



# COMPREHENSIVE POLYMER SCIENCE

*The Synthesis, Characterization, Reactions  
& Applications of Polymers*

CHAIRMAN OF THE EDITORIAL BOARD

**SIR GEOFFREY ALLEN, FRs**

*Unilever Research and Engineering, London, UK*

DEPUTY CHAIRMAN OF THE EDITORIAL BOARD

**JOHN C. BEVINGTON**

*University of Lancaster, UK*

**Volume 1**

**Polymer Characterization**

VOLUME EDITORS

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# Preface

It is only 60 years since Staudinger's model of the molecular nature of a polymer was becoming universally accepted and the physical states of rubbers, plastics and fibres understood. Unfortunately, for some time many academic chemists continued not to appreciate the full significance of polymerization reactions and physicists tended to regard polymeric materials as inevitably being of indeterminate composition and unamenable to study by conventional physical methods.

Nevertheless, in the 1930s the foundations were laid for the understanding of the main polymerization mechanisms. An industry based on synthetic rubbers, plastics and fibres was soon established. In World War II it played a major strategic role and afterwards grew to be one of the main elements of the heavy chemicals industry. It became recognized that synthetics may be superior to natural materials in their properties and that they may be used for completely new purposes.

Alongside the production of well-defined materials there grew the ability to characterize the structure of polymer molecules and to understand the relationships between methods of preparation and subsequent treatment, structure and properties, both chemical and physical. As a result, a vast literature of polymer science and technology has been generated and four Nobel prizes awarded specifically for contributions to polymer science. Add to this the fact that many biological molecules, including polypeptides, enzymes, antibodies, carbohydrates and so on, are polymers of varying degrees of complexity, then the universality of polymers in the physical and biological sciences and technologies forms a dominant modern theme.

*Comprehensive Polymer Science* is a series of volumes designed to set down the structure of this vast subject in such a way that researchers and teachers of polymer science and workers in associated fields can find an authoritative and comprehensive account of the topic of immediate interest. That topic is set out in a framework of related subjects. The text is focused on synthetic polymers with little reference to biological macromolecules *per se* but the science underpins both physical and biological systems.

To ensure that the wide coverage is maintained at an authoritative level, more than 250 authors from 20 countries have been enlisted. Their contributions have been organized into a series of major themes:

Volume 1	Polymer Characterization
Volume 2	Polymer Properties
Volumes 3-5	Polymerization Mechanisms
Volume 6	Polymer Reactions
Volume 7	Specialty Polymers & Polymer Processing

Because of the wide coverage the editors were presented with a particularly difficult decision with regard to symbols and nomenclature. The latter does not follow strictly the recommendations of IUPAC nor are symbols consistent throughout the whole work. However, usage in a particular chapter is consistent with the practice in the current literature. Thus a reader will be able to frame new publications in the context of the information presented in this series of volumes.

We should like to acknowledge the way in which the staff at the publisher, particularly Dr Colin Drayton (who initially proposed the project), Dr Helen McPherson and their editorial team, have supported the editors and authors in their endeavour to produce a text that is both complete and up-to-date and that will appeal to industrial and academic researchers alike. *Comprehensive Polymer Science* is a milestone in the literature of the subject in terms of coverage, clarity and a sustained high level of presentation.

GEOFFREY ALLEN  
London

JOHN C. BEVINGTON  
Lancaster

# Contributors to Volume 1

**Professor Sir Geoffrey Allen**

Unilever Research & Engineering, PO Box 68, Unilever House, Blackfriars, London EC4P 4BQ, UK

**Dr N. S. Allen**

Faculty of Science and Engineering, John Dalton Building, Manchester Polytechnic, Chester Street, Manchester M1 5GD, UK

**Professor E. D. T. Atkins**

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

**Professor D. C. Bassett**

Department of Physics, J. J. Thomson Physical Laboratory, University of Reading, Whiteknights, PO Box 220, Reading RG6 2AF, UK

**Dr G. S. Beddard**

Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

**Dr C. Booth**

Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

**Dr F. A. Bovey**

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, USA

**Dr D. Briggs**

ICI Plc, Petrochemicals and Plastics Division, PO Box 90, Wilton Centre, Middlesbrough, Cleveland TS6 8JE, UK

**Dr P. M. Budd**

BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, UK

**Professor G. G. Cameron**

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2HE, UK

**Professor B. T. P. Chu**

Department of Chemistry and of Materials Science and Engineering, State University of New York, Stony Brook, Long Island, NY 11794-3400, USA

**Professor F. Ciardelli**

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 35 Via Risorgimento, I-56100 Pisa, Italy

**Dr R. O. Colclough**

Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

**Dr J. V. Dawkins**

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK



Professor D. L. Dorset

Electron Diffraction Department, Medical Foundation of Buffalo Inc., 73 High Street, Buffalo, NY 14203, USA

Dr H. Geerissen

Johannes-Gutenberg-Universität, Institut für Physikalische Chemie, Jakob-Welder-Weg 13, D-6500, Mainz, Federal Republic of Germany

Professor J. C. Giddings

Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

Professor G. Glöckner

Technische Universität Dresden, Sektion Chemie, Wissenschaftsbereich, Hochpolymere und Textilchemie, Mommsenstrasse 13, DDR-8027 Dresden, German Democratic Republic

Dr J. J. Gunderson

Dow Chemical Co., Midland, MI 48667, USA

Dr I. H. Hall

Department of Pure and Applied Physics, University of Manchester Institute of Science and Technology, PO Box 88, Sackville Street, Manchester M60 1QD, UK

Professor A. E. Hamielec

McMaster Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

Dr T. Hammond

Birmingham Polymer Group, Department of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT, UK

Dr F. Heatley

Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

Mr D. A. Hemsley

Institute of Polymer Technology, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK

Dr D. M. Hindenlang

Analytical Research Division, Allied-Signal Inc., Corporate Technology, PO Box 1021R, Morristown, NJ 07960, USA

Professor S. L. Hsu

Department of Polymer and Engineering Science, University of Massachusetts, Amherst, MA 01003, USA

Professor A. D. Jenkins

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ, UK

Dr K. Kamide

Fundamental Research Laboratory of Fibers and Fiber-forming Polymers, Asahi Chemical Industry Company Ltd., 11-7 Hacchonawate, Takatsuki, Osaka 569, Japan

Professor I. A. Katime

Departamento Química Física, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao, Spain

Dr T. A. King

Department of Physics, Schuster Laboratory, University of Manchester, Manchester M13 9PL, UK

Dr L. A. Kleintjens

Tossaintstr. 5, 6171 HN Stein, The Netherlands

Dr R. Koningsveld

P Visschersstr. 23, 6174 RB Sweikhuizen, The Netherlands

Dr R. S. Lehrle

Birmingham Polymer Group, Department of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT, UK

Dr K. L. Loening

Chemical Abstracts Service, PO Box 3012, 2540 Olentangy River Road, Columbus, OH 43210, USA

Dr P. A. Lovell

Polymer Science and Technology Group, University of Manchester Institute of Science and Technology, PO Box 88, Sackville Street, Manchester M60 1QD, UK

Professor V. J. McBrierty

Department of Pure and Applied Physics, University of Dublin, Trinity College, Dublin 2, Ireland

Dr J. R. MacCallum

Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

Dr G. R. Mitchell

Department of Physics, J. J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 2AF, UK

Dr J. R. Quintana

Departamento Quimica Fisica, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao, Spain

Dr R. W. Richards

Department of Pure and Applied Science, Thomas Graham Building, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK

Dr M. J. Richardson

Division of Materials Applications, National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK

Dr D. M. Sadler<sup>†</sup>

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

Dr N. Schlotter

Bell Communications Research, Navesink Research Center, Room 3X 163, 331 Newman Springs Road, Red Bank, NJ 07701-7020, USA

Dr P. Schützeichel

Johannes-Gutenberg-Universität, Institut für Physikalische Chemie, Jakob-Welder-Weg 13, D-6500, Mainz, Federal Republic of Germany

**Dr R. D. Sedgwick**

Analytical Research Division, Allied-Signal Inc., Corporate Technology, PO Box 1021R,  
Morristown, NJ 07960, USA

**Dr M. Styring**

McMaster Institute for Polymer Production Technology, Department of Chemical Engineering,  
McMaster University, Hamilton, Ontario L8S 4L7, Canada

**Dr M. Tsuji**

Laboratory of Polymer Crystals, Institute for Chemical Research, Kyoto University, Uji,  
Kyoto-fu 614, Japan

**Dr B. A. Wolf**

Johannes-Gutenberg-Universität, Institut für Physikalische Chemie, Jakob-Welder-Weg 13,  
D-6500, Mainz, Federal Republic of Germany

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# 1

## Perspectives

GEOFFREY ALLEN

Unilever Research and Engineering, London, UK

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### 1.1 INTRODUCTION

From the standpoint of western science, the origins of plastics technology lie with the medieval Guilds of Horners. Horn softens at 125°C and can be shaped into a variety of utensils. Alternatively, it can be rolled into thin translucent sheets originally used in lanterns and windows. The Worshipful Company of Horners was founded in the City of London in the 12th century; it is extant but now many of its members are associated with the modern plastics industry.

The entry of rubber into western civilization is more precisely documented. Natural rubber in the form of balls was brought to Europe from the New World by Columbus returning from his second voyage in 1496. There were various reports of ball games played by the Indians, and in 1585 the chronicler Duran wrote, '... the ball is as big as a small ball used in 9-pins ... It has one property which is that it jumps and rebounds upwards and continues jumping from here to there so that those who run after it become tired before they catch it.'

### 1.2 THE ORIGINS OF RUBBER TECHNOLOGY

In 1748, Charles-Marie de la Condamine,<sup>1</sup> returning from a voyage of scientific exploration in South America, sent to his sponsors, the Academie de Science in Paris, specimens of natural rubber, called cauchu. He wrote, 'There grows a tree which the natives call Hleve. When the bark is cut a white, milky fluid runs out and hardens in the air.' He described the collection of latex from the *Hevea brasiliensis* tree and how rubber utensils were made by drying it down by smoking over leaf fires.



In 1763, cauchu, dissolved in turpentine, was sold as a rubber cement in France. Seven years later, in the preface to 'A Familiar Introduction to the Theory and Practice of Perspective', Joseph Priestley<sup>2</sup> wrote: 'Since this work was printed off, I have seen a substance excellently adapted to the purpose of wiping from paper the marks of a black-lead pencil. It must therefore be of a singular use to those who practice drawing. It is sold by Mr. Nairne, Mathematical Instrument Maker, opposite the Royal Exchange. He sells a cubial piece of about half an inch for three shillings and he says it will last several years'. Thus, cauchu became 'rubber' in English, whereas in France it remains 'caoutchou'.

The first waterproof clothes were manufactured from natural rubber in the UK in 1791, and in 1823 MacIntosh<sup>3</sup> produced much improved products laminated on both sides with cotton fabric. The world production of natural rubber rose to 100 tonnes per annum. One of the drawbacks of the raw rubber used to waterproof garments was its tendency to crystallize into a rigid form at about 0°C.

Charles Goodyear's work on the sulfur cure of natural rubber was announced<sup>4</sup> in 1844, and, shortly after, Hancock introduced the term 'vulcanization'. From the point of view of rubber technology, the suppression of flow and crystallization brought about by curing was a major step towards turning natural rubber into an engineering material.

By the end of the century, natural rubber plantations were established in Malaysia. The invention of the internal combustion engine and Dunlop's pneumatic tyre<sup>5</sup> (1888) swelled the increasing demand for natural rubber to 10 000 tonnes per annum worldwide.

This phase of rubber technology culminated with the development of synthetic rubbers. Harries,<sup>6</sup> in 1906, polymerized isoprene using a sodium catalyst to form the first synthetic analogue of natural rubber. Hofmann<sup>7</sup> (1907) of Bayer synthesized natural rubber by heating isoprene in an autoclave. However, because 2,3-dimethylbutadiene was more readily available at lower cost, Hofmann used this monomer to make 'methyl rubber'. The blockade of Germany during World War I revived this process, and production ultimately reached 1500 tonnes per annum.

### 1.3 THE ORIGINS OF PLASTICS TECHNOLOGY

The first synthetic plastic reported was cellulose nitrate, described by Schonbein<sup>8</sup> in 1846, but his attention quickly turned to its exploitation as gun cotton. However, in 1862 Parkes<sup>9</sup> won a medal for his novel material Parkesine and built a factory at Hackney Wick to manufacture this cellulose derivative. Not surprisingly, the factory burned down in 1868. Shortly after this, the material was patented as Celluloid in 1870 by the Hyatts<sup>10</sup> and they won a prize of \$10 000 for a substitute material for billiard balls! Next, cellulose acetate was introduced by Cross and Bevan in 1892<sup>11</sup> and it was later used to make viscose rayon fibre.

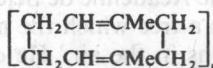
About the same period, Baekeland<sup>12</sup> emigrated from Ghent to the USA, via the UK. In 1907 he announced the first thermosetting resin, 'Bakelite', a member of the phenol-formaldehyde range of plastics.

Thus, at the outbreak of World War I, there were three industrial plastics: cellulose nitrate, cellulose acetate and 'Bakelite'. They were used principally in electrical and aeronautical applications.

### 1.4 THE CONCEPT OF A POLYMER MOLECULE

Early attempts to determine the chemical nature of polymeric materials were hampered by three factors which made chemists reluctant to adopt the modern concept.

First, organic chemists in the 19th century strove to find precise formulae and to isolate pure substances. Thus, in 1826, Faraday<sup>13</sup> determined the empirical formula of natural rubber to be  $C_8H_7$ . Isoprene was obtained<sup>14</sup> from natural rubber by destructive distillation in 1860 and, although the unit  $C_5H_8$  was firmly established, Harries, in 1905, argued<sup>15</sup> for the association of isoprene dimers (structure 1). Only in 1914 did he concede<sup>16</sup> that larger rings of five or seven isoprene units may be involved. A similar progression of ideas marked the evolution of chemical structures for cellulose, starch and proteins. At the turn of the century most scientists did not distinguish between large covalent structures and aggregates of smaller molecules formed by partial bonding or physical association.



(1)