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The Stereochemistry of Macromolecules *(In Three Volumes)*

Volume 3

Edited by A. D. KETLEY

W. R. GRACE & CO.
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**The Stereochemistry
of Macromolecules** (*In Three Volumes*)

VOLUME 3

“Nearly all great technological advances depend upon discoveries so unexpected as to be unplannable. Nature in her own time reveals her secrets to the patient questioner, and the plain fact is that nature is infinitely cleverer than man.”

SIR CYRIL HINSELWOOD, *The Listener*, Sept. 2, 1965.

Introduction to the Series

Most synthetic polymers contain either asymmetric atoms or double bonds which can give rise to geometrical isomers. As long as thirty years ago, the problem of stereoisomerism in polymer chains was discussed. However, the field lay dormant since, at that time, it was not possible either to synthesize polymers which were highly stereoregular or to measure the degree of regularity in the chains of those polymers which were known.

In the late 1940's, Schildknecht obtained indications that some steric control could be exerted by the catalyst in the polymerization of vinyl ethers and Morton developed catalysts which enabled him to influence the geometrical isomerism in diene polymers. However, it was not until Natta showed that transition-metal-based catalysts could exert a very high degree of steric control in the polymerization of simple olefins and a wide variety of other monomers that this field became a major area of research.

To some extent, the excitement surrounding the synthesis of highly stereoregular crystalline polymers has overshadowed another recent development of almost equal scientific significance—the enormous increase in our knowledge of the stereochemistry of polymers whose chains do not possess a high degree of stereoregularity. Undoubtedly the most important contribution to this latter problem has come from the application of nuclear magnetic resonance spectroscopy.

In Volume 1 of this three-volume series, we have attempted to bring together the latest knowledge of Ziegler-Natta polymerization. In Volume 2, we are concerned mainly with the stereospecific polymerization of monomers by catalysts other than the Ziegler-Natta type. In both volumes an attempt has been made to emphasize the mechanism of these reactions. In general there is very little real understanding of the way in which the stereochemistry of the growing chain is controlled, and even the starting point for any discussion, the structure of the catalyst, has not, in most cases, been elucidated. Many of the mechanisms which have been proposed in the literature are pure speculation and are not based on any experimental facts or accurate chemical knowledge. Consequently,

the authors were asked not to impartially present ideas of this kind but to critically evaluate them and emphasize those which seem most sound. In this respect, we have given a special place to the ideas of Cossee and Arlman on Ziegler-Natta catalysis, not because, as these authors themselves would agree, they represent a definitive mechanism and all controversy has now ceased, but because the ideas are most in keeping with current knowledge and their approach seems to be one which could be most fruitfully followed to plan further research.

In Volume 3, the ways in which the steric structure of polymers may be determined are discussed, together with the way such structural features influence the physical, mechanical, and chemical properties of polymers.* We have also chosen to include in this volume some discussion of the effects of stereochemistry in processes involving biological macromolecules. This, obviously, is a topic which is too huge in scope to receive comprehensive treatment in a book mainly concerned with synthetic polymers. On the other hand, it is far too important to neglect. We have, consequently, aimed at including some material which might stimulate polymer chemists to work at the interface between their own field and biochemistry. We feel strongly that this kind of interaction is of enormous importance. The direct study of biological systems is made difficult by their overwhelming complexity. Small molecules are often, on the other hand, too far removed as realistic models for meaningful extrapolation to biological systems to be made. Synthetic polymers, in many cases, may be the best compromise between reality and simplicity.

Perhaps because polymer chemistry has such great industrial importance, chemists and physicists working in other areas have, it seems, sometimes regarded it as a relatively uninteresting field for research. We hope that these volumes will help to show that polymer chemistry is, in fact, an area of almost infinite fascination. The problems are often tremendously complex but the rewards for solving them are correspondingly great.

Acknowledgments

To the following, our sincere thanks: Above all, to the authors who gave their time and also to their long-suffering wives, one of whom threatened to send me a bowl of poisoned fruit; to W. R. Grace & Co.

* It is assumed that most of the readers of Volumes 1 and 2 will be acquainted with the nomenclature used to describe steric arrangements in polymers. For any who are not, this nomenclature is described in Chapter 1 of Volume 3 and in *Die Makromolekulare Chemie*, **82**, 1 (1965).

and in particular to Dr. F. X. Werber and Dr. T. R. Steadman for their encouragement in this project and for putting the facilities of the Washington Research Center at my disposal; to Blanche White and Gabriella Schwarzman for their assistance in searching the literature and in a thousand other ways; to Doris Gardner and Lois deCheubel for being unflagging, loyal typists; and to Jennie Touchette for drawing and redrawing figures at short notice when she would rather have been skiing or sunning on the beach.

A. D. K.

August, 1967

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CHAPTER 1

Chain Conformation and Crystallinity

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I. CONFIGURATION OF STEREOREGULAR POLYMERS

A. Definitions

The constitution of a compound specifies which atoms in the molecule are bound to one another and with what type of bonds, without regard to

their spatial arrangement (1). A polymer is said to be regular when its constitution is regular; that is, its constitution is described by the enchainment of conventional base units all of the same type, in a head-to-tail sequence (2).

The configuration of a compound specifies the spatial arrangement of bonds in a molecule (of a given constitution) without regard to the multiplicity of spatial arrangements that may arise by rotation about single bonds. The configuration of a polymer is regular, and the polymer is said to be stereoregular, when its constitution is regular, and the law of succession of configurations of successive base units is assigned (3).

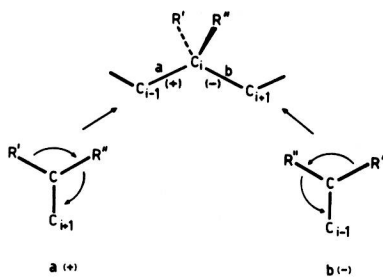
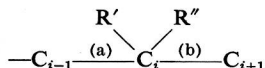


Fig. 1. Tetrahedral stereoisomeric centers. Definition of (+) and (-) bonds.

Different configurations of a regular polymer arise from the existence of stereoisomeric centers. The more important stereoisomeric centers that are found along the chain of a polymer are as follows:

1. Double bonds, which can have a *cis* or *trans* configuration
2. Tetrahedral stereoisomeric centers, that is, carbon atoms along the chain, bonded to two different substituents R' and R''

As regards the second type of stereoisomeric center, it is important to note that the two bonds of the chain adjacent to the carbon atom constituting the stereoisomeric center can be distinguished from a configurational viewpoint as (+) or (-) bonds (Fig. 1). This is also true where the carbon atom is not optically active. We shall designate by the (+) sign, with respect to the stereoisomeric center C_i , a bond adjacent to C_i along a chain



such that, as we look down the C_{i-1} — C_i bond (a) or the C_{i+1} — C_i bond (b), we see that the substituents C_{i+1} , R' , and R'' or C_{i-1} , R' , and R'' succeed each other by a clockwise rotation. R' is conventionally defined

as being bulkier than R'' (4). We can define a $(-)$ bond in an analogous manner. It is clear that, if (a) is $(+)$ with respect to the stereoisomeric center C_i , (b) must be $(-)$, and vice versa; bonds astride a tetrahedral stereoisomeric center are always opposite in sign by definition.

Two monomeric units are identical, from the configurational viewpoint, when corresponding bonds are characterized by the same set of $(+)$ and $(-)$ signs; they are configurationally enantiomorphous if corresponding bonds are characterized by opposite signs. Hence, insofar as the chain

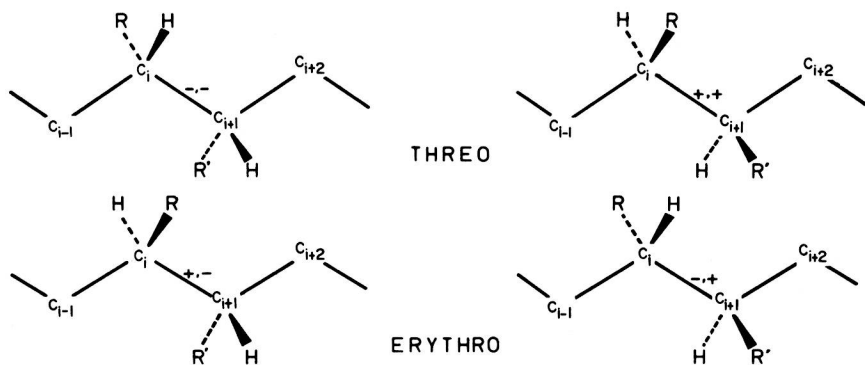


Fig. 2. *Threo* and *erythro* relative configurations.

atoms are concerned, enantiomorphous configurations of a monomeric unit can be obtained simply by changing all the configurational signs in an orderly manner.

As regards polymers having tetrahedral stereoisomeric centers, we call a polymer "isotactic" if it is formed from monomeric units with regular enchainment which are configurationally identical for long sequences of the chain and "syndiotactic" if it is formed from monomeric units with regular enchainment, alternately enantiomorphous from a configurational viewpoint. Isotaxy and syndiotaxy are the only two possibilities of stereo-regular enchainment of order 1.

Whenever a monomeric unit contains more than one tetrahedral stereoisomeric center, it is necessary to define the relative configuration of the centers. In the case of two adjacent stereoisomeric centers, for instance, $-\text{CHR}-$ and $-\text{CHR}'-$, the bond connecting them can be assigned two configurational signs (Fig. 2). The pairs $(-, -)$ or $(+, +)$ define a relative configuration *threo*, whereas the pairs $(-, +)$ or $(+, -)$ define a relative configuration *erythro*.