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The Chemistry of Polymers (Second Edition)

聚合物化学

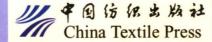
(第二版)

[英] 约翰·W.尼科尔森 编著

付中玉 译

The Royal Society of Chemistry

John W. Nicholson



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内 容 提 要

本书是配合高等院校高分子材料及相关专业实施双语教学而引进的英文原版经典教材,语言简洁、易懂,涵盖了聚合物化学领域的基本内容,注重实际应用,并反映了近年该领域的发展。

本书内容包括聚合物的结构和性质、聚合物的合成反应、 聚合物的力学性能及一些重要话题,如聚合物的降解、聚合物 的污染、多种聚合物的科技发展等。

本书可供高等院校高分子材料及相关专业师生使用,也可供高分子领域的科技人员参考。

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Preface

前言

This book seeks to introduce readers to the chemistry of polymers. It is aimed primarily at new graduates who have not previously studied polymer chemistry as part of their degree course, but it ought to prove useful to others as well. I hope that final year students studying polymer chemistry and more experienced chemists in industry looking for concise information on the subject will find their needs met as well.

In preparing this book I have attempted to do two distinct things: (i) to provide a brief, readable introduction to the chemistry of polymers and (ii) to emphasise the applied aspects of the scientific knowledge presented. I believe that any introductory book ought to be written in a way that encourages its proposed audience actually to read it. Also as an applied scientist myself I want to emphasise the applications of polymer chemistry since I believe that these are worth covering in a book of this type.

No book, however brief, is the product of just one person. In my own case, I have been very conscious of the help I have received from many sources. These include authors of those books on polymer chemistry that I have drawn on in preparing this one, all of which are listed in the Bibliography.

I also want to give special thanks to my colleague Eleanor Wasson for her generous assistance in reading the entire manuscript and for her numerous helpful suggestions.

Lastly I thank my wife Suzette for her forbearance and support during my involvement with this project. Her good-natured tolerance of my frequent absence from family life has considerably assisted me in the completion of this book.

John Nicholson

出版前言

进入 21 世纪, 各高校纷纷在提高教育素质、与国际接轨方面进行了积极的探索。其中"双语教学"成为推进素质教育的又一着陆点。教育部于2001 年 8 月发布文件, 针对本科教学工作提出 12 项措施, 其中明确要求各高校在三年内开设 5% ~ 10% 的双语课程, 并引进原版教材和提高师资水平。这使得高校双语教学势在必行。双语教学既是教育自身对课程设置的调整, 也是社会发展对教育改革的必然要求。实施双语教学不仅可提高学生的英语水平, 适应未来的发展, 更重要的是提高我国综合国力和国际竞争力的需要。

通过问卷调查、座谈等方式,我们了解到双语教材的缺乏是高校实施 双语教学的一大难点。作为科技出版社,我们拥有纺织、染化、服装、工美等 专业人才,并和英美等国家的专业出版社、院校、协会保持着良好的合作, 因此,我们希望利用自身专业优势,与高校合作出版双语教材,使之成为高 校实施双语教学的先行兵。

经过广泛的调研、深入的讨论,我们在双语教材的内容、出版形式等方面形成了较完整的思路。目前,我社出版的双语教材按专业分为四个系列:纺织工程专业双语教材、轻化工程专业双语教材、高分子材料专业双语教材、服装专业双语教材。所选图书均为国外的经典教材,其内容与国内相关专业课程相近,便于学生在掌握专业基础知识的同时,开阔视野,提高语言应用能力。我们将力求出版形式多样化,既有原汁原味的影印本,又有中译本和中文注释版本。部分教材将配有多媒体光盘,更加丰富了教材的表现手段,有助于提高学生的英语听说能力。

可以说,这是我们在双语教材出版方面所进行的一次有意义的尝试, 希望能对高校的双语教学的开展起到抛砖引玉之用,也希望读者对双语教 材的出版提出建议、意见,以便我们在今后的工作中逐步改进、完善。

> 出版者 2004 年 11 月

Preface to the Second Edition

第二版前言

The first edition of this book was, with one or two exceptions, gratifyingly well received by reviewers. It also sold well, thus confirming my belief that there is, indeed, place for an introductory book biased towards the more applied aspects of polymer science. It has been translated into Polish, suggesting that this need is international. Although it was not intended as a textbook for undergraduates, I have discovered that the first edition has been used for that purpose in certain universities, a point I have borne in mind in preparing the current edition.

In this second edition, I have stuck very much to the approach and level of the first edition, making changes only where absolutely necessary. In some cases this has been done to widen the coverage; in others it has been done to bring the text up to date. In making these changes, I have been helped by individuals who wrote to me after the publication of the first edition, with corrections or suggestions for additional material; I acknowledge my sincere gratitude for their help.

Despite this help, and the success of the first edition, I am sure that, even now, the book is not perfect. I am therefore still open to suggestions about how it could be improved. In the meantime, I take full responsibility for all the errors and infelicities that remain.

John Nicholson, March 1997

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Chapter 1

Polymer Chemistry

聚合物化学

BASIC CONCEPTS

A polymer is a large molecule built up from numerous smaller molecules. These large molecules may be <u>linear</u>, slightly <u>branched</u>, or highly <u>interconnected</u>. In the latter case the structure develops into a large <u>three-dimensional network</u>.

The small molecules used as the basic building blocks for these large molecules are known as monomers. For example the commercially important material poly(vinyl chloride) is made from the monomer vinyl chloride. The repeat unit in the polymer usually corresponds to the monomer from which the polymer was made. There are exceptions to this, though. Poly(vinyl alcohol) is formally considered to be made up of vinyl alcohol (CH₂CHOH) repeat units but there is, in fact, no such monomer as vinyl alcohol. The appropriate molecular unit exists in the alternative tautomeric form, ethanal CH₃CHO. To make this polymer, it is necessary first to prepare poly(vinyl ethanoate) from the monomer vinyl ethanoate, and then to hydrolyse the product to yield the polymeric alcohol.

The size of a polymer molecule may be defined either by its mass (see Chapter 6) or by the number of repeat units in the molecule. This latter indicator of size is called the degree of polymerisation, DP. The relative molar mass of the polymer is thus the product of the relative molar mass of the repeat unit and the DP.

There is no clear cut boundary between polymer chemistry and the rest of chemistry. As a very rough guide, molecules of relative molar mass of at least 1000 or a DP of at least 100 are considered to fall into the domain of polymer chemistry.

The vast majority of polymers in commercial use are organic in

基本概念

线型的 支化/交联 三维网状

单体 聚氯乙烯 重复单元

聚乙烯醇

互变(异构)的/乙醛 聚乙酸乙烯酯 水解 乙醇

聚合度 相对摩尔质量

有机 的

nature, that is they are based on covalent compounds of carbon. 共价的 This is also true of the silicones which, though based on silicon-硅氧烷 oxygen backbones, also generally contain significant proportions 主链 of hydrocarbon groups. The other elements involved in polymer chemistry most commonly include hydrogen, oxygen, chlorine, fluorine, phosphorus, and sulfur, i.e. those elements which are 氟/磷/硫 able to form covalent bonds, albeit of some polarity, with carbon. 极性 As is characteristic of covalent compounds, in addition to primary valence forces, polymer molecules are also subject to 化合价 various secondary intermolecular forces. These include dipole 偶极 forces between oppositely charged ends of polar bonds and dispersion forces which arise due to perturbations of the electron 色散力 clouds about individual atoms within the polymer molecule. Hydrogen bonding, which arises from the particularly intense 氢键 dipoles associated with hydrogen atoms attached to electronegative elements such as oxygen or nitrogen, is important in certain 负电性的 polymers, notably proteins. Hydrogen bonds have the effect of 蛋白质 fixing the molecule in a particular orientation. These fixed 取向 structures are essential for the specific functions that proteins have in the biochemical processes of life.

高分子概念的历史

生物化学的

THE HISTORY OF THE CONCEPT OF THE **MACROMOLECULE**

Modern books about polymer chemistry explain that the word polymer is derived from the Greek words 'poly' meaning many and 'meros' meaning part. They often then infer that it follows that this term applies to giant molecules built up of large numbers of interconnected monomer units. In fact this is misleading since historically the word polymer was coined for other reasons. The concept of polymerism was originally applied to the situation in which molecules had identical empirical formulae but very different chemical and physical properties. For example, **★** benzene (C₆H₆; empirical formula CH) was considered to be a polymer of acetylene (C₂H₂; empirical formula also CH). Thus the word 'polymer' is to be found in textbooks of organic chemistry published up to about 1920 but not with its modern meaning.

The situation is confused, however, by the case of certain chemicals. Styrene, for example, was known from the mid-nine-苯乙烯 teenth century as a clear organic liquid of characteristic pungent odour. It was also known to convert itself under certain circumstances into a clear resinous solid that was almost odour-free, this resin then being called metastyrene. The formation of metastyrene from styrene was described as a polymerisation and metastyrene was held to be a polymer of styrene. However, these terms applied only in the sense that there was no change in empirical formula despite the very profound alteration in chemical and physical properties. There was no understanding of the cause of this change and certainly the chemists of the time had no idea of what had happened to the styrene that was remotely akin to the modern view of polymerisation.

树脂/介苯乙烯 聚合

Understanding of the fundamental nature of those materials now called polymers had to wait until the 1920s, when Herman Staudinger coined the word 'macromolecule' and thus clarified thinking. There was no ambiguity about this new term – it meant 'large molecule', again from the Greek, and these days is used almost interchangeably with the word polymer. Strictly speaking, though, the words are not synonymous. There is no reason in principle for a macromolecule to be composed of repeating structural units; in practice, however, they usually are. Staudinger's concept of macromolecules was not at all well received at first. His wife once recalled that he had 'encountered opposition in all his lectures'. Typical of this opposition was that of one distinguished organic chemist who declared that it was as if zoologists 'were told that somewhere in Africa an elephant was found who was 1500 feet long and 300 feet high'.

大分子

重复结构单元

There were essentially three reasons for this opposition. Firstly, many macromolecular compounds in solution behave as colloids. Hence they were assumed to be identical with the then known inorganic colloids. This in turn implied that they were not macromolecular at all, but were actually composed of small molecules bound together by ill-defined secondary forces. Such thinking led the German chemist C. D. Harries to pursue the search for the 'rubber molecule' in the early years of the twentieth century. He used various mild degradations of natural rubber, which he believed would destroy the colloidal character of the material and yield its constituent molecules, which were assumed to be fairly small. He was, of course, unsuccessful.

胶体

无机的

橡胶

降解

The second reason for opposition to Staudinger's hypothesis was that it meant the loss of the concept of a single formula for a single compound. Macromolecules had to be written in the form

 $(CH_2CHX)_n$, where n was a large number. Moreover, no means were available, or indeed are available, for discretely separating molecules where n = 100 from those where n = 101. Any such attempted fractionation always gives a distribution of values of n and, even if the mean value of a fraction is actually n = 100, there are significant numbers of molecules of n = 99, n = 101, and so on. Now the concept of one compound, one formula, with one formula being capable of both physical (*i.e.* spatial) and chemical interpretation, had been developed slowly and at some cost, with many long, hard-fought battles. Organic chemists could not easily throw it out, particularly in view of the fact that it had been so conspicuously successful with much of the rest of organic chemistry.

聚合材料

非晶性的

萃取/结晶的

The third reason for opposition lay in the nature of many of the polymeric materials then known. Not only were they apparently ill-characterised, but they were also frequently non-crystalline, existing as gums and resins. Just the sort of unpromising media, in fact, from which dextrous organic chemists had become used to extracting crystalline substances of well characterised physical and chemical properties. To accept such resins as inherently non-crystallisable and not capable of purification in the traditional sense of the word was too much for the self-esteem of many professional organic chemists.

胶质的

Staudinger's original paper opposing the prevalent colloidal view of certain organic materials was published in 1920 and contained mainly negative evidence. Firstly, he showed that the organic substances retained their colloidal nature in all solvents in which they dissolve; by contrast, inorganic colloids lose their colloidal character when the solvent is changed. Secondly, contrary to what would have been expected, colloidal character was able to survive chemical modification of the original substance.

By about 1930 Staudinger and others had accumulated much evidence in favour of the macromolecular hypothesis. The final part in establishing the concept was carried out by Wallace Carothers of the Du Pont company in the USA. He began his work in 1929 and stated at the outset that the aim was to prepare polymers of definite structure through the use of established organic reactions. Though his personal life was tragic, Carothers was an excellent chemist who succeeded brilliantly in his aim. By the end of his work he had not only demonstrated the relationship between structure and properties for a number of polymers,

but he had invented materials of tremendous commercial importance, including neoprene rubber and the nylons.

氯丁橡胶/尼龙

聚合物的分类

热塑性塑料/热固性塑

热处理

料

分解

CLASSIFICATION OF POLYMERS

There are a number of methods of classifying polymers. One is to adopt the approach of using their response to thermal treatment and to divide them into thermoplastics and thermosets. Thermoplastics are polymers which melt when heated and resolidify when cooled, while thermosets are those which do not melt when heated but, at sufficiently high temperatures, decompose irreversibly. This system has the benefit that there is a useful chemical distinction between the two groups. Thermoplastics comprise essentially linear or lightly branched polymer molecules, while thermosets are substantially crosslinked materials, consisting of an extensive three-dimensional network of covalent chemical bonding.

Another classification system, first suggested by Carothers in 1929, is based on the nature of the chemical reactions employed in the polymerisation. Here the two major groups are the <u>condensation</u> and the <u>addition</u> polymers. Condensation polymers are those prepared from monomers where reaction is accompanied by the loss of a small molecule, usually of water, for example polyesters which are formed by the condensation shown in Reaction 1.1.

缩合/加成

聚酯

$$HO[-R-COO-R^{1}-COO-]_{n}H + (n-1)H_{2}O$$
 (1.1)

By contrast, addition polymers are those formed by the addition reaction of an <u>unsaturated</u> monomer, such as takes place in the polymerisation of vinyl chloride (Reaction 1.2).

不饱和的 氯乙烯

$$n \text{ CH}_2 - \text{CHCl} \longrightarrow [-\text{CH}_2 - \text{CHCl}-]_n$$
 (1.2)

This system was slightly modified by P. J. Flory, who placed the emphasis on the <u>mechanisms</u> of the polymerisation reactions. He reclassified polymerisations as <u>step</u> reactions or <u>chain</u> reactions corresponding approximately to <u>condensation</u> or <u>addition</u> in Carother's scheme, but not completely. A notable exception occurs with the synthesis of polyurethanes, which are formed by

机理逐步反应/链式反应

聚氨酯

异氰酸酯/羟基 动力学/消去 reaction of <u>isocyanates</u> with <u>hydroxy</u> compounds and follow 'step' <u>kinetics</u>, but without the <u>elimination</u> of a small molecule from the respective units (Reaction 1.3).

$$n ext{ OCN-R-NCO} + n ext{ HO-R}^1 - OH - - - - - OCN - [R-NHCO_2-R^1-]_n OH (1.3)$$

In the first of these, the kinetics are such that there is a gradual build up of high relative molar mass material as reaction proceeds, with the highest molar mass molecules not appearing until the very end of the reaction. On the other hand, chain reactions, which occur only at a relatively few activated sites within the reacting medium, occur with rapid build up of a few high relative molar mass molecules while the rest of the monomer remains unreacted. When formed, such macromolecules stay essentially unchanged while the rest of the monomer undergoes conversion. This means that large molecules appear very early in the polymerisation reaction, which is characterised by having both high relative molar mass and monomer molecules present for most of the duration of the reaction.

形态 无支化的/交联的 Step reactions can give molecules having a variety of morphologies from the simple unbranched linear to the heavily crosslinked network. The final structure depends on the number of functional groups in the parent monomers – the greater the proportion with a functionality of greater than two, the more extensive will be the branching until, at sufficient degrees of branching, a highly crosslinked network emerges. Chain reactions, by contrast, give only linear or lightly branched polymers. Thus, in terms of the thermoplastic/thermoset classification, chain reactions give thermoplastics, while step reactions may give either thermoplastics or thermosets.

聚合物的结构和性 质

STRUCTURE AND PROPERTIES OF POLYMERS

Having established the basic principles of classification in polymer chemistry, we will now turn our attention to individual polymers and consider a little about their physical and chemical properties. Most of the examples which follow are of commercial importance, though it is their properties that are emphasised rather than the complete chemistry of their industrial manufacture. In terms of