A Review on Polymer Technology

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ABSTRACT

Man's unending chase for new and improved materials has been growing with time. Polymers, is the class of materials which has prospective for use as rubbers, resins, plastics and composites, and as adhesives, laminates and coatings. In polymer chain small, simple chemical units appears to repeat a large number of times to form the structure of a macromolecule or polymer molecule. The large range and variety of natural, synthetic and semi-synthetic polymers known today reveal wide variety of properties or property range. Polymer technology is the branch of materials science that deals with the study of long chain macromolecules (polymers), which form an significant part of modern technology. They increasingly replace or supplement more traditional materials such as wood, metal, ceramics and natural fibres. Today these materials are present in practically every aspect of life and it is not possible to live without them. Polymerization is defined as a process in which reacting monomer molecules link together by a chemical reaction to form polymer chains or three-dimensional networks. These long chains set polymers apart from other chemical species and give them their exceptional characteristic properties. Polymerization reactions are divided into two groups; addition polymerization and condensation polymerization. The varying physical conditions lead to different polymerization techniques, such as bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization and solid and gas phase polymerization. The purpose of this review is to take a closer look at polymerization techniques used for the preparation of the various polymers. Based on ongoing research and existing techniques, some new approaches in this interesting area are thoroughly discussed.

Keywords: *Polymers, Polymerization, Polymerization Technique, Polymerization Mechanism.*

1. INTRODUCTION

Man's unending chase for new and improved materials has been growing with time. Though polymers came nearly in the end of the chain of discoveries and developments of materials, they occupy an important place and crucial position in our materials map today. Polymers, is the class of materials which has prospective for use as rubbers, resins, plastics and composites, and as adhesives, laminates and coatings. In application scenario and performance quality and in property range and diversity, polymers offer uniqueness and versatility which can hardly be corresponding by any other kind of materials. Polymers have deeply and widely moulded the present – day human civilization and culture.

The polymer literally means many units (poly means many and mer means units). In a polymer chain small, simple chemical units appear repeatedly a large number of times to form the structure of a polymer molecule or macromolecule. In case a polymer has more than one kind of repeat units in its molecular chain structure, it is called a copolymer. If a polymer chain contains more than one repeat units, it is called a copolymer. Polymers of the molecular weight range 1,000 – 20,000 are commonly

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called low polymers and those having molecular > 20,000 are commonly referred to as high polymers. The large range and variety of natural, synthetic and semi-synthetic polymers known today reveal wide variety of properties or property range. Some emerge rigid, hard, strong and dimensionally stable, while others appear soft, flexible or largely extensible under the influence of stress. Some show ready solubility and fusibility, while others appear more resistant to heat and solvents and may appear even insoluble and infusible. All such properties may vary from a polymer of one type to a polymer of a different type.

Polymer technology is the branch of materials science that deals with the study of long chain macromolecules (polymers), which form a significant part of modern technology. Materials that are typically classified as polymers are plastics, rubber, paints, sealants, foams, adhesives, etc. Today these materials are present in practically every aspect of life and it is not possible to live without them. polymer technology provides an understanding of polymer materials, properties, manufacturing processes, analyses and applications. Industries that are totally dependent on polymer include (but are not limited to) the packaging, automotive, music, clothing, medical, information technology, aerospace, building and construction industries. Polymers offer diversity in their molecular structure and properties due to availability of various monomers, varying molecular weight and ability to copolymerise. Due to this, it is possible to design a polymer tailor-made to suit any desired application. They increasingly replace or supplement more traditional materials such as wood, metal, ceramics and natural fibres.

2. POLYMERIZATION

In polymer chemistry, polymerization is defined as a process in which reacting monomer molecules link together by a chemical reaction to form polymer chains or three-dimensional networks. These long chains set polymers apart from other chemical species and give them their exceptional characteristic properties. Depending on the property ranges they display, the polymers are classified as rubbers, plastics and fibres. Factors that influence the polymer properties are: molar cohesion, polarity, molecular weight, crystallinity, overall molecular symmetry, linearity and non – linearity of chain molecules, thermomechanical history of the polymer and temperature of observation. Higher molecular weight permits greater degree of chain entanglements, thus resulting in higher melting temperature (Tm) and tensile strength (T.S.). The polymer chains can be linear, branched, or cross-linked (Fig. 1)

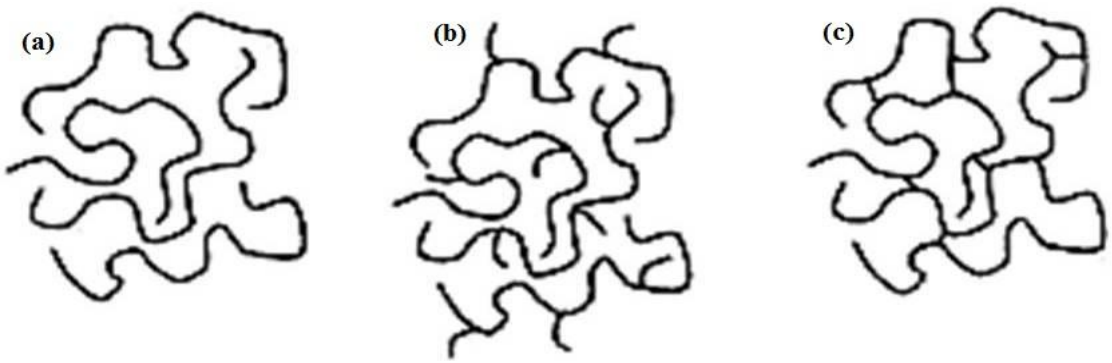

Figure 1 : Structure of (A) Linear, (B) Branched and (C) Crosslinked Polymer

Small extents of branching makes polymer less resistant to solvents, chemicals and heat due to increase in molecular mobility arising due to the branch units or pendent groups. On cross-linking, basic changes in the polymers structure are introduce and as a result, basic changes or improvements in properties are achieved. Polymerization is defined as the process by which polymer chains are

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formed by reacting monomer molecules. Polymerization reactions are divided into three groups: a) Addition polymerization or Chain Growth Polymerization, b) Condensation polymerization or Step Growth Polymerization and c) Ionic Polymerization.

2.1 Addition Polymerization or Chain Growth Polymerization

Chain – growth or addition polymerization is a process in which unsaturated (olefinic, diolefinic, vinylic) monomers are converted to polymers of high molecular weight which exhibit the characteristics of typical chain reactions and takes place very fast. In Chain growth polymerization the monomer adds one by one to the growing polymer chain so there is rapid increase in the molecular weight. It occurs via addition reaction. The polymerization requires an initiator, a substance that start the reaction. The reaction is so fast that can also lead to explosion. For example polythene, Polypropylene, polyvinyl chloride and polytetraflouroethene are formed by addition polymerization.

The reaction occurs via three successive, distinguishable stages:

1) Initiation or triggering off the chain reaction
2) Propagation of the chain i.e. addition of monomer to growing polymer chain
3) Termination or cessation of the chain

The polymerization requires an initiator, a substance that starts the reaction. The chain polymerization can be initiated or induced by heat, light radiations or initiators. If the process is initiated by light, it is called photo polymerization. The chain propagation may take place by free radical or ionic (cationic or anionic) mechanisms, depending on the initiator system used and the prevailing polymerization environment. Free radical polymerization is widely practiced and has been studied extensively.

2.2 Condensation Polymerization or Step Growth Polymerization

As the name implies, step-growth polymers are formed through a series of steps, and high molecular weight materials result from a large number of steps. Step Growth or condensation polymerization is a process in which polymer is formed by an intermolecular condensation reaction between bifunctional or polyfunctional compounds in a fashion that makes the process functionally capable of proceeding indefinitely, avoiding formation of ring or cyclic structures. At least two functional groups are required to form polymer. Functional groups through reactions of which polymerization takes place are: reactive hydrogen (*–H*), hydroxyl group (*–OH*), halogen atom (*–Cl*, *–Br*), carboxyl group (*–COOH*), amino group ($-NH_2$), isocyanate group (*–NCO*), aldehyde group (*–CHO*), double bond (*C = C*) etc.

The reaction is normally related to the formation of a condensed interunit chemical linkage and release of a small byproduct such as *H2O, HCl,* etc. at each step. Examples of condensation polymers are Polyesters and polyamides, polycarbonates, phenol (urea, melamine) – formaldehyde resins, epoxy resins etc. This is called step polymerization because the addition of monomer is step by step and the molecular weight builds up slowly. Most of the monomer gets exhausted rapidly in initial stages before any polymer is formed at latter stages as only oligomers are formed initially. So the Reaction should be carried out for long hours to build the molecular weight.

2.3 Ionic Polymerization

The addition polymerization that takes place due to ionic intermediate or through ionic mechanism is called ionic polymerization. Ionic polymerisation can be of two types depending on the type of ionic intermediate through which the reaction takes place: a) Cationic polymerization and b) Anionic polymerization.

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2.3.1 Cationic Polymerization: In this type of polymerization, cationic initiators are used including reagents capable of providing positive ions or H^+ ions. The cationic polymerization is effective in the case of monomers which contains electron releasing groups like methyl ($-CH_3$) or phenyl ($-C_6H_5$) etc, that include propylene (CH_3-CH=CH_2) and styrene (C_6H_5-CH=CH_2) etc.

2.3.2 Anionic Polymerization: In this type of polymerization, anionic initiators are used including reagents which are capable of providing negative ions. Typical catalysts include sodium in liquid ammonia, alkali metal alkyls, Grignard reagents and triphenylmethyl sodium. The anionic polymerization is effective in the case of monomers which contains electron withdrawing groups like nitrile (–CN) or chloride (-Cl), etc that include acrylonitrile [CH_2=CH(CN)], vinyl chloride [C H_2=CH(Cl)], methyl methacrylate [CH_2=C(CH3)COOCH3], etc.

3 POLYMERIZATION TECHNIQUES

Factors such as the nature of the monomer, the type of polymerization mechanism, the requires physical form of the polymer and the viability of the process for industrial production are some of physical conditions which dictates condition under which polymerization is carried out. Physical aspects of polymerization reactions decide in which state the monomer is polymerised along with other inert components such as solvents and non-solvents. These varying physical conditions lead to different polymerization techniques, such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization and solid and gas phase polymerization as enumerated in the following section.

3.1 Bulk Polymerization

Bulk polymerization is the simplest technique and leads to the highest-purity polymers. In bulk polymerization, the monomer is taken in liquid state and a monomer soluble initiator is dissolved in the monomer hence forming a homogeneous phase. The reaction mass is heated to proper temperature under agitation and stirring. Bulk polymerization leads to high conversion of monomer into polymer. This method helps easy recovery of polymer and the product obtained has minimum contamination. Free radical polymerization applies to the bulk polymerization. Bulk Polymerization is used for the monomers like ethylene, styrene, methyl methacrylate etc. Bulk polymerization is simple and the polymer obtained has a high purity and minimum contamination except initiator. But the reaction medium becomes increasingly viscous as the reaction proceeds, making stirring and processing difficult. Bulk polymerization leads to uneven polymerization and loss of monomer due to heat. It leads to the auto acceleration process in which the propagation rate is very higher than that of termination rate; therefore this method is seldom used in commercial manufacture.

3.2 Solution Polymerization

In solution polymerization, the monomer is dissolved in a suitable inert solvent. A solvent soluble suitable initiator is also dissolved in the monomer and solvent forming a homogeneous system of monomer, solvent and initiator. Vinyl acetate, acrylonitrile and esters of acrylic acid etc are prepared by solution polymerization. If the polymer is insoluble in the solvent, a heterogeneous system is formed which leads to the precipitation of the polymer, for example acrylonitrile in water and vinyl chloride in bulk. The presence of inert solvent medium helps in controlling the viscosity and in heat transfer. The solution polymerization follows the kinetics of free radical polymerization. Solution polymerization has the advantage that the solvent acts as a dilutent and helps in the removal of heat of polymerization. Solvent also helps in reducing viscosity which makes processing easier. Thermal control is better in solvent polymerization as compared to the bulk polymerization. But in solution polymerization chain transfer to solvent occurs, which leads to decrease in molecular weight. It is

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difficult to remove solvent from the final product due to which degradation of bulk properties of the polymer occurs. It also increases the cost and environmental pollution due to solvent release. Solution polymerization, nevertheless, can be used where the polymer is required to be used in solution form, for eg. adhesives and coating compositions.

3.3 Suspension or Bead or Pearl Polymerization

Only water-insoluble monomers can be polymerised by suspension polymerization technique. In this technique the water insoluble monomer is suspended in water system using suitable water soluble inorganic stabilizer ie surface active agents and an oil soluble initiator is used. Under stirring a suspension is formed in which the droplets are 0.001-1 cm in diameter. The size of the monomer droplets formed depends on the monomer to water ratio, the type and concentration of the stabilising agents and also on the type and speed of agitation. Suspension polymerization used for the preparation of styrene, methyl methacrylate, vinyl chloride and vinyl acetate etc. Kinetics of bulk polymerization are followed in suspension polymerization. In suspension polymerization each monomer droplet acts as independent bulk polymerization nucleus because each monomer droplet is isolated and independent of other droplets. The water phase helps in heat transfer and makes the process more economical. Suspension polymerization results in high molecular weight polymer with narrow weight distribution because of control on kinetic chain length. Polymerization gives 100% conversion of monomer into polymer. Suspension polymerization has advantage of low viscosity due to suspension and easy heat removal due to high heat capacity of water. Isolation of the product becomes easy as this involves only filteration of the beads and washing. Suspension Polymerization yields finely divided, stable latexes and dispersions to be used directly in coatings, paints, and adhesives. On the other hand this technique has disadvantage that it cannot be used for polymers whose glass transition temperature is less than the polymerization temperature, or else aggregation will occur. Also it is required to separate and purify the polymer or required to accept the contaminated product.

3.4 Emulsion Polymerization

In emulsion polymerization the monomer is dispersed in aqueous phase as in suspension polymerization, but not as a suspension. In this technique the monomer is dispersed in water as a uniform emulsion. To achieve this, a surface active agent (surfactant) is aggregated in micelles. The surfactant can be anionic (alkali salts of fatty acids and sulfonic acids), cationic (alkyl amine hydrochlorides and alkyl ammonium halides) or non-ionic (alkyl glycosides and saccharose esters of fatty acids). The water insoluble monomer is stabilized by surfactant and a water soluble initiator is dispersed in water. Surfactant lowers the surface tension at the monomer water interface and helps in stabilization of the emulsion. A small portion of water insoluble monomer or slightly water soluble monomer dissolves in solution. A large monomer portion enters the interior of micelles leading to increase in the size of the micelles. Hence the hydrocarbon core of the micelles becomes swollen by monomer molecules. Radicals are produced in the water phase, but the polymerization in the aqueous phase is insignificant due to low monomer concentration in aqueous phase. Polymerization mainly takes place in the micelle in emulsion polymerization due to:

- High monomer concentration
- High surface/volume ratio
- Presence of interface for organic monomer and water soluble initiator

During polymerization, the monomer is replenished by diffusion from droplets through the solution to micelles. Surfactant is then redistributed, with more adsorbed on swollen polymer particle and less on monomer droplets. Emulsion polymerization is predominant preparation process for vinyl acetate,

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chloroprene, butadiene/styrene/acrylonitrile copolymers, various acrylates and used somewhat for methyl methacrylate, vinyl chloride, vinylidene chloride and styrene.

The difference between suspension and emulsion is that the emulsion has micelles in which the monomer is solubilised. Emulsion systems generally utilises water soluble initiators such as persulfates or hydrogen peroxide. This technique has the advantage that the thermal and viscosity problems are minimized due to the high heat capacity and ease of stirring of the continuous aqueous phase.

3.5 Solid and Gas Phase Polymerization

Polymerization is carried out in pure liquid or in solution phase in all the above mentioned polymerization technique. In spite of liquid phase polymerization being very popular, the polymerization can also be carried out in solid or gaseous phases. Solid phase polymerization is mostly restricted to chain polymerization. Solid state polymerization can also be carried out using the cationic initiators such as BF_3. Gas phase polymerization is known in the case of very few olefinic monomers. The two methods used in gas phase polymerization are

- Spraying the catalyst (usually Zeigler-Natta type).
- Feeding the gaseous monomer into catalyst particles.

4. CONCLUSIONS

The varying physical conditions lead to different polymerization techniques, such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization and solid and gas phase polymerization. Bulk polymerization is simple and the polymer obtained has a high purity and minimum contamination except initiator. But the reaction medium becomes increasingly viscous as the reaction proceeds, making stirring and processing difficult. Solution polymerization has the advantage that the solvent acts as a dilutent and helps in the removal of heat of polymerization. Solvent also helps in reducing viscosity which makes processing easier. But in solution polymerization chain transfer to solvent occurs, which leads to decrease in molecular weight. In suspension polymerization each monomer droplet acts as independent bulk polymerization nucleus because each monomer droplet is isolated and independent of other droplets. Isolation of the product becomes easy as this involves only filtration of the beads and washing. Suspension Polymerization yields finely divided, stable latexes and dispersions to be used directly in coatings, paints, and adhesives. On the other hand this technique has disadvantage that it cannot be used for polymers whose glass transition temperature is less than the polymerization temperature, or else aggregation will occur. Emulsion polymerization technique has the advantage that the thermal and viscosity problems are minimized due to the high heat capacity and ease of stirring of the continuous aqueous phase. Each technique has its own advantages and disadvantages and has their applications according to that.

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