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Liquid Crystalline Polymers
2nd Edition
液晶高分子
第二版

(影印版)

〔英〕唐纳德（A. M. Donald）
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序　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了“中外物理学精品书系”，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，“中外物理学精品书系”力图完整呈现近现代世界和中国物理

科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是，在把西方物理的精华要义“请进来”的同时，也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻，引进和翻译世界物理的经典著作和前沿动态，可以满足当前国内物理教学和科研工作的迫切需求。另一方面，改革开放几十年来，我国的物理学研究取得了长足发展，一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域，使世界对中国物理学的过去和现状有更多的深入了解，不仅充分展示出中国物理学研究和积累的“硬实力”，也向世界主动传播我国科技文化领域不断创新的“软实力”，对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是，“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来，中国物理界诞生了很多经典作品，但当时大都分散出版，如今很多代表性的作品已经淹没在浩瀚的图书海洋中，读者们对这些论著也都是“只闻其声，未见其真”。该书系的编者们在这方面下了很大工夫，对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值，不仅可以很好地保护和传承我国物理学的经典文献，充分发挥其应有的传世育人的作用，更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统，真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出，“加强基础研究是提升国家创新能力、积累智力资本的重要途径，是我国跻身世界科技强国的必要条件”。中国的发展在于创新，而基础研究正是一切创新的根本和源泉。我相信，这套“中外物理学精品书系”的出版，不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣，也将进一步推动其他相关基础科学更好更快地发展，为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会 主任

中国科学院院士，北京大学教授

王恩哥

2010 年 5 月于燕园

LIQUID CRYSTALLINE POLYMERS

Second Edition

A. M. Donald
A. H. Windle
University of Cambridge

S. Hanna
University of Bristol

CAMBRIDGE
UNIVERSITY PRESS

Preface to first edition

Liquid crystalline polymers lead one into the heartland of interdisciplinary science, where it is an art in itself to thrive without becoming a Jack of all trades and master of none. To explore new frontiers requires depth, but in this subject probably more than any other there is need for a breadth of background, and often a breadth not catered for within the traditional divisions of school and college science education. The subject lies where organic chemistry, physical chemistry, physics and materials science meet. A physicist will discover the need to appreciate something of the chemical diversity of the molecular world, and will begin to become familiar with the chemical language of the trade. A chemist, skilled in the synthesis of new liquid crystalline molecules, will become increasingly familiar with the need of materials people for samples in kilogram rather than milligram quantities, and with the demands of the physicist that the samples be ever purer and better characterised. Indeed, any scientist meeting the field for the first time will almost certainly be confronted with some unfamiliar areas which must be assimilated and understood in depth. This book is written as a handbook for anyone entering the liquid crystalline polymer arena, from whatever background. We hope it will serve the graduate student embarking on any project associated with these novel materials, the academic desiring a broader knowledge and the scientist whose research efforts become focused into the field. The authors also intend it as a reference text for any course at the undergraduate or masters degree level which includes liquid crystalline polymers within its syllabus. Recognising the likely diversity of experience of its readers, the authors have taken a liberty with the second chapter, *Terminology and concepts*. This they present encyclopaedically, with a wide range of topics appearing in alphabetical order. It is unlikely to be read before the remainder of the book, and is not really meant to be. It is offered as a resource to serve areas in which a reader's background knowledge may need support, and is there to be dipped into as needed.

Liquid crystalline polymers, as a subject area, has arisen from the interaction of two well-established sciences. The more mature of these is liquid crystalline science, now a little over 100 years old (see Chapter 1) which comparatively recently experienced a great upsurge of interest in its own right as the application of liquid crystals to display devices fuelled it with funds and new challenges. Polymer science, by comparison, is somewhat younger, albeit the fore-runner of the plastics industry. The recognition that there are polymers which show liquid crystallinity has, for the device scientist, opened up the possibility of attaching

mesogenic molecules onto or into polymer chains, and led to a wide range of new electro-optical opportunities. On the other hand, the polymer field now has available to it a range of new materials with novel processing capabilities and with the prospect of unique (and marketable!) combinations of properties. Indeed in the heady days of the mid 1980s, there was hardly a large chemical company which was not active in the field, although hopes of a rapid return on investment meant that the subject tended to be oversold. Six years and a world recession later, there are perhaps only four major chemical companies sharing the market for structural liquid crystalline polymers, while device applications are in the advanced development stage. The basic research effort worldwide remains at a high level and is maturing. Integrated teams now follow programmes through from the synthesis of new molecules, to chemical, physical and microstructural characterisation, then to properties and finally to applications, with feedback loops established to the chemistry. This is the current climate in which this book appears. It is perhaps surprising, but, as far as the authors are aware, it is the first dedicated textbook to be published on the subject. There are, of course, a number of multi-author, edited volumes of papers and articles which continue to serve the field in providing up to date research reviews. Indeed, the latest of these, edited by Ciferri and published by VCH (1991) is too recent to be referenced formally in this text but is warmly commended to the reader.

The *contents* pages have already mapped this book. After a brief history of liquid crystalline polymers and the background chapter on terminology and concepts already described, Chapter 3 concentrates on relating the stability of liquid crystalline polymers, as a function of temperature and solvent content, to their molecular architecture. It builds strongly on the established knowledge of small molecule liquid crystalline phases, and will be an especially appropriate entry point to any who are familiar with that side of the subject. While Chapter 3 focuses on the influence of chemical detail on stability, Chapter 4 takes the reader through the different theories which describe liquid crystalline polymers using, deliberately, the simplest of molecular models. Attention is given to the search for the critical molecular parameters which are the essence of chain mesogenicity, and which determine transition temperatures and microstructures both in thermotropic melts and lyotropic solutions. Chapter 5 examines aspects of local molecular order in more detail and introduces the reader to the Friedelian classification of polymeric mesophases. Chapter 6 moves up in scale to the continuum level where the microstructure of liquid crystalline polymer phases is accounted for in terms of distortion energies and defects within the elastic distortion fields, while Chapter 7 represents a further increase in scale, describing the response to external applied fields. While most emphasis is placed on flow fields and the associated rheological issues, there are also five pages or so devoted to the effect of electromagnetic fields. In writing Chapter 8 on practical aspects of liquid crystalline polymers, the authors have sought to provide a snapshot of current applications of the materials. They have done this in the knowledge that this chapter is likely to age rather more quickly than the preceding ones, but it is a risk taken in the belief that an appreciation of the applications of the science to technology and thus to commerce, makes the best possible context for fundamental research in providing a spur to new ideas.

In addition to the references, by chapter at the end of the book, there are also indices both of symbols used and of chemical formulae of the vast majority of molecules referred to in the book. The molecules are indexed by numbers in angle brackets, the references in square brackets, while the equations are numbered in round brackets. The units used are SI, although some more esoteric ones such as N tex^{-1}, are briefly introduced, more to prepare the reader for what may be encountered elsewhere than to serve the needs of the text itself. In addition e.s.u. still tends to be used in electromagnetic experiments. Particularly, we ask the reader's bilingual indulgence in the matter of temperature units. While we have used Kelvin (K) where there are no other constraints, so many data are still published in centigrade units (°C) that we have not converted reported values, either in figures or in the text.

With the book now complete it is our great pleasure to thank those who have helped us to make it appear at all. In the first place, it was Professor Ian Ward who recognised the need for such a text and encouraged us to go ahead. We are especially grateful to him for his leadership, support and constructive comments on the manuscript, and his unfailing patience. We must also acknowledge with gratitude, all those who have influenced us in our scientific careers and thus indirectly contributed here. In particular we wish to thank our various mentors in (respectively) Materials Science at Cornell University and the Department of Physics at Bristol University, as well as here at Cambridge. We also recognise the contribution of our University through its enlightened attitude to the sabbatical principle. Our research students, past and present, have given much, not only in their tolerance of our reduced availability at times, but also through their candid critique of various drafts of chapters. Our respective spouses, Matthew and Janet, and our families, have a big part in this too. For their love and assistance over six summers, we thank them.

Preface to second edition

Over ten years have passed since the first edition of this book was published, a period marked by continued growth in liquid crystalline polymer research and a gradual maturing of understanding of the key scientific issues. Whereas the first edition was the first textbook to cover the field, this second edition has been able to draw on a very much wider range of textbooks and research papers than was available in 1992. It is thus a rather different book. Certainly, it is about twice the length as it embraces more recent and more detailed understanding of particular topics such as theory and modelling and disclination structures, while at the same time introducing necessary new topics. Amongst these is the extension of a discussion of liquid polymeric structures across into the biological field, an important and potentially far-reaching area and marked in the new edition by an additional chapter (Chapter 7). The whole area of liquid crystalline elastomers, has now advanced to the point where there is a satisfying blend of experiment and theory and, accordingly, it is now covered in some detail in Sections 4.8.7 and 8.7. Even carbon nanotubes feature briefly, as they show liquid crystalline phases and disclination defects. The strong growth in the field of computational modelling of polymers means that, in addition to its contribution to theoretical understanding, it can provide a means of illustrating various liquid crystalline processes involving microstructure and defects. Considerable use is now made of this capability. Treatments of side-chain polymers are organised to stand out more clearly than before, although it has to be said that the current impact of liquid crystalline polymers on devices is probably more main-chain than side-chain. Having duly noted the differences, it should be emphasised that the overall structure of the first edition has stood the test of time and has been retained. The chapter structure is largely the same but with two exceptions: the insertion of the biologically related chapter already mentioned, and the division of the applications chapter into two (Chapters 9 and 10), which deal with structural and functional liquid crystalline polymers respectively. Some of the more applied aspects of rheology have also been transferred into Chapter 9. As before, Chapter 2 reviews terminology and concepts, arranged so that any reader coming into this field from another is able to acquire essential background material as conveniently as possible; additionally, the terms which are explained in this chapter appear as bold italic throughout the text so that it serves also as a glossary. Furthermore, the cross-indexing of molecular structures drawn within the text, and their collation into an index is retained. The authors are pleased to note that the vast

majority of the material in the first edition, including many of the figures, is still highly relevant and finds its just place in the second. The second edition is thus largely built upon the base of the first, but with significant expansion in both depth and breadth necessary to represent the significant progress in the field.

It is pertinent to enquire of the impact which liquid crystalline polymers are having on industry and society. From the days when almost every primary polymer company in the world was investing in liquid crystalline polymer research, the perspective has been scaled back to the point where many of the important applications of these materials may be properly described as niche applications. Certainly, they are high performance polymers and not commodity materials. It is interesting to note that the applications chapters have not had to be recast, they are simply longer as there is much more to describe. Main-chain, structural polymers are proving their worth in high strength, high precision mouldings, and are used extensively in the electronics industry with applications ranging from computer connectors to casings for mobile phones. Medical applications are also being developed. In fibre form, liquid crystalline polymers have been woven into cloth for high endurance sails, and were used for the airbags that cushioned the landing of NASA's highly successful missions to Mars. Main-chain polymers are also proving of value as functional materials, with many polymeric light-emitting diodes being processed in a liquid crystalline phase.

On the other hand, side-chain materials, originally identified as future display materials, have fared less well. The high viscosity of polymeric liquid crystals compared with their small-molecule cousins, has been the key reason that side-chain polymers have not been adopted as the active element in any commercial device. Although ferroelectric systems showed early promise, the change of mindset required, not to mention the cost of re-equipping factories to handle new production processes, has ensured that such materials remain on the shelf for now. It is important to note, however, that applications for side-chain liquid crystalline polymers are gradually emerging, and they do appear to have a healthy future. Perhaps the most significant application to appear so far *is* in the field of displays. But, rather than providing the active element, they are being used to create passive films with carefully tailored optical properties, which are leading to dramatic improvements in the brightness and viewing angles available from conventional liquid crystal displays (see Section 10.3). In other areas, careful design of new molecules is leading to applications in non-linear optics, in piezo- and pyroelectric sensors, and when cross-linked, as tunable lasers and artificial muscles.

The second edition provides a new opportunity to thank those who have contributed, directly or indirectly, to the work. Professor Ian Ward persuaded us to persevere with the new edition, and continued to provide necessary steers as we wrestled with a plethora of available material. Our respective research groups in Bristol and Cambridge, have perhaps seen rather less of us because of the book, while the love and forbearance of our families have been invaluable as ever.

Contents

Part I

Fundamentals