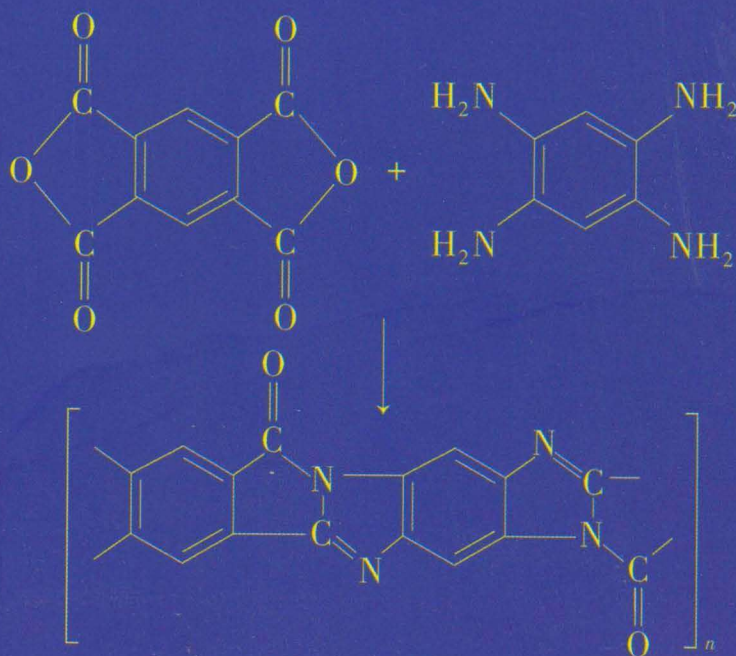


Polymer Materials and Their Applications

高分子材料与应用

王选伦 吕 军 编著



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重庆大学出版社

内 容 提 要

本书共 8 章,内容主要包括高分子材料的发展历史和分类,热塑性常用塑料、热固性塑料、工程塑料的制备方法,合成原理、品种、性能及用途,常见天然纤维和化学纤维的分类、制备原理、性能特点及用途,橡胶的常用品种、加工方法、配方体系、性能及用途,涂料及黏合剂的分类、性能及用途,一些功能高分子的性能特点、合成路线及用途等。

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编写说明

“高分子材料与应用”在国内很多高校是高分子材料与工程专业的一门专业必修课,有些同时是双语课。该课程旨在帮助高分子材料与工程专业的学生了解并掌握常见高分子材料的种类以及高分子材料的基本特性,使其具备高分子材料制备、结构与性能、成型加工、制品种类及应用领域等方面的基本知识。

这门课程理论不深,但教学内容广泛,实用性很强,很适合开设为双语课。很多高校的高分子材料专业开设了“高分子材料与应用”课程,但是有的不是双语课,就使用中文教材,是双语课的,也一般用自编讲义,没有合适的教材。在近5年的教学过程中,我们发现只使用中文教材,难以取得较好的教学效果。学生往往只看中文教材,而不去听教师的英文讲解,达不到提高学生阅读专业文献的能力和掌握专业词汇的目标。如使用英文原版教材,则存在与我国教学大纲不完全相符、内容过于全面且难度无法调节等问题。在实际讲课过程中,教师为了照顾到各个层次的学生和教学大纲的要求,往往对教材内容进行选择性讲解,实际教学内容覆盖率低,且学生学习起来知识点散,不易系统组织,同时也造成了教材的浪费。因此,编写一本符合国内需求的,内容比较丰富而实用的双语课教材是很有意义而且必要的。

本书的内容主要包括介绍高分子材料的发展历史和分类,重点讲解了通用塑料、工程塑料、热固性塑料的合成原理、常见品种、加工工艺、改性途径、主要性能及应用,介绍了常见天然纤维和化学纤维的分类、制备原理、性能特点及应用,橡胶的常见品种、加工方法、配方体系、性能及应用,涂料及黏合剂的分类、合成工艺、主要性能及应用,一些重要功能高分子材料的性能特点、合成路线及应用等。

本书每章节后有课后练习,练习答案在本书的课件中,课件可在重庆大学出版社的官网上下载。

在本书的编写过程中,得到了重庆理工大学材料学院杜长华院长的鼓励和支持。全书共分 8 章,第 1—6 章由王选伦编写,第 7,8 章由吕军编写。本书内容系统全面,围绕当前高分子材料的种类、性能、加工与应用以及技术发展均给出了详细的论述和介绍,不仅可作为高分子材料与工程相关专业的教材,也是材料工程技术人员的一本很好的参考书。

本书由重庆理工大学市级重点学科材料科学与工程,中国国家自然科学基金委员会(51373139)及聚合物分子工程国家重点实验室(复旦大学)开放研究课题基金(K2014-02)资助出版,在此表示感谢。

由于编者水平及时间所限,书中不足或谬误之处在所难免,恳请读者批评指正。

编 者
2015 年 1 月

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CHAPTER ***I***

INTRODUCTION

1.1 What are polymers?

Plastics, rubbers, fibers are all polymers. What is a polymer? The simplest definition of a polymer is something made of many units. Think of a polymer as a chain (Figure 1.1). The term *polymer* is derived from the Greek words *poly* and *meros*, meaning many parts^[1]. Each link of the chain is the “mer” or basic unit that is usually made of carbon, hydrogen, oxygen, and/or silicon. To make the chain, many links or “mers” are hooked or polymerized together. Polymerization can be demonstrated by linking strips of construction paper together to make paper garlands or hooking together hundreds of paper clips to form chains.

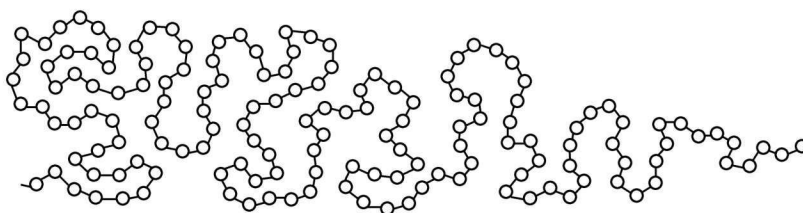


Figure 1.1 Model of a polymer molecule

Polymers have been with us since the beginning of time. Natural polymers include such things as tar and shellac, tortoise shell and horns, as well as tree saps that produce amber and latex. These polymers were processed with heat and pressure into useful articles like hair ornaments and jewelry. Natural polymers began to be chemically modified during the 1800s to produce many materials. The most famous of these were vulcanized rubber, gun cotton, and celluloid. The first semi-synthetic polymer produced was Bakelite in 1909 and was soon followed by the first synthetic fiber, rayon, which was developed in 1911.

Even with these developments, it was not until World War II that significant changes took place in the polymer industry. Prior to World War II, natural substances were generally available; therefore, synthetics that were being developed were not a necessity. Once the world went to war, our natural sources of latex, wool, silk, and other materials were cut off, making the use of synthetics critical. During this time period, we saw the use of nylon, acrylic, neoprene, SBR, polyethylene, and many more polymers take the place of natural materials that were no longer available. Since then, the polymer industry has continued to grow and has evolved into one of the fastest growing industries in the U.S. and in the world.

Table 1.1 gives a list of some polymers, their year of introduction, and some of their applications. It is obvious that the pace of development of plastics, which was painfully slow up to the 1920s, picked up considerable momentum in the 1930s and the 1940s. The first generation of man-made polymers was the result of empirical activities; the main focus was on chemical composition with virtually no attention paid to structure. However, during the first half of the 20th century, extensive organic and physical developments led to the first understanding of the structural concept of polymers—long chains or a network of covalently bonded molecules. In this regard the classic work of the German chemist Hermann Staudinger on polyoxymethylene and rubber and of the American chemist W. T. Carothers on nylon stand out clearly. Staudinger first proposed the theory that polymers were composed of giant molecules, and he coined the word *macromolecule* to describe them. Carothers discovered nylon, and his fundamental research (through which nylon was actually discovered) contributed considerably to the elucidation of the nature of polymers. His classification of polymers as *condensation* or *addition* polymers persists today.

Table 1.1 Brief history of polymeric materials

Date	Material	Typical Use
1868	Cellulose nitrate	Eyeglass frames
1909	Phenol-formaldehyde	Telephone handsets, knobs, handles
1919	Casein	Knitting needles
1926	Alkyds	Electrical insulators
1927	Cellulose acetate	Toothbrushes, packaging
1927	Poly(vinyl chloride)	Raincoats, flooring
1929	Urea-formaldehyde	Lighting fixtures, electrical switches
1935	Ethyl cellulose	Flashlight cases
1936	Polyacrylonitrile	Brush backs, displays
1936	Poly(vinyl acetate)	Flashbulb lining, adhesives
1938	Cellulose acetate butyrate	Irrigation pipe
1938	Polystyrene	Kitchenwares, toys
1938	Nylon (polyamide)	Gears, fibers, films

continued

Date	Material	Typical Use
1938	Poly(vinyl acetal)	Safety glass interlayer
1939	Poly(vinylidene chloride)	Auto seat covers, films, paper, coatings
1939	Melamine-formaldehyde	Tableware
1942	Polyester (cross-linkable)	Boat hulls
1942	Polyethylene (low density)	Squeezable bottles
1943	Fluoropolymers	Industrial gaskets, slip coatings
1943	Silicone	Rubber goods
1945	Cellulose propionate	Automatic pens and pencils
1947	Epoxies	Tools and jigs
1948	Acrylonitrile-butadiene-styrene copolymer	Luggage, radio and television cabinets
1949	Allylic	Electrical connectors
1954	Polyurethane	Foam cushions
1956	Acetal resin	Automotive parts
1957	Polypropylene	Safety helmets, carpet fiber
1957	Polycarbonate	Appliance parts
1959	Chlorinated polyether	Valves and fittings
1962	Phenoxy resin	Adhesives, coatings
1962	Polyallomer	Typewriter cases
1964	Ionomer resins	Skin packages, moldings
1964	Polyphenylene oxide	Battery cases, high temperature moldings
1964	Polyimide	Bearings, high temperature films and wire coatings
1964	Ethylene-vinyl acetate	Heavy gauge flexible sheeting
1965	Polybutene	Films
1965	Polysulfone	Electrical/electronic parts
1970	Thermoplastic polyester	Electrical/electronic parts
1971	Hydroxy acrylates	Contact lenses
1973	Polybutylene	Piping
1974	Aromatic polyamides	High-strength tire cord
1975	Nitrile barrier resins	Containers

The initial compound that is used to form polymers is the “mer” or monomer. Monomers are chemically joined together in one of two ways: addition polymerization or condensation polymerization.

Addition polymerization is comprised of three basic steps: initiation, propagation, and

termination. For example, during the initiation phase of the polymerization of polyethylene, the double bonds in the ethylene “mers” break and begin to bond together. A catalyst or promoter may be necessary to begin or speed up the reaction. The second phase, propagation, involves the continued addition of monomers together into chains.

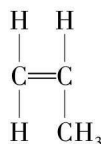
The final step is termination. During termination all monomers may be used, causing the reaction to cease. A polymerization reaction can cease by quenching the reaction. Similar to quenching someone’s thirst, water can be used to quickly cool a reaction. Polymers formed by addition polymerization include acrylic, polyethylene, and polystyrene, to name a few.

Very simply, addition polymerization describes the process of “mers” joining by each one adding on to the end of the last “mer”. A simple visual of the process is paper clips joined together to form a long chain. Polymers formed by addition polymerization are often thermoplastic in nature. Thermoplastics are like hot melt glue sticks that can be heated and made soft and then become hard when cooled. Thermoplastic polymers are easily processed and reprocessed or recycled. The majority of polymers used today are thermoplastics.

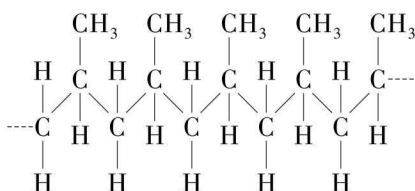
The other group of polymers is formed by condensation polymerization. During the chemical reaction of condensation polymerization, a small molecule is eliminated as the monomers join together. Common polymers in this group include nylons, some polyesters, urea formaldehyde, and urethanes. These polymers can be thermoplastic in nature or thermosetting. Once a thermoset polymer is formed, it cannot be melted and reformed. All plastics flow at some time during their processing and are solid in the finished state, but once a thermoset is processed, it is dramatically different and cannot be reformed.

The means of polymerization will affect the heat reaction of the formed polymer; likewise, the arrangement of the “mers” within the molecule will affect the physical characteristics of the formed polymer. “Mers” joined together in long chains have a linear configuration very similar to a paper clip chain, even though in actuality tetrahedral bonds give the molecule a zigzag arrangement. During polymerization, if the “mers” not only form straight chains but also form long side chains off the main backbone, the resulting configuration is described as branched, like a tree branch or grape stem. A third configuration is achieved by the long chains being chemically linked together. An example would be natural rubber (isoprene) being reacted with sulfur. The sulfur bonds the chains to form a giant meshwork molecular structure that is known as vulcanized rubber. This is a cross-linked configuration.

Polyethylene has the simplest “mer” structure. Even though the backbone of other polymers will be similarly formed by a broken bond between two carbons, the remaining carbons in the “mer” will form a functional group whose orientation about the backbone will affect the physical nature of the resulting polymer. For example, propylene is the “mer” that will form polypropylene:



Polymerization will be initiated by the double bond breaking and the “-mers” joining together. Therefore, the methyl group on the propylene “-mer” has the potential to be located at various points along the backbone. If the methyl group (CH_3) is oriented repeatedly on one side of the chain on alternating carbons, it is called isotactic. Ninety to nine-five percent of all polypropylene polymers have this configuration.



1.2 Classification of polymers

Polymers can be classified in many different ways. The most obvious classification is based on the origin of the polymer, i.e., natural vs. synthetic. Other classifications are based on the polymer structure, polymerization mechanism, preparative techniques, or thermal behavior^[2].

1.2.1 Natural vs. synthetic

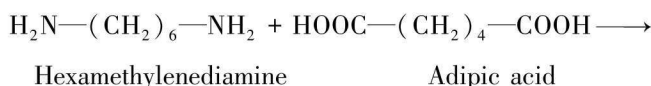
Polymers may either be naturally occurring or purely synthetic. All the conversion processes occurring in our body (e.g., generation of energy from our food intake) are due to the presence of enzymes. Life itself may cease if there is a deficiency of these enzymes. Enzymes, nucleic acids, and proteins are polymers of biological origin. Their structures, which are normally very complex, were not understood until very recently. Starch—a staple food in most cultures—cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin and have relatively simpler structures than those of enzymes or proteins. There are a large number of synthetic (man-made) polymers consisting of various families: fibers, elastomers, plastics, adhesives, etc. Each family itself has subgroups.

1.2.2 Polymer structure

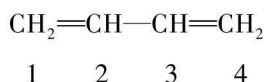
(1) Linear, branched or cross-linked, ladder vs. functionality

As we stated earlier, a polymer is formed when a very large number of structural units (repeating units, monomers) are made to link up by covalent bonds under appropriate conditions. Certainly even if the conditions are “right” not all simple (small) organic molecules possess the

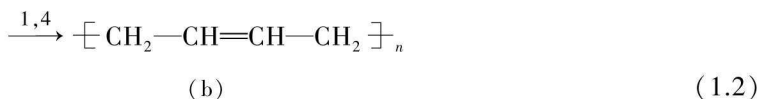
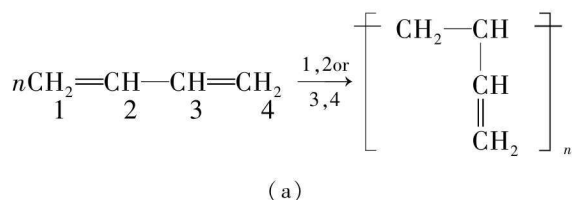
ability to form polymers. In order to understand the type of molecules that can form a polymer, let us introduce the term *functionality*. The functionality of a molecule is simply its interlinking capacity, or the number of sites it has available for bonding with other molecules under the specific polymerization conditions. A molecule may be classified as monofunctional, bifunctional, or polyfunctional depending on whether it has one, two, or greater than two sites available for linking with other molecules. For example, the extra pair of electrons in the double bond in the styrene molecules endows it with the ability to enter into the formation of two bonds. Styrene is therefore bifunctional. The presence of two condensable groups in both hexamethylenediamine (—NH_2) and adipic acid (—COOH) makes each of these monomers bifunctional. However, functionality as defined here differs from the conventional terminology of organic chemistry where, for example, the double bond in styrene represents a single functional group. Besides, even though the interlinking capacity of a monomer is ordinarily apparent from its structure, functionality as used in polymerization reactions is specific for a given reaction. A few examples will illustrate this.



A diamine like hexamethylenediamine has a functionality of 2 in amide-forming reactions such as that shown in Equation 1.1. However, in esterification reactions a diamine has a functionality of zero. Butadiene has the following structure:



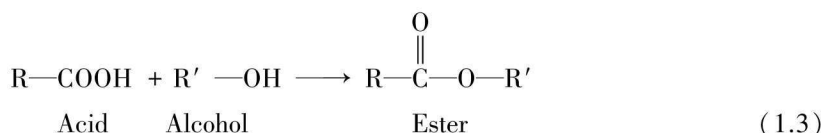
From our discussion about the polymerization of styrene, the presence of two double bonds on the structure of butadiene would be expected to prescribe a functionality of 4 for this molecule. Butadiene may indeed be tetra-functional, but it can also have a functionality of 2 depending on the reaction conditions (Equation 1.2).



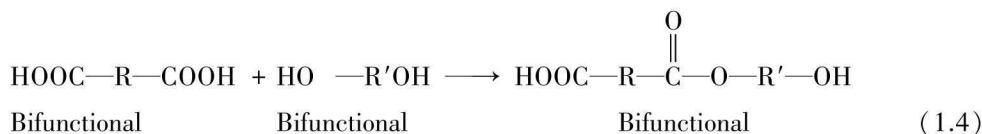
Since there is no way of making a distinction between the 1,2 and 3,4 double bonds, the

reaction of either double bond is the same. If either of these double bonds is involved in the polymerization reaction, the residual or unreacted double bond is on the structure attached to the main chain [i.e., part of the pendant group (a)]. In 1,4 polymerization, the residual double bond shifts to the 2,3 position along the main chain. In either case, the residual double bond is inert and is generally incapable of additional polymerization under the conditions leading to the formation of the polymer. In this case, butadiene has a functionality of 2. However, under appropriate reaction conditions such as high temperature or cross-linking reactions, the residual unsaturation either on the pendant group or on the backbone can undergo additional reaction. In that case, butadiene has a total functionality of 4 even though all the reactive sites may not be activated under the same conditions. Monomers containing functional groups that react under different conditions are said to possess latent functionality.

Now let us consider the reaction between two monofunctional monomers such as in an esterification reaction (Equation 1.3).



You will observe that the reactive groups on the acid and alcohol are used up completely and that the product ester is incapable of further esterification reaction. But what happens when two bifunctional molecules react? Let us use esterification once again to illustrate the principle (Equation 1.4).



The ester resulting from this reaction is itself bifunctional, being terminated on either side by groups that are capable of further reaction. In other words, this process can be repeated almost indefinitely. The same argument holds for polyfunctional molecules. It is thus obvious that the generation of a polymer through the repetition of one or a few elementary units requires that the molecule(s) must be at least bifunctional.

The structural units resulting from the reaction of monomers may in principle be linked together in any conceivable pattern. Bifunctional structural units can enter into two and only two linkages with other structural units. This means that the sequence of linkages between bifunctional units is necessarily linear. The resulting polymer is said to be linear. However, the reaction between polyfunctional molecules results in structural units that may be linked so as to form nonlinear structures. In some cases the side growth of each polymer chain may be terminated before the chain has a chance to link up with another chain. The resulting polymer molecules are said to be branched. In other cases, growing polymer chains become chemically linked to each other, resulting

in a cross-linked system (Figure 1.2).

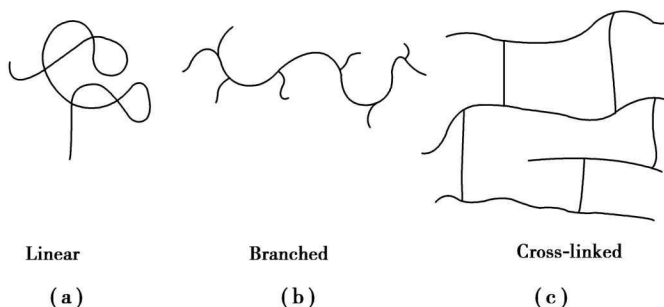
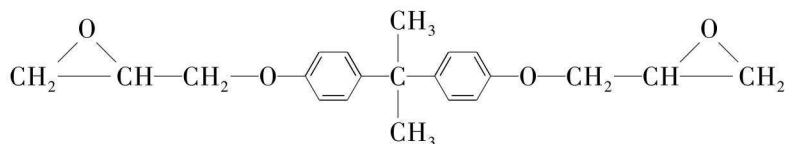


Figure 1.2 Linear, branched, and cross-linked polymers

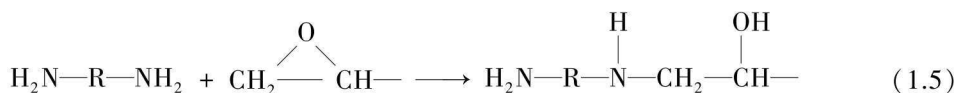
The formation of a cross-linked polymer is exemplified by the reaction of epoxy polymers, which have been used traditionally as adhesives and coatings and, more recently, as the most common matrix in aerospace composite materials. Epoxies exist at ordinary temperatures as low-molecular-weight viscous liquids or prepolymers. The most widely used prepolymer is diglycidyl ether of bisphenol A (DGEBA), as shown below:



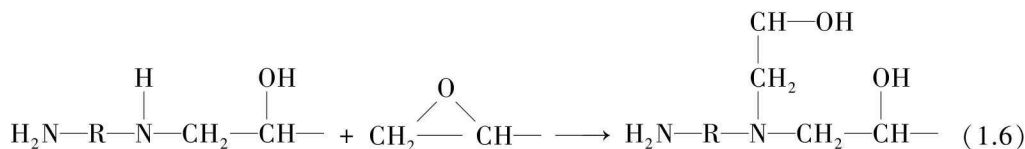
Diglycidyl ether of bisphenol A (DGEBA)

The transformation of this viscous liquid into a hard, cross-linked three-dimensional molecular network involves the reaction of the prepolymer with reagents such as amines or Lewis acids. This reaction is referred to as curing. The curing of epoxies with a primary amine such as hexamethylenediamine involves the reaction of the amine with the epoxide. It proceeds essentially in two steps:

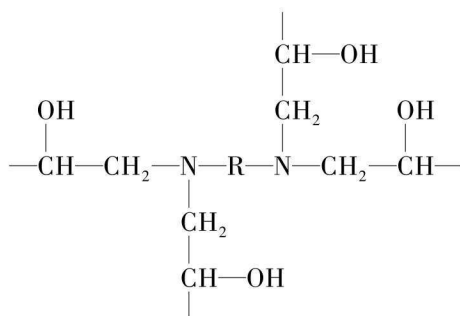
- ① The attack of an epoxide group by the primary amine



- ② The combination of the resulting secondary amine with a second epoxy group to form a branch point



The presence of these branch points ultimately leads to a cross-linked infusible and insoluble polymer with structures as follows.



In this reaction, the stoichiometric ratio requires one epoxy group per amine hydrogen. Consequently, an amine such as hexamethylenediamine has a functionality of 4. Recall, however, that in the reaction of hexamethylenediamine with adipic acid, the amine has a functionality of 2. In this reaction DGEBA is bifunctional since the hydroxyl groups generated in the reaction do not participate in the reaction. But when the curing of epoxies involves the use of a Lewis acid such as BF_3 , the functionality of each epoxy group is 2; that is, the functionality of DGEBA is 4. Thus the curing reactions of epoxies further illustrate the point made earlier that the functionality of a given molecule is defined for a specific reaction. By employing different reactants or varying the stoichiometry of reactants, different structures can be produced and, consequently, the properties of the final polymer can also be varied.

Polystyrene, polyethylene, polyacrylonitrile, poly (methyl methacrylate) and poly (vinyl chloride) are typical examples of linear polymers.

Substituent groups such as —CH_3 , $\text{—O—}\overset{\text{O}}{\parallel}\text{C—CH}_3$, —Cl , and —CN that are attached to the main chain of skeletal atoms are known as pendant groups. Their structure and chemical nature can confer unique properties on a polymer. For example, linear and branched polymers are usually soluble in some solvent at normal temperatures. But the presence of polar pendant groups can considerably reduce room temperature solubility. Since cross-linked polymers are chemically tied together and solubility essentially involves the separation of solute molecules by solvent molecules, cross-linked polymers do not dissolve, but can only be swelled by liquids. The presence of cross-linking confers stability on polymers. Highly cross-linked polymers are generally rigid and high-melting. Cross-links occur randomly in a cross-linked polymer. Consequently, it can be broken down into smaller molecules by random chain scission. Ladder polymers constitute a group of polymers with a regular sequence of cross-links. A ladder polymer, as the name implies, consists of two parallel linear strands of molecules with a regular sequence of cross-links. Ladder polymers have only condensed cyclic units in the chain; they are also commonly referred to as double-chain or double-strand polymers. A typical example is poly (imidazopyrrolone), which is obtained by the polymerization of aromatic dianhydrides such as pyromellitic dianhydride or aromatic tetracarboxylic acids with ortho-aromatic tetramines like 1,2,4,5-tetraaminobenzene: