普通高等教育“十三五”规划教材

Polymer Chemistry

（双语教学用）

周　明　代加林　编

化学工业出版社

扫描二维码　拓展基础知识

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·北京·

The textbook is divided into eight chapters. In the introduction, the basic concept of polymer, classification and nomenclature of polymer, reaction type of polymer, development history of polymer and application of polymer are introduced in brief. In the next six chapters, free radical polymerization, free radical copolymerization, ionic polymerization, step polymerization, ring-opening polymerization and chemical reactions of polymers are introduced in detail. The implementation methods of polymerization are introduced systematically in the last chapter. The new words and terminology are noted in Chinese in detail, and the large exercises are attached at the end of each chapter, which is helpful for the students who are new to polymer chemistry to study smoothly.

This book is used as the textbook for colleges and universities. It is suitable for the major of Polymer Materials and Engineering, Material Chemistry, Material Science and Engineering, New Energy Materials and Devices, New Energy Materials and Engineering, Chemical Engineering and Technology, Applied Chemistry in engineering, Chemistry, Organic Chemistry, Analytical Chemistry, Polymer Chemistry and Polymer Physics in science, and Chemistry in normal colleges. It can also be used as the reference for junior college, scientific researchers and production technicians.

《Polymer Chemistry（双语教学用）》共分 8 章。首先在绪论中介绍了聚合物的基本概念、聚合物的分类和命名、聚合物的反应类型、聚合物的发展历程、聚合物的应用等。接下来 6 章分别就自由基聚合、自由基共聚、离子聚合、逐步聚合、开环聚合、聚合物的化学反应进行详细介绍。最后 1 章较系统地介绍聚合实施方法。书中对专业生词和专业术语做了较详细的中文注解，另每章后都附有习题，有利于初接触到高分子化学的学生顺利学习。

本书适合作为高等院校教材，适用于工科的高分子材料与工程、材料化学、材料科学与工程、新能源材料与器件、新能源材料与工程、化学工程与工艺和应用化学专业，理科的化学、有机化学、分析化学、高分子化学及物理专业，师范院校的化学专业。也可供大专院校师生以及科研人员和生产技术人员参考。

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Preface

Polymer chemistry is a compulsory basic course of polymeric materials and engineering and interrelated specialities in engineering colleges. It is also listed as a compulsory or optional course for students majoring in science in universities of science and technology and chemistry in teacher universities. In addition, many non-polymer majors are also engaged in polymer research, production and application after graduation because of the large production, variety, wide application and high economic benefits of polymers. In particular, the internationalization of China's development requires that trained students can engage in scientific research, production technology and management abroad. This is urgently required for a bilingual textbook or a reference book with high value in English and Chinese.

There are many English textbooks for polymer chemistry in foreign countries. Because there are so many local words and unfamiliar words, even university teachers have difficulty in dealing with the skimming and scanning. It is difficult to find suitable original English textbook for the students in local universities in China to master professional vocabulary and professional knowledge. Therefore, on the basis of our fifteen years' experience in bilingual teaching, a bilingual textbook on polymer chemistry has been written to suit for local universities in China. Try to be literal and easy to understand, and professional words and new words are annotated in Chinese. To improve the readability and applicability of the textbook, it offers opportunities for students from a variety of backgrounds to gain basic knowledge, understanding and skills in polymer materials.

In the teaching plan of polymer materials and engineering specialty, there are courses such as polymer chemistry, polymer physics (structure and performance), fundamentals of polymer molding and processing. In this case, the emphasis of polymer chemistry should be put on the principle of polymerization, but relationship between structure, properties and application should not be neglected. In the introduction of this textbook, the basic concepts of polymers, molecular weight and distribution of polymers, microstructure, classification of polymers, types of polymerization reactions, nomenclature of polymers, and development history of polymers are highlighted one by one in order to draw attention to them and hopefully penetrate them into later chapters. When we need to know more about these contents, we should refer to other textbooks or monographs.

From the point of view of polymer materials, the synthesis, structure, properties and applications of polymers can be introduced according to the types of polymers. This book, on the one hand, is classified according to polymerization mechanism, kinetics and polymerization methods, and then discusses free radical polymerization, free radical copolymerization, ionic polymerization (including anionic polymerization, coordination polymerization and cationic polymerization), step polymerization, chemical reactions of polymers and polymerization methods in turn. On the other hand, ring-opening polymerization includes anionic poly-

merization, cationic polymerization and step polymerization, so it is written as an independent chapter. This will contribute to deepen the problem.

The three chapters of free-radical polymerization, free-radical copolymerization and step polymerization are the major ones, and their theoretical system and content are the most mature. At the same time, students should be aware that the material literature in ionic polymerization and coordination polymerization are very abundant, however, from the overall opinion, theoretical research is still in immature, imperfect stage. Therefore, we only introduce the basic concepts, basic principles and other basic knowledge in these chapters. In general polymer chemistry textbooks, except for emulsion polymerization, the other polymerization methods are very brief. Considering that there is not the course of polymer production technology in many engineering colleges and universities, and that polymerization mechanism and kinetics should be closely related to practice, this book extends the content of polymerization method (process) appropriately from polymerization reaction engineering, and gives some examples. The chapter on chemical reactions of polymers, especially the rapid development of functional polymers in recent years, covers a wide range of topics. Each section of this chapter can be developed into an independent course or monograph. Unfortunately, under the condition of limited space, we can only comprehensively consider the content of each part, and make a brief introduction not in-depth discussion. The purpose is to give students some ideas in order to open up their horizons and broaden thinking.

The structure and form of olefin monomers have little change by chain polymerization, but the properties of polymers are obviously different. However, the monomers with functional groups can form condensate polymers with different structures and properties after condensation or step polymerization. Therefore, in the chapter of step polymerization, the syntheses of many kinds of condensate polymers are introduced systematically through the practical application on the mechanism of condensation polymerization and polymerization methods. Such treatment can reflect the diversity of condensation polymerization and supplement much knowledge about condensate polymers.

This book was written by Ming Zhou and Jialin Dai. Chapters 1-6 were written by professor Zhou of Southwest Petroleum University. Chapters 7 and 8 were written by professor Dai of Southwest Petroleum University. Professor Zhou revised the whole textbook. Zhou's postgraduates Yiping Chen, Yinghua Gu and Rongjun Yi helped to change the format and handle words.

Ming Zhou

CATALOGUE

Chapter 1 INTRODUCTION

Polymers（聚合物）are macromolecules（molecular weight ～10000 or greater）built up by linking large numbers of smaller molecules together. Polymers are complex and giant molecules and different from low molecular weight compounds such as common salt sodium chloride（氯化钠）. The molecular weight of sodium chloride is only 58.5, while that of polymers can be up to as high as several hundred thousand, even more than thousand thousand. The small molecules that combine with each other to form polymer molecules are termed as monomers（单体）, and the reaction that small molecules become polymer molecules is termed as polymerization（聚合反应）. This interlinking of many units has given the polymer its name, with poly meaning "many" and mer meaning "part". As an example, a gaseous compounds called ethylene（乙烯）, with a molecular weight of 28, combines nearly 5×10^3 times and gives a polymer known as polyethylene（聚乙烯）(a synthetic plastic) with about 1.4×10^5 molecular weight.

Polymer is defined as a substance composed of thousands of small molecules which have long sequences（序列）of one or more species（种类）of atoms or atom groups linked to each other by primary covalent bonds. Usually, a molecule is considered to be polymer or macromolecular when it only exhibits the typical properties of high molecular weight substances.

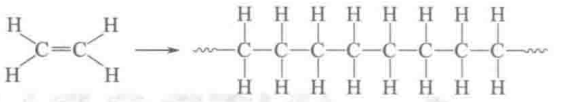
Polymer chemistry is a multidisciplinary（多学科的）science that deals with the chemical synthesis and chemical properties of polymers. The challenge in polymer chemistry is the application of fundamental chemical and physical techniques and ideas to large and complex molecules. It is obvious that polymer chemistry, perhaps more than any other research area, is often related to organic, inorganic, physical, and analytical chemistry; physics; engineering; biology; advanced mathematics; electronics and even medicine. A beginner to polymer science needs to be able to blend knowledge together from all these fields.

1.1 BASIC CONCEPTS AND DEFINITIONS

1.1.1 Monomers and Polymers

A monomer is any substance that can be converted（转变）into a polymer. For exam-

ple, ethylene $CH_2=CH_2$ is a monomer that can be polymerized to polyethylene:



Monomer: ethylene　　Polymer: polyethylene(PE)

Overall reaction:

$$n\ CH_2=CH_2 \longrightarrow +CH_2-CH_2+_n$$

In addition: propylene+propylene+propylene+…→polypropylene (PP)

$$n\ CH_2=\underset{\displaystyle CH_3}{\underset{|}{CH}} \longrightarrow +CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}+_n$$

Poly (hexamethyleneadipamide) (聚己二酰己二胺, Nylon-66) is made from two monomers, hexanedioic acid or adipic acid and 1,6-diaminohexane (also known as hexane-1,6-diamine).

$$HOOCCH_2CH_2CH_2CH_2COOH + H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$$

Monomers: hexanedioic acid　　1,6-diaminohexane

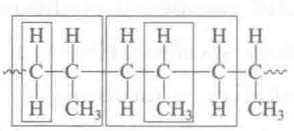
$$\longrightarrow \sim\!\sim OC(CH_2)_4CONH(CH_2)_6NHOC(CH_2)_4CONH(CH_2)_6NH\sim\!\sim$$

Overall reaction:

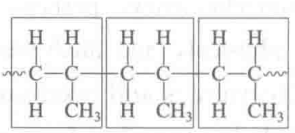
$$n\ HOOC(CH_2)_4COOH + n\ H_2N(CH_2)_6NH_2 \longrightarrow$$
$$+NH(CH_2)_6NHOC(CH_2)_4CO+_n + (2n-1)H_2O$$

1.1.2 Structural Unit and Repeating Unit

A structural unit (结构单元) is an elementary unit connected to one another in the chain of polymer molecules, or polymeric structure by covalent bonds (共价键). It is the result of a monomer residue (残留部分) that has been polymerized. All atom groups in each following square frames are called as structural units.



A repeating unit (重复单元) is defined as the shortest sequence that can be found repeatedly in a polymer. This distinction is necessary in order to estimate the molecular weight of polymers correctly. The atom groups in each following square frames are called as repeating units.



The structures of polymers vary largely, but almost all polymers may be expressed as the combinations of many different structure units. In a large number of cases, a single type of structural unit is sufficient for the representation of the entire polymer molecule. This feature is the basic characteristics of polymeric substances (这一特性是高分子物质的基本特征).

For example, the monomers which could be used to create this polymer polyethylene are ethylene $CH_2=CH_2$. The structural unit and repeating unit both are $-CH_2CH_2-$.

The molecule or structure of polyethylene may be represented by

$$+CH_2-CH_2+_n$$

where n is termed as the degree of polymerization (聚合度) or the number of repeating units in the molecules. (参见本章二维码：1-1 单体单元和聚合度概念)

Since poly (hexamethylene adipamide) is made from two monomers, $HOOC(CH_2)_4COOH$ and $H_2N(CH_2)_6NH_2$, there are two structural units in the polymer, which are

$$-HN(CH_2)_6NH- \text{ and } -OC(CH_2)_4CO-$$

The repeating unit is

$$-HN(CH_2)_6NHOC(CH_2)_4CO-$$

Therefore, the molecule or structure of poly (hexamethylene adipamide) may be described by

$$+NH(CH_2)_6NHOC(CH_2)_4CO+_n$$

The structural units may be connected together in any imaginable (想得到的) pattern to form so called linear polymer (线型聚合物), branched polymer (支化聚合物), graft polymer (接枝聚合物), block polymer (嵌段聚合物) or crosslinked polymer (交联聚合物).

1.1.3 Dimers, Trimers and Oligomers

The polymerization of a monomer often occurs in a sequential (序列) manner. In other words, two monomer molecules first react together to form a dimer (二聚体). The dimer may then react with a third monomer to yield a trimer (三聚体), and so on. Dimers are usually linear molecules, but trimers, tetramers (四聚体), pentamers (五聚体), and so on, can be linear or cyclic (环化的).

$$\underset{\text{Glycolic acid (monomer)}}{2HOCH_2COOH} \longrightarrow \underset{\text{Dimer}}{H+OCH_2CO+_2OH} + H_2O$$

$$\underset{\text{Dimer}}{H+OCH_2CO+_2OH} + \underset{\text{Monomer}}{HOCH_2COOH} \longrightarrow \underset{\text{Trimer}}{H+OCH_2CO+_3OH} + H_2O$$

The reactions outlined in the above scheme indicate the relationship between monomers, dimers, and trimers. Low molecular weight products obtained by polymerization, for example, dimers, trimers, tetramers, pentamers, and so on, which may be cyclic or linear, are known as oligomers (低聚体或低聚物). Some care should be taken to avoid use of the term "polymer" to describe materials that are real oligomers because the two types of products have distinctly different properties.

1.1.4 Linear Polymers

A linear polymer (线型聚合物) consists of a long chain of skeletal atoms which are attached to the substituent groups. Polystyrene (聚苯乙烯, PS) or polyethylene is one of the simplest examples. Linear polymers are usually soluble in some solvent, and in the solid state at normal temperatures, they exist as elastomers (弹性体), flexible materials (韧性材料), or glasslike thermoplastics (热塑性树脂). In addition to polyethylene, typical linear-type polymers include poly (vinyl chloride) (聚氯乙烯, PVC), poly (methyl methacrylate) (聚甲基丙烯酸甲酯, PMMA), polyacrylonitrile (聚丙烯腈, PAN) and Nylon-

66 (尼龙-66).

Chain structure of a linear polymer:

~~MMMMMMMMMMMMMMMMMMMMMM~~

1.1.5 Branched Polymers

A branched polymer (支链型聚合物) can be visualized as (被看成) a linear polymer with branches of the same basic structure as the main chain. A branched polymer structure is illustrated in Figure 1.1. Branched polymers are often soluble in the same solvents as the corresponding linear polymer. In fact, their many properties are similar to (与……相似) those of linear polymers. However, they can sometimes be distinguished from (区别于) linear polymers by their lower tendency to crystallize or by their different solution viscosity or light-scattering (光散射) behavior. Heavily branched polymers may swell in certain solvents without dissolving completely.

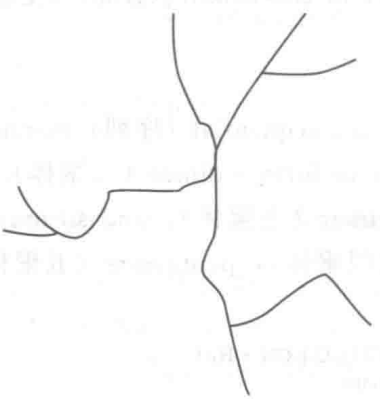


Figure 1.1 Branched polymer

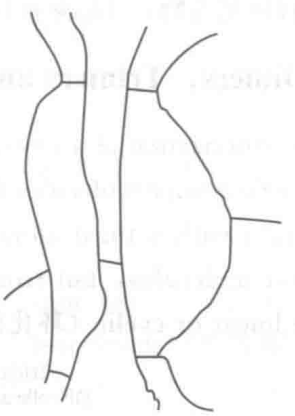


Figure 1.2 Crosslinked polymer

1.1.6 Crosslinked Polymers

A crosslinked or network polymer (交联或网状聚合物) is one in which chemical bonds exist between the chains, as showed in Figure 1.2. The materials can be usually swelled (溶胀) by "solvents", but they can't be dissolved.In fact, this insolubility can be used as a cautious criterion of a crosslinked structure. Actually, the amount of the swelled polymer in a solvent depends on the crosslinking density. The bigger crosslinking density presents, the smaller the amount of swelled polymer is. If the crosslinking degree is high enough, the material may be a rigid, high-melting, unswellable solid. Light crosslinking of chains favors the formation of rubbery elastomeric (弹性的) properties.

1.1.7 Stars and Dendrimers

Star polymers (星形聚合物) have mutli-arms radiating from a common core (Figure 1.3). The number of arms may vary from three to six or more. Star polymers are prepared either by growing the arms by polymerization from a multifunctional core, or by linking preformed

polymer molecules（预聚物分子）to a core through reactive end groups on the polymer. In principle, there is no limit to the length of the arms in a star polymer, but in the process of actual synthesis, the arm length is restricted by the influence of the steric hindrance, group reaction activity and so on.

Dendrimeric polymers（枝状聚合物）have the arborization（树枝状）structures in the chain of polymer molecules, as shown in Figure 1.4. Except for usually three-dimensional structure, there is a sphere structure in the overall final outer shape.

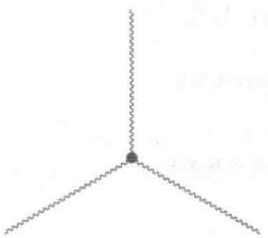


Figure 1.3 Tri-star polymer

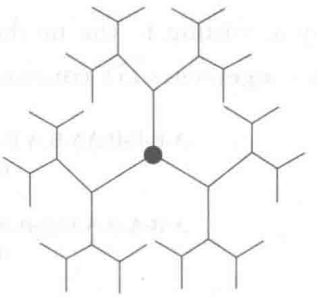


Figure 1.4 Dendrimeric polymer

The solution and solid-state properties of star polymers and especially dendrimers（枝状聚合物）are usually noticeably different from those of their linear correspondent polymer with the same molecular weight. The spherical shape of a dendrimer restricts intermolecular entanglements（缠绕）. Hence, both the solution and bulk viscosities are lower than expected.

1.1.8 Ladder Polymers

As the name suggests（顾名思义）, a ladder polymer（梯形聚合物）consists of linear molecules in which two skeletal strands（骨架主链）are linked together in a regular sequence（序列）by crosslinking units, as illustrated diagramatically（图解地）in Figure 1.5. In practice, aromatic rings（芳环）may constitute the linking units. As might be expected（可以预料的）, ladder polymers have a more rigid（刚性的）molecular structure than conventional linear polymers, and they are often much less soluble. However, they frequently display very good thermal stability（热稳定性）, because the decrease of molecular weight must be preceded（在……之前发生）by the cleavage（断裂）of two bonds at each cleavage site.

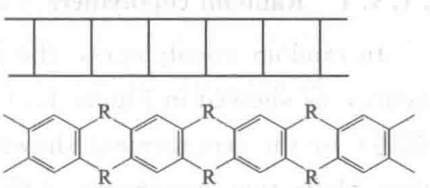
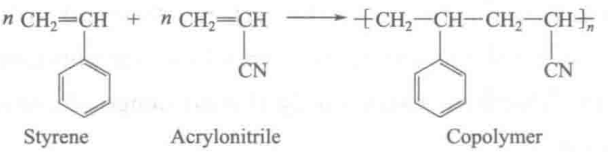


Figure 1.5 Ladder polymer

（参见本章二维码：1-2 聚合物按结构分类）

1.1.9 Copolymers

A copolymer（共聚物）is a polymer made from two or more different monomers. For example, if styrene and acrylonitrile are allowed to polymerize in the same reaction vessel（容器）, a copolymer will be formed which contains both styrene monomer units and acrylonitrile monomer units.



Many commercial（商品化的）synthetic polymers are copolymers, because they can improve some properties of the materials and enhance the ability for adapting the environment. The common copolymers are in the following four categories, as shown in Figure 1.6. It is attracted to wide attention that the sequence of monomer units along a copolymer chain could vary according to the method and mechanism of synthesis. Four different types of sequencing arrangements are commonly found in Figure 1.6.

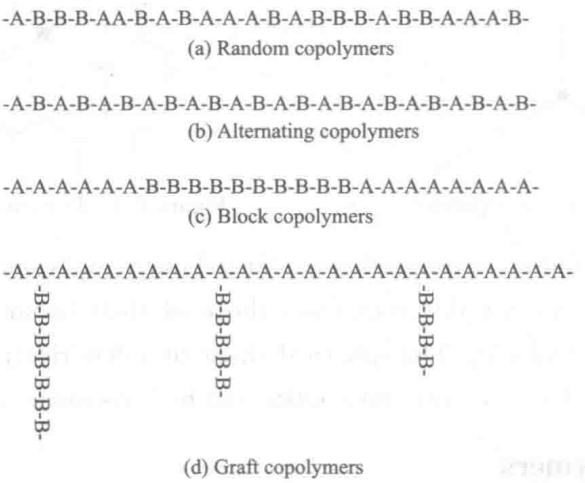


Figure 1.6 Structure of copolymers

1.1.9.1 Random copolymers（无规共聚物）

In random copolymers, the arrangement of the monomer units has not definite sequence, as showed in Figure 1.6(a). A copolymer of monomers A and B might be depicted（描述）by the arrangement shown in Figure 1.6(a). Random copolymers are often formed when olefin-type monomers（烯烃类单体）copolymerize（共聚）by free-radical-type processes. The properties of random copolymers are usually quite different from those of the corresponding homopolymers（均聚）.

1.1.9.2 Alternating copolymers（交替共聚物）

As the name implies（顾名思义）, alternating copolymers contain a regular alternating sequence of two monomer units, as showed in Figure 1.6(b). Again, the properties of the copolymer are usually markedly different from those of the two corresponding homopolymers.

1.1.9.3 Block copolymers（嵌段共聚物）

Block copolymers contain a block of one monomer connected to a block of another, as showed in Figure 1.6(c). Block copolymers are often formed by ionic polymerization（离子聚合反应）processes. Unlike other copolymers, they retain many of the physical characteristics of the two homopolymers.

1.1.9.4 Graft copolymers（接枝共聚物）

A graft copolymer is defined as a polymer that the atoms or groups of backbone chain（主链）are attached to the branched chains（支链）in which the monomeric unit contains different atoms or groups, as shown in Figure 1.6(d). In general, the backbone chain is composed of one A monomeric unit and the branched chain is composed of another B monomeric unit. The main chain also may be a copolymer or may be derived from a single monomer. Graft copolymers can be obtained in two ways. First, monomer B can be polymerized from sites along the length of polymer A. Second, two preformed polymers derived from A and B can be induced to react with each other to form a graft structure. For example, if polymer B has end-groups that will react with the side groups on polymer A, a graft copolymer will be formed. Graft copolymers are sometimes produced when two polymers are mixed and either irradiated（辐射）with X-rays or gamma-rays, or are subjected to mechanical shearing（机械剪切）. The chains of polymer B may be broken and the active chain ends will then be grafted onto polymer A. Graft copolymers often display the properties that are derived from the two homopolymers.

（参见本章二维码：1-3 共聚物分类及标记）

1.2 AVERAGE MOLECULAR WEIGHT AND DISTRIBUTION

A major distinguishing feature of polymers is their enormous（巨大的）molecular weight. Molecular weights of 2×10^4 are routine（常规）, and values as high as 2×10^7 are not uncommon. However, unlike small molecules such as benzene（苯）or chloroform（氯仿）, a sample of a synthetic polymers has no single, fixed molecular weight. Instead, there is a distribution of different molecular weights in the same sample of material (Figure 1.7). For this reason, it is necessary to talk about average molecular weights rather than a single defining value.

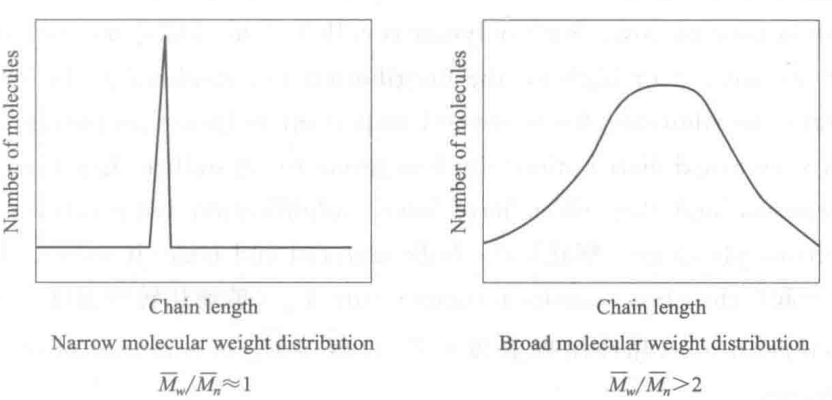


Figure 1.7 Molecular weight distributions

Several different types of average molecular weights are used in polymer chemistry, the most important of which are known as number average molecular weight $\overline{M}_n$, and weight