's pamphlet, has held good, without correction and almost without addition, during a period of at least half a century; and even today it is so

sound that modern electronic formulae may be judged very largely by their conformity to the principles laid down by van't Hoff in 1874."

Now more than 128 years later this concept endures and has been one of the foundations of chemistry inspiring and guiding chemists in their endeavors to design and study molecular architectures of increasing complexity. Although unexpected in those early years in the development of chemistry, the concept connecting the three-dimensional arrangements of atoms in space to isomerism and chiral optical phenomena has been critical in both the development of polymer science and later in supramolecular chemistry. These fields can be gathered under the descriptor materials-chirality, a term first created in 1996 for an American Chemical Society symposium honoring the memory of Mario Farina. Professor Farina played an early role in the understanding of how the formation of isotactic polymers required chiral information in the catalyst, a key piece of the puzzle leading to the Nobel Prize for Ziegler and Natta. His chapter in *Topics in Stereochemistry* in 1987 still stands as a masterpiece in this field. And chirality is no less important in the field of supramolecular chemistry, another area distinguished by Nobel Prizes to Pederson, Cram, and Lehn. It was thought timely to focus in Volume 24 of this series on these two fields and organize a volume of *Topics in Stereochemistry* titled *Materials-Chirality*.

The different chapters in Volume 24 have been arranged in such a way that some justice is given to history and the chronological order of events in materials-chirality.

Chapter 1, by Guerra, Cavallo, and Corradini, discusses in detail both the historical and modern aspects of stereoregular olefin polymerization, a field that arose with the first uses of the catalyst that came to be known as Ziegler-Natta, and a field that these authors greatly contributed to and therefore write about with an intimate knowledge.

De Rosa's overview in Chapter 2 effectively links up with the first chapter in that polymer crystallinity yielded the essential first insight into the workings of the Ziegler-Natta catalyst. This chapter provides a penetrating analysis of the origins of the helical conformations found in stereoregular polymers in the solid state, including newly discovered phenomena, such as frustration and symmetry-breaking effects, which regulate the crystal packing of polymer chains.

Many studies, the first of which began shortly after the discovery of stereoregular polymerization of olefins, demonstrated that macromolecules could adopt stable helical conformations not only in the solid state but also in solution. These efforts have led to the realization that certain helical polymers reach a level of chiral recognition adequate for commercial development as an important aspect of chromatography. Researchers from the leading laboratory in this field, Okamoto, Yashima, and Yamamoto, have written Chapter 3 painting a detailed picture of the current status and future possibilities in this

field. The authors provide insights into the origins of the chiral separations and the mechanisms of the recognition processes found between the racemates and the chiral polymeric materials.

Optically active poly(silanes) constitute a special and intriguing class of helical polymers because they contain a sigma-conjugated main chain. As a result of this conjugation, polymers and copolymers of this type display very interesting chiroptical properties, which are analyzed and discussed together with other features of poly(silanes) in a state-of-the-art account by Fujiki, Koe, Nakashima, and Toyoda in Chapter 4. There are several other classes of helical polymers with fascinating chiral properties, which were not included in this volume but which can be recommended for study. Among these are the polyisocyanates, which are responsible for quantitatively defining the cooperative characteristics of chiral amplification but which have been adequately reviewed in recent years, and as such do not require incorporation in this volume.

Well into the twentieth century, chemists and physicists struggled with the problem of whether very large molecules could exist. Staudinger contributed greatly to resolving this quandary by a series of elegant experiments demonstrating that macromolecules are held together with the same kinds of bonds as in small molecules. It is interesting to note that with the advent of supramolecular chemistry we discover how the physical bonding forces so vigorously but incorrectly defended as solely responsible for the formation of polymers can, in fact, lead to macromolecules via self-assembly and self-organization. These phenomena have led to new and sometimes unexpected architectures with interesting properties, sometimes reminiscent of those found in nature. The next chapters bring us into this area.

In Chapter 5, Spector, Selinger, and Schnur describe such supramolecular architectures, which are formed in water from compounds derived from natural materials that have been altered in their ability to pack. Chirality plays an essential role in this area. However, there are the questions as to why these supramolecular structures are formed, the answers to which can improve approaches to control their architectures and dimensions. These authors evaluate several theories proposed to answer these fundamental questions.

The number of building blocks for supramolecular self-assembly is virtually unlimited. Chapter 6, by Brunsveld, Rowan, Nolte, and Meijer, describes studies on disk-shaped molecules which are programmed to stack in a helical fashion, leading to novel kinds of twisted fibers as well as lyotropic and thermotropic liquid crystalline materials.

In Chapter 7, Gottarelli and Spada extend further the theme of liquid crystalline materials. They note that although much is understood, important mysteries remain about the relationships between the handedness of cholesteric liquid crystalline phases and the chirality of the constituting building blocks. This may seem surprising given the intense interest in these materials, including their

widespread commercial use, but it testifies to the subtlety of chiral interactions. Their chapter provides a detailed analysis with directions pointed to for further study and with the conclusion that the problem is far from being solved.

This volume of *Topics in Stereochemistry* could not be complete without hearing about ferroelectric liquid crystals, where chirality is the essential element behind the wide interest in this mesogenic state. In Chapter 8, Walba, a pioneering contributor to this area, provides a historical overview of the earlier key developments in this field and leads us to the discovery of the unique banana phases. This discussion is followed by a view of the most recent results, which involve, among others, the directed design of chiral ferroelectric banana phases, which display spontaneous polar symmetry breaking in a smectic liquid crystal.

Nonlinear optical techniques are extremely useful in characterizing the chiral properties of materials, as is pointed out by Verbiest and Persoons in Chapter 9. These authors give an in-depth discussion of this tool, both from an experimental and theoretical point of view, paying special attention to the characterization of chiral surfaces and thin films. In the second part of their contribution they highlight the role chiral materials can play in the field of nonlinear optics and photonics, which opens the way for a variety of applications.

The idea of a *Topics in Stereochemistry* volume on materials-chirality was conceived following the 1996 American Chemical Society meeting entitled Materials-Chirality dedicated to the memory of Mario Farina noted above. One hundred and twenty-five years after van 't Hoff and Le Bel, chirality in its various forms has pervaded all molecular science and now is finding its way increasingly into fields under the heading of materials. It is rewarding to see that the various contributions of the authors bear out this increasing importance of chirality in the materials area. We hope that the nine chapters in this volume will inspire many readers and act as seeds of inspiration which grow into sparkling ideas, in particular for the younger generation of chemists who are supposed to take the lead in the further development of science, in a similar way that Pasteur and then van 't Hoff and Le Bel did as young scientists in their time.

As a final note, there was a tenth chapter intended for this volume to be written by André Collet. He had agreed to write this chapter but could not, adding one additional loss among many of far greater importance arising from the death of this eminent stereochemist and gentleman and friend to so many.

July, 2003

MARK M. GREEN  
BERT MEIJER  
ROELAND NOLTE

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# Chapter 1

## Chirality of Catalysts for Stereospecific Polymerizations

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## 1 INTRODUCTION

Ziegler–Natta catalysts are formed from reactions involving transition metal compounds of groups 4–10 (mainly titanium, vanadium, zirconium) with alkyl, aryl, or hydrides of groups 1–4 under inert conditions.<sup>1–3</sup> These catalysts are of great industrial relevance since they are used for the production of several polymeric materials: thermoplastics like high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and isotactic polypropylene (and, in much smaller volumes, isotactic poly-1-butene and poly-4-methyl-pentene) and rubbers like polybutadiene, polyisoprene, and ethene–propene copolymers. Ziegler discovered these catalytic systems in 1953,<sup>4</sup> while Natta and co-workers discovered the synthesis of stereoregular polymers in 1954 by using similar catalytic systems.<sup>5</sup>

According to International Union of Pure and Applied Chemistry (IUPAC) nomenclature we define as a *regular polymer* a linear polymer whose molecules can be substantially described by a unique species of constitutional units in a unique sequential arrangement. We define a polymer as *stereoregular* if the succession of configurations is regular too (we mean by configuration the spatial arrangement of the various bonds without considering the multiplicity of arrangements which arise from rotation around single bonds).

Cellulose, guttapercha, and natural rubber are examples of stereoregular polymers which nature is able to synthesize. Research conducted in the three decades after 1922, when Staudinger first proposed the term *macromolecule*, led to the synthesis of semicrystalline polymers—nylons by polycondensation and low-density polyethylene by polyaddition, for example—all polymers of great practical importance. These are regular polymers whose constitutional units can have only a unique configuration. Consequently, they do not show problems of stereoregularity. On the other hand, the vinyl polymers already known at the time—poly(vinyl chloride) or polystyrene obtained by radical polymerization processes, for example—resulted substantially or totally amorphous at a roentgenographic examination even if they had a quite regular constitution. In any case, the researchers of those years, in general, did not recognize that the lack of crystallinity was to be related to the lack of regularity in the succession of configurations.

In the early 1950s there was the quite contemporary discovery—in three different laboratories—of processes for the polymerization of ethene at low pressure using solid catalysts: The catalyst used by the Standard Oil of Indiana was Mo(VI) oxide supported on aluminum oxide; the one by Phillips Petroleum was Cr(VI) oxide still supported on silica/alumina; the catalyst studied by Ziegler and his co-workers at the Max Planck Institute at Mühlheim

resulted from the reaction between  $\text{AlEt}_3$  and  $\text{TiCl}_4$ . Nowadays it is hypothesized that the mechanism of polymerization (insertion of a monomer molecule into a metal-carbon bond) is quite similar for all the three catalytic systems.

The polyethylene obtained (the already cited HDPE) is more highly crystalline and more rigid and dense and has a much more regular structure than the one previously known and obtainable at very high temperature and pressure and which had been industrially produced in the previous 15 years (now called low-density polyethylene, LDPE). The latter shows macromolecules with both long and short branches and is consequently less crystalline than the almost completely linear HDPE. It is obvious that polyethylene does not present tertiary carbon atoms in its constitutional unit, hence it does not show problems of stereoisomerism.

In the laboratories of Natta in Milan it was found that the Ziegler catalysts could polymerize (besides ethene) propene, styrene, and several  $\alpha$ -olefins to high linear polymers. These polymers appeared crystalline when examined by X-ray diffraction techniques and were able to give oriented fibers. In less than one year since the preparation of the first polymer of propene, Natta was able to communicate, in the meeting of the Accademia dei Lincei of December 1954 in Rome, that a new chapter had been disclosed in the field of macromolecular chemistry, due to the discovery of processes to obtain polymers with an extraordinary regularity in their structure in terms of both chemical constitution and configuration of the successive monomeric units along the chain of each macromolecule.

This regularity is particularly impressive considering that each propene monomer unit can be inserted in a polymer molecule in four (constitutionally and/or configurationally) different ways. It follows that a chain molecule with 1000 monomer units, for instance, can be built up in  $4^{1000} \approx 10^{600}$  different ways. The lattice constants of several new crystalline polymers like polypropylene, poly-1-butene, and polystyrene were determined by X-ray studies. The identity period along the chain axis, as determined by fiber diffraction patterns, resulted to be of the order of  $6.5 \text{ \AA}$  and could be attributed to a chain segment containing three monomeric units. Therefore, it was to be excluded that the crystallinity could have originated from a regular alternance of monomeric units characterized by enantiomeric steric configurations. On the contrary, it was evident that the polymeric chains had to be constituted by regular successions of monomeric units with the same steric configuration.<sup>5</sup> This kind of structure was denominated *isotactic* (from the greek words *isos*, "the same", and *tassein*, "to put in order"). The examination of the crystal structure of isotactic polymers showed that the chain conformation of these polymers is always helical.