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Spectroscopy of Polymers

2nd Edition

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Spectroscopy of Polymers
2nd Edition

Dedication

My grandchildren have enlightened my life and I want
to dedicate this book to them.

Robert

Brian

Chelsea

Dustin

Christopher

Alexander

Delaynie

Tess

Preface to the second edition

How time flies! How rapidly things change! It is hard to believe that the first edition of *Spectroscopy of Polymers* is not only out of date but also out of print. Therefore, I took the opportunity to rewrite major sections of the book in an effort to bring in the large number of recent advances in the spectroscopy of polymers. The challenges of characterizing the molecular structure of synthetic polymers continue to grow as the polymer chemists for a broad range of new materials applications are synthesizing exciting new structures.

The first chapter on the theory of polymer characterization is essentially unchanged with only minor editions and tightening of some of the text. The second chapter has been substantially modified to include both Raman and Infrared in the description of the molecular basis of vibrational spectroscopy. This makes for a more consistent approach and will better guide the student to the more subtle differences in the applications of the two complementary methods of vibrational spectroscopy. The chapter on infrared instrumentation and sampling techniques has been modified to include innovations in instrumentation such as step-scan and focal array detector imaging interferometers. The sections in this chapter on data processing and quantitative analysis have been updated to reflect the major impact in this field of fast computers with large memories. The chapter on applications of infrared has been updated by including some of the new developments in the continuing astronomical growth in the applications of infrared to polymers. It is possible to include only a small number of the numerous new examples that are available and those selected were based on the utility as pedagogical examples for the student.

Raman spectroscopy has become a most important tool for characterization of polymers as low frequency lasers have improved so Raman spectroscopy excited in the infrared frequency range can be used to minimize the effect of fluorescence. Advances in Raman instrumentation have been dramatic and the polymer spectroscopists must now seriously consider the use of Raman as complementary to infrared. In many cases Raman spectroscopy will be the preferred method as the many new applications in this revised chapter illustrate.

Advances in solution NMR arise from the greater availability of high field instruments and the fast computers with large memories. The higher applied magnetic field results in greater dispersion so the resolution is higher and the information content is extended as longer stereo and comonomer sequences are observed. The improved computers allow the complex computational problems associated with two-dimensional techniques to be overcome so the multidimensional NMR techniques are available to the ordinary user. The spectral editing chapter of the first edition has been incorporated in this chapter. The applications of solution NMR chapter has been expanded to reflect the advances made using the higher applied magnetic field. A large number of new chemical structures are resolved including endgroups, branches, crosslinks and stereosequences.

The utility of solid state NMR continues to grow. Many new applications, particularly those based on motional differences of the phases, are developing, as experiments are easier to do with better spinners and decoupling methods.

The final chapter is an entirely new one describing mass spectrometry and its increasing importance in polymer characterization. Vaporization and ionization techniques are being developed that make macromolecules fly with little fragmentation. Therefore, the advantages of short measurement and analysis times make mass spectrometry an important tool in polymer characterization. I wish to thank Robert Latimer of B.F. Goodrich for introducing me to the potential of the technique and for kindly making a number of valuable suggestions on the manuscript.

I want to thank my professional colleagues and those many students from around the world that have made comments on the first edition of the *Spectroscopy of Polymers*. I have made an effort to incorporate many of the constructive suggestions in the second edition.

I want to thank Barbara Leach and June Ilhan for their efforts in turning rough text and figures into a readable manuscript and pursuing all of the innumerable details associated with production of a second edition.

Again, I want to thank my wife, Jeanus, for her giving up time that we would ordinarily share together for me to work on the book. Her constant support is appreciated.

Finally, it is unusual to have a second edition of a book published by a different publisher. The first edition was published by ACS publications. However, ACS decided not to publish monographs any longer and kindly released the copyright of the first edition to me. Elsevier has agreed to publish the second edition. Jonathan Glover was instrumental in making the selection of Elsevier as the publisher and I thank him for his efforts.

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Chapter 1

Theory of polymer characterization

The primary motivation for determining the molecular structure of a polymer chain is to relate the structures to the performance properties of the polymer in end use. If the polymer chains are completely characterized and the structural basis of its properties are known, the polymerization reaction can be optimized and controlled to produce the optimum properties from the particular chemical system.

Elements of polymer structure

The following basic terms are used for defining a polymer structure.

- The *composition* (or *constitution*) of a molecule defines the nature of the atoms and the type of bonding irrespective of the spatial arrangement.
- The *configuration* of chemical groups characterizes the chemical state of a polymer. Different configurations constitute different chemical entities and cannot be interconverted into one another without rupture of chemical bonds.
- The *conformation* of chemical groups characterizes the geometrical state of a polymer. Different conformations of a polymer can be produced by rotation about single bonds without rupture of chemical bonds. Changes in conformation arise from physical considerations such as temperature, pressure, or stress and strain.

Polymer chains are made up of sequences of chemical repeating units that may be arranged regularly or irregularly on the backbone.

- The chemical *microstructure* is defined as the internal arrangement of the different chemical structures or sequences on the polymer chain.

Polymers can exhibit phase transitions and show a number of fundamental spatial distributed macroconformations that define the crystalline and amorphous phases.

- The polymer *morphology* defines the intermolecular packing of the polymer molecules as crystals or spherulites in the bulk.
- Polymer chains can exhibit different chain topologies where topology describes the molecular packing of the chains. Chain alignments, orientation and entanglements are topologic features.

The mechanical properties such as modulus, tenacity, and yield are properties which depend on the dynamics of the polymer chain.

- The *molecular motion* depends on the intramolecular and intermolecular constraints imposed on the structure of the chain and the non-bonded neighbors in the vicinity.

From a structural point of view polymers are chainlike molecules.



The structural elements of an *ideal* polymer molecule with a single structural repeating unit can be represented by the molecular formula, $X(A)_nY$, where A represents the repeating unit of the polymer molecule and n is the number of repeating units of A. X and Y are the end-group units which are chemically different from A. The number of connected repeating units, n , can range from 2 to greater than 100,000. The chemical nature of the repeating unit A determines the chemical properties of the polymer. The chemical structure of the repeating unit can be very simple (e.g., CH_2 for polyethylene) or very complicated.

The end-group units X and Y can be substantially different in chemical structure from A or very similar depending on the nature of the polymerization process.

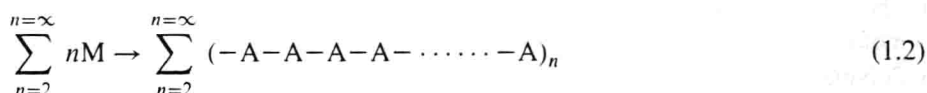
Structural variations within the chain can be represented by the letters B, C, etc., to indicate the differences in the chemical, configurational, or conformational structure.

The polymerization reaction converts the initial bifunctional monomers into a chain of chemically connected repeating units. The process of polymerization can be written in the following form:



where M is the monomer. We have neglected for the moment the fact that the end groups X and Y are different structures from A.

However, this representation of the ideal polymerization reaction is incomplete, as the polymerization reaction is statistical in nature and does not generate a single molecule of a specified length n . Rather millions of polymerization reactions are occurring simultaneously, generating millions of molecules of various lengths ranging from 1 to a very large number (e.g., 100,000) depending on how many reactions have occurred between the individual molecules during the polymerization. So more precisely, the polymerization reaction must be written



Thus, in contrast to chemistry of simple molecules, which produce a single molecular

species, the polymerization batch contains a mixture of chain molecules ranging in length from very short to very long. For this simple ideal polymer system, the only structural variables are the lengths n of the chains and the number of molecules of these various lengths $N(n)$. In other words, to determine the structure of the polymer we need to know the number fractions of molecules having different specific lengths.

Approach to polymer structure determination using probability considerations

Let us start with the simplest structural example: the degree of polymerization (DP). With the polymerization model just described, and assuming an equal likelihood for the selection of any polymer molecule from the mixture, it is possible to calculate the *probability distribution function for the chain length n* . The probability distribution function for n is the probability of finding a molecule with a given chain length n in a polymer sample. For experimental purposes, the probability function is the fraction of all polymer molecules that possess the stated chain length, n .

You can visualize the probability approach as one of reaching into the reaction mixture and pulling out a single polymer molecule. You must then calculate the probability that the molecule selected has a specified length.

Let P be the probability that a propagation polymerization reaction has occurred and Q be the probability of termination; that is, the molecule has not undergone propagation and is terminated from further polymerization. This is a simple description of an ideal simple chain/addition polymerization (a chain reaction in which the growth of a polymer chain proceeds exclusively by reactions between monomers and reactive sites on the polymer chain with regeneration of the reactive sites at the end of each growth step). This is illustrated in the following diagram:

Polymerization	Event	Probability
Propagation	$\sim A_n^* + A \rightarrow A_{n+1}^*$	P
Termination	$\sim A_n^* \rightarrow A_n$	Q

The instantaneous probability of propagation, P , in this case, is given by

$$P = \frac{\text{Number of propagation events}}{\text{Total number of events}} = \frac{\text{Rate of propagation}}{\text{Rate of propagation} + \text{Rate of termination}}$$

For termination

$$Q = \frac{\text{Number of termination events}}{\text{Total number of events}} = \frac{\text{Rate of termination}}{\text{Rate of propagation} + \text{Rate of termination}}$$