

Chapter 1

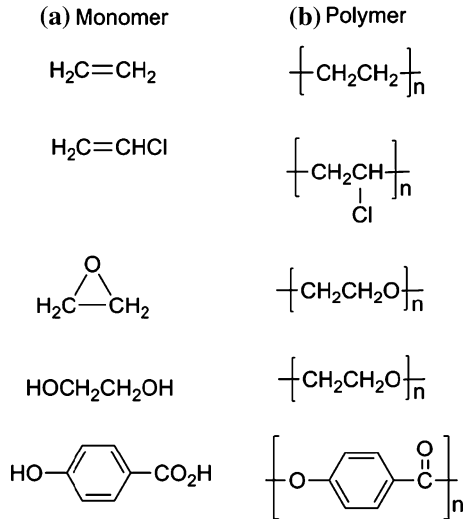
Introduction

Synthetic polymers [1] are vital materials used in modern daily life from packaging, electronics, medical devices, clothing, vehicles, buildings, etc., due to their ease of processing and light weight. The first synthetic polymer, a phenol-formaldehyde resin, was invented in the early 1900s by Leo Baekeland [2]. It was a commercial success invention although most of scientists had no clear concept of polymer structure at that time. Wallace Carothers invented very important polymers of neoprene rubber and Nylon in 1930s which shaped the leadership of DuPont in polymer industry. Hermann Staudinger developed theoretical explanations of remarkable properties of polymers by ordinary intermolecular forces between molecules of very high molecular weight. He was awarded the Nobel Prize in Chemistry in 1953 for this outstanding contribution. World War II led to significant advances in polymer chemistry with the development of synthetic rubber as natural rubber was not accessible to the Allies. Karl Ziegler and Giulio Natta won the Nobel Prize in Chemistry in 1963, jointly for the development of coordination polymerization to have controlled stereochemistry of polymers using coordination catalysts. Their work has revolutionized the polymer industry to synthesize stereoregular polymers that have mechanical properties superior than that of non-stereoregular polymers. Equally significant work was done by Paul Flory 1974, Nobel laureate on the quantitative investigations of polymer behaviors in solution or in bulk.

Most of polymers are insulators, so they have passive functions and used as a bulk material for structure or as thin layer for coating barrier. In 1977, Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa reported high conductivity in iodine-doped polyacetylene. This research earned them the 2000 Nobel Prize in Chemistry. Since then, the application of polymer has expanded into active functional area such as light emitting diode, sensor, solar cell, etc. Polymers can be tailor made to meet the requirements of specific application through molecular design and synthesis. Therefore, they have become the material of choice to face the ever fast changing world from electronics to medical applications.

The physical properties of polymers are mainly determined by their chemical structures. Chemical structures of polymers affect their flow and morphology that results in different physical properties. The processability of polymers is controlled

Fig. 1.1 Chemical structures of (a) monomers and (b) their corresponding polymers

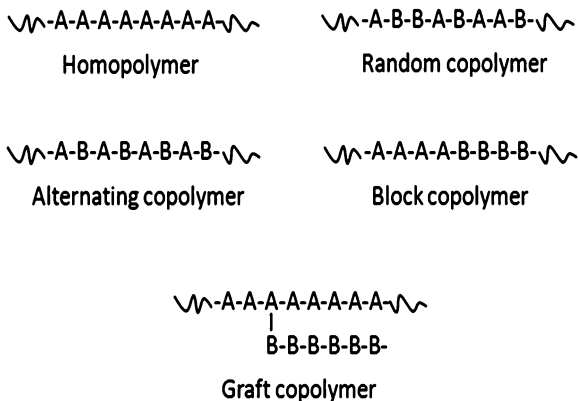


by their flow characteristics in neat form or in solution which affects by their molecular weight.

Polymers are built up by linking together of large number of “monomers.” Monomers are small molecules with functional groups (organic compounds) and they can react with each other to form a large molecule. Figure 1.1 shows some commonly used polymers with their chemical structures of monomers and their corresponding polymers. The polymers have to have molecular weight larger than 10,000 to exhibit good mechanical properties for structural use. Oligomer is a molecule that has molecular weight between 1,000 and 10,000. The oligomer has been widely used in coating applications. End group is the chemical structure at the end of the polymer chains. When the polymer is ended with a functional group, such as $\text{CH}_3\text{CH}_2-\left[\text{CH}_2\text{CH}_2\right]_n-\text{CH}=\text{CH}_2$, the polymer is called telechelic polymer. In the same way, reactive oligomer is oligomer that contains end groups and capable to undergo polymerization.

The size of polymer is determined by the degree of polymerization (DP). It is a total number of structural units, including end groups, and is related to both chain length and molecular weight. For example, the molecular weight of polymethacrylate with $\text{DP} = 500$ is 500 multiplying by 74 (weight of unit) = 37,000. Because polymer chains within a given polymer sample are always of varying lengths, we need to use average value, such as number-average molecular weight (\bar{M}_n), weight-average molecular weight (\bar{M}_w), etc. The molecular weight distribution (PDI) is defined as dividing \bar{M}_w over \bar{M}_n .

Fig. 1.2 Possible arrangements of repeating units to form different type polymers



1.1 Types of Polymers

There are many different types of polymers that can be differentiated from the arrangement of repeating units, and the different arrangements of molecular segment [3]. A polymer prepared from one kind of monomer is called homopolymer. A polymer prepared from more than one kind of monomer is called copolymer, including random copolymer, alternating copolymer, block copolymer, and graft copolymer (Fig. 1.2). These homopolymer and copolymers also can be prepared into polymers with different arrangement of molecular segment, such as star polymer, comb polymer, ladder polymer, dendrimer, and so on. (Fig. 1.3).

1.2 Types of Polymerization

The types of polymerizations are generally classified into chain polymerization and step polymerization according to chemical reactions in the polymerization [4]. The molecular weight of polymers can be built either gradually by step reactions or simultaneously by chain reaction depending on the chemical structure of the monomer. For the step polymerization, the monomers need to have bifunctional groups to link 1 molecule at one time. If the bifunctional groups are the same such as ethylene glycol (OH-CH₂CH₂-OH), one will need different type of bifunctional monomer such as terephthalic acid (COOH-C₆H₄-COOH) to synthesize polyester [-CH₂-CH₂-O-C(=O)C₆H₄C(=O)O-]_n at relative high temperature to remove water. This type of polymerization is also called polycondensation polymerization due to the loss of molecule during the polymerization.

The monomers containing double bond can be polymerized by chain reaction. The polymerization proceeds by three steps of initiation, propagation, and termination. Depending on the type of initiation, the chain polymerization can be classified into free radical chain polymerization, ionic chain polymerization, and

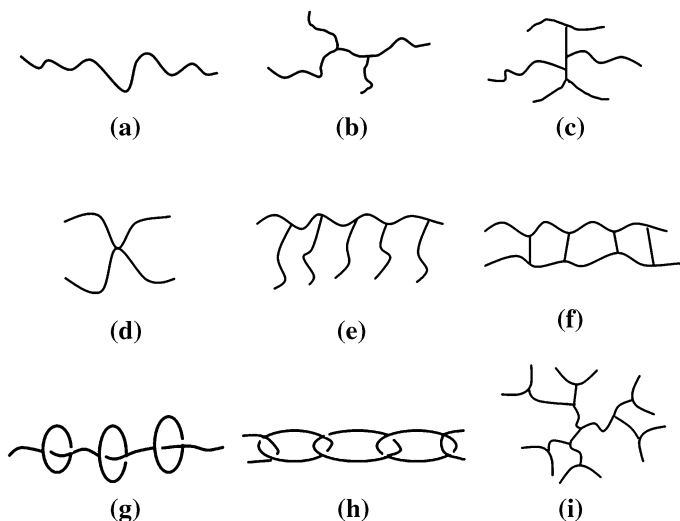


Fig. 1.3 Possible arrangements of molecular segment to form different type polymers: (a) linear polymer, (b) branched polymer, (c) crosslinked polymer, (d) star polymer, (e) comb polymer, (f) ladder polymer, (g) polyrotaxane, (h) polycatenane, (i) dendrimer

coordinating chain polymerization. Their principles will be addressed in the subsequent chapters. Copolymers are made from more than one kind of monomer to meet balanced properties required in many different applications. The differences in the reactivity of different monomer and growing polymer chain need to be considered in the synthesis of copolymer. We will also discuss this subject in the later chapter.

Ring opening polymerization has been extensively used in synthesis of polyether, polyamide, polysiloxane, and the curing of the epoxy resin. The reaction mechanism of ring opening polymerization is unique in its own way which shows a combination behavior of step polymerization and chain polymerization. The detailed reaction mechanism will be present in the last chapter of this book.

1.3 Nomenclature of Polymers

The nomenclature of polymers [1, 3] is usually based on the source of monomer, for example, poly(vinyl chloride) $-(\text{CH}_2\text{CHCl})_n-$ is made from vinyl chloride monomer, and poly(ϵ -caprolacton) $-\text{[NH-CO-(CH}_2)_5\text{]}_n-$, that is the same as poly(6-aminocaproic acid), is made from ϵ -caprolacton. Many polymers commonly are named basis on their structures such as poly(hexamethylene sebacamide) $-\text{[HN-(CH}_2)_6\text{-NHCO-(CH}_2)_8\text{-CO]}_n-$, poly(ethylene terephthalate) $-\text{[O-CH}_2\text{CH}_2\text{-O-CO-C}_6\text{H}_5\text{-CO]}_n-$, and poly(trimethylene ethylene urethane) $-\text{[O-CH}_2\text{CH}_2\text{CH}_2\text{-O-CO-NH-CH}_2\text{-CH}_2\text{-NH-CO]}_n-$.

Table 1.1 Comparison between common name and IUPAC name of polymers

Structure	Common name	IUPAC name
$-(\text{CH}_2-\text{CH}_2)-$	polyethylene	poly(methylene)
$-(\text{CH}(\text{CH}_3)-\text{CH}_2)-$	polypropylene	poly(propylene)
$-(\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2)-$	polystyrene	poly(1-phenyl ethylene)

The International Union of Pure and Applied Chemistry (IUPAC) polymer nomenclature system is a more systematic approach. The basis of the IUPAC polymer nomenclature system is the selection of a preferred CRU (constitutional repeating unit), i.e., structural repeating unit, as tabulated in Table 1.1. The name is made according to the seniority among the atoms or subunits making up the CRU. The steps including (1) CRU is identified, (2) substituent groups on the backbone are assigned the lowest possible number, and (3) the name is placed in parentheses and prefixed with *poly*.

For the copolymers, they are named according to the arrangements of the repeating units in copolymers. For example, for a copolymer that consists of polystyrene and poly(methyl methacrylate), this copolymer can be abbreviated as either poly[styrene-co-(methyl methacrylate)] or copoly(styrene/methyl methacrylate). For an alternating copolymer, an abbreviation of *alt* can be placed between these two homopolymers, as poly[styrene-alt-(methyl methacrylate)]. Therefore, the *alt* is replaced by *block* and *graft* that can represent the block copolymer [polystyrene-block-poly(methyl methacrylate)] and graft copolymer [polystyrene-graft-poly(methyl methacrylate)], respectively.

The source-based nomenclature system is still one of choices in the polymer community, although the important reference sources such as Chemical Abstracts and Polymer Handbook have adopted the IUPAC system. Polymers used in business for long time usually have their own trade name, due to sometimes a polymer named by IUPAC name is not read easily and too long to use

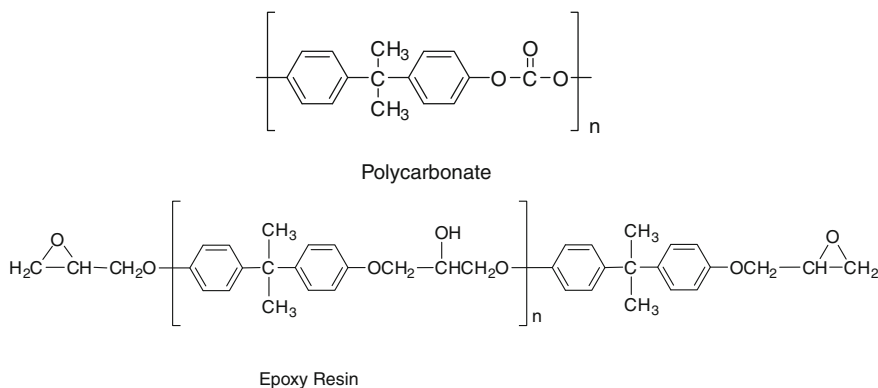
**Fig. 1.4** Chemical structures of polycarbonate and epoxy resin

Table 1.2 Representative polymers used in modern society

Common name	Abbreviation	Chemical structure
Polyethylene	PE	$\left[\text{CH}_2\text{CH}_2 \right]_n$
Polypropylene	PP	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{CH}_3 \end{array} \right]_n$
Poly(vinyl chloride)	PVC	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Cl} \end{array} \right]_n$
Poly(ethylene terephthalate)	PET	$\left[\text{CH}_2\text{CH}_2\text{-O-C(=O)-C}_6\text{H}_4\text{-C(=O)-O} \right]_n$
Polystyrene	PS	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$
Phenol-formaldehyde	none	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3\text{-CH}_2 \end{array} \right]_n$
Polyisoprene	PI	$\left[\begin{array}{c} \text{H}_2\text{C} \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ \text{H}_3\text{C} \quad \text{H} \end{array} \right]_n$
Polyacrylonitrile	PAN	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{CN} \end{array} \right]_n$
Poly(vinyl acetate)	PVA	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{O-C(=O)-CH}_3 \end{array} \right]_n$
Poly(methyl methacrylate)	PMMA	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{C} \\ \\ \text{C(=O)-O-CH}_3 \end{array} \right]_n$
Polycaprolactam	Nylon 6	$\left[\text{NH(CH}_2\text{)}_5\text{-C(=O)} \right]_n$
Polycarbonate	PC	$\left[\text{O-C(=O)-O-C}_6\text{H}_4\text{-C(CH}_3\text{)}_2\text{-C}_6\text{H}_4 \right]_n$
Poly(3-hexyl thiophene)	P3HT	$\left[\begin{array}{c} \text{C}_6\text{H}_{13} \\ \\ \text{C}_4\text{H}_2\text{S} \end{array} \right]_n$

Table 1.3 Recycling codes of plastics [3]

Number	Letters	Plastic
1	PET	Poly(ethylene terephthalate)
2	HDPE	High density polyethylene
3	V <i>or</i> PVC	Poly(vinyl chloride)
4	LDPE	Low density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	OTHER	Others or mixed plastics

conveniently. For example, IUPAC name for polycarbonate is poly(oxy carbonyl oxy -1,4-phenylene-isopropylidene -1,4-phenylene) and the repeating unit is $-\text{[O-CO-O-C}_6\text{H}_4\text{-C(CH}_3\text{)}_2\text{-C}_6\text{H}_4\text{]}_n\text{-}$. Bisphenol A epoxy resin has an IUPAC name of 4,4'-dimethoxy oxirane -2,2-diphenyl propane. Figure 1.4 shows the chemical structures of polycarbonate and bisphenol A epoxy resin.

Table 1.2 organizes some representative polymers in modern society with their common name, abbreviation, and chemical structure according to the amount of usage. Their synthesis and properties will be discussed throughout this text book. The abbreviated name of polymer has been adapted for subsequent chapter for simplicity.

1.4 Polymer Recycling

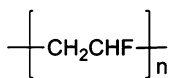
Polymer recycling [3] is an important matter being carried out worldwide to reduce pollution and conserve material. Poly(ethylene terephthalate) (PET) and high density polyethylene (HDPE) share more than 70 % of the demand for recycled plastics. The recycling industry sometime encounters economic difficulties because most “virgin” plastics are not only of better quality than their recycled counterparts, but are often less expensive. In Taiwan, the majority of used plastics are burned as fuel or pyrolyzed to make fuel. The Society of the Plastics Industry (SPI) of USA has adopted plastic recycling codes to be used internationally as shown in Table 1.3, so the recycled polymers can be sorted according to their code before they are used as raw materials for specific applications.

1.5 Problems

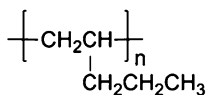
1. Write a concise definition of each term listed below, using examples as appropriate, (a) polymer, (b) monomer, (c) functional group, (d) oligomer, (e) telechelic polymer, (f) degree of polymerization, (g) molecular weight distribution, (o) copolymer, (p) chain polymerization, (q) step polymerization.

- Write the name and structure of the monomers that are required to synthesize the following polymers. Please write the IUPAC name of each polymer.
- Please discuss the importance of plastic recycling.

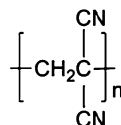
(a)



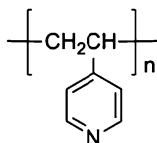
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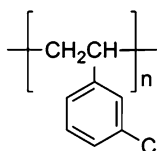
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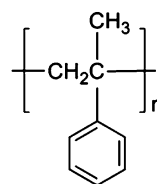
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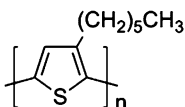
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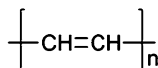
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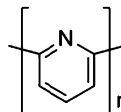
(g)



(h)



(i)



References

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