

**Newer Methods
of Polymer Characterization**

Edited by B. K_E

NEWER METHODS OF POLYMER CHARACTERIZATION

Edited by BACON KE

*Charles F. Kettering Research Laboratory
Yellow Springs, Ohio*

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INTRODUCTION TO THE SERIES

This series was initiated to permit the review of a field of current interest to polymer chemists and physicists *while* the field was still in a state of development. Each author is encouraged to speculate, to present his own opinions and theories and, in general, to give his work a more "personal flavor" than is customary in the usual reference book or review article. Where background material is required to explain a new development in the light of existing and wellknown data, authors have included it and, as a result, some of the volumes are lengthier than one would expect of a "review."

We hope that the books in this series will generate as much new research as they attempt to review.

H. F. MARK

E. H. IMMERGUT

PREFACE

This volume represents a collective effort to present the newest methods and new refinements of established methods of characterizing high polymers. The tremendous growth of polymer science in recent years and especially the discovery of stereo-regular polymers have created a demand for advanced physical techniques and sophisticated instrumentation as tools of investigation. However, descriptions of the newer methods are mostly still scattered in the current journal literature, where, because of space limitation, detailed treatment is usually not found. The present volume has been conceived in the hope of presenting these newer methods in a more comprehensive manner that may lead to their wider use and thus stimulate further development.

Because the stereo-regular polymers are so intimately associated with the newer characterization methods, a separate chapter on the subject of "microtacticity" was included. Only one chapter deals with the preparative aspect, namely, fractionation. Even here only the elution chromatographic method for polyolefins was singled out. Six chapters may be placed in the category of optical methods. These are polarization and deuteration in infrared spectra, birefringence and light scattering from solid polymers, optical rotatory dispersion, fluorescence polarization, small-angle x-ray diffraction, and electron diffraction. The chapter on nuclear magnetic resonance deals only with the high-resolution technique. The two thermal methods are differential thermal analysis and the novel method of measuring heat effect during mechanical deformation. The remaining five chapters deal either with solution properties or topics of a miscellaneous nature: light scattering and osmometry at elevated temperatures, density-gradient ultracentrifugation, flow birefringence, elasto-osmometry and polymer monolayers.

We have endeavored to include in this volume most of the newer methods useful for modern polymer research but have also tried to avoid overlapping on any information that can be readily found in standard monographs. The editor is well aware of the difficulties posed by diversity in subject matter and multiple authorship. Effect has been made to achieve insofar as possible a balanced and uniform presentation. Each author was asked to give a brief exposition of the theoretical basis of the method, describe the apparatus and experimental manipulations only when such

information is not easily available, concentrate on illustrating the application of the technique with a wide range of examples, and most important of all, inform the reader of the scope of the method and its potentialities for polymer research.

As editor, I have been fortunate in being able to secure the collaboration of an international team of authors well known in their respective fields, and my thanks goes to each one of them. In the preparation of this volume I have received helpful advice from Dr. E. H. Immergut and patient assistance from the staff of Interscience Publishers, to whom I express my sincere appreciation.

Yellow Springs, Ohio
January 1964

BACON KE

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I. STUDIES OF MICROTACTICITY

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Natta's announcement (1) in 1955 describing the stereoregular polymerization of olefins set into motion a concerted effort by polymer chemists throughout the world to prepare and characterize a variety of stereoregular polymers. It is difficult to explain why these important problems should have received such scant attention prior to Natta's disclosure, for the concept of stereoregularity had been clearly formulated at an earlier date (2), and the profound influence of stereoregularity upon the mechanical properties of polymers had previously been demonstrated by at least two published examples (3,4). However, once this effort was begun, it assumed prodigious proportions. The development of polymerization procedures received first priority, but, as these began to come under control,

the need for adequate means for characterizing tacticity grew more urgent. This presented a challenge to the physico-chemical methods previously developed for polymer structure characterization, and nearly all of these were re-examined for possible usefulness in the assessment of tacticity.

Three years ago, although it would have been perfectly feasible to describe all of the relevant investigations in considerable detail, a judgment of the relative merits of the various methods would have been a hazardous undertaking. Today the overall picture is more clearly in focus, while the number of investigations has become so large as to preclude a detailed consideration of each. I have chosen to bypass much of this detail and to stress instead a relative evaluation of the various procedures, in the belief that this will be of more value to the average reader than a comprehensive coverage of all of the pertinent literature. This decision involved some selection of the examples to be presented, and in a few cases this choice was rather arbitrarily made.

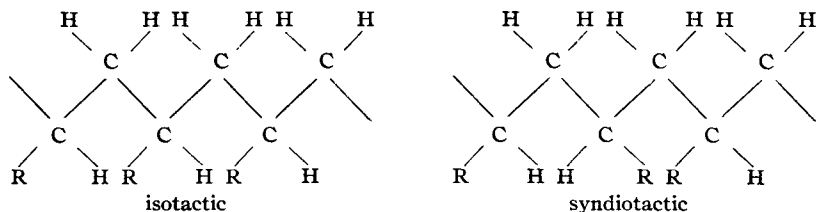
As the contents of this chapter will show, a completely general solution to the problem of determining microtacticity is not yet available; however, considerable progress toward this goal has been achieved. In a few specific cases the experimental procedures permit quantitative characterization, while, for other polymers, we must be content with more qualitative information. Apart from this progress toward the direct objective, some of the achievements along related lines have been fully as noteworthy. Theoretical treatments have furnished much needed insight concerning the minimum number and nature of the parameters which must be evaluated experimentally in order to obtain an adequate description of a tactic polymer. Secondly, our ability to interpret data in terms of molecular structure has been considerably sharpened. Finally, the theoretical problems connected with the calculation of the unperturbed molecular dimensions and the associated physical properties, such as the dipole moment and optical anisotropy, have been approached with renewed vigor and with remarkable success.

A. THEORY

1. The Problem of Nomenclature (5-8)

Natta is, of course, the originator of much of our present terminology. The contrast between the crystallinity of his polymers and the complete lack of crystallinity in the same polymers when polymerized in the usual manner led him to define a *stereoregular polymer* as one possessing a perfectly regular structure, completely devoid of branching, and having the repeating

units entirely in head-to-tail arrangement. From unit cell dimensions he concluded that vinyl polymers could exhibit either of two stereoregular forms, which he termed *isotactic* or *syndiotactic*,



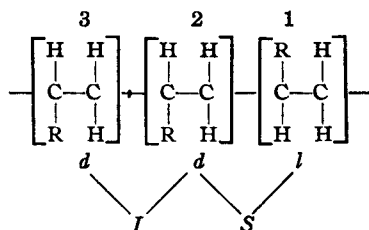
depending upon whether the successive pseudoasymmetric carbon atoms had the same or opposite enantiomorphic configurations. By definition, these terms were to apply only if the entire chain (or very long sections comprising almost the entire chain) exhibited the indicated structure. All possible structures having a lesser degree of order were termed *atactic*. This terminology simplified the problem of experimental evaluation, but the need for modification to enlarge its scope soon became apparent.

The results (9) reported for poly(methyl methacrylate) by Fox *et al.* in 1958 demonstrated two important points. First, the properties of the conventional atactic polymer indicated that its structure was not midway between the isotactic and syndiotactic forms but, instead, was much closer to the latter than to the former. Second, they obtained evidence for a fourth form, a *stereoblock polymer*, which had distinctly different properties from those of the other three forms. These observations indicated that the isotactic and syndiotactic forms of Natta were end points of a scale, and that some means of designating an intermediate degree of isotacticity or syndiotacticity was needed. Also, one should be able to specify whether, in a particular case, the isotactic or syndiotactic sections of the chain are long or short. Fortunately, theoretical studies of the tactic sequence distribution soon provided a terminology that could cope with these problems of description. However, this entire development rendered the experimental evaluation of tacticity a much more difficult task, since the complete characterization now entailed a very detailed knowledge of the sequence of diastereoisomeric forms along the chain. For this reason the descriptive term *microtacticity* was coined. Whereas the Natta terminology suggested that long-range properties would be the most useful ones for characterization studies, the revised terminology implied that the most fruitful experimental measurements for the study of microtacticity would be those concerned with near-neighbor effects along the chain.

2. Diastereosequence Distribution

The first papers concerned with the theoretical description of tactic polymers were those of Coleman (10) and Hughes (11), both of which appeared in 1958. These treatments were subsequently refined and extended by a number of authors (12-18). It will only be possible here to give an outline of the problem and an indication of the way in which the results can aid in the experimental assessment of tacticity. The interested reader must therefore consult the original literature for details. It is perhaps not out of place to mention in this regard that Miller (15) has provided a rather extensive tabulation of the symbolisms used by these various authors, which greatly facilitates comparison of the results.

Let us start numbering the repeating units from one end of the chain. We then consider adjacent pairs, and follow Coleman (10) in designating these as being in *isotactic placement* (*I*) or *syndiotactic placement* (*S*), depending upon whether the configuration of the two successive pseudo-asymmetric carbon atoms is the same (*dd* or *ll*) or different (*dl* or *ld*):



When we come to consider the addition of another repeating unit to the chain, several possibilities arise. In the simplest case, the probability of a specified outcome (for example, an isotactic placement) is uninfluenced by the placements of any or all of the units previously added. This corresponds to Bernoulli statistics, as exemplified by the tossing of a (possibly biased) coin. If the probability of an isotactic placement is symbolized by α , then the probability of a syndiotactic placement, β , is just $1 - \alpha$. Hence for processes involving Bernoulli trials only one parameter must be evaluated from experiment. There is no correlation of the units along the chain, so the probability of finding a sequence of ζ units having isotactic placement is

$$P_{\zeta} = \alpha^{\zeta}$$

Whether this simple situation applies in practice must be decided by experiment, and there is now considerable evidence that Bernoulli statistics