



AN EMPIRICAL STUDY ON POLYMERS AND ITS UTILITY

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ABSTRACT:

Most polymers are formed from monomers either of hydrocarbon or hydro-carbon derivatives. The most basic synthetic monomer is ethylene (C₂H₄), a name whose -ene ending identifies it as an alkene, a hydrocarbon formed by double bonds between carbon atoms. Another alkene hydrocarbon monomer is butadiene, whose formula is C₄H₆. The butadiene's structure is much more complex. Still more complex is styrene, which includes a benzene ring. Several other monomers involve other elements: chloride, in vinyl chloride; nitrogen, in acrylonitrile; and fluorine, in tetrafluoroethylene. Polymers, both natural and synthetic, are created via polymerization of many monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, visco elasticity, and a tendency to form glasses and semi crystalline structures rather than crystals. Here we are going to study the polymerization process, the micro structure, biological synthesis of polymers, biopolymers, chain length of polymers, modification of natural polymers, their characterization, degradation and their real life application.

The process by which polymers are formed from monomers is called polymerization. Polymerization occurs by one of two basic reactions: addition or condensation. Another variety of polymerization, the process whereby monomers join to form polymers. If monomers of a single type join, the resulting polymer is called a homo polymer, but if the polymer consists of more than one type of monomer, it is known as a copolymer. This joining may take place by one of two processes. Also Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain or network.

Keywords: Addition polymerization: Alkanes, Copolymers, Dimer, Doublebond, Functional groups, Homopolymers, Hydrocarbons, Hydrocarbon derivatives, monomers, organic, plastics, polymerization, Valence Electrons.



Introduction:

Though "plastic" has a number of meanings in everyday life, and in society at large (as we shall see), the scientific definition is much more specific. Plastics are materials, usually organic, that can be caused to flow under certain conditions of heat and pressure, and thus to assume a desired shape when the pressure and temperature conditions are withdrawn. Most plastics are made of polymers.

Polymers are long chain giant organic molecules are assembled from many smaller molecules called **monomers**. **Polymers** consist of many repeating monomer units in long chains. A polymer is analogous to a necklace made from many small beads (monomers).

Another common name for many synthetic polymers is **plastic** which comes from the Greek word "plastikos", suitable for molding or shaping. Many objects in daily use from packing, wrapping, and building materials include half of all polymers synthesized. Other uses include textiles, TV's, CD's, automobiles, and many other all are made from polymers. A quarter of the solid waste from homes is plastic materials - some of which may be recycled. . Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Polymers range from familiar synthetic plastics such as polystyrene (or styrofoam) to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function

Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which includes polymer chemistry and polymer physics). Polyisoprene of latex rubber and the polystyrene of styrofoam are examples of polymeric natural/biological and synthetic polymers, respectively. 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—e.g., isoprenylated/lipid-modified glycoproteins, where small lipidic molecule and oligosaccharide modifications occur on the polyamide backbone of the protein.

Review:

Standardized polymer nomenclature:

There are multiple conventions for naming polymer substances. Many commonly used polymers, such as those found in consumer products, are referred to by a common or trivial name. The trivial name is assigned based on historical precedent or popular usage rather than a standardized naming convention. Both the American Chemical Society (ACS) and IUPAC have proposed standardized naming conventions; the ACS and IUPAC conventions are similar but not identical. Examples of the differences between the various naming conventions are given in the table below:

Common name	ACS name	IUPAC name
<u>Poly(ethylene oxide)</u> or PEO	Poly(oxyethylene)	Poly(oxyethene)
<u>Poly(ethylene terephthalate)</u> or PET	Poly(oxy-1,2-ethanedioxydicarbonyl-1,4-phenylenecarbonyl)	Poly(oxyetheneoxyterephthaloyl)
<u>Nylon 6</u>	Poly[amino(1-oxo-1,6-hexanediy)]	Poly[amino(1-oxohexan-1,6-diy)]

In both standardized conventions, the polymers' names are intended to reflect the monomer(s) from which they are synthesized rather than the precise nature of the repeating subunit. The polymerization process:

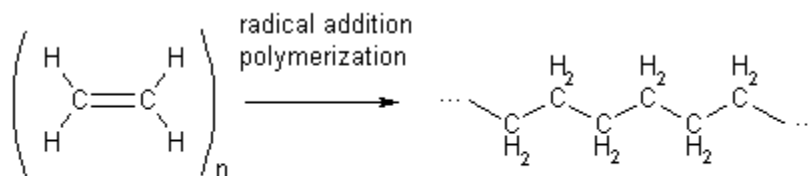
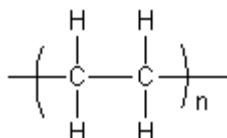
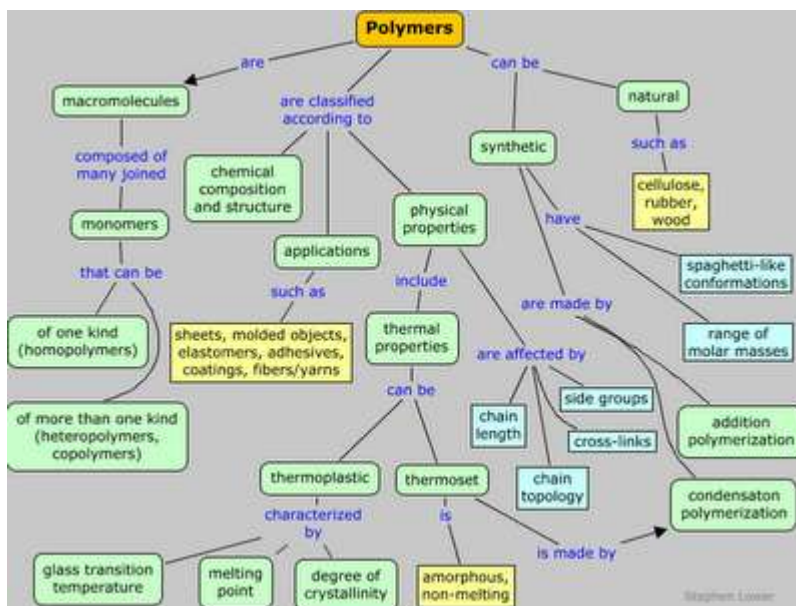


Fig 1: The polymerisation of ethene in to poly(ethene)



The flowchart of polymers



Chain length

The physical properties of a polymer are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase quickly. Impact resistance also tends to increase with chain length, as does the viscosity, or resistance to flow, of the polymer in its melt state. Melt viscosity η is related to polymer chain length Z roughly as $\eta \sim Z^{3.2}$, so that a tenfold increase in polymer chain length results in a viscosity increase of over 1000 times. Increasing chain length furthermore tends to decrease chain



mobility, increase strength and toughness, and increase the glass transition temperature (T_g). A common means of expressing the length of a chain is the degree of polymerization, which quantifies the number of monomers incorporated into the chain. The ratio of these two values (number average molecular weight and weight average molecular weight.) is the polydispersity index, commonly used to express the "width" of the molecular weight distribution. A final measurement is contour length, which can be understood as the length of the chain backbone in its fully extended state. The flexibility of an un branched chain polymer is characterized by its persistence length.

Method:

Polymer Synthesis

The process by which polymers are formed from monomers is called polymerization. Polymerization occurs by one of two basic reactions: addition or condensation. In addition polymerization, entire monomers are linked together to form long chains. In condensation polymerization, some small molecules (such as water) are released as polymer is formed. Polymerization reactions may be divided into two major categories: stepwise processes and chain-type processes. In the step-wise process, reactants are brought together and heated. Initially short chains are formed and only at the end of the reaction are long chains formed. Reactions generally require hours to form the polymers. It is by this process that condensation polymers are generally made.

Polymerization: A reference to the breaking of carbon double bonds.

One variety of polymerization - the process whereby monomers join to form polymers. If monomers of a single type join, the resulting polymer is called a homopolymer, but if the polymer consists of more than one type of monomer, it is known as a copolymer. This joining may take place by one of two processes. The first of these, addition polymerization: monomers add themselves to one another, usually breaking double



bonds in the process. This results in the creation of a polymer and no other products.

Much more complex is the process known as condensation polymerization, in which a small molecule called a dimer is formed as monomers join. The monomers in condensation polymerization must be bi functional, meaning that they have a functional group at each end. When characteristic structures at the ends of the monomers react to one another by forming a bond, they create a dimer, which splits off from the polymer. The products of condensation polymerization are thus not only the polymer itself, but also a dimer, which may be water, hydrochloric acid (HCl), or some other substance.

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain or network. During the polymerization process, some chemical groups may be lost from each monomer. This is the case, for example, in the polymerization of PET polyester. The monomers are terephthalic acid ($\text{HOOC-C}_6\text{H}_4\text{-COOH}$) and ethylene glycol ($\text{HO-CH}_2\text{-CH}_2\text{-OH}$) but the repeating unit is $\text{-OC-C}_6\text{H}_4\text{-COO-CH}_2\text{-CH}_2\text{-O-}$, which corresponds to the combination of the two monomers with the loss of two water molecules. The distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue.

Laboratory synthetic methods are generally divided into two categories, step-growth polymerization and chain-growth polymerization. The essential difference between the two is that in chain growth polymerization, monomers are added to the chain one at a time only, such as in polyethylene, whereas in step-growth polymerization chains of monomers may combine with one another directly, such as in polyester. Synthetic polymerization reactions may be carried out with or without a catalyst. Laboratory synthesis of biopolymers, especially of proteins, is an area of intensive research.



In general, polymeric mixtures are far less miscible than mixtures of small molecule materials. This effect results from the fact that the driving force for mixing is usually entropy, not interaction energy. In other words, miscible materials usually form a solution not because their interaction with each other is more favorable than their self-interaction, but because of an increase in entropy and hence free energy associated with increasing the amount of volume available to each component. This increase in entropy scales with the number of particles (or moles) being mixed. Thus, concentrated solutions of polymers are far rarer than those of small molecules.

In dilute solution, the properties of the polymer are characterized by the interaction between the solvent and the polymer. In a good solvent, the polymer appears swollen and occupies a large volume. In this scenario, intermolecular forces between the solvent and monomer subunits dominate over intra molecular interactions. In a bad solvent or poor solvent, intra molecular forces dominate and the chain contracts. In the theta solvent, or the state of the polymer solution where the value of the second virial coefficient becomes 0, the intermolecular polymer-solvent repulsion balances exactly the intramolecular monomer-monomer attraction. Under the theta condition (also called the Flory condition), the polymer behaves like an ideal random coil. The transition between the states is known as a coil-globule transition.

Modification of natural polymers.

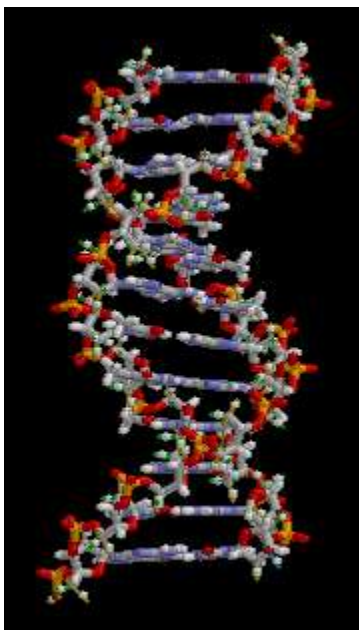
Naturally occurring polymers such as cotton, starch and rubber were familiar materials for years before synthetic polymers such as polyethene and perspex appeared on the market. Many commercially important polymers are synthesized by chemical modification of naturally occurring polymers. Prominent examples include the reaction of nitric acid and cellulose to form nitrocellulose and the formation of vulcanized rubber by heating natural rubber in the presence of sulfur. Ways in which polymers can be modified include oxidation, cross-linking and end-capping.

Especially in the production of polymers, the gas separation by membranes has acquired increasing importance in the petrochemical industry and is now a relatively well-established unit operation. The process of polymer degassing is necessary to suit polymer for extrusion and pelletizing, increasing safety, environmental, and product quality aspects. Nitrogen is generally used for this purpose, resulting in a vent gas primarily composed of monomers and nitrogen.

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. Structure has a strong influence on the other properties of a polymer. For example, two samples of natural rubber may exhibit different durability, even though their molecules comprise the same monomers.

Biological synthesis



Microstructure of part of a DNA double helix **biopolymer** **Biopolymer**

There are three main classes of biopolymers: polysaccharides, polypeptides, and polynucleotides. In living cells, they may be



synthesized by enzyme-mediated processes, such as the formation of DNA catalyzed by DNA polymerase. The synthesis of proteins involves multiple enzyme-mediated processes to transcribe genetic information from the DNA to RNA and subsequently translate that information to synthesize the specified protein from amino acids. The protein may be modified further following translation in order to provide appropriate structure and functioning.

Results:

Polymer properties

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents. A polymer molecule containing ionizable subunits is known as a polyelectrolyte or ionomer.

Physical Properties of Polymers

The properties of polymers are dependent on many factors including inter- and intrachain bonding, the nature of the backbone, processing events, presence/absence of additives including other polymers, chain size and geometry, and molecular weight distribution.

Polymers do not boil because the energy necessary to put a polymer into the vapor state is greater than the bond energies of the atoms that hold the polymer together, thus they degrade prior to boiling. In order for a



polymer to be flexible, its various units or segments must be able to move. The glass transition temperature (T_g) is the temperature where polymer units or segments can move but the entire chain cannot. Most vinyl polymers have T_g values below room temperature so that they appear to be flexible and act as rubber and plastic materials. Most condensation polymers have T_g values above room temperature and are used as hard plastics and fibers. The temperature where entire chain movement occurs is called the melting point (T_m) and is greater than the T_g . Many polymers are themselves brittle at room temperature.

The inflexible regions of a polymer, such as crystalline regions, are often referred to as "hard" regions. Conversely, the flexible regions of a polymer, where segmental mobility occurs, are referred to as "soft" regions. This combination of hard and soft can be illustrated with so-called segmented polyurethanes .

Chemical properties

The attractive forces between polymer chains play a large part in determining a polymer's properties. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. The stronger forces typically result in higher tensile strength and higher crystalline melting points.

The intermolecular forces in polymers can be affected by dipoles in the monomer units. Polymers containing amide or carbonyl groups can form hydrogen bonds between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one chain are strongly attracted to the partially negatively charged oxygen atoms in C=O groups on another.



Discussion:

Polymer characterization

The characterization of a polymer requires several parameters which need to be specified. This is because a polymer actually consists of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties.

Techniques such as wide angle X-ray scattering, small angle X-ray scattering, and small angle neutron scattering are used to determine the crystalline structure of polymers. Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity. FTIR, Raman and NMR can be used to determine composition. Thermal properties such as the glass transition temperature and melting point can be determined by differential scanning calorimetry and dynamic mechanical analysis. Pyrolysis followed by analysis of the fragments is one more technique for determining the possible structure of the polymer. Thermogravimetry is a useful technique to evaluate the thermal stability of the polymer. Rheological properties are also commonly used to help determine molecular architecture (molecular weight, molecular weight distribution and branching) as well as to understand how the polymer will process, through measurements of the polymer in the melt phase. Another polymer characterization technique is Automatic Continuous Online Monitoring of Polymerization Reactions (ACOMP) which provides real-time characterization of polymerization reactions. It can be used as an analytical method in R&D, as a tool for reaction optimization at the bench and pilot plant level. It is applicable in the areas of free radical and controlled radical homo- and copolymerization, polyelectrolyte synthesis, heterogeneous phase reactions, including emulsion polymerization, adaptation to batch and continuous reactors, and modifications of polymers.



Polymer degradation

A plastic item with thirty years of exposure to heat and cold, brake fluid, and sunlight. Notice the discoloration, swelling, and crazing of the material. Polymer degradation is a change in the properties—tensile strength, color, shape, or molecular weight—of a polymer or polymer-based product under the influence of one or more environmental factors, such as heat, light, chemicals and, in some cases, galvanic action. It is often due to the scission of polymer chain bonds via hydrolysis, leading to a decrease in the molecular mass of the polymer. Degradation can also be useful in biomedical settings. For example, a copolymer of polylactic acid and polyglycolic acid is employed in hydrolysable stitches that slowly degrade after they are applied to a wound.

The susceptibility of a polymer to degradation depends on its structure. Epoxies and chains containing aromatic functionalities are especially susceptible to UV degradation while polyesters are susceptible to degradation by hydrolysis, while polymers containing an unsaturated backbone are especially susceptible to ozone cracking. Carbon based polymers are more susceptible to thermal degradation than inorganic polymers such as polydimethylsiloxane and are therefore not ideal for most high-temperature applications. High-temperature matrices such as bismaleimides (BMI), condensation polyimides (with an O-C-N bond), triazines (with a nitrogen (N) containing ring), and blends thereof are susceptible to polymer degradation in the form of galvanic corrosion when bare carbon fiber reinforced polymer CFRP is in contact with an active metal such as aluminium in salt water environments.

The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. They literally unzip or depolymerize back to the constituent monomer. The sorting of polymer waste for recycling purposes may be facilitated by the use of the Resin identification codes developed by the Society of the Plastics Industry to identify the type of plastic.



Conclusion:

REAL-LIFE APPLICATIONS

Types of Polymers and Polymerization

Many polymers exist in nature. Among these are silk, cotton, starch, sand, and asbestos, as well as the incredibly complex polymers known as RNA (ribonucleic acid) and DNA (deoxyribonucleic acid), which hold genetic codes. The polymers discussed, however, are primarily of the synthetic kind. Artificial polymers include such plastics such as polyethylene, styrofoam, and Saran wrap; fibers such as nylon, Dacron (polyester), and rayon; and other materials such as Formica, Teflon, and PVC pipe.

Once the carbon double bonds in tetrafluoroethylene (C_2F_4) are broken, they form the polymer known as Teflon, used in the coatings of cooking utensils, as well as in electrical insulation and bearings. Vinyl chloride breaks its double bonds to form polyvinyl chloride, better known as PVC, a material used for everything from plumbing pipe to toys to Saran wrap. Styrene, after breaking its double bonds, forms polystyrene, used in containers and thermal insulation.

A DAY IN THE LIFE.

A silent revolution has been brought—a world surrounded by polymers, plastics, and synthetic materials—represents a very recent phenomenon. Every day, a person comes into contact with dozens, if not hundreds, of plastics and polymers. Consider a day in the life of a hypothetical teenage girl. She gets up in the morning, brushes her teeth with a toothbrush made of nylon, then opens a shower door—which is likely to be plastic rather than glass—and steps into a molded plastic shower or bathtub. When she gets out of the shower, she dries off with a towel containing a polymer such as rayon, perhaps while standing on tile that contains plastics, or polymers.

She puts on makeup (containing polymers) that comes in plastic containers, and later blow-dries her hair with a handheld hair dryer



made of insulated plastic. Her clothes, too, are likely to contain synthetic materials made of polymers. When she goes to the kitchen for breakfast, she will almost certainly walk on flooring with a plastic coating. The countertops may be of formica, a condensation polymer, while it is likely that virtually every appliance in the room will contain plastic. If she opens the refrigerator to get out a milk container, it too will be made of plastic, or of paper with a thin plastic coating. Much of the packaging on the food she eats, as well as sandwich bags and containers for storing food, is also made of plastic.

And so it goes throughout the day. The phone she uses to call a friend, the computer she sits at to check her e-mail, and the stereo in her room all contain electrical components housed in plastic. If she goes to the gym, she may work out in Gore-tex, a fabric containing a very thin layer of plastic with billions of tiny pores, so that it lets through water vapor (that is, perspiration) without allowing the passage of liquid water. On the way to the health club, she will ride in a car that contains numerous plastic molds in the steering wheel and dashboard. If she plays a compact disc—itsself a thin wafer of plastic coated with metal—she will pull it out of a plastic jewel case. Finally, at night, chances are she will sleep in sheets, and with a pillow, containing synthetic polymers. And yet 'plastic' —as polymers-- remains, as often as not, a term of opprobrium."



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