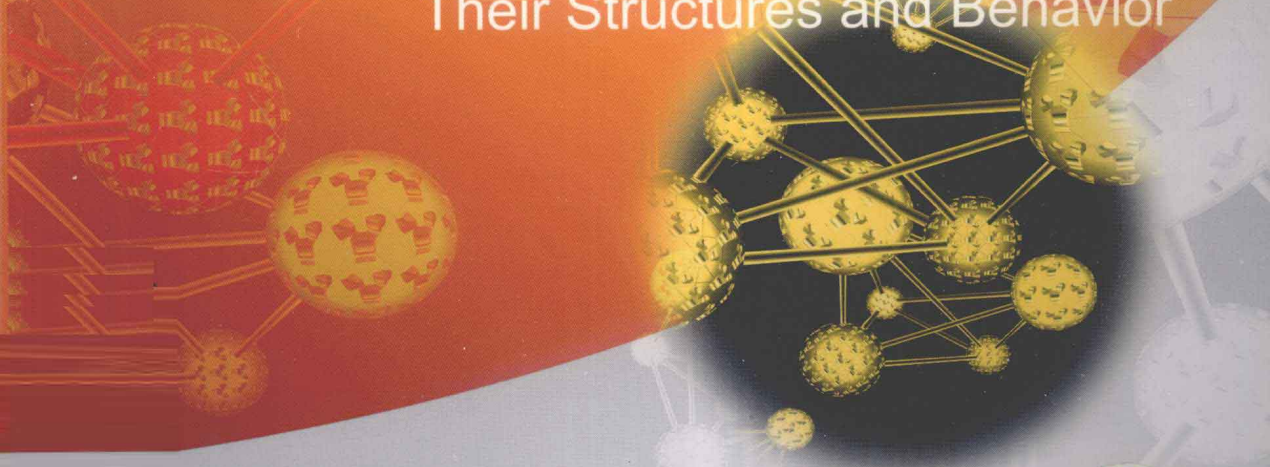
时代教育·国外高校优秀教材精选

Third Edition
(英文版·原书第3版)

高分子物理
——“结构与性能”背后的概念

◎ (德)G.斯特罗伯(Gert Strobl) 著

The Physics of Polymers
Concepts for Understanding Their Structures and Behavior



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推　荐　序

本书是我最推崇的一本《高分子物理》教材。作为本书的一名忠实读者，从中得到了丰富的教益，其中最重要的是作者对高分子物理这门课程的认识与理解。高分子物理之所以不同于普通物理，是由于高分子物质的运动单元（常称作高分子链）与小分子有显著的不同，主要区别在于分子形状的严重不对称性以及多层次性。高分子物理正是描述高分子链物理运动规律的一门学问。

其他作者虽然也看到了这一点，但在高分子物理的教材编撰中却走上另一条路。许多高分子物理教材脱胎于传统的金属学教材，基调为结构与性能。一本书中往往是前半部分介绍结构，后半部分介绍性能，甚至把一些典型材料的加工与应用也引进了高分子物理的范畴。从某种意义上说，“结构与性能”是属于材料学而不是物理学的内容。经过多年的演进，国外的高分子物理课程早已是单纯的物理教学，绝大多数学校采用本书或迈克尔·鲁宾斯坦（Michael Rubinstein）所著的《高分子物理》作为教材，把描述高分子链的物理运动规律作为讲授重点。

从编写体例与内容上看，本书是一本纯粹的物理学书籍。就如副标题中所说：“结构与性能”背后的概念（而不是“结构与性能”本身）。本书以一个实验科学家多年的研究视角，对高分子物理的多个领域作了生动而详细的介绍，内容涵盖了链构象，高分子溶液，共混物和嵌段共聚物，半晶态聚合物，聚合物网络，聚合物流体等多种体系。介绍的内容可以一言以蔽之：对微观、宏观物理现象的机理阐释以及数学处理。作者还使用了大量的数学处理与实验结果，对提出的机理与数学模型进行示例与验证，勾勒出一幅浓墨重彩的高分子物理画卷。

除了以上所谈的编撰理念，该书还有以下几个特点：

1）第3章溶液部分加入了电解质溶液。

2）将聚合物共混物与嵌段聚合物独立设章（第4章）。

3）力学松弛与介电松弛合并处理。这是慧眼独具的一种做法，无论在力学场还是在电场中，高分子链的松弛行为在性质上是相同的。合并处理不仅节省篇幅，且更有利于知识的融会贯通。

4）将凝胶归入橡胶网络，这又反映出作者的见解独到，与其他书把凝胶放在溶液中处理形成鲜明对比。凝胶被溶胀后呈现出的主要是网络性质而非溶液性质，读者很容易体会到这一点。

5）第7章标题为共轭聚合物，实际上是在讲光电效应的物理本质。在其他书中，光电效应都是作为一种性能来讲，相比之下，本书作者是在讲原理而非

性能。

6）散射的表征贯穿全书，且在书后附有散射的入门知识。作者本人是散射学家，通过“如影随形”的散射表征，能够使读者认识到散射是高分子物理研究最重要的手段之一。离开了散射，高分子的物理结构就只能是空谈。散射是一门很难的课程，通过对本书的学习，读者可以同时学到散射的入门知识。

当然本书在有些概念的理解上可能有些问题，如半结晶聚合物一章中对平衡结晶温度和平衡熔点温度的理解等，这些都值得广大老师和学生在阅读中思索。

机械工业出版社以英文原版的形式出版此书，原汁原味地呈现给广大作者，无疑为高分子界的广大读者做了一件好事。本书可作为化学化工、材料科学和物理学等专业的本科生和研究生相关课程的教材和参考书，也可供相关领域的专家、学者阅读参考。

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出 版 说 明

随着我国加入 WTO，国际间的竞争越来越激烈，而国际间的竞争实际上也就是人才的竞争、教育的竞争。为了加快培养具有国际竞争力的高水平技术人才，加快我国教育改革的步伐，国家教育部出台了一系列倡导高校开展双语教学、引进原版教材的政策。以此为契机，机械工业出版社拟于近期推出一系列国外影印版教材，其内容涉及高等学校公共基础课，以及机、电、材料等领域的专业基础课和专业课。

引进国外优秀原版教材，在有条件的学校推动开展英语授课或双语教学，自然也引进了先进的教学思想和教学方法，这必将对提高我国自编教材的水平，加强学生的英语实际应用能力，使我国的高等教育尽快与国际接轨，起到积极的推动作用。

为了做好教材的引进工作，机械工业出版社特别成立了由著名专家组成的国外高校优秀教材审定委员会。这些专家对实施双语教学作了深入细致的调查研究，对引进原版教材提出了许多建设性意见，并慎重地对每一本将要引进的原版教材一审再审，精选再精选，确认教材本身的质量水平以及权威性和先进性，以期所引进的原版教材能适应我国学生的外语水平和学习特点。在引进工作中，审定委员会还结合我国高校教学课程体系的设置和要求，对原版教材的教学思想和方法的先进性、科学性严格把关，同时尽量考虑原版教材的系统性和经济性。

这套教材出版后，我们将根据各高校的双语教学计划，及时地将其推荐给各高校选用。希望高校师生在使用教材后及时反馈意见和建议，使我们更好地为教学改革服务。

机械工业出版社

Preface

More than ten years have passed now since the first printing of this book, and I am happy to say that it is a success. Many thousands of volumes can today be found worldwide in libraries, laboratories of polymer science and private hands, with a special edition for China and an edition in Japanese. The book obviously filled a gap. After such a period the time had come for a revision and moderate expansion of the book's contents and I continuously worked on it during the last years. The basis of the new sections and chapters were again lectures given to students of physics and chemistry in Freiburg. Proceeding in this manner, the original 'pedagogical style' of the writing was continued. The results of the effort are presented here and they include some major changes:

- The electro-optically active conjugated polymers have attracted many scientists during the last decade and approach commercial uses as display materials. The newly written Chap. 7 deals with the physical basis of the electrooptic response and in addition discusses the spectacular electrical conduction properties of conjugated polymers created by doping.
- Quite peculiar properties are also shown by polyelectrolytes. They became popular in particular by their use as superabsorbers. Many researchers, both theoreticians and experimentalists, are fascinated by the ordering phenomena caused by the Coulomb forces. Polyelectrolyte properties are now discussed in different chapters of the book, in Sects. 3.3, 8.4.2 and 9.2.
- The basic understanding of melt crystallization, a classical field of polymer physics, has changed during the last decade; new experiments have provided novel insights. As a consequence, Chap. 5 was completely rewritten. It presents the new results in a selection of figures, formulates the deduced laws and also includes in Sect. 5.3.1 the – not yet generally accepted – 'multistage model' developed as an explanation of all the new observations.
- Chapter 10 also includes some substantial changes, again triggered by progress in understanding. Some principles governing shear deformation in semicrystalline polymers were revealed and enabled the construction of a mechanic-rheological model (Sect. 10.1).

In addition to these major changes, which resulted in an increase of the book volume by more than one hundred pages, many minor corrections and modifications have been made. Many of them are reactions to remarks from readers, and I would like to express here my high appreciation for the constructive criticism. I hope that it will continue, because it is a real help. There were also a few changes in the choice of symbols, necessitated by additional variables introduced in the new parts. The changed symbols appear in the updated Glossary in the Appendix.

When writing the new chapters I obtained advice by my renowned colleagues Prof. Heinz Bässler (Marburg), Prof. Jürgen Heinze (Freiburg), Prof. Manfred Schmidt (Mainz) and Prof. Stephan Förster (Hamburg), and I would like to express my gratitude to them here.

Last but not least, many thanks go to my secretary Christina Skorek. Without her most effective support in processing the TEX file and preparing all figures, the book with all its three editions would not have come into being.

Gert Strobl
Freiburg, November 2006

Preface to the First Edition

In our faculty, we offer to the graduate students in physics a course on 'Condensed Matter Physics' which goes beyond the usual lectures on solid state physics, by also including the physics of simple liquids, liquid crystals and polymers. While there is a large selection of textbooks on solid state physics and also a choice of excellent treatises on the physics of liquids and liquid crystals, a book on a comparable level covering the major parts of the physics of polymers apparently does not exist. The desire is to have a textbook on polymer physics which, ideally, would stand in line with the 'Kittel', the 'Egelstaff' and 'de Gennes' books on the physics of liquid crystals, to cite only some of the best known volumes. This book is a first attempt to comply with these needs and to fill the gap. Certainly the aim is high, too high to be reached with this first approach, but hopefully other polymer physicist will also take on the task in future and then do better, once a frame is set and a first trial exists.

For me personally, writing such a textbook was indeed highly valuable and a worthwhile experience. In a time when science has such a strong tendency for diversification, there is a great danger of losing contact even with the neighboring branches and simultaneously the ability to see and assess the relevance of one's own activities. Students have this sensitivity and often have a better feeling about the importance of a topic. When teaching students as a lecturer, it is of primary importance always to provide the motivation and to make clear the role and relevance of a certain problem. Indeed, for me this amounts to a true check which helps me to discriminate between the major phenomena and secondary effects. Senior scientists with time tend to become acquainted with complicated, sometimes even artificial concepts; the young student, however, being confronted for the first time with an explanation, reacts naturally and distinguishes intuitively between reasonable, illuminating concepts and less attractive complicated ways of thinking. Hence, writing a textbook also means to put the state of the art of polymer physics to the test. If it is possible to present this field coherently and to explain convincingly the main properties with the aid of clear and appealing concepts, then it is in good shape. It is my impression, already gained in the lectures and now further

corroborated during writing, that this is the case. The level of understanding is quite satisfactory and compares well with the understanding of simple liquids or liquid crystals. Therefore, the goal to write a coherent textbook on polymer physics can be reached, I am only rather uncertain if I have succeeded in demonstrating it.

As I am not sufficiently familiar from own experience with all the topics treated in the various chapters I am certainly not in a position to eliminate all errors. Hopefully, the ones I have made, are only minor ones. In any case, I would be grateful for reactions and comments from readers and any indication of faults in the treatment. Some incorrect conclusions have already been eliminated, after comments by Professor M.H. Wagner (Stuttgart) and Dr. L. Könczöl (Freiburg), who were kind enough to go through Chaps. 7 and 8 and I wish to thank them here once again for their advice.

Even if all of us in the scientific community use the English language, for a non-native speaker, the writing of a book is a different matter. As I do not like to read something in bad German I guess that Anglo-American scientists must feel the same. I received help at the beginning of my writing from Dr. Sandra Gilmour, who was working at this time as a postdoctoral student in Freiburg, and would like to express my gratitude again. Then, after completion, the manuscript was thoroughly revised by the copy editor, but he remarked that 'the sentence structure is very German which often makes it sound strange to a native speaker'. So I can only hope that this does not amount to a problem in understanding and offer my apologies.

In the first version produced two years ago the manuscript was dictated immediately after given lectures. This is the reason for the 'pedagogical style' of the writing. The emphasis is on the various concepts which have successfully established the present-day understanding of polymer physics. The focus is on the major phenomena, both in the formation of structures and the behavior under forces applied externally, mainly mechanical ones. This implies that many further effects, although important in certain cases, remain untouched. Hence, this textbook does not represent a comprehensive treatise and, therefore, should be better considered as an 'interface', providing help to enter into the various fields of polymer science, emanating from a basis which shows the interrelations. The recommendations given under the 'Further Readings' at the end of each chapter, the selected works included as figures, and the bibliography supplied in the Appendix are meant to open the way for more detailed studies.

One active area of research is completely missing. These are the optical and electrical properties, with effects such as the high conductivity of doped conjugated polymers, electro-luminescence in polymeric light emitting diodes, or the ferro- and piezoelectricity of poly(vinylidene fluoride), to cite only a few examples. There is no good reason for this omission, only that I did not want to overload the book with another topic of different character which, besides, mostly employs concepts which are known from the physics of semi-conductors and low molar mass molecules.

As already mentioned, this book is primarily written for students of physics and physicists wishing to enter into polymer science for the first time. Interested macromolecular chemists and chemical engineers may also find it useful. The prerequisite for an understanding is not a special one, all that is needed is a background in phenomenological and statistical thermodynamics on the level of the respective courses in physical chemistry, together with the related mathematical knowledge.

Of course, I will be happy if the book finds many readers. It is a matter of fact that polymer physics is largely unknown to the majority of physicists. As a consequence, it is only rarely included in university courses on condensed matter behavior. This is difficult to comprehend considering the widespread uses of polymeric materials and in view of the appealing physical concepts developed for the description of their properties. It is therefore my wish that this book will contribute a little to change the present situation by helping to widen the physicists' general knowledge with a better understanding of the physics of polymers.

Gert Strobl

Freiburg, November 1995

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1

Constitution and Architecture of Chains

Polymers, also known as **macromolecules**, are built up of a large number of molecular units that are linked together by covalent bonds. Usually they represent organic compounds, containing carbon atoms together with hydrogen, oxygen, nitrogen, and halogens, etc. In this first chapter, we briefly survey the main characteristics of their chemical constitution and molecular architecture and introduce the notions employed for their description, using examples for the explanation.

Let us begin with a look at polyethylene (PE), which has a particularly simple structure. It is depicted in Fig. 1.1. The chemical repeat unit or **monomeric unit** building up the chain is the CH_2-(methylene)group and their number determines the **degree of polymerization**, denoted by the symbol N. Macromolecules are generally obtained by a polymerization process starting from reactive low molar mass compounds. The name 'polyethylene' indicates that here the process is usually based on ethylene. Figure 1.2 shows, as a second example, the chemical composition of another common polymer, that of polystyrene (PS). Here phenyl groups are attached as **sidegroups** to the C–C **backbone chain**. Table 1.1 presents a selection of further conventional polymers, giving the chemical constitution of the repeat units and commonly used short forms. The majority (from polypropylene to polycarbonate) has a flexible backbone set-up of carbon atoms, in some cases in combination with some heteroatoms. The four polymers following in the listing (poly(ether ether ketone) to polyimide) are examples for polymers with a stiff backbone.

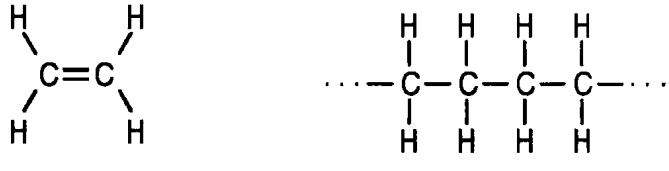

Fig. 1.1. Ethylene and polyethylene

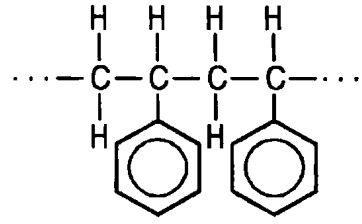

Fig. 1.2. Polystyrene

Rather than being carbon-based, the backbone chain can also be composed of silicon atoms, again together with other elements. The last two materials, poly(dimethylsiloxan) and poly(tetramethyl-p-silphenylene-siloxane) are corresponding examples.

All these polymers are electrically neutral. If chains are built up of monomers that contain an ionizable group, i.e., a group that can dissociate into a chain-fixed kation or anion and a mobile counter-ion bearing the opposite charge, a **polyelectrolyte** is obtained. Table 1.2 collects a few typical examples. The first three compounds are synthetic polymers, the other two samples are biopolymers; cellulose and starch in the form of derivatives which include ionizable substitutes.

Charges on a chain can also be created by doping processes. For **conjugated polymers**, i.e., chains with conjugated C–C double bonds, this is particularly easy. Even more importantly, the produced charges are mobile and thus provide electrical conductivity. Table 1.3 compiles some of these special materials.

Rather than leading to polymers with a unique degree of polymerization, reactions usually result in a mixture of macromolecules with various molar masses. Therefore, for a full characterization, the **molar mass distribution** function has to be determined, and this is usually accomplished by gel permeation chromatography. We choose the symbol M for the molar mass and introduce the distribution function $p(M)$ as a number density, adopting the definition that the product

$$p(M)\,\mathrm{d}M$$

gives the fraction of polymers with molar masses in the range from M to $M + \mathrm{d}M$. As a distribution function $p(M)$ must be normalized

$$\int_0^\infty p(M)\,\mathrm{d}M = 1\,. \tag{1.1}$$

The average molar mass follows by

$$\overline{M}_\mathrm{n} = \int_0^\infty p(M) M\,\mathrm{d}M\,. \tag{1.2}$$

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