LIQUID CRYSTALLINE POLYMERS

SECOND EDITION

The new edition of this authoritative guide on liquid crystalline polymer (LCP) science has been produced in response to the wealth of new material recently generated in the field. It takes the reader through the theoretical underpinnings to real-world applications of LCP technology in a logical, well-integrated manner. A chapter on liquid crystalline biopolymers has been introduced, whilst the in-depth discussion on applications describes not only maturing fields of high strength structural LCPs, but also a detailed analysis of the developing area of functional materials. The in-depth coverage and detailed glossary establish this as an indispensable text for graduate students and researchers in the polymer field, as well as being of interest to those working in chemistry, physics and materials science.

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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.