



**Benchmark Papers  
in Polymer Chemistry / 1**

**POLYMER SOLUTION  
PROPERTIES  
PART I  
STATISTICS AND  
THERMODYNAMICS**

Edited by  
**J. J. HERMANS**



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A BENCHMARK® Books Series

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STATISTICS AND  
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**J. J. HERMANS**

University of North Carolina



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# Benchmark Papers in Polymer Chemistry

Series Editor: Eric S. Proskauer

## Volume

- 1 POLYMER SOLUTION PROPERTIES, PART I: Statistics and  
Thermodynamics / *J. J. Hermans*  
POLYMER SOLUTION PROPERTIES, PART II: Hydrodynamics and  
Light Scattering / *J. J. Hermans*

## SERIES EDITOR'S FOREWORD

Polymers or macromolecules are the most abundant natural substances. They are the carriers of most of the live processes, contribute the greatest part of the biomass of our planet, are the most widely produced industrial organic compounds, and occupy the highest percentage of all chemists in the American Chemical Society. Ten percent of all abstracts in Chemical Abstracts for the period of 1971-1976 relate to the chemistry and physics of polymers. Herman T. Mark, however, could still state recently in an historical review that: "It is interesting to register today with the benefit of hindsight that the development from 1920 to 1930 did not create very much impression on the classical, organic and physical chemists. Of course some enlightened leaders realize the importance of this new branch of chemistry, but many organic chemists of great stature and overwhelming influence remain unimpressed, and they are not ready to accept polymer chemistry as a truly scientific discipline which deserves to be promoted and incorporated into the curriculum of modern science. Strangely enough, this reluctance exists even today in certain quarters."

Perhaps one of the reasons that polymer science did not evolve into a separate branch of science is that the study straddles the areas of chemistry and physics. It is one of the purposes of this Benchmark series to bridge this gap and to help make the practitioners of these different areas familiar with the original literature in the related field. The Series will examine the structure, the behavior and the properties of polymers. The first volume treats the behavior of polymers in solutions and it is planned that further volumes will deal with polymers in the solid state and with historical development of the polymer concept.

The Benchmark Series in Polymer Chemistry will provide those engaged in polymer research with an easy source of reference. The novice is also provided with a "guided tour" through the state of the art based on its classical publications. The reading of the originals might not only lead to better understanding of the historical development of the concepts and experimental findings, but might also stimulate new insights which will help to generate progress and evaluation.

ERIC S. PROSKAUER

## PREFACE

The physical chemistry of macromolecular solutions came of age, roughly, in the late thirties with the works of Mark, Kuhn, Burgers and others. This was followed by rapid developments (Flory, Huggins, Debye, Kirkwood, and many more) which gave the science of polymer solutions its place in the disciplines of statistical mechanics, hydrodynamics, and electromagnetics. The present two volumes are an attempt to summarize the salient features of this development.

The books address themselves to students who need a survey that goes beyond the usual introductory textbook, and to polymer scientists who like to look back upon the steps taken by their predecessors. Although a student to whom polymer science is a new field of study can find excellent books to orient himself, he must often consult the original literature in order to become familiar with the details of the models used, the mathematical techniques involved, and the approximations needed to obtain explicit results. These are nevertheless essential for a good understanding not only for a scientist, who contributes to further developments and refinements, but also for those who must interpret experimental data. All too often theories are applied to phenomena for which they were not developed or to situations that are not compatible with the approximations made.

For these reasons, a collection of papers dealing with the fundamental aspects of polymer solutions may also be very useful to those who perhaps do not consider themselves as polymer scientists per se, but who apply the results of the theories in their own disciplines. This applies in particular to the disciplines of biochemistry and biophysics.

It is further hoped that scientists who are already familiar with the physical chemistry of polymers will find this collection refreshing and informative. Many of them will doubtless criticize the absence of numerous important papers. I share this regret with them, but hope that enough material is left to make this collection relevant to the study of polymer solutions.

The collected papers cover polymer statistics, hydrodynamics, thermodynamics, and light-scattering. The selection was made on the basis of their importance in the development of new concepts and techniques. It is one of the fascinating aspects of polymer science that, although it is

## *Preface*

part of general physical chemistry, the application of physical chemical principles to molecules of exceptionally large size has almost always certain characteristics that make it different and new. This explains why new approaches were needed to understand and to describe polymer solution properties.

The papers selected introduce or apply models and techniques that are still of great value and have had a notable effect on the development of polymer science. Only very occasionally has part of a paper been included primarily for its historical interest. Many of the articles reproduced are still quoted frequently because later work is based on them or uses similar models. Nevertheless, an article of equal importance may be missing, sometimes simply because the available space did not allow its inclusion. Often, however, it is because the material has been incorporated in textbooks that are readily available. For this and for many other reasons, the collection must, on no account, be considered as an attempt to offer an historical review. For the sake of completeness and clarity, however, occasional historical remarks have been added in the introduction to a new field of topics.

J. J. HERMANS

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# INTRODUCTION

All solution properties of polymers are intimately related to each other. There exists a close relation, for example, between equilibrium thermodynamics and light scattering, and between irreversible thermodynamics and the frequency distribution in scattered light. But thermodynamic considerations have also played a role in the statistics of molecular size (excluded volume effect) and, conversely, the size is an important factor in determining the second virial coefficient. Finally, the molecular statistics are inseparably interlinked with all hydrodynamic properties.

As a result of this situation, the order in which the various subjects are presented is to a large extent arbitrary. In the present two volumes the order is (1) statistics, (2) thermodynamics, (3) hydrodynamics, (4) light-scattering, but arguments of a thermodynamic nature are occasionally introduced in the statistics of molecular conformations. Moreover, some articles cannot be classified under a single heading because they deal with more than one subject; for example, chain statistics and light-scattering or chain statistics and viscosity.

The present volumes are an attempt to put together a more or less continuous story of the application of basic physical principles to polymer solutions. It is hoped, for example, that the collection in Part II gives a good idea of the manner in which hydrodynamics has been applied to polymer solutions: the early work considered free-drained gaussian chains but was soon made to include hydrodynamic interaction and was extended to non-gaussian chains. The treatment of hydrodynamic interaction, in its turn, has undergone subsequent developments.

What is inevitable in a book of this kind is the arbitrary omission of a great many important papers. The reasons for such omissions are

## Introduction

varied. One reason may be that excellent textbooks and review articles are easily available. This argument should not play too important a role in a book such as this, but it plays some role, especially when the subject deals with refinements of a discipline rather than with the discipline itself.

Omissions have also been motivated by other reasoning. To mention an example, there are two reasons for the absence of articles on centrifugation, density gradient centrifugation, and centrifugation equilibria. In the first place, these phenomena can be understood as straightforward applications of the principles outlined in Part II. For example, once the driving force in a centrifugation experiment is understood, the treatment becomes essentially an *application* of the hydrodynamic and thermodynamic results obtained for polymer molecules. In the second place, the centrifuge is of particular practical importance to biologists and biochemists, and a compilation of articles dealing with ultracentrifugation might therefore be more appropriate if combined with work on proteins.

This second consideration also played a role in the decision to omit all work concerned with polyelectrolytes.

In essence, then, this volume is concerned primarily with certain basic concepts; it attempts to show how these concepts have been applied to polymer solutions, but it makes no attempt to follow any particular trend of thought to its latest stage of development. For example, the reader will find a reproduction of the well-known Flory-Huggins theory to demonstrate the principles of the statistical method used, but later refinements by Prigogine and others are merely touched upon in the comments. Similarly, light-scattering results are derived, but the application to molecules deformed by a shear-rate or by some other external field is not included. At the same time it is not claimed that this philosophy is always adhered to in a fully logical manner.

Although papers on the same or closely related subjects are reproduced in chronological order, this collection is not by any means a reliable guide in a historical study, because there are too many omissions. The history of the developments reconsidered in these volumes is interesting but cannot be shown to full advantage in books of this kind. Nor would the editor have the competence to write such a history even if he aspired to do so. Remarks of a historical nature are included in the comments from time to time, but no attempt is made to be complete. Likewise, the references to related work which occasionally are given in the comments are by no means complete, but it is hoped that they will be helpful.



Part I

STATISTICS OF  
CHAIN MOLECULES

# Editor's Comments on Papers 1 Through 11

- 1 **TAYLOR**  
*Average Square Length and Radius of Unbranched Long-Chain Molecules with Restricted Internal Rotation*
- 2 **TAYLOR**  
*Average Length and Radius of Normal Paraffin Hydrocarbon Molecules*
- 3 **FLORY and FOX**  
*Treatment of Intrinsic Viscosities*
- 4 **GOBUSH, ŠOLC, and STOCKMAYER**  
*Statistical Mechanics of Random-Flight Chains. V. Excluded Volume Expansion and Second Virial Coefficient for Linear Chains of Varying Shape*
- 5 **WALL and ERPENBECK**  
*New Method for the Statistical Computation of Polymer Dimensions*
- 6 **WALL and ERPENBECK**  
*Statistical Computation of Radii of Gyration and Mean Internal Dimensions of Polymer Molecules*
- 7 **GANS**  
*Self-Avoiding Random Walks. I. Simple Properties of Intermediate-Length Walks*
- 8 **DOMB, GILLIS, and WILMERS**  
*On the Shape and Configuration of Polymer Molecules*
- 9 **CURRO**  
*Computer Simulation of Multiple Chain Systems—the Effect of Density on the Average Chain Dimensions*
- 10 **KRATKY and POROD**  
*Röntgenuntersuchung Gelöster Fadenmoleküle*

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*The Statistics of Stiff Chains, with Applications to Light-Scattering*

The theory of the statistics of molecular size and shape in the absence of any interaction between chain segments originates with W. Kuhn<sup>1</sup> and, independently, Guth and Mark.<sup>2</sup> The concepts used were known well before that time in the form of "random flight problem" (theory of Brownian motion). Extensive treatments can be found in many textbooks and review articles, of which two in particular may be mentioned: Chandrasekhar's<sup>3</sup> classical review and the book edited by Wax.<sup>4</sup> Kuhn's application of the random flight concept to polymer chains was made possible by the introduction of a simplified model. The real polymer molecule was replaced by a model in which rigid segments are bonded together by freely jointed links on the assumption that the orientation of each segment is random and is independent of that of the other segments in the molecule. This treatment leads to the well-known gaussian distribution of end-to-end distances in linear chain molecules when there is no interaction between segments. Such chains are commonly called gaussian chains.

In view of the fact that the random flight problem is discussed in many introductions to physics or physical chemistry, only two short articles by Taylor are reproduced here. The case of a fixed valency angle but unrestricted rotation was discussed already by Eyring.<sup>5</sup> Taylor (Paper 1) shows how to account for restricted rotation about successive bonds, a problem that was considered also by others, for example Sadron.<sup>6</sup> We may further refer to Volkenstein's textbook.<sup>7</sup>

Applications to special polymers were worked out by Benoit<sup>8</sup> and by others. An example is shown in Paper 2. Further examples, and a much more general formulation of the problem can be found in Flory's textbook,<sup>9</sup> where attention is paid also to the interaction between non-adjacent units in the chain.

This brings us to the so-called excluded volume effect, which is the subject of the next seven papers in this book. The attraction and repulsion between the units in a chain molecule raises a complicated many-body problem for which a rigorous solution is not known. Paper 3 by Flory and Fox treats the molecule in a manner which may be characterized by saying (a) the tendency of the polymer chain to expand is described by a free energy of mixing, which is borrowed from the thermodynamics of polymer solutions, (b) this tendency is counter-

acted by the elastic force in the molecule, which is related to the manner in which the number of possible conformations depends on the end-to-end distance (and which was known already from rubber elasticity theory).

Paper 3 then considers the application to intrinsic viscosity, and it may be emphasized at this point that it is the relation between thermodynamic and hydrodynamic properties which has made this theory so attractive and useful. This relation finds its origin in the fact that both the hydrodynamic behavior and the second virial coefficient depend on the molecular dimensions, and it explains the remarkable ability of the theory to predict, to a considerable extent, the effect of the solvent on the viscosity.

Deviations from the constancy of  $(\alpha^5 - \alpha^3)M^{-1/2}$  predicted by the Flöry-Fox theory have been reported by Krigbaum and Flory<sup>10</sup> and by Notley and Debye,<sup>11</sup> and the theory has been slightly refined by Krigbaum.<sup>12</sup> The entire problem of the relation between intrinsic viscosity  $[\eta]$ , expansion factor  $\alpha$  and molecular weight  $M$  has been further discussed in detail by Stockmayer and coworkers,<sup>13-15</sup> and one of the relevant papers is included in this book (Paper 4).

The approach chosen by Flory and Fox and by the later authors mentioned can be characterized as attempts to develop a "mean field theory," and it may be mentioned at this point that other, quite sophisticated field theories have been worked out. None of them is reproduced here, but some references may be in order: Edwards,<sup>16</sup> Freed,<sup>17</sup> Gillis and Freed.<sup>18</sup>

Another approach to the problem is by means of computer calculations. Four of these are included as Papers 5-8. Other work along these lines was done by Wall and coworkers,<sup>19</sup> Martin, Sykes, and Hioe,<sup>20</sup> Domb,<sup>21</sup> Fisher and Sykes,<sup>22</sup> Fischer and Hiley.<sup>23</sup>

The final papers (Papers 9, 10, 11) in this section concerns the statistics of the "worm-like" chain, which has played a considerable role in studies of DNA.

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Reprinted from *J. Chem. Phys.* 15(6):412-413 (1947)

## Average Square Length and Radius of Unbranched Long-Chain Molecules with Restricted Internal Rotation

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(Received March 27, 1947)

EYRING<sup>1</sup> has derived a well-known formula for the average square length of an unbranched long-chain molecule with  $n$  bonds, each of length  $\sigma$ , with a fixed valence angle  $\theta$  between successive bonds, and *free internal rotation* about each bond, and Debye<sup>2</sup> has given a formula for the average square radius of the molecule. These quantities appear as parameters in theories of the physical properties (elasticity, intrinsic viscosity, streaming double refraction, etc.) of long-chain molecules. However, the assumption of free rotation is now known to be inadequate for a quantitative treatment of properties affected by internal rotation. In actual molecules in which rotations occur, the latter are, in general, partially restricted by potential functions with one or more minima separated by intervening maxima (potential barriers).

The only published attempt to calculate the effect of a restricting potential of which the writer is aware, is that of Bresler and Frenkel,<sup>3</sup> who, however, considered only the special case of small torsional oscillations about the equilibrium configuration.<sup>4</sup> Their treatment fails for large oscillations or for potential functions with more than one minimum, so that they have not in fact treated restricted rotation.

The present communication reports formulas for the average square length and radius of an unbranched long-chain molecule for the case in which the rotation about each bond is restricted by the same potential function  $V(\phi)$  ( $\phi$ =angle

of rotation, defined so that  $\phi=0(\pi)$  for the planar *trans* (*cis*) configuration of three successive bonds). It is assumed that there are no interactions between different rotations (because of terms in the potential function or of steric hindrance), but there are no restrictions on the form of the function  $V(\phi)$ , or on the extent of the rotation. The exact solution has been obtained in a very general form which allows also for variation of the bond angle and bond length. However, in actual molecules the effect of these latter variations on the length and radius should be much less important than that of internal rotation. Only the formulas for restricted internal rotation will be presented here, and, in addition, only the approximate formulas valid for long chains. The derivation (which is based on Eyring's method<sup>1</sup>) and the general solution will be presented in a subsequent paper.

According to classical statistics, the probability that a given bond rotation lies in the range  $(\phi, \phi+d\phi)$  is  $p(\phi)d\phi$ , where

$$p(\phi) = C \exp[-V(\phi)/kT] \quad (1)$$

and  $C$  has a value such that,

$$\int_{-\pi}^{\pi} p(\phi) d\phi = 1 \quad (2)$$

$k$  is Boltzmann's constant and  $T$  is the absolute temperature. The average square length and radius depend on the function  $V(\phi)$ , and on the temperature, only through the two parameters,  $a$  and  $b$ , defined by the equation,

$$\begin{Bmatrix} a \\ b \end{Bmatrix} = \int_{-\pi}^{\pi} p(\phi) \begin{Bmatrix} \cos\phi \\ \sin\phi \end{Bmatrix} d\phi \quad (3)$$

$a$  and  $b$  are clearly the average values of  $\cos\phi$  and  $\sin\phi$ , respectively. The solution has been obtained for the general case,  $a \neq 0$ ,  $b \neq 0$ . However the only case likely to be of physical interest is that corresponding to an *even* potential function,  $V(\phi) = V(-\phi)$ , for which  $b = 0$ .

\* Research Associate on the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons."

<sup>1</sup> H. Eyring, *Phys. Rev.* 39, 746 (1932); E. Gorin, J. Walter, and H. Eyring, *J. Am. Chem. Soc.* 61, 1885 (1939); see also, F. T. Wall, *J. Chem. Phys.* 11, 67 (1943).

<sup>2</sup> P. Debye, *J. Chem. Phys.* 14, 636 (1946).

<sup>3</sup> S. E. Bresler and J. I. Frenkel, *Acta Physicochimica U.R.S.S.* 11, 485 (1939). In English.

<sup>4</sup> R. Simha, in reviewing the present paper, has brought to the attention of the author a paper by B. H. Zimm, R. S. Stein, and P. Doty (*Polymer Bulletin*, Vol. 1, October 1945, page 109 and Eq. (64)) in which brief mention is made of a treatment of this problem by Debye. It is not immediately clear whether the result quoted agrees with Eq. (4) of the present paper.