Introduction to polymer

A polymer is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits. Due to their broad spectrum of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday lifeA **polymer** (/ˈpɒlɪmər/; Greek *poly*-, "many" + *-mer*, "part") is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits. Due to their broad spectrum of properties,[7] both synthetic and natural polymers play essential and ubiquitous roles in everyday life.[8] Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass, relative to small molecule compounds, produces unique physical properties including toughness, high elasticity, viscoelasticity, and a tendency to form amorphous and semicrystalline structures rather than crystals.

The term "polymer" derives from the Greek word πολύς (*polus*, meaning "many, much") and μέρος (*meros*, meaning "part"), and refers to large molecules whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties.[3] The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition. The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis.

Polymers are studied in the fields of polymer science (which includes polymer chemistry and polymer physics), biophysics and materials science and engineering. Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science. An emerging important area now focuses on supramolecular polymers formed by non-covalent links. Polyisoprene of latex rubber is an example of a natural polymer, and the polystyrene of styrofoam is an example of a synthetic polymer. In biological contexts, essentially all biological macromolecules—i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides—are purely polymeric, or are composed in large part of polymeric components.

Natural Polymers

Natural polymeric materials such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

Synthetic Polymers

The list of synthetic polymers, roughly in order of worldwide demand, includes polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic rubber, phenolformaldehyde resin (or Bakelite), neoprene, nylon, polyacrylonitrile, PVB, silicone, and many more. More than 330 million tons of these polymers are made every year (2015).

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeating unit is based on ethylene monomer. Many other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

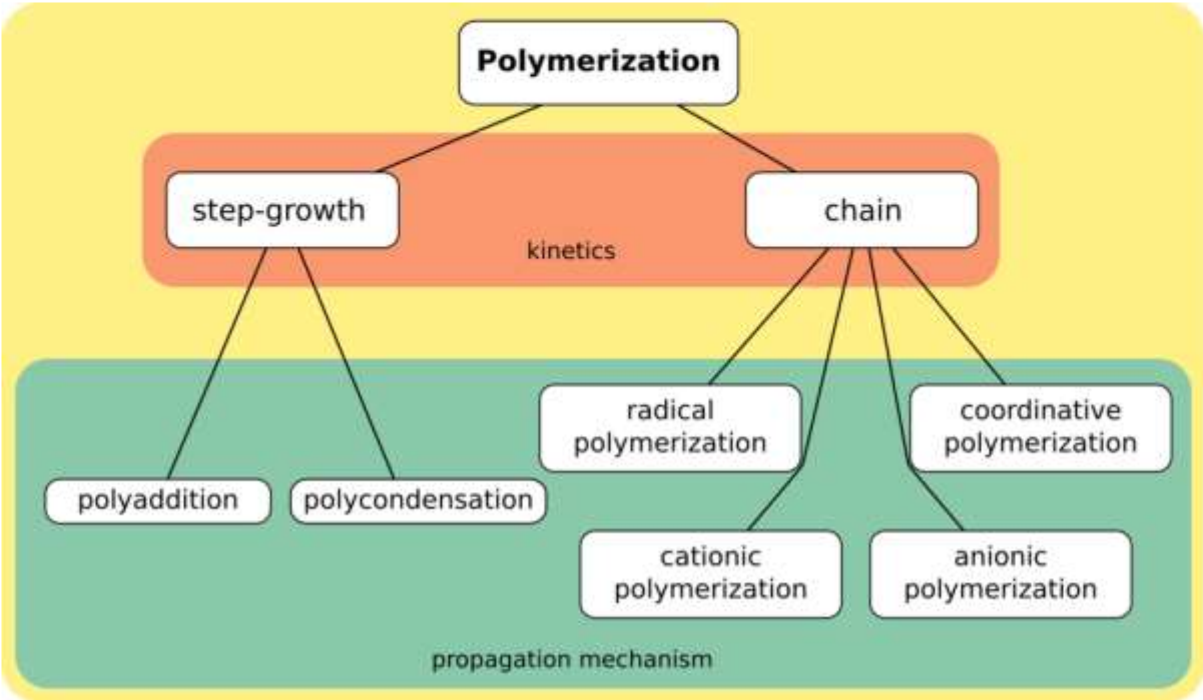

Figure: **Types of mechanism of polymerization**

Structure

The structure of a polymeric material can be described at different length scales, from the sub-nm length scale up to the macroscopic one. There is in fact a hierarchy of structures, in which each stage provides the foundations for the next one. The starting point for the description of the structure of a polymer is the identity of its constituent monomers. Next, the microstructure essentially describes the arrangement of these monomers within the polymer at the scale of a single chain. The microstructure determines the possibility for the polymer to form phases with different arrangements, for example through crystallization, the glass transition or microphase separation. These features play a major role in determining the physical and chemical properties of a polymer.

Monomers and repeat units

The identity of the repeat units (monomer residues, also known as "mers") comprising a polymer is its first and most important attribute. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. A polymer which contains only a single type of repeat unit is known as a homopolymer, while a polymer containing two or more types of repeat units is known as a copolymer. A terpolymer is a copolymer which contains three types of repeat units.

Polystyrene is composed only of styrene-based repeat units, and is classified as a homopolymer. Polyethylene terephthalate, even though produced from two different monomers (ethylene glycol and terephthalic acid), is usually regarded as a homopolymer because only one type of repeat unit is formed. Ethylene-vinyl acetate contains more than one variety of repeat unit and is a copolymer. Some biological polymers are composed of a variety of different but structurally related monomer residues; for example, polynucleotides such as DNA are composed of four types of nucleotide subunits.

Microstructure

The microstructure of a polymer (sometimes called configuration) relates to the physical arrangement of monomer residues along the backbone of the chain. These are the elements of polymer structure that require the breaking of a covalent bond in order to change. Various polymer structures can be produced depending on the monomers and reaction conditions: A polymer may consist of linear macromolecules containing each only one unbranched chain. In the case of unbranched polyethylene, this chain is a long-chain *n*-alkane. Linear polymers may fold into diverse conformations with distinct circuit topology. There are also branched macromolecules with a main chain and side chains, in the case of polyethylene the side chains would be alkyl groups. In particular unbranched macromolecules can be in the solid state semi-crystalline, crystalline chain sections highlighted red in the figure below.

While branched and unbranched polymers are usually thermoplastics, many elastomers have a wide-meshed cross-linking between the "main chains". Close-meshed crosslinking, on the other hand, leads to thermosets. Cross-links and branches are shown as red dots in the figures. Highly branched polymers are amorphous and the molecules in the solid interact randomly.

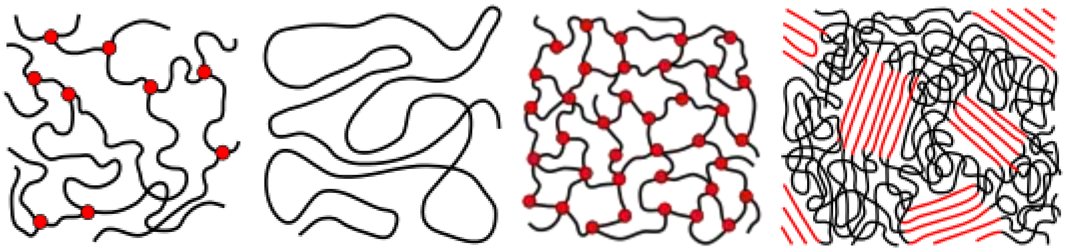

Figure: Branched, linear, highly crosslinked, slightly crosslinked polymers

An important microstructural feature of a polymer is its architecture and shape, which relates to the way branch points lead to a deviation from a simple linear chain. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. Types of branched polymers include star polymers, comb polymers, polymer brushes, dendronized polymers, ladder polymers, and dendrimers. There exist also two-dimensional polymers (2DP) which are composed of topologically planar repeat units. A polymer's architecture affects many of its physical properties including solution viscosity, melt viscosity, solubility in various solvents, glass-transition temperature and the size of individual polymer coils in solution. A variety of techniques may be employed for the synthesis of a polymeric material with a range of architectures, for example living polymerization.