book reviews

Polymer Update: Science and Engineering

W. D. Cook and G. B. Guise (Eds)
Royal Australian Chemical Institute, Victoria, 1989, 285 pages
ISBN 0 909589 67 4

The Polymer Division of the Royal Australian Chemical Institute, like the Plastics and Rubber Institute in the UK, is a national forum for discussion, education and training. This book is the second in a series, edited by G. B. Guise, with which it has entered the arena of publication for a wider international scientific community. Its objective is clear from its origin in an intensive two-day course for scientists and engineers whose careers had led them into the area but who lacked a formal training in polymer engineering, physics or chemistry: the book is an 'update' in the sense of a review of currently accepted basic understanding ('dogma'?) to frame an appreciation of new research developments. Cook and Guise have mastered the formidable editing task of integrating 'course notes' from seven contributors into a substantial, linear and consistent text, with little duplication, few omissions and research hobby horses firmly reined.

Guise opens with a readable historical review, which highlights the quantum jumps in which polymer science and engineering has progressed. Like biological evolution seen on the 'punctuated equilibrium' model, the pace of progress has often been forced by acute stimuli, both external (war, oil price changes) and internal (the 'discovery' of macromolecular structure and Ziegler-Natta catalysts). It is interesting—especially as we currently face another emergency of uncertain feedstock supply and price—to reflect that the current emphasis on special small-tonnage, functional and high performance polymers was partly determined by the oil price rises of the early 70s.

The next two chapters focus on polymer synthesis. This route to a basic understanding of microstructure and properties has been adopted by some textbooks (e.g. Rodriguez) and can be very effective even for those whose first subject is not chemistry. E. Rizzardo's exhaustive review of the mechanisms of chain growth polymerization is followed by R. A. Shanks on step-growth polymerization reactions, in which many of the more exciting new high-performance polymers are introduced; this chapter also considers some microstructural topics, such as rubber toughening in epoxies and gelation in networks, as they arise.

A didactic path from molecular structure through amorphous melt to amorphous glass and the crystalline phase continues with Z. H. Stachurski's chapter on Melt Properties and Solidification. The approach remains firmly based in the underlying molecular phenomena; polymer melt properties are introduced by moving from concepts of mobility, diffusion and viscosity in gases and simple liquids, to chain conformation, configuration and reptation. The section on solidification provides both a platform for presenting Stachurski's own work on TTT diagrams and a bridge to the following chapter by K. R. Chynoweth on Glass Transition and Crystallization.

R. P. Burford's chapter on Elastomers recognises the subject as one which has evolved in weaker communication with the main population of polymer science. Thus all aspects of these materials, from physics through formulation and processing to mechanical testing, are dealt with, before turning to a material-by-material account of specific materials, from natural rubber through to block copolymer and IPN structured thermoplastic elastomers.

The final chapter, by D. R. G. Williams, on Mechanical Behaviour of Amorphous and Semicrystalline Polymers, opens by reconsidering transitions as modulus/temperature variations. Physical and processing properties are touched on as well as the microstructure of copolymers and blends. Some of this depth has been achieved at the expense of broader mechanical phenomenology. Williams declares an equivalence of 'brittle' fracture to primary bond breakage, ductile fracture to secondary bond slippage—although it is known that microductile deformation dominates 'brittle' surface fracture work. Surely, after a 20 year contribution to polymer engineering research, Fracture Mechanics has earned more than a single paragraph, and could have served to deepen discussion of this and other areas?

In general, this book is a valuable resource for travellers through the vast landscape of research literature in polymer science and engineering. The overall standard of writing, illustration and typography are high, and this book can be recommended as a particularly good investment for readers from a background in chemistry.

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Applied Polymer Light Microscopy

D. A. Hemsley (Ed)
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Light microscopy has been sadly neglected as an investigative tool, following the development of more perceivedly glamorous techniques such as electron imaging microscopy. The ultimate in resolution, however, frequently blinds the observer to the necessary statistical relevance of viewing structures large enough to contribute to the macroscopic properties of a material. This is unequivocally the case in the ever-burgeoning field of polymer science. It is, therefore, timely to re-evaluate the potential uses and applications offered by the optical microscope, especially in those branches of scientific study outside the field of biology—a conventional stronghold for light microscopists—in which its value has been largely forgotten or unrealised.

For the want of other texts, this collection of contributions from various authors, each individually respected in their discipline, suffices as an introduction to the subject. However, it disappoints in its lack of coherence—not unique to the practice of collating monographs—and more importantly its failure to impress the value and quality of the images attainable. Primarily, the problem lies in the dated style of presentation, especially noticeable in the early chapters describing specimen preparation and basic microscope construction. The graphics are poor and suffer from being hand-drawn. The photography is often ill-composed and monochrome reproduction proves wholly unsuitable for illustrating images formed by methods of colour contrast (although it is a means of achieving economy).

It has to be recognised that a book of limited size (271 pages) aimed at an introductory audience must suffer from omissions. Perhaps the most obvious is the lack of discussion of the role of fillers, not only from the aspects of microscopic imaging but the fundamental constraints imposed on sample preparation (Chapter 1, A. D. Curson, ICI). For example, it would have been valuable to have included comments on the precautions necessary in preparing sections from polymers filled with a hard crystalline mineral, such as calcium carbonate, or a soft 'smearable' talcum. Furthermore, some fillers are soluble and the practice

of lubricating and floating thin sections for transmission microscopy may not be possible, in which case reflected light microscopy from surface finished sample blocks, with enhanced contrast/reflectivity by metal coating, yields rewarding results.

The inclusion by Hemsley of a brief excursion into Information Theory and optical transfer functions is to be commended as a tantalising approach to the basic principles of light microscopy (Chapter 2).

The theory and measurement principles of polarized light microscopy are adequately described in the contribution by B. P. Saville, University of Loughborough (Chapter 3). It is to be expected that the usual crop of errors will appear, most of which are interpretable from the context. However, this chapter contains more than its fair share. Those readers attempting to apply the algebraic expressions given in Section 3.3 and Figure 3.4, p. 82, could become confused by the interchange of axial systems y, z for x, y and the alternate presence and absence of subscripts. Similarly, equation 3.14, p. 96, should read,

$$fz = fy = \frac{1 - 3\overline{\cos^2 \phi_{1x}}}{2},$$

not

$$\frac{1 - 3\overline{\cos^2 \phi_{1x}}}{z}.$$

The contribution in Chapter 4 from the same author contains a wealth of practical observation, and particular attention is drawn to concepts of texture in relation to polymer crystallization.

Hoffman's contribution (Modulation Optics, NY) in Chapter 5 contains a good description of the physical systems required to obtain modulation contrast, and offers the greatest sense of unity by cross reference to the other contributions. But, sadly, here is the worst example of constraint by monochrome graphics—how can an author adequately describe Newton's colour sequence in the context of Differential Interference Contrast when the reader is rendered colour blind? It also shows the microscopist's desire to stress the resolution limit of an observation when referring to an optical path difference of 'about 0.200 μm'—is one to assume 0.200 ± 0.0005 μm? I suspect not.

Hemsley's discussion of interference microscopy reveals descriptive powers at their best (Chapter 6), with an excitement and enthusiasm surrounding practical observation and including many examples of the investigative power of the technique when applied to material identification.

Calvert and Billingham (University of Sussex) continue the excellent theme of applied techniques to polymer science in their updated review (Chapter 7) of ultraviolet and fluorescence microscopy. In the closing pages the reader obtains a glimpse of the sophistication and elegance of the light microscope for the study of such phenomena as molecular mobility and diffusion throughout polymer structures, with specific examples describing the diffusion: spherulitic growth ratios of impurities associated with their relative solubilities in the crystalline and amorphous phases.

It is to be hoped that, despite the book's overall shortcomings, the inclusion of these concluding chapters, together with a well compiled bibliography and reference list, will enable the publication to inspire the investigative polymer scientist with at least a sense of awareness of the many significant advantages the methodology has to offer.

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N.m.r. Spectroscopy and Polymer Microstructure: The Conformational Connection

A. E. Tonelli (Ed)
VCH Publishers (UK) Ltd, Cambridge, UK, 1989, 252 pages
ISBN 0-89573-737-X

Without doubt, n.m.r. spectroscopy is the principal method for determining the molecular structure of polymers. Evidence for this is obtained merely by noting the number of papers in polymer journals which report the use of n.m.r. spectroscopy as the primary means of polymer characterization. In the 1970s, books by Bovey ('High Resolution NMR of Macromolecules', Academic Press, New York, 1972) and Randall ('Polymer Sequence Determination', Academic Press, New York, 1977) championed the application of n.m.r. methods to the study of polymers. Given the rapid progress made in n.m.r. spectroscopy since then, such as the advent of two-dimensional n.m.r. and high-resolution solid-state n.m.r., and ever-increasing magnetic field strengths, this new text is long overdue.

The stated aim of this book is to enable polymer scientists to determine more readily the microstructures and conformations of polymers using n.m.r. spectroscopy. The book begins with a relatively brief chapter providing clear and useful definitions of polymer microstructure. The following three chapters, which are also reasonably short, introduce the reader to the general concepts of n.m.r. spectroscopy and its application to polymers. The author has sensibly kept the n.m.r. theory to a minimum, providing only the bare essentials of the technique. Thus, for example, two-dimensional n.m.r. is dealt with in a couple of pages. In later chapters, the author then quite rightly prefers to concentrate on the kinds of information available from 2D n.m.r. measurements, rather than on the intricate theory of how the experiments work. In this way, the non-specialist is informed without being put off by lengthy discussion.

In Chapter 5, discussion of the link between polymer microstructure, conformation, and observed n.m.r. spectra begins in earnest. The chapter shows how carbon-13 chemical shifts of a polymer may be predicted using the rotational isomeric state model of a polymer and the *gamma-gauche* effect. Indeed, this connection between microstructure, conformation, and n.m.r. spectra provides a unifying theme for the rest of the book.

Chapters 6–9 provide a wide range of examples of the use of n.m.r. spectroscopy to study polymer microstructure, dealing with determination of vinyl polymer stereosequence, microstructural defects, copolymer microstructure, and chemically-modified polymers. Throughout these chapters, great emphasis is placed on the use of the *gamma-gauche* effect method, the success of which justifies its pre-eminence. These chapters also include useful sections on the use of 2D n.m.r. techniques to study microstructure and conformation, and a discussion of copolymerization mechanisms. The majority of the examples presented in these chapters (indeed, throughout the book) are taken from the work of the author and his colleagues. However, no criticism can be levelled at this, given that the examples chosen cover all the major areas of polymer microstructure. Moreover, the author's familiarity with the examples means that they are presented in a logical and comprehensible manner.

Chapter 10 provides a brief introduction to the elucidation of biopolymer microstructure using n.m.r. techniques. Of course, a whole text could be devoted to this area. However, the author brings out the key elements of biopolymer characterization, emphasising the importance of 2D-COSY and NOESY measurements in this area. The book concludes with a chapter on solid-state n.m.r. spectroscopy of polymers. Although a number of recent texts are already available on this subject, its inclusion is justified since its context is again the link between microstructure, conformation and n.m.r. properties.

Overall, the book is well-written and the quality of presentation is generally excellent. However, one small criticism stems from the way the figures are interspersed with the text, particularly in Chapter 10. I found it slightly annoying to have to flick four or five pages ahead to find a figure referred to in the text.

In conclusion, I feel that the book will achieve its aim and is worthy of a place on the bookshelves of polymer scientists and n.m.r. spectroscopists alike.

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