

“十二五”普通高等教育本科规划教材

Introduction to Polymer Materials

高分子材料导论 (双语教学用)

李 坚 俞 强 万 同 张洪文 编



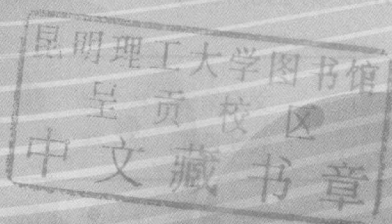
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· 北 京 ·

本书是为高分子及其相关专业的学生编写的双语教学用教材。全书共分 10 章,依次介绍了聚合物合成,聚合物的结构、分子运动及转变,聚合物固体性能,聚合物的测试与表征,塑料,弹性体,聚合物复合材料,涂料以及聚合物科学与技术进展。教材覆盖面广、内容丰富,既包含了高分子专业的基础知识,如高分子化学、高分子物理等方面的内容;又介绍了一些基本的高分子材料品种,如聚乙烯、聚丙烯、聚苯乙烯及弹性体等;还对高分子材料在涂料方面的应用作了介绍。每章编写有相应的习题供复习使用。希望本教材能起到在学习英语的同时,既能复习巩固专业基础知识,又能拓宽相应专业知识的作用,为今后的学习与研究打下良好的基础。

本书可供高分子材料、材料化学、精细化工及应用化学以及相关专业的低年级学生学习使用,也适合相关专业的研究生参考学习。

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前 言

随着教学改革深入,各高校相继开设了高分子材料及相关专业的双语教学课程。在教学过程中,首先面临的是教材的选择问题。目前国内还没有合适的高分子材料及相关专业的双语教材可供选择。若采用国外原版教材,则专业内容及深度等方面不尽合适,且普遍价格相对较高。由鉴于此,结合我们多年双语教学的实践积累,编写了《高分子材料导论(双语教学用)》这本教材。

本书编写的指导思想如下。一是选择英语难度不大,专业知识相对较浅,容易讲授和学习的内容作为教材内容。二是选择的高分子化学和高分子物理的内容在大学二年级或大学三年级时已经用中文讲授过,学生具有一定的基础,容易接受。三是选择的内容覆盖面相对较广,几乎涉及高分子材料的各个方面,如聚合物的合成,聚合物的性能,聚合物的结构表征,塑料,弹性体,涂料及复合材料等方面。这为教师对讲课内容的选择提供了很大的空间。还介绍了国内外高分子科学部分领域的最新进展,这为学生以后的学习与科研提供了有益的帮助。四是以多本原版英文教科书为基础,参考国外著名期刊上的综述性文章,编写了相关的章节,由此形成了双语教材。

本书由以下老师完成编写。Chapter 1、Chapter 5、Chapter 6 由常州大学俞强教授编写;Chapter 2、Chapter 4、Chapter 9 由常州大学李坚教授编写;Chapter 3 由常州大学张洪文副教授、李坚教授编写;Chapter 7 由天津科技大学万同教授、李坚教授编写;Chapter 8 由万同教授编写;Chapter 10 由俞强教授、李坚教授、万同教授编写。全书由李坚教授最后统稿、编排完成。

由于时间仓促,加上编者的学术水平、英语水平有限,以及资料的收集、内容的取舍等方面的不足,本书一定存在有待完善与改进的地方,敬请广大师生、读者批评指正。

编 者

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Contents

Chapter 1 Introduction	1
1.1 Classification of polymerizations	1
1.1.1 Condensation and addition polymerization	1
1.1.2 Step and chain polymerizations	3
1.2 Classification of Polymers	5
1.2.1 Classification by source	5
1.2.2 Classification by mechanical behavior and application	5
1.2.3 Classification by synthesis reaction	6
1.2.4 Classification by chain structure	6
1.2.5 Classification by processing characteristics	7
1.3 Physical State, Property and Application of Polymers	8
1.3.1 Crystalline and amorphous behavior	8
1.3.2 Thermal transitions	8
1.3.3 General properties of polymers	9
1.3.4 Applications of polymer materials	10
1.4 Polymer Processing	10
1.4.1 Ingredients of polymer materials	11
1.4.2 Processing methods	11
1.5 Development of Polymer Science and Engineering	13
1.5.1 Brief history of polymer materials	13
1.5.2 Establishment of polymer science	14
1.5.3 The development of synthetic polymers	14
Problems	19
Chapter 2 Polymer Synthesis	20
2.1 Step Polymerization	20
2.1.1 Basis for analysis of polymerization kinetics	21
2.1.2 Kinetics of step polymerization	22
2.1.3 Molecular weight control in linear polymerization	28
2.2 Radical Chain Polymerization	33
2.2.1 Rate of radical chain polymerization	33
2.2.2 Molecular weight	38

2.2.3	Chain transfer	40
2.2.4	Inhibition and retardation	42
2.2.5	Process conditions	43
Problems		47
Chapter 3 Polymer Structure, Molecular Motions and Transitions of Polymers		50
3.1	General Introduction for Polymer Structures	50
3.1.1	Structural groups	50
3.1.2	Linear chain polymers	51
3.1.3	Configurations of polymer chains	53
3.1.4	Conformation	55
3.1.5	Copolymers	55
3.1.6	Network polymers	56
3.2	Characteristics of Macromolecular Motions and Transitions	56
3.2.1	The Glassy Region	57
3.2.2	The Glass Transition Region	57
3.2.3	The Rubbery Plateau Region	58
3.2.4	The Rubbery Flow Region	59
3.2.5	The Liquid Flow Region	59
3.3	Molecular Motion and Thermal Transitions	59
3.3.1	Theories of glass transition	60
3.3.2	Factors affecting glass transition temperature	62
3.3.3	The crystalline melting point	69
3.3.4	Factors affecting the crystalline melting point, T_m	70
Problems		74
Chapter 4 Solid State Properties of Polymers		76
4.1	Mechanical Properties	76
4.1.1	Forces Versus Deformation Properties	77
4.1.2	Toughness	83
4.1.3	Creep	87
4.2	Optical Properties	88
4.2.1	Haze	88
4.2.2	Transparency	89
4.2.3	Gloss	90
4.3	Surface Contact Properties	90
4.3.1	Friction	90
4.3.2	Cling	92
4.3.3	Wear Resistance	92
4.4	Barrier Properties	93
4.4.1	Permeation through Polymers	94

4.4.2	Barrier Property Analysis	95
4.5	Electrical Properties	96
4.5.1	Electrical Resistance	96
4.5.2	Capacitive Properties	97
4.5.3	Dielectric Strength	98
4.5.4	Arc Resistance	99
4.5.5	Corona Treatment	99
4.5.6	Factors Influencing Polymers in Electrical Applications	99
4.6	Weather Resistance	100
4.6.1	Natural Outdoor Weathering	100
4.6.2	Accelerated Outdoor Weathering	101
4.6.3	Artificial Weathering	101
Problems		101
Chapter 5	Characterization and Testing of Polymers	103
5.1	Gel Permeation Chromatography	103
5.1.1	GPC Instrumentation	103
5.1.2	Calibration	105
5.1.3	Selection and Assembly of Detectors	106
5.2	Infrared Spectroscopy	106
5.2.1	Instrument and Experimental Method	107
5.2.2	Applications to Polymers	108
5.3	X-ray Diffraction Analysis	110
5.3.1	Experimental Methods	110
5.3.2	Application to Polymers	111
5.4	Nuclear Magnetic Spectroscopy	112
5.4.1	Experimental Methods	112
5.4.2	Application to Polymers	113
5.5	Thermal Analysis	118
5.5.1	Thermogravimetry Analysis (TGA)	118
5.5.2	Differential Scanning Calorimetry (DSC)	119
5.6	Light and Electron Microscopy	122
5.6.1	Light Microscopy	122
5.6.2	Electron Microscopy	123
Problems		126
Chapter 6	Plastics	128
6.1	Polyethylene	128
6.1.1	Low Density Polyethylene (LDPE)	130
6.1.2	High density polyethylene (HDPE)	134
6.1.3	Linear low density polyethylene (LLDPE)	135

6.1.4	Ethylene-vinyl acetate copolymer (EVA)	136
6.1.5	Crosslinked polyethylene (XPE)	137
6.2	Polypropylene (PP)	137
6.2.1	Isotactic polypropylene	138
6.2.2	Syndiotactic polypropylene (sPP)	139
6.3	Polyvinyl Chloride (PVC)	140
6.3.1	Polymerization	140
6.3.2	Structure and Properties	141
6.3.3	Copolymers	142
6.3.4	Application	142
6.4	Polystyrene (PS) and Related Polymers	143
6.4.1	Polymerization of styrene	143
6.4.2	Structure and properties	143
6.4.3	Copolymers of styrene	144
6.4.4	Syndiotactic polystyrene (sPS)	145
6.4.5	Application	145
6.5	Polymethyl Methacrylate (PMMA)	146
6.5.1	Polymerization	146
6.5.2	Structure and property	146
6.5.3	Application	147
6.6	Polyamide (Nylon)	147
6.6.1	Polyhexamethylene adipamide (nylon-66)	147
6.6.2	Other important polyamides	149
6.7	Polyethylene terephthalate (PET)	150
6.7.1	Polymerization	150
6.7.2	Property and application	150
6.8	Polyoxymethylene (POM)	151
6.8.1	Polymerization	151
6.8.2	Property	152
6.8.3	Application	152
6.9	Polycarbonate (PC)	152
6.10	Polytetrafluoroethylene (PTFE)	152
6.10.1	Polymerization	153
6.10.2	Structure	153
6.10.3	Property	154
6.10.4	Effect of structure on property	154
6.10.5	Fabrication and processing	154
6.10.6	Application	156
6.10.7	Fluorocarbon copolymers	156
	Problems	156

Chapter 7 Elastomers	158
7.1 Basics for Elastomers	158
7.2 Morphology of Thermoplastic Elastomers	162
7.2.1 General characteristics	162
7.2.2 Properties and effect of structure	163
7.2.3 Mechanical properties	165
7.2.4 Thermal and chemical properties	168
7.3 Diene Elastomers	169
7.3.1 Butadiene-based elastomers	169
7.3.2 Polyisoprene	170
7.3.3 Polychloroprene	170
7.3.4 Styrene-butadiene rubber (SBR)	170
7.3.5 Metathesis elastomers	173
7.3.6 Nondiene elastomers	174
7.3.7 Thermoplastic elastomers	176
Problems	178
Chapter 8 Polymer Composites	179
8.1 Introduction to Composites	179
8.2 A Brief History of Polymer Composites	180
8.3 General Use Considerations	182
8.4 Technology Overview	184
8.4.1 Reinforcements	184
8.4.2 Matrices	186
8.4.3 Coupling agents	189
8.4.4 PMC forms	189
8.4.5 Fabrication processes	190
8.5 Applications of Polymer Composites	192
8.6 Nanocomposites	193
8.7 View of the Future	194
Problems	195
Chapter 9 Paint and Coatings	197
9.1 Principles of Coating	197
9.1.1 Rheology	198
9.1.2 Viscosity behavior	199
9.1.3 Surface chemistry	201
9.2 Composition of Paint	209
9.2.1 Introduction	209
9.2.2 Binder	209
9.2.3 Pigments	210

9.2.4	Solvents	211
9.2.5	Additives	212
9.2.6	Fillers (Extenders)	213
9.3	Theory of Adhesion	213
9.3.1	Introduction	213
9.3.2	Mechanical bonding	213
9.3.3	Electrostatic attraction	214
9.3.4	Chemical bonding	215
9.3.5	Paint diffusion	215
9.4	Coating Materials	216
9.4.1	Acrylics	218
9.4.2	Alkyd resins	218
9.4.3	Epoxies	220
9.4.4	Polyurethanes	221
Problems		223
Chapter 10	Developments in Polymer Science and Technology	224
10.1	Synthesis Technology	224
10.1.1	Living radical polymerization	224
10.1.2	Living cationic polymerization	235
10.2	New Polymer Materials and Applications	239
10.2.1	Dendritic (highly branched) polymers	239
10.2.2	Conducting Polymers	243
10.2.3	Bio-degradable polymers	254
Problems		260
References		262

Chapter 1 Introduction

When one speaks of polymers, one is concerned with materials whose molecular weights may reach into the hundreds of thousands or millions. For this reason, the term “macromolecules” is frequently used when referring to polymer materials. More strictly, polymers are such materials whose molecules are composed of a large number of low molecular weight compounds held together by covalent bonds. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reactions by which they combined are termed polymerizations. Through a polymerization, many monomers react together chemically to form either linear chains or a three-dimensional network of polymer chains.

Over the past decades, people have witnessed a fast and enormous increase in production and application of polymer materials. A hundred and thousand of new kinds of polymers have been successfully synthesized and many of them have been used as plastics, rubbers, fibers in different fields. The fast growing of polymer production and consumption is mainly attributed to the good performance involved in their applications. In comparison with conventional materials such as metals and ceramics, polymer materials demonstrate many excellent properties, such as ease of fabrication, low density, chemical inertness, high electrical resistivity, etc. On the other hand, some of their properties are still needed to be improved in order to fit the requirements in high-demanding applications.

Polymer science was born and grows with the rapid development of polymer production and applications, in the need to make new kinds of polymers, to understand the interrelationships among polymer structure, morphology and properties, to better use polymers, and to further extend their applications. Perhaps because of its origins, polymer science tends to be more interdisciplinary than most sciences, combining chemistry, chemical engineering, materials, and other fields as well. Therefore, it is more suitable to name this discipline as polymer science and engineering.

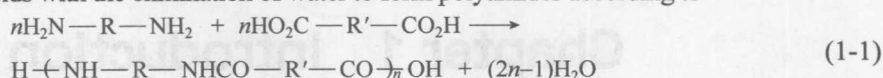
1.1 Classification of polymerizations

In polymerization, monomers react with each other to give polymer molecules. During the development of polymer science, different types of polymerizations are found and two types of classifications have come into use. One classification is based on polymer structure and divides polymerizations into condensation and addition polymerization. The other classification is based on polymerization mechanism and divides polymerizations into step and chain polymerizations.

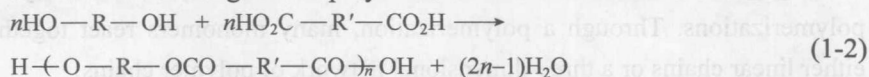
1.1.1 Condensation and addition polymerization

Polymerizations were originally classified by Carothers into condensation and addition polymerization on the basis of the compositional difference between the polymer and the monomers from which it was synthesized. Condensation polymerizations run with a series of condensation reactions from polyfunctional monomers and their intermediates by eliminating some

small molecules such as water. An example of such a condensation polymerization is the polyamidation from diamines and diacids with the elimination of water to form polyamides according to

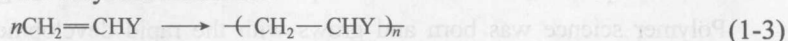


Where R and R' are aliphatic or aromatic groupings. The unit in parentheses in the polyamide formula repeats itself many times in the polymer chain and it is termed the repeating unit. The elemental composition of the repeating unit differs from that of the two monomers by the elements of water. The polyamide synthesized from hexamethylene diamine, $\text{R} = (\text{CH}_2)_6$, and adipic acid, $\text{R}' = (\text{CH}_2)_4$, is the extensively used fiber and plastic known commonly as nylon 66 or poly(hexamethylene adipamide). Other example of condensation polymerizations is the polyesterification from diacids and diols to generate polyester, with the elimination of water:



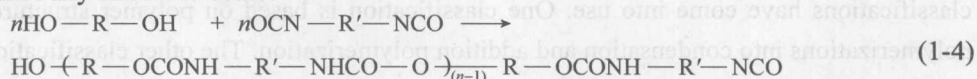
Most condensation polymerizations are carried out by the reaction of functional groups in the monomers. The polymers produced by condensation polymerizations always contain repeating units joined together by functional units of one kind or another such as the ester, amide, and ether linkages.

Unlike condensation polymerizations, addition polymerizations proceed without the loss of small molecules, and in the polymer chains formed through addition polymerizations the repeating unit has the same composition as the monomer. The simplest type of addition polymerizations is the formation of polyethylene from ethylene monomer:



In the addition polymerization of ethylene, thousands of monomers (ethylene) add to a growing chain sequentially and rapidly to form a polyethylene chain. The addition of ethylene monomer to the growing chain is performed by conversion of its double bonds into saturated linkages. For the most common forms of addition polymerization to occur, the monomer must contain carbon-carbon double bond. Such monomers are referred to as vinyl monomers, such as methyl methacrylate, vinyl chloride, and styrene.

With the development of polymer science, study of new polymerization processes and polymers showed that this classification was not entirely adequate. For example, consider the synthesis of polyurethanes, which are formed by the reaction of diols with diisocyanates without the elimination of any small molecule:



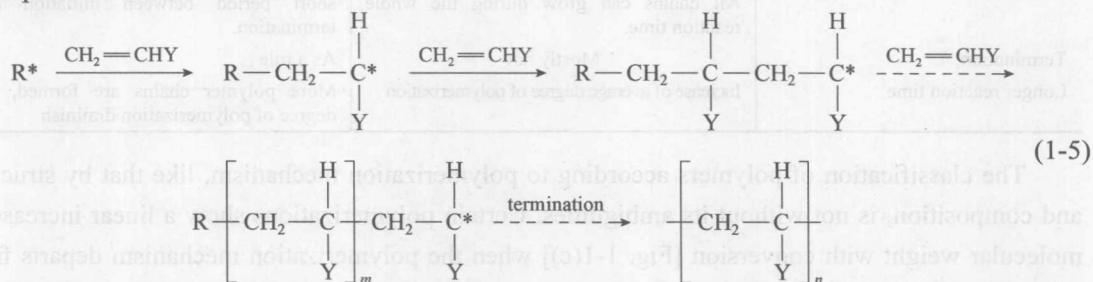
Based on Carothers' classification, this reaction would be classified as addition polymerization, since the polymer has the same elemental composition as the sum of the monomers. However, the polyurethanes are structurally much more similar to the condensation polymers than to the addition polymers. The urethane linkage ($-\text{NH}-\text{CO}-\text{O}-$) has much in common with the ester ($-\text{CO}-\text{O}-$) and amide ($-\text{NH}-\text{CO}-$) linkages. It seems that the synthesis reaction of polyurethanes could be classified into either addition polymerization or condensation

polymerization. It is also true to the ring opening polymerization of ϵ -caprolactam. No H_2O molecules are eliminated and chain growth takes place by successive additions of opening monomeric rings to a chain end. However, when the reaction is initiated by adding a small amount of water, the final product is identical to the polymer obtained by condensation polymerization of ϵ -aminocaproic acid with elimination of water.

1.1.2 Step and chain polymerizations

Flory suggested a new classification principle based on the mechanism by which polymer molecules are built up. This system classifies polymerizations into step and chain polymerizations. Chain and step polymerizations differ in several features, but the most important difference is in the identities of the species that can react with each other. Another difference is the manner in which polymer molecular size depends on the extent of conversion. Step polymerizations proceed by the stepwise reaction between the functional groups of reactants as in reactions such as those described by Eqs. 1-1, 1-2. The size of the polymer molecules increases at a relatively slow pace in such polymerizations. One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on, until eventually large-sized polymer molecules have been formed. The reaction occurs between any of the different-sized species present in the reaction system.

The situation is quite different in chain polymerization where the reaction occurs in three stages. In the initiation step an initiator is used to produce an initiator species R^* with a reactive center. The reactive center may be a free radical, cation, or anion. It attacks and opens the double bond of a molecule of the monomer, producing a new activated species. In the propagation step, a growing chain is formed by the propagation of the reactive center through the successive additions of large numbers of monomer molecules to the reactive center. Each monomer molecule that adds to a reactive center regenerates the reactive center. The growth of the polymer chain ceases when the reactive center is destroyed by one or more of a number of possible termination reactions. The distinguishing characteristic of chain polymerization is that polymer chain growth takes place by monomer reacting only with the reactive center. By far the most common example of chain polymerization is that of vinyl monomers. The process can be depicted as



The typical step and chain polymerizations differ significantly in the relations between polymer molecular weight and the percent conversion of monomer. If we start out step and chain polymerizations side by side, the molecular weights of the polymers produced at any time after the start of the reactions will always be very characteristically different for the two polymerizations. If

the two polymerizations are stopped at 0.1%, 1%, 10%, 40%, 90% conversion, and so on, one will always observe the same behavior. The chain polymerization will show the presence of high-molecular-weight polymer molecules at all percents of conversion. There are no intermediate-sized molecules in the reaction mixture — only monomer, high-molecular-weight polymer, and initiator species. The only change that occurs with conversion (i.e., reaction time) is the continuous increase in the number of polymer molecules [Fig. 1-1(a)]. On the other hand, high-molecular-weight polymer is obtained in step polymerizations only near the very end of the reaction [Fig. 1-1(b)]. Thus both polymer size and the amount of polymer are dependent on conversion of functional groups in step polymerization. The characteristics of step and chain polymerizations are summarized in Table 1-1.

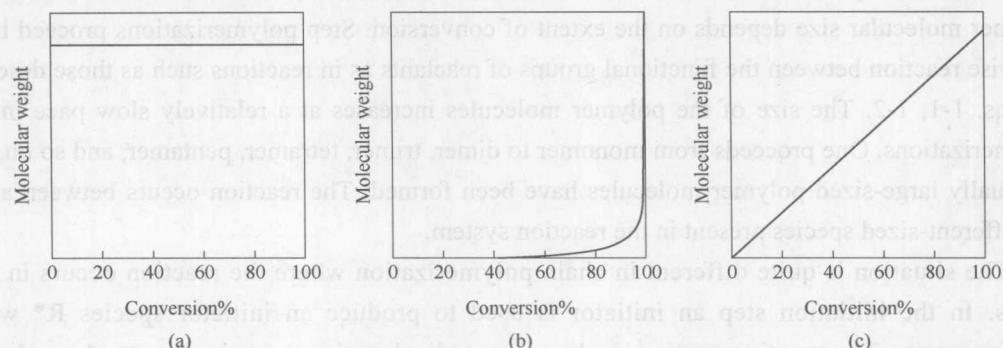


Fig. 1-1 Variation of molecular weight with conversion; (a) chain polymerization; (b) step polymerization; (c) non-terminating chain polymerization and protein synthesis.

Table 1-1 Differences between step-growth and chain-growth polymerizations

Reaction steps	Step-growth	Chain-growth
Elimination of a small molecule	often (e.g. H_2O)	never
Initiator (for starting reaction)	not necessary	necessary
Propagation (growth of polymer chains)	Two complementary end groups condense to form a linkage in the polymer chain thus formed. All complementary chain ends can react with each other. All chains can grow during the whole reaction time.	An active end group yields again an active end group (chain reaction). Only initiated chains react with monomer exclusively. Chain growth is fast and takes place in the short period between initiation and termination.
Termination	Mostly not	As a rule
Longer reaction time	Increase of average degree of polymerization	More polymer chains are formed, the degree of polymerization diminish

The classification of polymers according to polymerization mechanism, like that by structure and composition, is not without its ambiguities. Certain polymerizations show a linear increase of molecular weight with conversion [Fig. 1-1(c)] when the polymerization mechanism departs from the normal chain pathway. This is observed in certain chain polymerizations, which involve a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers. Biological syntheses of proteins also show the behavior described by Fig. 1-1(c), because the various monomer molecules are directed to react in a very specific manner by an enzymatically controlled process.

1.2 Classification of Polymers

“Polymer” is actually a general name given to a variety number of materials with macromolecular structures. These materials exist in countless forms and numbers because of a very large number and types of atoms present in their molecular chains. Polymers with different chemical structures will show different physical and mechanical behavior. Therefore, it is necessary to classify polymers based on their source, mechanical performance, polymerization mechanism, and processing characteristic.

1.2.1 Classification by source

Depending on their source or origin, polymers can be classified as natural and natural modified polymers, synthetic polymers, and biopolymers.

(1) Natural and natural modified polymers

Those isolated from natural materials are called natural polymers. The typical natural polymers include cotton, silk, wool, lignin, and natural rubber. In practice, some of natural polymers have experienced chemical modification in order to have more desirable properties. They are called natural modified polymers. The examples are casein, cellulose, gelatin, etc.

(2) Synthetic polymers

Polymers obtained through synthetic reactions with low molecular weight compounds are called synthetic polymers. Typical examples are polyethylene (PE), polyvinyl chloride (PVC), nylon, and polyester. The original sources of this group of polymers are petroleum, coal, and agricultural products. Synthetic polymers are the most important group of polymer materials, because most polymeric materials used widely today belong to them.

For synthetic polymers, not all the molecular chains have the same length, i.e. the molecular weight of synthetic polymers is polydisperse. Consequently, by the strict sense, such polymers are not pure compounds but mixtures of polymer chains with different chain lengths.

(3) Biopolymers

This case involves substances like proteins, polysaccharides (cellulose, starch), polyaminoacid and several gums. The molecules of proteins contain many types of monomers (up to 20 amino acids), linked in a specific sequence (according to the genetic code) to chains of definite length. So these biopolymer molecules are identical, the polymer is monodisperse, and represents a single, pure compound.

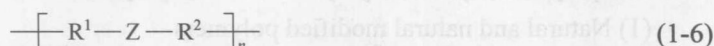
1.2.2 Classification by mechanical behavior and application

According to their ultimate forms and applications, polymers can be classified as plastics, elastomers or rubbers, fibers, coatings and adhesives. When a polymer is shaped into hard and tough utility articles by exerting heat and pressure, it is used as a “plastic”. Some very important plastics are PE, PP, PS, PVC, PMMA. Elastomers are those polymers which have flexible chains and exhibit long elongation and elasticity. Typical examples are

natural rubber (polyisoprene), polybutadiene, polychlorobutadiene. As fibers we already know nylon, polyester, polyacrylonitrile, etc. In the field of coatings and adhesives, some linear and crosslinked polymers will be covered, they are polyvinyl acetate, polyacrylates, epoxy resin, etc.

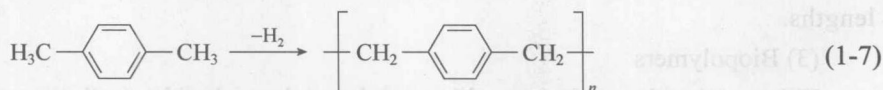
1.2.3 Classification by synthesis reaction

Polymers were classified into addition polymers and condensation polymers based on the involved synthetic reaction of either addition polymerization or condensation polymerization. A polymer is classified as a condensation polymer if its synthesis involves the elimination of small molecules, or it contains functional groups as part of the polymer chain, or its repeating unit lacks certain atoms that are present in the (hypothetical) monomer to which it can be degraded. Thus the structure of condensation polymers has been defined by



where R^1 and R^2 are aliphatic or aromatic grouping unit and Z is a functional unit such as $-\text{OCO}-$, $-\text{NHCO}-$, $-\text{S}-$, $-\text{OCONH}-$, $-\text{O}-$, $-\text{OCOO}-$, and $-\text{SO}_2-$.

Addition polymers are those obtained through addition polymerization. They do not contain functional groups as part of the polymer chain. Such groups may, however, be present in addition polymers as pendant substituents hanging off the polymer chain. According to this classification, the polyurethanes are readily and more correctly classified as condensation polymers. However, with or without functional groups in the polymer chain can not be taken as the only criterion for polymer classification. Some condensation polymers do not contain functional groups such as ester or amide in the polymer chain, such as phenol-formaldehyde polymers produced by the reaction of phenol with formaldehyde. It really is condensation polymer, since water is split out during the polymerization process. Another example is poly(*p*-xylene), which is produced by the oxidative coupling (dehydrogenation) of *p*-xylene:



1.2.4 Classification by chain structure

Polymers can be classified as linear, branched, or crosslinked polymers depending on their structure. In the previous discussion on the different types of polymers and polymerizations, we have considered only those polymers in which the monomer molecules have been linked together in one continuous length to form the polymer molecule. Such polymers are termed linear polymers. Under certain reaction conditions or with certain kinds of monomers, polymers would be generated with more than two chain ends per molecule, which are called branched polymers. For branched polymer molecules, there are side branches of linked monomer units protruding from various central branch points along the main polymer chain. The difference between the shapes of linear and branched polymer molecules can be seen from

the structural representations in Fig. 1-2.

The branch points are indicated by heavy dots. The illustrations show that there are several different kinds of branched polymers. The branched polymer can be comblike in structure with either long (A) or short (B) branches. When there is extensive branching, the polymer can have a dendritic structure in which there are branches protruding from other branches, that is, branched branches (C). The presence of branching in a polymer usually has a large effect on many important polymer properties. The most significant changes brought about by branching are the crystallization capability and flow property. Branched polymers do not pack as easily into a crystal lattice as do linear polymers, leading to decrease of crystallinity. It is important to point out that the term branched polymer does not refer to linear polymers containing side groups that are part of the monomer structure. Only those polymers that contain side branches composed of complete monomer units are termed branched polymers.

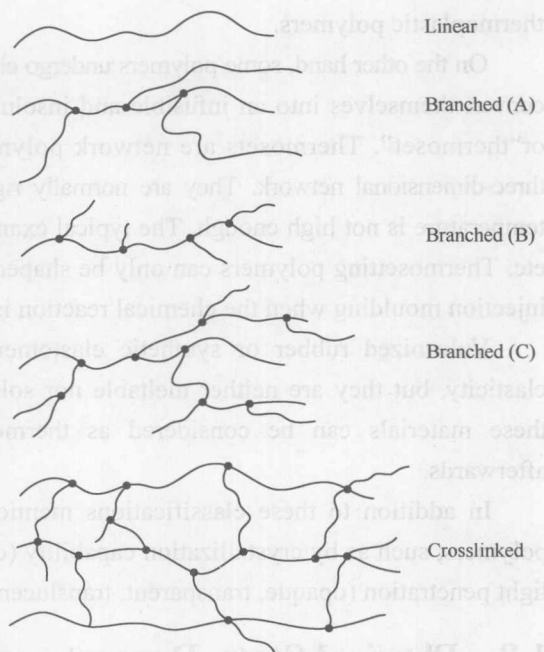


Fig. 1-2 Structure of linear, branched, and crosslinked polymers.

When polymers are produced in which the polymer molecules are linked to each other at points other than their ends, the polymers are said to be crosslinked (Fig. 1-2). Crosslinking can be made to occur during the polymerization process by the use of appropriate monomers. It can also be brought about after the polymerization by various chemical reactions. The crosslinks between polymer chains can be of different lengths depending on the crosslinking method and the specific conditions employed. One can also vary the number of crosslinks so as to obtain lightly or highly crosslinked polymers. When the number of crosslinks is sufficiently high, a three-dimensional or space network polymer is produced in which all the polymer chains in a sample have been linked together to form one giant molecule. Light crosslinking is used to impart good recovery (elastic) properties to polymers to be used as rubbers. High degrees of crosslinking are used to impart high rigidity and dimensional stability (under conditions of heat and stress) to polymers such as the phenol-formaldehyde and urea-formaldehyde polymers.

1.2.5 Classification by processing characteristics

Some polymers become soft and fluid upon heating, and then can be converted into any desired shape, which is solidified by subsequent cooling. This cycle can be repeated several times at will. Such polymers, which soften on heating and stiffen on cooling, are termed "thermoplastics". Thermoplastics are composed of polymers with linear or branched chain structures. They account for almost 90 weight percent of the processed polymers. PE, PVC, nylon, PS are examples of