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A review of: "Markov Chains and Monte Carlo Calculations in Polymer Science"

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BOOK REVIEW

"Markov Chains and Monte Carlo Calculations in Polymer Science"

Although many strides have been made in the synthesis and characterization of high polymers, only recently has the full potential of advanced statistics and chain analysis been applied to the field. For example, the power of Markov chain statistics in the analysis of the problems of copolymerization and polymer chain tacticity was recognized only as recently as 1962 by Fraser P. Price [*J. Chem. Phys.*, **36**, 209 (1962)]. The advances in mathematical treatment of copolymerization, tacticity, and chain conformation had followed other avenues with other assumptions, involving such factors as steady-state conditions or partition functions for rotational isomeric chains.

Reasonably valid answers can be obtained by these less precise approaches. However, growing realization of the power and precision of the Markov chain approach has led to its increasing dominance as a means of treating polymer chain problems. Indeed, simplified models are now derived from Markov chain calculations with reducing assumptions added in the derivations.

The continuing intermeshing of polymer chains with related mathematics must be noted. Even now, certain extensions of Markov mathematics bear the imprint of concepts arising from polymer chemistry. Opportunities for the amplification of Markov chain mathematics are probably only beginning to be considered. Indeed, the typical conformational polymer chain or sequential copolymer chain may be regarded as kind of a computer tape, subject to detailed inspection with growing insight into the nature of polymerization processes and polymer properties.

Chapter I of this volume* is entitled "Introduction: Deterministic and Stochastic Approaches," by George G. Lowry, and is an unusually concise treatment of the background and definitions of Markov chain theory and its application to polymer chemistry.

**Markov Chains and Monte Carlo Calculations in Polymer Science*, George G. Lowry, ed., Dekker, New York, 1970, xiv + 329 pp., $19.75.

Chapter II, "Markov Chains" by Janet M. Myhre, is, unfortunately, one of the weakest chapters in the book. The information here is strictly mathematical and presents no real insight into the particular purposes of the monograph.

Chapter III, "Monte Carlo Methods" by Malcolm Fluendy, is exceptionally insightful. The usefulness of the Monte Carlo method is fortified by descriptions of recent breakthroughs in computer technology. This powerful tool lends renewed importance to the Monte Carlo approach. The Monte Carlo method, of course, is an empirical technique for "growing" sequential chains, using certain mathematical assumptions about the way in which units are added. The final chain may then be viewed with respect to gross properties such as chain conformation and molecular weight distribution.

This chapter is followed by one of the most important chapters of the book–Chapter IV, "Polymer Conformation as a Markov Chain Problem" by Jack B. Kinsinger. Dr. Kinsinger, who has made important contributions to the field, describes in an exceptionally lucid manner the scope of conformational problems and Markov chain analysis of lattice models. A variety of approaches covering both Markovian and Ising treatments are presented. Chain growth on two-dimensional square lattices and the diamond lattice is treated. The conclusions drawn do not appear, however, to match precisely experimental fact. Indeed, it is difficult to check the various predictions, since physical measurements have a commensurate error of 5 to 15%. Furthermore, bond and rotational angles are taken from analysis in the crystalline state and may not necessarily apply to those exhibited in amorphous or solution state. Angles in crystalline polymers are often extended because of distortions caused in this state. In view of these limitations the success of these complex mathematical descriptions is even more remarkable.

Chapter VII, "Copolymer Composition and Tacticity" by Fraser P. Price, is also unusually worthy of detailed study. Dr. Price has made important contributions to the treatment of copolymer compositions and tacticity in polymer systems. Breakthroughs in Monte Carlo treatment of copolymer composition have been extended to multicomponent polymers, distributions of degree of polymerization, and compositional distributions. In the remainder of the chapter, stereoregular polymers are covered with emphasis on such topics as compositional transients and sequence distributions.

Further treatment of this general topic occurs in Chapter VIII, entitled "Molecular-Weight Distributions," by George G. Lowry. This chapter covers,

in a somewhat clearer, but more brief, manner, the subject of molecular weight distributions and comparison with molecular weights measured by physical methods. The general role of absorbing Markov chains and their role in determining molecular weight distributions is also covered. Perhaps no other chapter sets forth in as powerful a manner the uses of Markov chain techniques in elucidating polymer chain properties.

In conclusion, few books in the polymer field more ably convey the theoretical breakthroughs in mathematics and their implications for polymer chemistry and physics. After reading this book the polymer chemist is tempted to conclude that the day is not far away when mathematical techniques will offer possibilities for understanding polymer chain behavior that will compare well with those possible through experimentation.

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