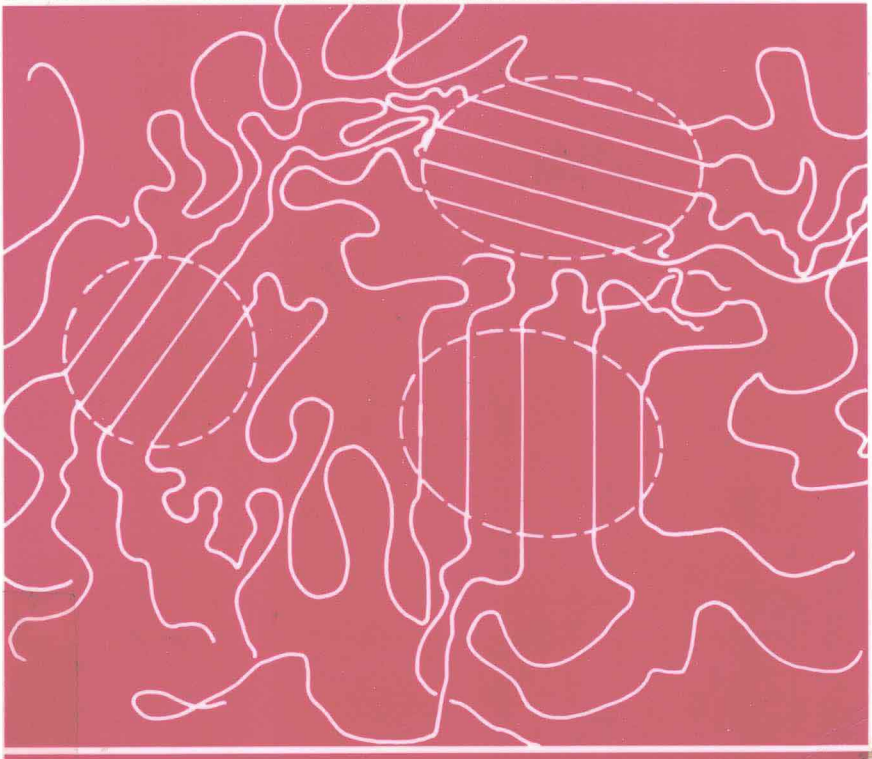
IAN M. CAMPBELL

Introduction to Synthetic Polymers



OXFORD SCIENCE PUBLICATIONS

Introduction to Synthetic Polymers

Ian M. Campbell
School of Chemistry,
University of Leeds

Oxford New York Tokyo
OXFORD UNIVERSITY PRESS
1994

Oxford University Press, Walton Street, Oxford OX2 6DP
Oxford New York
Athens Auckland Bangkok Bombay
Calcutta Cape Town Dar es Salaam Delhi
Florence Hong Kong Istanbul Karachi
Kuala Lumpur Madras Madrid Melbourne
Mexico City Nairobi Paris Singapore
Taipei Tokyo Toronto
and associated companies in
Berlin Ibadan

Oxford is a trade mark of Oxford University Press

Published in the United States by
Oxford University Press Inc., New York

© Ian M. Campbell, 1994

First published 1994
Reprinted 1994

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, without the prior permission in writing of Oxford University Press. Within the UK, exceptions are allowed in respect of any fair dealing for the purpose of research or private study, or criticism or review, as permitted under the Copyright, Designs and Patents Act, 1988, or in the case of reprographic reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency. Enquiries concerning reproduction outside those terms and in other countries should be sent to the Rights Department, Oxford University Press, at the address above.

This book is sold subject to the condition that it shall not, by way of trade or otherwise, be lent, re-sold, hired out, or otherwise circulated without the publisher's prior consent in any form of binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

A catalogue record for this book is available from the British Library

Library of Congress Cataloging in Publication Data
Campbell, Ian M. (Ian McIntyre), 1941–
Introduction to synthetic polymers / Ian M. Campbell.
(Oxford chemistry series ;)
Includes bibliographical references and index.
1. Polymers. I. Title. II. Series.
QD381.C34 1994 547.7—dc20 93–1953
ISBN 0 19 855399 4 (Hbk)
ISBN 0 19 855398 6 (Pbk)

Printed in Great Britain by
Redwood Books, Trowbridge, Wiltshire

Introduction to Synthetic Polymers

Preface

Ten or so lectures on synthetic polymers are a usual component of undergraduate chemistry courses. The available textbooks have usually been written for more specialist interests. These books, apparently full of 'thousands' of polymeric chain structures, can discourage the students and make it an uphill struggle to instil confidence that a reasonable understanding of the main principles underlying the synthesis and properties of polymers can be achieved.

The aim of this book is to use a relatively small number of polymers as the background for an introduction to the most important aspects of modern polymer science. The amounts involved in commerce are the main basis of the particular polymers which are used as examples. A book of this length must be somewhat selective, focusing on the more important facets. For example, books on polymers are often overburdened with the range of methods for molecular weight determination: here it is recognized that just a few of these cover the large bulk of relevant activity in modern laboratories. There is little need beyond this for a reader seeking an introduction to the topic.

There are two main questions of fundamental importance here. How do the properties of a polymeric substance in bulk relate to the sizes and architectures of the molecules in it? How may the desired features be imposed on polymeric chains during synthesis? To illustrate the possible variations for just one polymeric substance, it may contain chains which are all around the same length or which cover a substantial range of lengths; the chains may be linear (unbranched) or branched or, indeed, of more complex forms such as 'comb-like' or 'star-like'; there may be chiral (asymmetric) centres in the chains and in sequence these may be all the same, randomly different or alternating. What effects do these subtle differences produce at the macroscopic level and how may the syntheses of the different types of polymer be brought about?

Chapter 1 defines terminology before giving historical and industrial perspectives: it then introduces general aspects of polymerization processes. The averages and distributions of molecular masses of polymers, their definitions and main methods of measurement, are the topics of Chapter 2. The microscopic structures of bulk polymers and their effects on the physical properties are assessed in Chapter 3, whilst Chapter 4 goes on to discuss how modern techniques may be applied to obtain detailed information on microstructural features. Chapters 5–7 describe the major mecha-

试读结束，需要全本PDF请购买 www.ertongbook.com

nisms of polymerizations, step-growth, radical-addition, and ionic/coordination-addition types respectively, using important industrial processes for exemplification. Chapter 8 relates various main features of chemical and physical structures to the properties of common polymers. It also considers the problems associated with polymer disposal. In the course of Chapter 9, a number of polymers of interest on account of their specialized usages rather than large-scale productions are brought in, such as those which are able to retain strength at high temperatures or which combine elasticity with remouldability. Finally, in Chapter 10 we peer into the future to some extent, considering some of the exciting new polymeric materials with astonishing properties which have become available recently.

A particular feature of this book is the appearance at the end of each chapter of a set of exercises, some drawing on recently published research papers. These are designed to allow readers to test their level of understanding and, in some cases to advance it. At the end of the book are selected suggestions for further reading.

It is hoped that readers will find it easier to gain an understanding of the basic principles of polymer chemistry and physics against this background of a limited number of different polymers. Thereafter, these principles may be carried forward into some of the more advanced textbooks with enough confidence to cope with the much larger number of different polymers usually found therein.

Leeds I.M.C.
April 1993

Contents

1 Introduction 1

1.1 Definitions and nomenclature 1
1.2 Some historical perspectives 4
1.3 The synthetic polymers industry 6
1.4 General features of polymerization processes 11
Exercises 15

2 Average molecular masses and polydispersity 18

2.1 Definitions and illustrations 18
2.2 Experimental determinations 21
2.3 Liquid-phase osmometry 32
Exercises 34

3 Microscopic features of bulk polymers 36

3.1 General aspects 36
3.2 Microcrystallinity and drawing 39
3.3 Amorphous polymers 42
3.4 Glass transition temperatures (T_g) 45
3.5 Melting temperatures (T_m) 50
3.6 Measurement of T_g and T_m 55
3.7 Concluding remarks 57
Exercises 57

4 Major techniques for analysis and structure determination 61

4.1 Infrared absorption spectroscopy 61
4.2 Nuclear magnetic resonance (NMR) spectroscopy 65
4.3 X-ray scattering 70
Exercises 78

5 Step growth polymerizations 85

5.1 General features 85
5.2 Linear step-growth systems with two monomers 90
5.3 Some important linear step-growth polymers 93
5.4 Network polymers 96
Exercises 102

6 Addition polymerization via free radicals 105

6.1 General features 105
6.2 Physical forms of synthesis media 107
6.3 Initiation processes 111
6.4 The growth and termination of chains 113
6.5 The control of chain growth 118
6.6 Generation of side chains 123
Exercises 126

7 Addition polymerization via ionic and coordination mechanisms 128

7.1 General features of ionic polymerization 128
7.2 Cationic polymerization 130
7.3 Anionic polymerization 133
7.4 Coordination polymerization 136
Exercises 142

8 Properties of common polymers in bulk 144

8.1 Crystallinity 144
8.2 Variation of glass transition temperature (T_g) 146
8.3 Drawn thermoplastics 151
8.4 Elastomers 153
8.5 Polymer degradation and recycling 160
Exercises 164

9 Some speciality polymers 167

9.1 Graft copolymers and comb copolymers 167
9.2 Liquid crystal polymers 170
9.3 High-temperature polymers 175
9.4 Polycarbonate 179
9.5 Ionomers and polymeric solid electrolytes 180
Exercises 185

10 Looking to the future 189

10.1 The synthesis of block copolymers 189
10.2 Side-chain liquid crystals 193
10.3 Synthetic metals 195
10.4 Polymers with active surfaces 197
10.5 Concluding remarks 201

Appendix Systematic names of common monomers 202

Further reading 203

Index 209

1
Introduction

'Polymer' as a scientific term was used first by the famous Swedish chemist, J. J. Berzelius, in 1827. But almost a century elapsed thereafter before a properly controlled synthesis of a polymer was achieved. We are familiar with a range of synthetic polymers nowadays, even if most of these have only made their debut in the last 60 years or so. New polymers continue to be developed and 'plastics' can be expected to turn up in even more commercial products in the future.

1.1 Definitions and nomenclature

A *polymer* is defined as a substance composed of very large molecules (or *macromolecules*). The molecular structure corresponds to a *chain* composed of many small molecules joined by chemical bonds. In synthetic polymers one structure, termed a *constitutional repeating unit (CRU)*, can be considered as producing the polymer molecule by its replication. Each CRU is joined to its neighbours by covalent bonds which are part of the *backbone*, defined as the minimum set of bonds and intervening atoms which extend continuously from end to end of the polymer molecule. The *monomer(s)* is (are) the small molecule(s) of one or more sorts which are incorporated into the polymer as it is synthesized. A *monomer residue* results from the incorporation of one monomer molecule into the chain. In many cases the CRU and monomer residue may be identical, as with a vinyl polymer where both correspond to $-CH_2-CH(X)-$. But the CRU is larger than any monomer residue in other cases, such as *copolymers* which incorporate more than one monomer. Polymers show special properties in comparison with *oligomers* which have molecules composed of up to a few tens of CRUs only, rather than the at least 50 in a polymer molecule.

Synthetic polymers are made by reacting monomers or their derivatives under controlled conditions. When a single monomer is concerned, the result is commonly a *homochain* polymer composed of just one monomer residue: polyethylene ($-CH_2-CH_2-$) and poly(vinyl chloride) (often known by its acronym PVC) ($-CH_2-CH(Cl)-$) are examples. Other common polymers require two monomers. Poly(ethylene terephthalate) (acronym PET) has the CRU represented as $-O-CH_2-CH_2-O-C$

(=O)−C_6H_4−C(=O)− and may be regarded as being the *alternating copolymer* of ethylene (CH_2=CH_2) and terephthalate (O(O=)C−C_6H_4−C(=O)O),where C_6H_4 represents a doubly substituted (1,4- or *para-* in this case) aromatic ring. In principle, the monomers for the synthesis of PET are ethylene glycol ($HOCH_2$−CH_2OH) and terephthalic acid (HO(O=)C−C_6H_4−C(=O)OH), repeatedly condensed together (or esterified) with elimination of a water molecule for each linkage. Thus PET is often termed a *polyester*.

The common names of monomers are used in most of the science and technology and essentially all of the commerce of polymers. This demands that this book should follow custom and most practice in *not* using the systematic names of organic compounds. Corresponding names are listed for monomers in Appendix 1.

All polymers have a very long backbone and this is the only macromolecular feature of a *linear* or *unbranched* chain. Evidently *branched* polymers have other chains joined to the backbone at various points along its length. *Crosslinks* are short linkages, commonly involving just a few covalent bonds, between polymer chains. Figure 1.1 represents these types of chain features in a simple way in two-dimensional projection. In considering how the chain backbones, such as the carbon atoms of polyethylene (shown as irregular lines here) are represented, it should be realized that

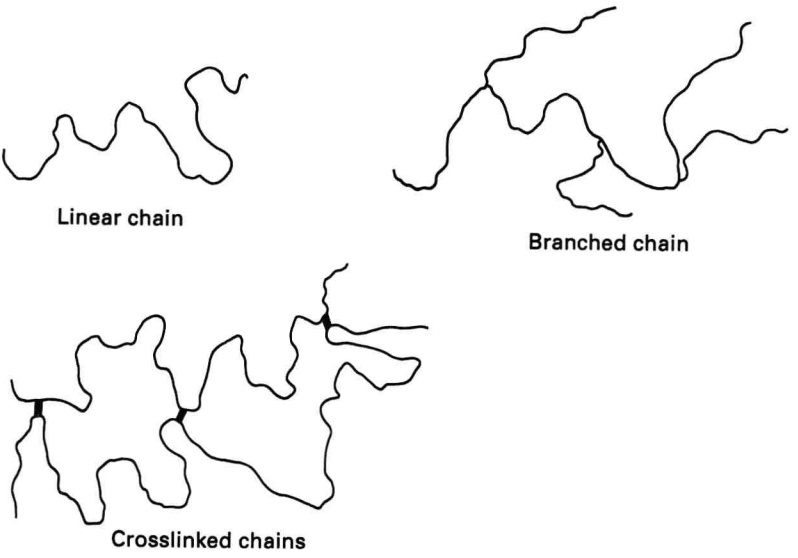


Fig. 1.1. Simple representations of linear, branched, and crosslinked chains (crosslinks are indicated by short thick lines).

individual chains are tangled with one another in the typical bulk sample. An apt description might be 'polymer spaghetti'.

At the general level, there are several types of copolymer. Consider two monomer residues designated as A and B. Figure 1.2 shows microscopic sequences and identifying class names. Any monomer must have at least two functional groups which have reacted or at least one double bond which has become a single bond when the corresponding residue has been incorporated into the polymer, i.e. the monomer must be *bifunctional, trifunctional* or occasionally *tetrafunctional.* Many common monomers are bifunctional, such as vinyl chloride in producing PVC. Some monomers can be trifunctional, giving monomer residues which each have *up to* three covalent linkages to other residues, as is seen for A in the network copolymer in Fig. 1.2. *Network copolymers* evidently require that one of the corresponding monomers has a functionality greater than 2.

One of the major interests explored in this book will be how structural differences at the microscopic level result in different properties of bulk samples of polymers, i.e. at the macroscopic level. The response to mechanical stress is one basis of differentiation. Some bulk polymers are *rigid*; that is to say that the shape does not deform significantly under moderate applied stress. Other polymers are *flexible*, so that they deform noticeably (for example bend) but will recover slowly and sometimes only partially on release. Another class is composed of *rubbery* or *elastic* solids, distinguished by the abilities to be deformed quite severely (for example

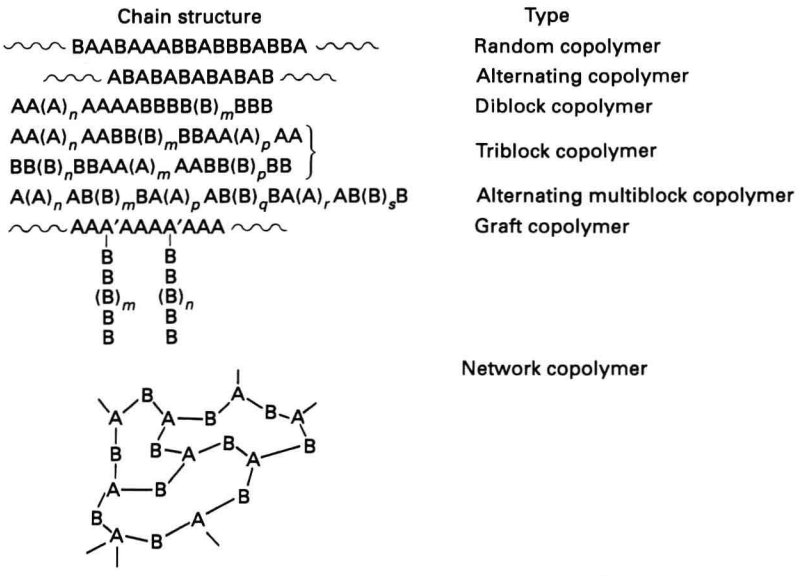


Fig. 1.2. Types of AB copolymers, where A and B are different monomer residues.

试读结束，需要全本PDF请购买 www.ertongbook.com

stretched) by quite small applied stress and to 'snap back' quickly to regain their original shape on release. A lump of a 'rubber' or *elastomer* (i.e. a polymer showing elastic properties) gives to a prod from a finger (say) far more than would a lump of polyethylene, a typical flexible solid.

There are also obvious differences between some of the polymers which are rigid at ambient temperatures when they are heated. Network copolymers are more commonly referred to as *thermoset(ting) resins*; these do not soften at all before the temperature becomes high enough to induce thermal decomposition. Polymers of the largest class, *thermoplastics*, become flexible above a particular temperature, becoming rigid again on cooling through this temperature: this rigid $\leftrightharpoons$ flexible cycle can be repeated on reheating and cooling again. In its flexible condition a thermoplastic is solid but can be moulded into complex shapes which are preserved in the rigid state after cooling. Remoulding can be done after reheating. Thermoplastics can be subdivided on the basis that only some are *fibre-formers*, which means that they can be *drawn* (i.e. pulled out) into strands which are permanent unless the polymer is melted and have considerable tensile strength and durability. PET is an example, giving rise to fibres known under various trade names such as Terylene (ICI) and Dacron (Du Pont).

1.2 Some historical perspectives

Natural polymeric materials, such as wood and horn, have been used by humans since prehistoric times. Modified forms of natural polymers were produced during the last century: the dramatic improvement in the properties of natural rubber (such as loss of tackiness and gain of elasticity) which resulted from its heating with sulphur, a process now referred to as *vulcanization*, was discovered independently in the USA (Goodyear in 1839) and the UK (Hancock in 1843). Modified forms of cellulose, initially cellulose nitrate (nitrocellulose) and later cellulose acetate and reconstituted cellulose itself were produced. But none of these can be considered as truly synthetic polymers.

The first fully synthetic polymers were the phenol–formaldehyde thermoset resins prepared by Baekeland in the early years of this century. These resins, known as Bakelites, achieved their main commercial significance in the 1920s. Several of today's most familiar polymers made their first appearances in Du Pont laboratories in the 1930s. Dashes of serendipity are apparent in the brief accounts of the discoveries which follow.

Carothers is the name associated with the first appearance of what we now know as nylon 6,6. At first, all that seemed to have come from the synthesis was a sticky lump, for which it did not seem worth seeking a patent. The true value only became evident when a glass rod was inserted and withdrawn, pulling silky fibres of remarkable tensile strength out from the lump. A patent was then sought with alacrity!

The reaction of hydrogen chloride with vinylacetylene ($CH_2{=}CH{-}C{\equiv}CH$) was being investigated and the critical event occurred reportedly when a sample of the resultant liquid was inadvertently left exposed to the air over a weekend. This had become solid by the time it was seen again and vitally important was the fact that the material was dropped and observed to bounce. Here then was the debut of the first synthetic rubber, a material now known generally as neoprene (see Exercise 1.3 at the end of this chapter).

Plunkett, with Du Pont in 1940, is credited with the discovery that tetrafluorethylene ($CF_2{=}CF_2$) can be polymerized; many failed attempts had led to the consensus that this monomer was unpolymerizable. The critical point came when a new cylinder of the monomer gas would not deliver any, even though the weight was correct for 'full'. Plunkett's curiosity persisted to the extent that he had the cylinder sawn open, when

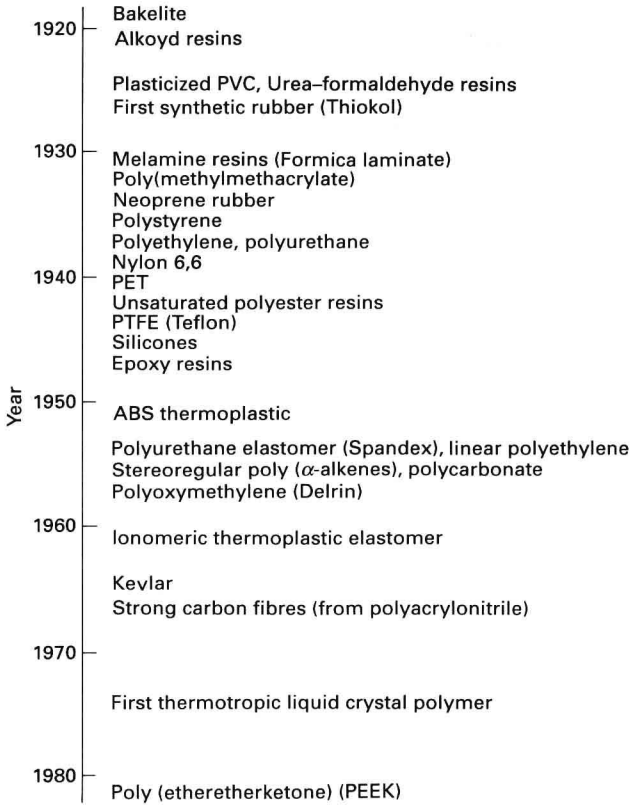


Fig. 1.3. Chronological list indicating the first *commercial* appearance of various polymers.

a white waxy powder was discovered within, thus exposing polytetrafluoroethylene (PTFE) to human gaze for the first time. This soon spurred the renewed effort which has now resulted in PTFE or Teflon being widely applied to produce nonstick finishes. In fact Plunkett and his coworkers ran an unrealized risk in their procedure of preparing tetrafluoroethylene and keeping it in steel cylinders. These cylinders were potential bombs since spontaneous conversion of the monomer to carbon and tetrafluoromethane liberates around one third of the energy released by the same molar amount of TNT in an explosion (see Exercise 1.6 at the end of this chapter).

Figure 1.3 completes this brief review of the history of synthetic polymers by indicating the chronological order in which various polymers made their first *commercial* appearance.

1.3 The synthetic polymers industry

Each year some 7×10^{10} kg of synthetic polymers are produced worldwide. Figure 1.4 shows the dominance of the industrial nations in this connection. The large production in the USA is evident. Table 1.1 indicates the contributions of the various types to total production of synthetic polymers by weight in the USA.

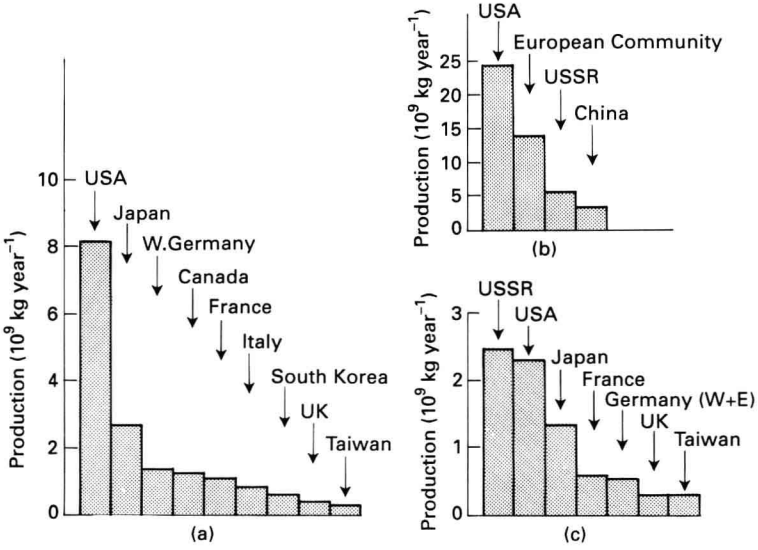


Fig. 1.4. Amounts of polymers made in the main producing nations in 1989. (a) Polyethylene (low and high density types), (b) all plastics and synthetic fibres, and (c) synthetic rubbers. Based upon entries given in 'Facts and figures for the chemical industry' given in *Chemical and Engineering News*, 18 June 1990, Volume **68**, Number 25, pp. 34–83.

Table 1.1 Main components of total polymer production in the USA

Type	Fraction of total (%)	Main specific polymers (Fraction of total)
Thermoplastics (non-fibres)	68	Polyethylene (23%) Poly(vinyl chloride) (13%) Polypropylene (11%) Polystyrene (8%)
Thermoplastics (fibres)	14	PET (5%) Nylon 6,6 (4%) Poly(alkenes) (2%)
Thermoset resins	10	Phenol–formaldehyde (5%) Urea–formaldehyde (2%)
Synthetic rubbers	8	SBR (2%) Poly(butadiene) (1%)

Based upon data given in *Chemical & Engineering News*, 18 June 1990, pp. 40–1.

It is evident that a small number of polymers dominate these production statistics: a similar situation can be expected in other industrial nations.

The capital cost of bringing a new thermoplastic into commercial production is enormous. Two to three thousand million pounds sterling (three to five thousand million US dollars) is a reasonable estimate for bringing on stream a new monomer production facility, new designs of polymer production plants and novel types of processing and fabrication operations. On this basis it can be expected that there will be relatively little change in the relative proportions of the amounts of main polymers produced on a national or global scale in the near future. This is supported by profiles representing the histories of annual productions of main polymers in the USA appearing in Figs. 1.5–1.7. Synthetic rubbers are not accorded similar representation since little change has occurred. Total productions in the years 1969 and 1989 were in fact not significantly different and there are only minor fluctuations during the intervening years.

It is obvious from Fig. 1.5 that production of thermoplastics in the USA has been increasing steadily, trebling over around 20 years in fact. Although the 'oil price shocks' of 1974–5 and 1979–80 make clear impacts on the profiles, apparently they have not disturbed the longer term trends. There have been almost parallel rises in the main individual thermoplastics except that two, high density polyethylene and polypropylene, have risen noticeably faster than the others. In Chapter 7 it will become apparent that this reflects the widespread commissioning of production plants within which relatively novel catalysts are used to synthesize these polymers.

Overall production of synthetic fibres has shown lower growth than total production of thermoplastics, several of the individual polymers being

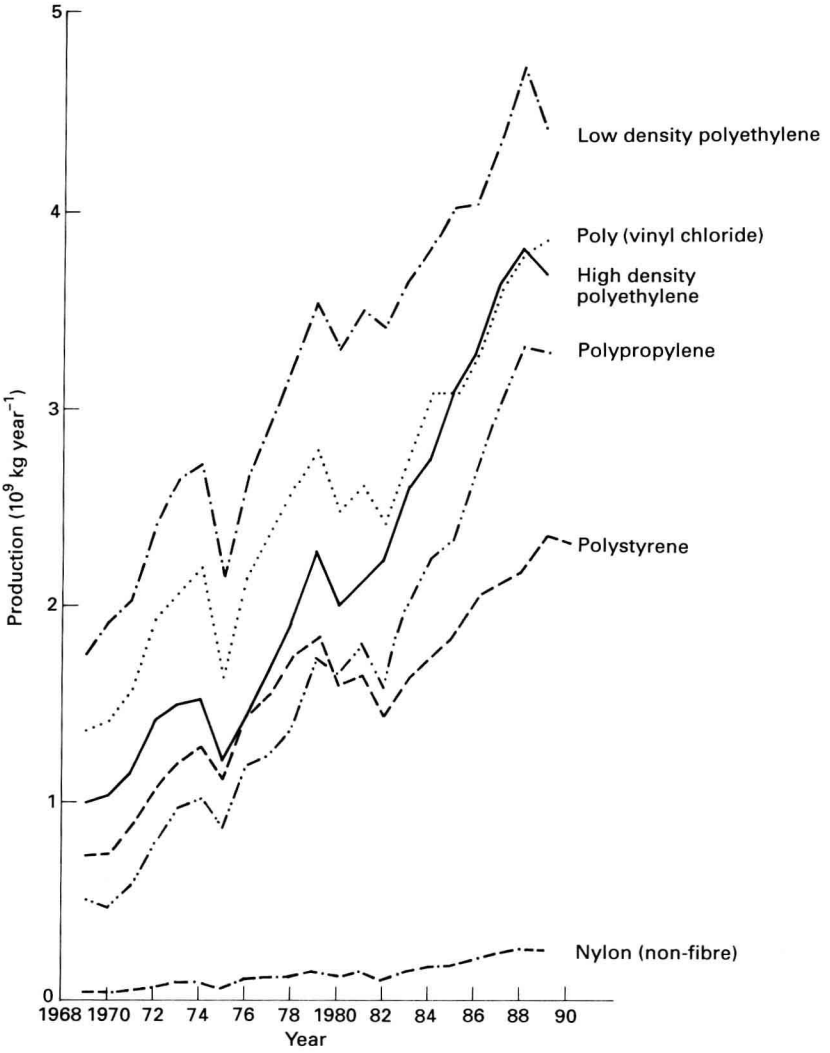


Fig. 1.5. Profiles of annual productions of the major thermoplastics in the USA from 1969 to 1989. Based upon entries given in the annual statistical surveys titled 'Facts and figures for the chemical industry' presented each year from 1970 in *Chemical and Engineering News*, terminating with the issue dated 18 June 1990, Volume **68**, Number 25, pp. 34–5.

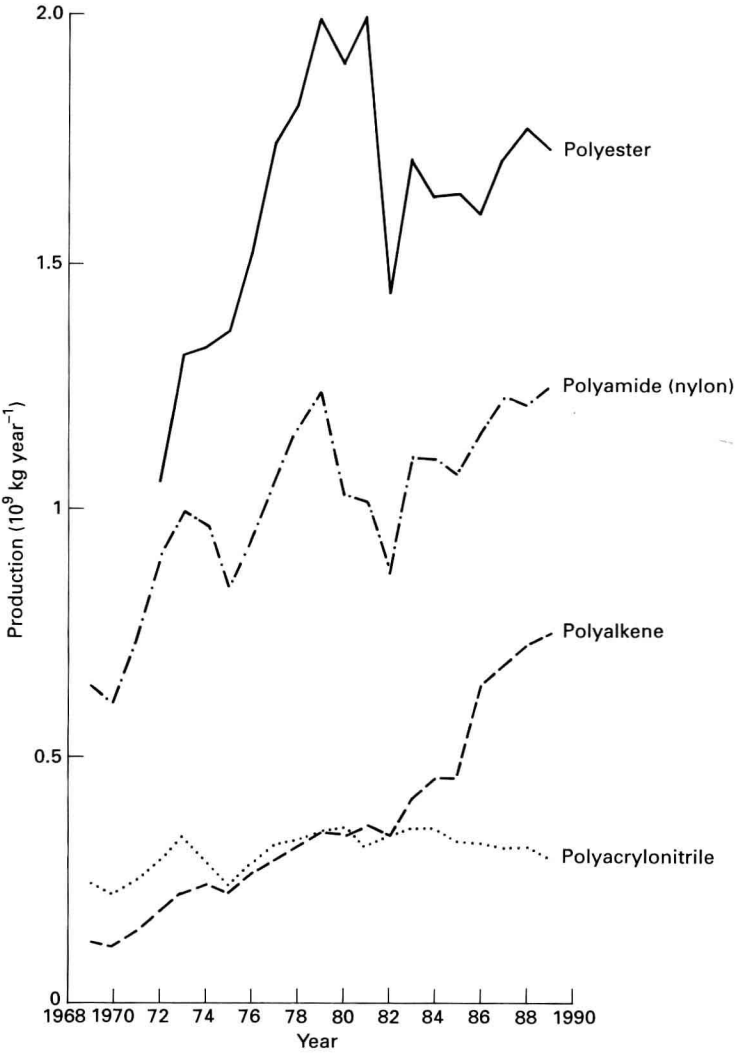


Fig. 1.6. Profiles of the annual productions of the major synthetic fibres in the USA from 1969 to 1989. Source as for Fig. 1.5.

试读结束，需要全本PDF请购买 www.ertongbook.com