International Plastics Handbook

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The Resource for Plastics Engineers

CHAPTER 2

MATERIALS SCIENCE OF POLYMERS

This chapter is intended to give the reader a general overview of polymer materials science. It presents the general chemistry, structure and morphology of polymers as well as common modifications done on polymeric materials to enhance their properties. At the end of the chapter the topic of recycling is briefly discussed.

2.1 POLYMER STRUCTURE

The material behavior of polymers is totally controlled by their molecular structure. In fact, this is true for all polymers; synthetically generated polymers as well as polymers found in nature (bio-polymers), such as natural rubber, ivory, amber, protein-based polymers or cellulose-based materials. To understand the basic aspects of material behavior and its relation to the molecular structure of polymers, in this chapter we attempt to introduce the fundamental concepts in a compact and simple way, leaving out material that has academic and scientific interest, but that is not needed to understand the basic technological aspects of plastics. Further information is presented in subsequent chapters. For more details on specific plastics and polymers the reader should consult Chapter 6 of this handbook.

2.1.1 Chemistry

As the word itself suggests, polymers are materials composed of molecules of very high molecular weight. These large molecules are generally referred to as *macromolecules*. Polymers are macromolecular structures that are generated synthetically or through natural processes. Historically, it has been always said that synthetic polymers are generated through *addition* or *chain growth polymerization*, and *condensation* or *radical initiated polymerization*. In addition polymerization, the final molecule is a repeating sequence of blocks with a chemical formula of the monomers. Condensation polymerization processes occur when the resulting polymers have fewer atoms than those present in the monomers from which they are generated. However, since many additional polymerization pro-

cesses result in condensates, and various condensation polymerization processes are chain growth polymerization processes that resemble addition polymerization, today we rather break-down polymerization processes into *step polymerization* and *chain polymerization*. Table 2.1 shows a break-down of polymerization into step and chain polymerization, and presents examples for the various types of polymerization processes.
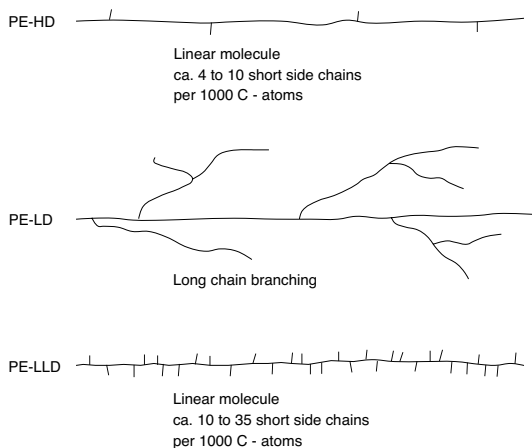
Table 2.1: Polymerization Classification

Classification	Polymerization	Examples
Step linear	Polycondensation	Polyamides
		Polycarbonate
		Polyesters
		Polyethers
		Polyimide
		Siloxanes
	Polyaddition	Polyureas
		Polyurethanes
Step non-linear	Network polymers	Epoxy resins
		Melamine
		Phenolic
		Polyurethanes
		Urea
Chain	Free radical	Polybutadiene
		Polyethylene (branched)
		Polyisoprene
		Polymethylmethacrylate
		Polyvinyl acetate
		Polystyrene
	Cationic	Polyethylene
		Polyisobutylene
		Polystyrene
		Vinyl esters
	Anionic	Polybutadiene
		Polyisoprene
		Polymethylmethacrylate
		Polystyrene
	Ring opening	Polyamide 6
		Polycaprolactone
		Polyethylene oxide
		Polypropylene oxide
	Ziegler-Natta	Polyethylene
		Polypropylene
		Polyvinyl chloride
		Other vinyl polymers
	Metallocene	Polyethylene
		Polypropylene
		Polyvinyl chloride
		Other vinyl polymers

Linear and non-linear step growth polymerization are processes where the polymerization occurs with more than one molecular species. On the other hand, chain growth polymerization processes occur with monomers with a reactive end group. Chain growth polymerization processes include *free-radical polymerization, ionic polymerization, cationic polymerization, ring opening polymerization, Ziegler-Natta polymerization and metallocene catalysis polymerization*. Free-radical polymerization is the most widely used polymerization process and it is used to polymerize monomers with the general structure $CH_2 = CR_1R_2$. Here, the polymer molecules grow by addition of a monomer with a free-radical reactive site called an active site. A chain polymerization process can also take place when the active site has an ionic charge. When the active site is positively charged, the polymerization process is called a *cationic polymerization*, and when the active site is negatively charged it is called *ionic polymerization*. Finally, monomers with a cyclic or ring structure such as caprolactam can be polymerized using the ring-opening polymerization process. Caprolactam is polymerized into poly-caprolactam or polyamide 6.

The atomic composition of polymers encompasses primarily non-metallic elements such as carbon (C), hydrogen (H) and oxygen (O). In addition, recurrent elements are nitrogen (N), chlorine (Cl), fluoride (F) and sulfur (S). The so-called semi-organic polymers contain other non-metallic elements such as silicon (Si) in silicone or polysiloxane, as well as bor or beryllium (B). Although other elements can sometime be found in polymers, because of their very specific nature, we will not mention them here. The properties of the above elements lead to specific properties that are common of all polymers. These are:

- Polymers have very low electric conductance (electric insulators)
- Polymers have a very low thermal conductance (thermal insulators)
- Polymers have a very low density (between 0.8 and 2.2 g/cm^3)
- Polymers have a low thermal resistance and will easily irreversibly thermally degrade

There are various ways that the monomers can arrange during polymerization, however, we can break them down into two general categories: uncross-linked and cross-linked. Furthermore, the uncross-linked polymers can be subdivided into linear and branched polymers. The most common example of uncross-linked polymers that present the various degrees of branching is polyethylene (PE), as schematically depicted in Figure 2.1. Another important family of uncrosslinked polymers are copolymers. Copolymers are polymeric materials with two or more monomer types in the same chain. A copolymer that is composed of two monomer types is referred to as a *bipolymer* (e.g., PS-HI), and one that is formed by three different monomer groups is called a *terpolymer* (e.g., ABS). Depending on how
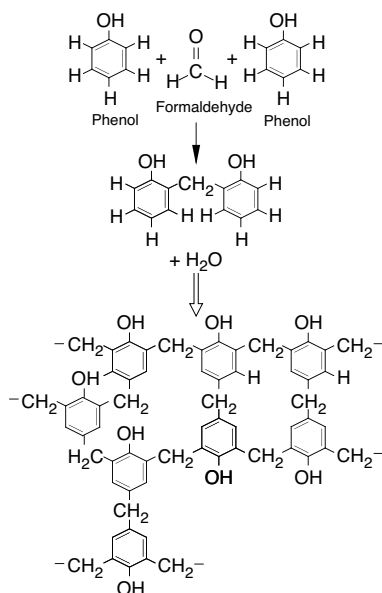
Figure 2.1:   Schematic of the molecular structure of different polyethylenes.

Figure 2.2:   Schematic representation of different copolymers.

the different monomers are arranged in the polymer chain, one distinguishes between *random*, *alternating*, *block*, or *graft* copolymers. The four types of copolymers are schematically represented in Fig. 2.2.

   Although thermoplastics can cross-link under specific conditions, such as gel formation when PE is exposed to high temperatures for prolonged periods of time, thermosets, and some elastomers, are polymeric materials that have the ability to cross-link. The cross-linking causes the material to become heat resistant after it has solidified. The cross-linking usually is a result of the presence of double bonds that break, allowing the molecules to link with their neighbors. One of
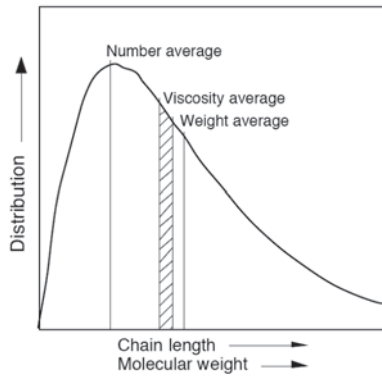
Figure 2.3: Symbolic representation of the condensation polymerization of phenol-formaldehyde resins.

the oldest thermosetting polymers is phenol-formaldehyde, or phenolic. Figure 2.3 shows the chemical symbol representation of the reaction where the phenol molecules react with formaldehyde molecules to create a three-dimensional cross-linked network that is stiff and strong, and leaving water as the by-product of this chemical reaction. This type of chemical reaction is called *condensation polymerization*.

Molecular Weight The size of the resulting macromolecules is the primary factor resulting from a polymerization reaction. After such a reaction, a polymeric material will consist of polymer chains of various lengths or repeat units. Hence, the molecular weight is determined by the average, or mean, molecular weight, which is defined by $M = W/N$. Here, W is the weight of the sample and N the number of moles in the sample. Figure 2.4 presents a schematic of a molecular weight distribution. The figure presents three molecular weight distributions. These are the *number avarage*, $\bar{M}_n$, defined by,

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \tag{2.1}$$

Figure 2.4: Molecular weight distribution of a typical thermoplastic.

the weight average, $\bar{M}_w$, defined by,

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \qquad (2.2)$$

and the *viscosity average*, $\bar{M}_v$. The viscosity average is a function of the viscosity of the polymers,
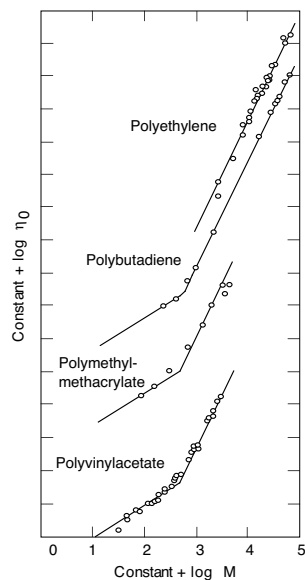
$$[\eta] = k\bar{M}_v^{\alpha} \qquad (2.3)$$

where α is a material dependent parameter, which varies from $\alpha = 1$ for short molecules to $\alpha = 3.4$ for long molecules. The linear relation for short molecules is directly related to the intra-molecular friction, while the power relation of long molecules is related to the molecular entanglement.
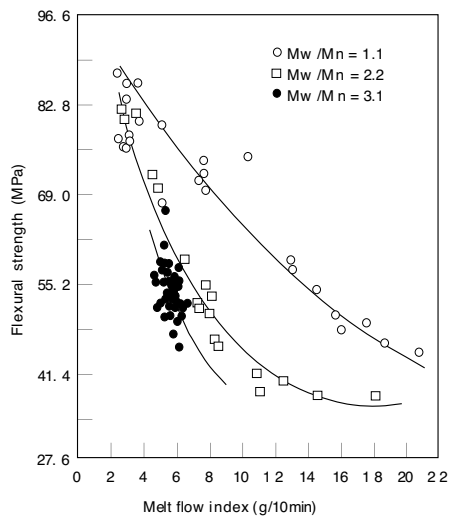
Figure 2.5 presents the viscosity of various polymers as a function of molecular weight. The figure shows how for all these polymers the viscosity goes from the linear to the power dependence at some critical molecular weight. The linear relation is sometimes referred to as Staudinger's rule and applies for a perfectly monodispersed polymer. In a monodispersed polymer most molecules have the same molecular weight. A measure of the broadness of a polymer's molecular weight distribution is the polydispersity index defined by,

$$PI = \frac{\bar{M}_w}{\bar{M}_n} \qquad (2.4)$$

Figure 2.6 presents a plot of flexural strength versus melt flow index for polystyrene samples with three different polydispersity indices. The figure shows that low

Figure 2.5: Zero shear rate viscosity for various polymers as a function of molecular weight.

Figure 2.6: Effect of molecular weight on the strength-MFI interrelationship of polystyrene for three polydispersity indeces.
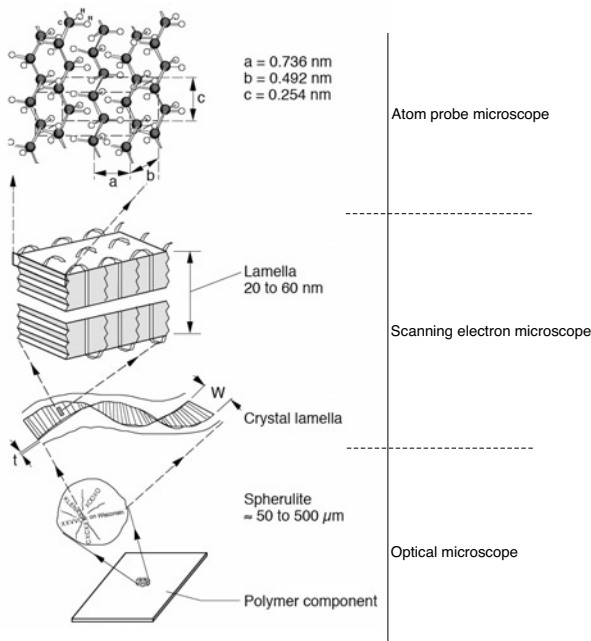
polydispersity index grade materials render higher strength properties and flowability, or processing ease, than high polydispersity index grades. Table 2.2 summarizes the various techniques used to measure molecular weight of polymers and the molecular weight range at which they can adequately perform the measurement.

Table 2.2:   Various techniques used to measure molecular weight of polymers and oligomers

Method	Measurement	Range
Sedimentation and diffusion with centrifuge (a)	$\bar{M}_w$	Up to 10^8
Light scattering (a)	$\bar{M}_w$	Up to 10^7
Electron microscopy (a)	$\bar{M}_i, \bar{M}_n$	*
Gel-Permeation-Chromatography (r)	$\bar{M}_w, \bar{M}_n, \bar{M}_v$	*
Solvent viscometry (r)	$\bar{M}_v$	*
Melt viscometry (r)	$\bar{M}_w$	‡
Membrane osmometry (a)	$\bar{M}_n$	$2 \cdot 10^4$ to 10^6
Vapor pressure osmometry (a)	$\bar{M}_n$	Up to 10^5
End-group determination (e)	$\bar{M}_n$	Up to $5 \cdot 10^4$
Cryoscopy (a)	$\bar{M}_n$	Up to $5 \cdot 10^4$
Ebullioscopy (a)	$\bar{M}_n$	Up to 10^4
(a) Absolute method, (r) Relative method, and (e) Equivalent method.		
* Dependent on solubility.		
‡ Dependent on melting point.		

Physically, the molecules can have rather large dimensions. For example, each repeat unit of a carbon backbone molecule, such as polyethylene, measures 0.252 nm in length. If completely stretched out, a high molecular weight molecule with say 10,000 repeat units can measure over 2 mm in length. Figure 2.7 serves to illustrate the range in dimensions associated with polymers as well as which microscopic devices are used to capture the detail at various orders of magnitude. If we go from the atomic structure to the part geometry, we easily travel between 0.1 nm and 1 mm, covering 8 orders of magnitude.

Conformation and Configuration   The conformation and configuration of the polymer molecules have a great influence on the properties of the polymer component. The conformation describes the preferential spatial positions of the atoms in a molecule, which is described by the polarity flexibility and regularity of the macromolecule. Typically, carbon atoms are tetravalent, which means that they are surrounded by four substituents in a symmetric tetrahedral geometry. The configuration gives information about the distribution and spatial organization of the molecule. The general structure and symmetry of a molecule can be greatly influenced during polymer synthesis. This is illustrated in Fig. 2.8. Due to energy issues, linear polymers such as polyethylene, polypropylene, polystyrene and polyvinyl chloride prefer to polymerize through 1,2-addition. For technical polydienes, such as natural rubber (polyisoprene), polybutadiene and poly-
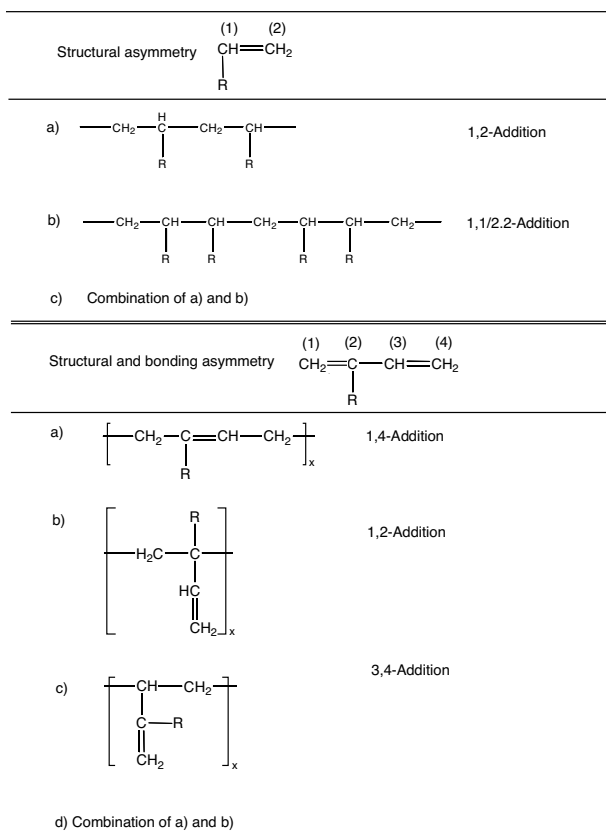
Figure 2.7: Schematic representation of the general molecular structure of semi-crystalline polymers and magnitudes as well as microscopic devices associated with such structures.

chloroprene, the preferred mode of polymerization is 1,4-addition. In effect, one can control the mode of polymerization by use of stereocatalysts as well as methalocene catalysts.

During polymerization it is possible to place the X groups on the carbon-carbon backbone in different directions. The order in which they are arranged is called the tacticity. The polymers with side groups placed in a random matter are called atactic. The polymers whose side groups are all on the same side are called isotactic, and those molecules with regularly alternating side groups are called syndiotactic. Figure 2.9 shows the three different tacticity cases for polypropylene. The tacticity in a polymer determines the degree of crystallinity that a polymer can reach. For example, polypropylene with a high isotactic content will reach a high degree of crystallinity and as a result will be stiff, strong, and hard.

Another type of geometric arrangement arises with polymers that have double bonds between carbon atoms. Double bonds restrict the rotation of the carbon atoms about the backbone axis. These polymers are sometimes referred to as

Figure 2.8: Constitutional isomer classification.

geometric isomers. The X groups may be on the same side (cis-) or on opposite sides (trans-) of the chain as schematically shown for polybutadiene in Fig. 2.10. The arrangement in a cis-1,4- polybutadiene results in a very elastic rubbery material, whereas the structure of the trans-1,4- polybutadiene results in a leathery and tough material. A cis-1,4- polybutadiene can be used to manufacture the outer tread of an automotive tire. A trans-1,4- polybutadiene can be used to make the outer skin of a golf ball. The same geometric arrangement is found in natural rubber, polyisoprene. The cis-1,4- polyisoprene is the elastic natural rubber used for the body of a tire, and the latex used to manufacture "rubber" gloves and condoms. The trans-1,4- polyisoprene, or the so-called gutta percha or ebony, was used to make dentures, statues, and other decorative items in the 1800s.
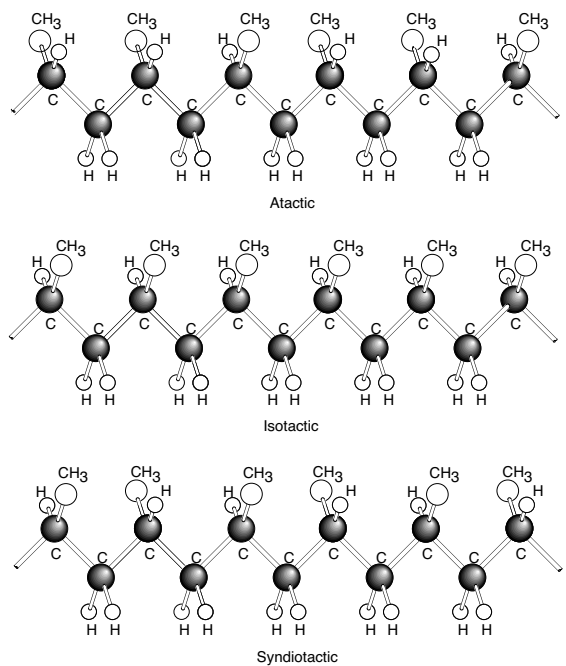
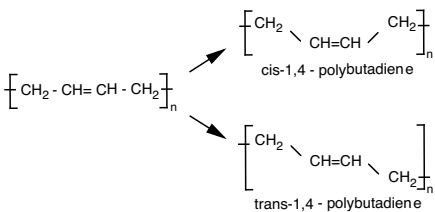**Figure 2.9:** Different polypropylene structures.

Figure 2.10: Symbolic representation of cis-1,4- and trans-1,4-polybutadiene molecules.