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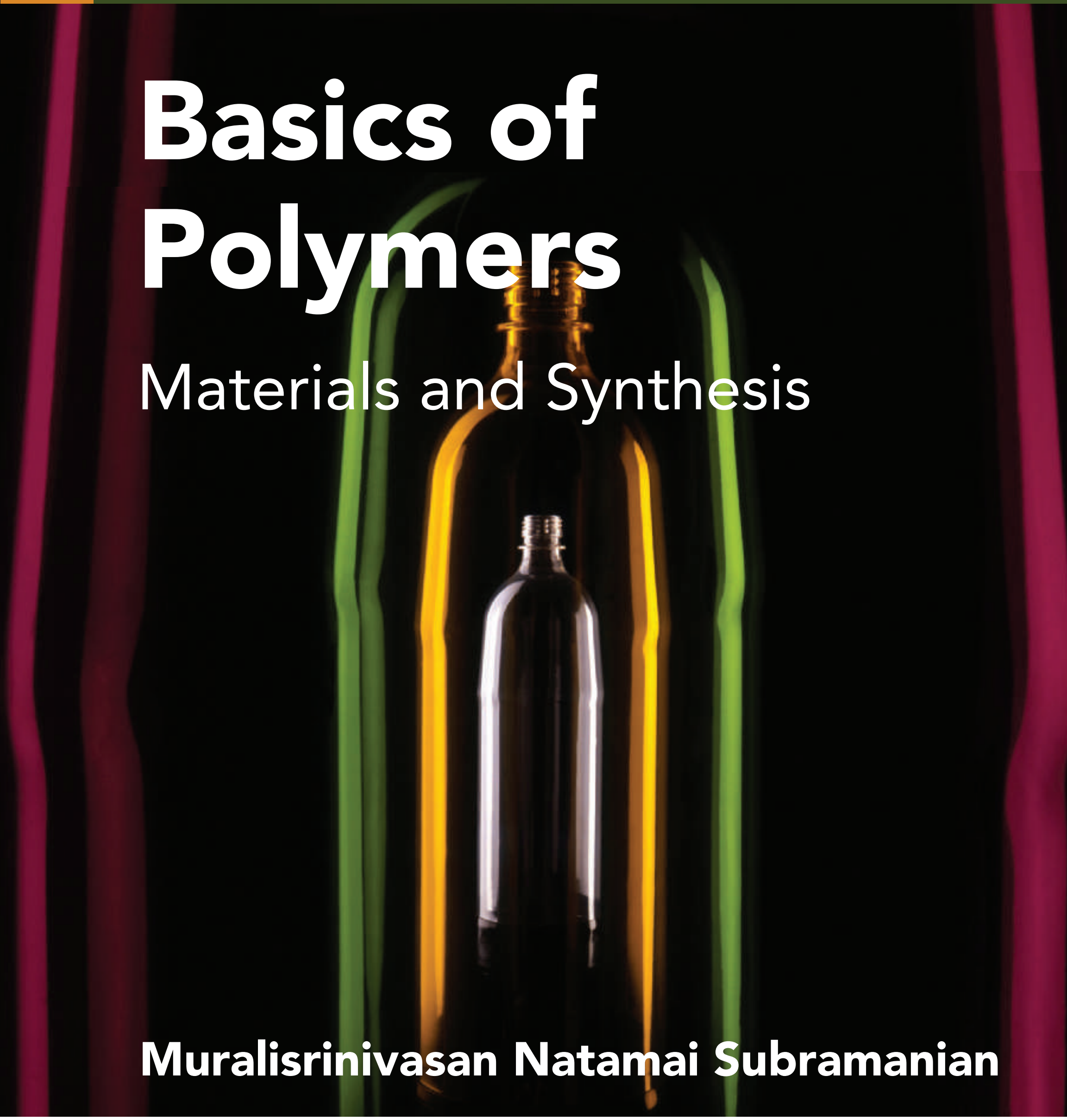

Basics of Polymers

Materials and Synthesis

Muralisrinivasan Natamai Subramanian

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ENGINEERING

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MATERIALS AND SYNTHESIS

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Basics of Polymers: Materials and Synthesis

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ABSTRACT

Polymer materials and synthesis play a most important role in the successful use in making the plastics properties and their possible extension. Several thousands of polymer syntheses are as a crucial element of the success of the polymer industry with constant evolution of technologies and procedures.

This book provides specialists with a comprehensive approach of the developments made in all the areas of polymer synthesis. It critically discusses the latest polymerization techniques. It provides industrial engineers and scientists with methods defining their limits of application. Polymer synthesis is continually challenged to develop new and exciting ways to produce polymer. Polymer synthesis is evaluated based on formation, potential consumer interest, realistic ingredients, design and regulations.

This book will be able to help and start with a handful of carbon atoms, a synthesis procedure, and understand what affects the polymer at each stage, rather than being limited to understanding a given molding process. It will allow students to adapt to industrial needs and the push towards a scientific approach to problem solving, rather than acting as traditional molding machine processors. Students will also be able to correlate the polymerization process to the performance derived in plastics processes and molded articles

The objectives included: apply knowledge and skills to integrate polymer synthesis methods. The changing environment is challenging polymer about the methods of educating practitioners. The measurement and justification of outcomes in material and synthesis practice will become increasingly important in the next few years as methods of synthesis which are required to document the effectiveness of the methods.

This book presents the fabrication of polymers and macromolecules. Current commercial techniques are covered in detail and encompass the reactions and processes currently being used in the plastics industry today. This book is designed to address the materials and synthesis issues competency statement in the Standards of teaching. This book is taught on campus and by distance using the Internet. The purpose of this book is to determine

to what extent students could learn for information on polymer synthesis and qualitatively evaluate the potential usefulness of the book.

This book gives a solid background in materials and synthesis and place the emphasis on understanding the underlying principles rather than enumerate information. It is designed to inspire a large audience of industrial and academic scientists as well as students interested in polymer chemistry. It also gives productive idea on the area of polymer synthesis. This book will become a reference for polymer specialists in the present situation and future also.

KEYWORDS

Macromolecules, monomer, synthetic polymer, natural polymer, organic material, molecular weight, composition, architecture, polymerization, oligomer, morphological, topological, homopolymer, copolymer, reaction mechanism, free radical, addition, condensation, anionic, cationic, co-ordination, metallocene, ring-opening, electro-polymerization, degree of polymerization, mono-functional, bi-functional, polyfunctional, cyclic, modification, living polymerization, biopolymer, surface science, drug discovery, medicine, conducting, conjugated, polymer waste, industrial research

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BASICS OF POLYMERS: MATERIALS AND SYNTHESIS

Basics of Polymers: Materials and Synthesis plays an important role in many technological, industrial, natural, and biological processes. Polymer reactions require a better fundamental understanding of complex interactions of mechanisms that include monomer(s) and other ingredients. Its origin is predicated on the assumption that a more fundamental understanding of the reaction mechanisms of existing polymers would lead to better polymers in the future.

The discussion of organic and inorganic types and reaction mechanism makes the book one of the most significant reference books. In view of the intense academic and industrial interest, this book on polymer reaction mechanisms will help to pave the way for research. This book is written as a practical and academic reference for polymer chemists, scientists, engineers, technicians, academicians, researchers, and processors.

Reaction mechanism is truly an interdisciplinary subject, as is evidenced by the vast amount of literature being published from diverse laboratories. Reaction mechanism at interfaces ranges from reactions of small molecules to macromolecules. *Materials and polymer synthesis* proceeds from synthesis that relates to types, kinetics, and further to degradation. Biopolymers continue to explore as a small portions of this book due to perplexing problems of degradability of polymers.

There are many good books on polymers in the market that vary widely in scope and coverage. *Basics of Polymers: Materials and Synthesis* is addressed primarily to students and professionals. It is also designed to meet the needs of both researchers and practitioners in industry. This book meets every need both academically and in terms of its other components. This book works in a broad and deep knowledge source in the classic Plastics and Polymers collection of the publication.

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I wish to express my sincere thanks to the professors who built my career during my studies and in the creation of this book. Many thanks to Mr. Joel Stein, Ms. Chitra Rajasekaran, Ms. Charlene Kronstedt, and other members of M/s. Momentum Press. I also thank my wife, Mrs. Himachalaganga, for her significant, inspiring, and indispensable support, and my children (Venkatasubramanian, who is studying at KLN College of Information Technology, and Sailesh, who is studying at Vellammal College of Engineering and Technology), who worked hard with me to get this book finished on time. Above all, I would like to thank God for his blessings, and my parents, who brought me into this world to enhance my writing.

CHAPTER 1

INTRODUCTION

Polymers are synthesized either by humans or by nature. Regarded as being among the most versatile and diverse materials, synthetic polymers have been a source of exciting developments in a variety of application. High-molecular-weight macromolecules and polymerization processes link together individual small monomer molecules by means of covalent bond formation [1–3]. Many synthetic materials are of potential value in many fields as they possess a combination of physical and chemical properties not found in natural macromolecules. Polymer synthesis may involve a simple repetition of classical organic reactions such as esterification. An important factor in polymer synthesis is the controlled rise in temperature during polymerization of monomers in the reactor.

Polymer molecule properties and utility enable most of the new inventions. Emphasis is being placed upon new approaches and opportunities to synthesize polymeric materials with new property profiles. Polymers are key elements, and nature also continues to teach much related to molecules to synthesize. Polymers that are made by modifying a natural polymer or synthesizing an entire polymer have become valuable. Therefore polymerization is giving variable results and most of the are unorganized structures. Physical properties are important in polymers. Organic materials such as wood, silk, cotton, wool, and flax are known to have great strength, but none of these can be synthesized in the laboratory.

Although polymers are incapable of reproducing the precise sequence control found in nature, they have still been found useful as substitutes for many steel products, and are also used in electronic applications and in human body parts. Polymer synthesis is critical to the realization of properties. It accounts for current and future generations to create ever more useful and diverse materials. Sustainable energy, affordable health care, and personal protection are all bound by current limitations in polymer materials; yet polymers will continue to be enabling materials to make the world a better place [4].

Polymer synthesis is a process of developing a synthetic polymer with a well-defined molecular weight, a high stereo regularity, and controlled monomer sequence for the creation of functional polymers. The synthesized polymer may challenge a nature-synthesized macromolecule with a perfectly ordered structure [5]. Therefore, the objective of polymer synthesis should be to control perfectly molecular weight, molecular weight distribution, composition, and architecture while producing polymers [6].

Polymer synthesis starts from the atoms present before they become a part of a polymer molecule. It is a key link between molecule and end product. The choice of polymer is governed by the application in question. In some cases, the polymer is specifically selected for its physical characteristics. It is the process of making the desired polymer using different polymerization techniques. Polymer synthesis involves many steps. The synthesis of a polymeric material with specific properties, such as strength and flexibility, is contingent upon the polymerization reaction taking place [7].

In the era of polymer science, polymer synthesis is the improvement of physical, thermal, and mechanical properties, as well as the modification of processing characteristics and cost reduction of the polymers. The synthesis and design of new polymeric materials to achieve specialized polymer applications to find interesting applications involving advanced structures and architectures is in continuous and parallel development. Initial period of polymer discovery and investigation of fundamental polymerization principles, new or advanced technologies, and investigation of fundamental principles of polymerization to ensure the synthesis reach their full potential.

In modern synthetic polymer chemistry, the goal of polymer synthesis is to prepare polymers with controlled molecular weight and well-defined architecture. New applications and modern technologies have required the synthesis of tailor-made macromolecules with precisely controlled dimensions, polydispersities, sequences, tacticities, and terminal functionalities. Novel phenomena and properties that include mechanical, electrical, optical, surface, and other properties can be observed for well-defined polymers and copolymers [8]. Polymer syntheses have been extensively from the part of the knowledge built up on the relationship between synthesis and molecular structure in polymeric materials.

The "simple properties" that are useful are not always simple in polymer synthesis. The polymer synthesis and design is for purpose. Polymer synthesis comes after need recognition, and is achieved only in a mature field of science with a wealth of knowledge. It is possible by achieving either to do or discover means of research of known promise. The fact is to provide knowledge and remarkable ways of synthesizing polymers of all sorts of shapes and sizes. Different shapes and sizes result in an equal diversity of properties. It is particularly striving toward understanding properties of polymers after synthesis.

The synthesis of polymers offers a potentially rich source of possibilities for desirable materials with different or required properties. However, understanding the reaction behavior, for instance, predicting its properties, a priority, based on the properties of two proposed monomers has proven to be much more elusive than is the case for simple, small molecular mixtures.

Polymer synthesis therefore has a key role to play in the following areas:

- Industrially important polymers
- Polymers of theoretical interest and their use in industry
- Development of new synthetic methods.
- Polymers that are important in other areas of science and technology
- Total synthesis of interesting and/or useful polymers
- A key link between the atoms present before they become a part of a polymer molecule and the molded article, the end produce of the molding operation.
- Molecular fragments joining the nuclei can be chosen so as to give melt process ability.
- Providing polymer resistance to thermal, oxidative, and photochemical attack.

Process in synthesis is conceded by skill in the art of being scientific exploit of something clever. Technical feasibility and ingredients to make polymer in clever synthesis process is to be organized, systemized or even automated. The focus of polymer synthesis research is to illustrate that some of the results are beginning to have a real impact on industrial practice.

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CHAPTER 2

POLYMER

Research is being carried out to produce more versatile polymeric structures to cover a wide range of properties and to replace or supplement more traditional materials. Polymers can be effectively used in material of commercial importance and everyday significance. They are molecules made up of many monomer segments and are produced from the sequential reaction of monomer units to form distributions of related molecules that can vary in the number of reacted monomer units, or chain length, the chemical species at the ends of the chains, end groups. They also have end groups that cap the repeat units composed of the monomers used to produce them. A polymer is any material that is composed of related monomer molecules. However, oligomers with small chain lengths have multiple monomer units with relative amounts of different units.

Polymers are fundamentally different structures of macromolecular substances with special physical and chemical properties. Polymers are scarcely or only slightly soluble in the usual solvents. They can be vaporized, generally, only under decomposition. With the increasing number of different polymers prepared, the interactions between macromolecules have become equally important in explaining the materials' properties at the molecular level. They are substantially different in most physical characteristics from simple organic compounds.

Polymers are non-regular with irregularity and may display at different levels, namely, molecular, topological, and morphological.

- Polymer molecules have a chain like structure, and non-equivalency (anisotropy) exists along and across the polymer chain.
- Topological irregularity is due to the existence of ends of polymer chains and various polymer chain entanglements surrounded by relatively ordered substances in which the short-range order is obeyed.

- Morphological irregularity is based on the existence of relatively large zones markedly differing in the character of arrangement of segments of macromolecules forming these zones.

The polymer is characterized by the chemical composition of the repeat units, the end groups, and the molecular weight distribution of the individual monomers. Structure–property relationships can be dealt with as chemical and architectural aspects.

CHEMICAL ASPECTS

Chemical aspects deal with solid-state structures, and physical properties with information on the molecular structure of the macromolecules, including the type of monomer repeat units and parameters, relate ultimately to the three-dimensional aggregate. Solubility and bulk properties such as glass transition temperatures, melting temperatures, crystallinity, and modulus depend on the chain flexibility, chain symmetry, and intermolecular interactions. Therefore, these properties depend mainly on the chemical nature of the macromolecules.

ARCHITECTURAL ASPECTS

Architectural aspects concern polymer chains as a whole. Architectural arrangements (topology) have considerably different properties such as linear polymers versus networks, branched and cyclic polymers, as well as block and graft copolymers, primarily because of the different motional constraints imposed and the consequent effects on solvent and molecular entanglement.

Rheological properties of polymers are affected by molecular structure [1, 2].

MONOMER

The monomer units in the random or statistical copolymer are statistically distributed along the copolymer chain. Based on constituent monomer related polymer presents abundance in the copolymer tends to produce properties in average. The properties of the copolymers are characterized by combining the properties of the two monomers along with structural regularity. Small molecules have the benefits of structural versatility, simplicity, and low molecular weight, resulting in higher overall yields, easier scale-up, and more precise structure–function relationships as compared with their broader distributed polymer relatives. Monomers are used to produce polymers industrially and traditionally. The majority of them are from petroleum-sourced crude oil.

MACROMONOMER

A macromonomer is defined as a functional oligomer with a polymerizable end group [3]. The chain length of the macromonomer defines the length of branches in the graft copolymer. It is predetermined and precisely controlled using living polymerization strategies. The choice of monomers and the order of monomer addition control the composition of the branch and backbone upon subsequent copolymerization [4].

MOLECULAR WEIGHT

Molecular weight refers to molecular weight distribution and its number, weight and z-average molecular weight, polydispersity index, and degree of branching, namely, short- and long-chain branching. Polymers exhibit a more or less broad molecular weight distribution (molar mass distribution) [5], which influences many properties of macromolecular materials.

Polymer materials are typically characterized by measuring the chemical structure of the repeat units and the end groups and by measuring the molecular weight distribution of the series of oligomers. The molecular weight distribution is determined by the number average molecular weight, MN, the weight average molecular weight, MW, and the polydispersity. The two average molecular weights are the first two moments of the distribution of oligomer molecules, where Mi is the mass of an observed ion and Ni is the number of ions observed:

$$M_N = \Sigma M_i N_i / \Sigma N_i \tag{1}$$

$$M_W = \Sigma (M_i)^2 N_i / \Sigma M_i N_i \tag{2}$$

$$\text{polydispersity} = \text{PD} = M_W / M_N \tag{3}$$

The molecular weight is, by definition, not uniform. Stereo regularity of polymers is important in view of its physical and chemical characteristics, which are influenced by tacticity. The introduction of bulkiness on monomer substituents provides significant tactics to control stereo regularities. Polymers are classified in the order of increasing number of chain ends. However, the network polymer represents one enormous molecule with relatively few chain ends. Each class of polymers has its unique properties.

HOMOPOLYMERS

In homopolymers, all the monomer segments are of the same type. Homopolymers are formed from the polymerization of single monomers. The physical behavior of a homopolymer is primarily due to interactions among its molecules in the solid state. The magnitude of interactions is dependent on the nature of intermolecular bonding forces, molecular weight, and chain packing and flexibility of the polymer.

MACROMOLECULAR AND SUPRAMOLECULAR STRUCTURES

Synthetic polymer chemistry has recently focused on the control of macromolecular and supramolecular structures. This includes the preparation of polymers with novel architectures such as cyclic, threaded, and ladder structures as well as various types of block and star polymers and copolymers, which may microphase separate into domains of various geometries. Synthesis of well-defined polymers requires high chemoselectivity, regioselectivity, and stereoselectivity.

As a consequence of demands for specialty polymers with a range of new and improved properties, the past decade has seen the synthesis of a staggering number of different block polymers, macromonomers, macrocrosslinking agents, stars, and other polymer architectures. The challenge now is to develop ways to prepare new polymer architectures and to use these advanced materials to produce advanced products.

COPOLYMERS

Copolymers are made up of two (or more) monomer types present as segments in the polymer (Figure 1). Copolymers can have star, random, graft,

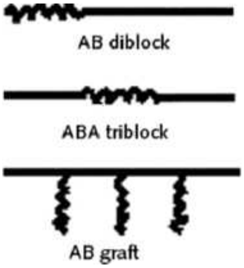

Figure 1. Structures of copolymer with monomer representation as A and B

block, and branched architectures. Polymers can also be neutral or charged macromolecules, such as biopolymers.

A copolymer uses two or more different repeat unit structures to polymerize. Copolymers with considerably different properties are obtained by varying the amounts of each monomer and technique, and can be classified according to the sequence of monomer units in the macromolecular chains. The nature of the spatial disposition of the components provides an additional design tool.

Alternating structures present in copolymers are capable of interactions that can affect solubility, chemical reactivity, and mechanical properties. The covalent bonding dictates the conformation properties, solvents interaction, and intermacromolecular interactions. The properties and behavior of various arrangements are distinctly different even with the same overall compositions.

During processing, the use of block or graft copolymers plays an important role by causing entanglements or bridging different polymer chains near the interface [6–11]. The main chain of branched polymers is either short- or long pendant chains. Series branching results in main chain branches themselves being branched. Block copolymers and graft copolymers often exhibit microphase separation, and this morphological control dramatically influences the physical properties of the polymer. Occurrence of microphase separation depends on many factors, including compositional dissimilarity, molecular weight, and crystallizability [12].

GRAFT COPOLYMERS

Graft copolymers (Figure 2) enable a wide variety of emerging applications owing to their unique macromolecular architecture. Intra- and intermolecular interactions are crucial for tuning the functionality and performance of

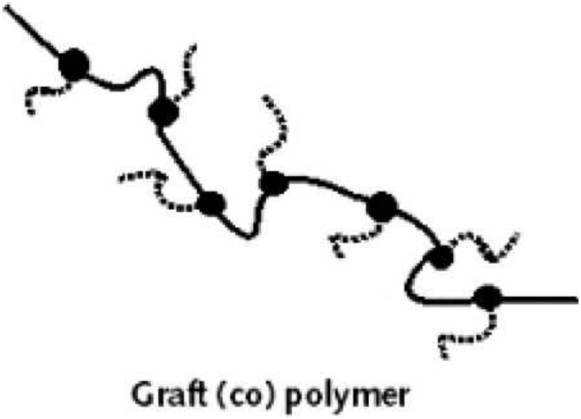

Figure 2. Structure of Graft (co)polymer

graft copolymers. It is necessary to understand structure–property relationships in order to synthesize and characterize graft copolymers [13]. It is either regularly spaced tetrafunctional branch points or randomly placed trifunctional and tetrafunctional branch points. Graft copolymers exhibit less well-ordered morphologies than analogues with regularly spaced branch points with randomly placed branch points [14].

Graft copolymers are branched polymers. The branches are structurally different from the primary or backbone chain. Phase-separated morphologies analogous to the block copolymers in graft and graft base depend on the compatibility and crystalline tendencies. One of the important applications is improved hydrophilicity through the grafting of polar units. A range of composition of monomer present as sensitive phase and morphological behavior with the resultant graft copolymer will have improvement in properties. Graft copolymers are used mainly as in situ compatibilizers for polymer blends, that is, they are formed during processing (extrusion) of the polymers. The main graft monomers are maleic anhydride, maleic acid, dibutyl maleate, and acrylic acid and its esters.

Graft copolymers are most commonly prepared from preformed polymers that possess groups along the chain that can be activated to initiate polymerization of a second monomer. Ionizing radiation (X-ray, -rays, and e-beams) in the presence of air, ozone, UV radiation with accelerators, and free-radical initiators (mostly organic peroxides [15]) have all been used to form polymeric peroxides. Heating of the polymeric peroxides in the presence of monomer(s) can initiate graft reactions. This free-radical grafting technique can be applied to a wide range of polymers, but is not suited to prepare well-defined graft copolymers because of such side reactions as cross-linking and chain scission, resulting in loss of mechanical properties.

Graft copolymers derived from commercial polymers offer an effective approach for incorporating specific properties into a material while retaining desirable properties of the parent polymer. Poly (vinyl chloride) (PVC) is one of the most widely used vinyl polymers in the world [16,17]. Replacing chlorine atoms of PVC with other atoms or groups would yield new polymer properties (or effects), such as thermal stability, polymer–solvent interactions, and dielectric response

BLOCK COPOLYMERS

Block copolymers are smaller architectural subunits of graft copolymers that dictate the morphological behavior of the large complex architectures of graft copolymers [18]. Block copolymers contain relatively long separate sequences of two or more different repeat units [19, 20]. The blocks or chemically different sequences in block copolymers are not mutually miscible. Therefore, phase separation results in microdomain formation. Hence, material has some of the properties of separate blocks. The importance can be realized from the arrangement of the blocks, compatibility, and crystalline tendencies. They are more versatile, high-tensile-strength materials usable in a relatively larger temperature window. Microphase separation with glassy or crystalline blocks tend to segregate into domains that serve to anchor elastomeric blocks and act as effective physical cross-linking points with reversible nature.

Block copolymers are high-molecular-weight polymers comprising two or more distinct regions of differing properties. The block copolymers consist of a hard polyamide block and a soft polyester block. The soft block contributes high toughness, elongation, and flexibility, whereas the crystalline hard amide blocks impart high strength, rigidity, chemical resistance, and high melting temperature.

Block copolymers are a specific class of copolymers (polymers comprising more than one chemically distinct monomer) where the different monomers are not distributed within the polymer chain in random or alternating fashion, but instead are grouped in discrete homogeneous sections (or blocks) of the chain [21]. Conceptually, a block copolymer can be thought of as two or more distinct homopolymers linked end to end through covalent bonds. The number of distinct homopolymer homogeneous sections determines the molecular architecture of block copolymer; diblock, triblock, and higher multiblock copolymers are possible [22]. Diblock copolymers, which contain two distinct homopolymers, are the simplest molecular architecture of block copolymers and have been studied most extensively for generating a variety of nanostructures.

RANDOM COPOLYMERS

Random copolymers of propylene and ethylene produced with a metallocene catalyst have advantages over similar types of copolymers made with classical Ziegler–Natta catalysts. In the metallocene type, molar mass distribution and interchain distribution of the comonomer are narrow, and the intrachain comonomer distribution follows Bernoullian statistics. Conversely, classical Ziegler–Natta catalysts lead to broadly distributed copolymers in both molar mass and comonomer concentration, complicating the study of structure–properties relations [23].

LINEAR POLYMERS

Linear polymers have a strong tendency to crystallize, and therefore show anisotropic charge transport properties; the introduction of branching and two- or three-dimensional architectures has been proposed in terms of isotropic properties [24]. The majority of linear polymers containing the aromatic nucleus are synthesized by using polycondensation techniques. Examples include poly (ethylene terephthalate) (PET), poly (teraphthalamide) (Kevlar), poly (phenylene ether sulfone) (PES), and poly (phenylene ether ether ketone) (PEEK). Polyphenylene would be the most thermally stable structure of all the linear polyaromatics.

The majority of linear polymers containing the aromatic nucleus are synthesized using polycondensation techniques...

An advantage of this synthetic route is that molecular fragments joining the aromatic nuclei can be chosen so as to give melt process ability. The disadvantage to this method of synthesis is that the molecular fragments joining the phenyl groups are more susceptible to thermal, oxidative, and photochemical attack. These facts have been extensively debated over the last 20 years and form part of the knowledge built up on the relationship between molecular structure and stability in polyaromatic materials. Polyphenylene is believed to be the most thermally stable structure of all the linear polyaromatics, and, consequently, various attempts have been made to synthesize this material.

BRANCHED POLYMERS

Well-defined branched polymers involve copolymerization of macromonomers with backbone-forming monomers. Highly branched polymers have resulted in the development of numerous methods for the synthesis of stars, combs, dendritic polymers, and polymers of more complex architectures [25–27]. Furthermore, the solubility is often increased in branched architectures compared with linear systems.

Branched polymers are characterized by the presence of branch points or more than two end groups, and comprise a class of polymers between linear polymers and polymer networks. Although undesirable branching can occur in many polymerization reactions, controlled branching is readily achieved. In fact, numerous studies on polymer structure–property relationships have shown that branched polymers display enhanced properties and performance for certain applications [28]. Long-chain branched polymers offer significantly different physical properties than linear polymers and polymer networks. For example, a low concentration of long-chain branching in the polymer backbone influences melt rheology, mechanical behavior, and solution properties, while large degrees of branching readily affect crystallinity [29,30]. The strong influence of only one long chain branch per chain can be visualized by looking at Fig. 1. The "slip-links" along the polymer backbone represent entanglements with other chains. The linear polymer is free to diffuse along a tube imposed by other chains, while it is clear from Fig. 1b that the mobility of the long-chain branched polymer is restricted, and must diffuse through some other mechanism. Thus, it is not surprising that long-chain branched polymers exhibit very different properties where chain entanglements play a role.

The number of branching points within the molecule strongly influences the optical and electrochemical properties: a high degree of sterically demanding branching points leads to a decrease in the efficiency of conjugation and therefore results in properties that would be expected for shorter conjugated systems.

The ultimate branched architecture with the intrinsically highest branching density is a dendrimer. The unique properties of larger dendrimeric systems make them a valuable building block in a variety of functional higher-dimensional systems.

Branched small molecules, oligomers, and polymers exhibit unique properties such as broadened absorption spectra and frontier orbitals that are influenced by their conformation and the branching degree. Linear conjugated polymers, on the other hand, are extensively used in optoelectronic devices due to high charge carrier mobilities, low-cost solution process ability, and the possibility to tune the material properties by chemical engineering. Through the incorporation of branched units in linear conjugated polymers, one seeks to combine the benefits of both architectures.

Branching along the main backbone of synthetic polymers significantly alters rheological and other physicochemical properties [31, 32], which in turn influences the process ability of many commercial polymers [33]. Branches may be distributed regularly or randomly along the main backbone, or several branches may originate from a single point to generate a star-shaped molecule. When polymer molecules are branched, their rheological behavior varies with the number, location, and length of the branches [31]

STAR-SHAPED POLYMERS

Star-shaped polymers (Figure 3) have branches with homopolymers or diblock copolymers. They are of almost equal length, radiating outward from a single branch point. They are characterized by low hydrodynamic volume owing to their low radius of gyration. The characteristics are reflected in the solution properties of the polymer. Low intrinsic viscosity depends on the number of branches relative to linear polymers of the same molecular weights. Star-block copolymers represent the best defined group of block copolymers with specific arm number, composition, and molecular weight with narrow molecular weight distribution. They can be prepared by anionic polymerization techniques.

Star-shaped polymers are called homostars when all arms have the same chemical structure. Arms may be built of homo-, co-, or even terpolymers; therefore, the final properties of the resulting star-shaped polymers (e.g., star-block and heterostar copolymers) may be adjusted by choosing the respective chemical structure of an arm and core, depending on the required application. Thus, star-block copolymers have each arm constituted of two homopolymeric blocks of different chemical nature, whereas

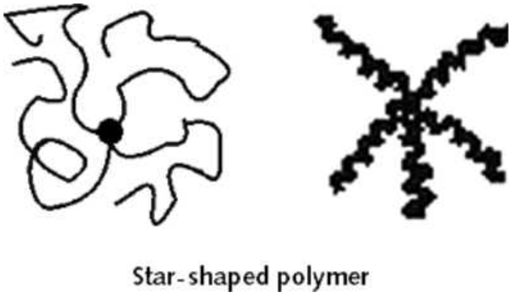

Figure 3. Structures of star-shaped polymer

heterostar copolymers have equal numbers of arms of two kinds, differing in chemical nature as well as average length, attached to the core (cf. Scheme 2) [34–36].

Star-shaped polymers consist of at least three linear polymeric chains of comparable lengths radiating from one single multifunctional branched point, usually called the core or the central nodule, and that can itself be polymeric. In a star-shaped polymer, the core radius should be much smaller than the dimension, e.g., the root-mean-square end-to-end distance of the arm. If the core size is much larger, such an entity can be considered a "nanoparticle," as its property will be dominated by the cross-linked nanometer-sized core. If the nanoparticles are approximately spherical in shape, they are referred to as "nanospheres" (cf. Fig. 1). The main feature of star-shaped polymers, distinguishing them from the linear analogues of identical molar masses (M_n), is their compact structure (smaller hydrodynamic volume and radius of gyration, and therefore lower viscosity) and the multiple functionality of the polymer which is useful in some of their applications.

DENDRIMERS

Dendrimers (Figure 4) have attracted interest because of their unusual, globular, and perfectly branched structures [37, 38]. Well-defined architectures, high numbers of functional groups on their surface, excellent solubility in a vast range of solvents, and very low viscosity make dendrimers good candidates for a wide range of applications, from viscosity modifiers to catalyst supports and drug carriers. The production of dendrimers, however, requires multistep syntheses, with drastic purifications between each step, making it a costly and time-consuming process. Hyperbranched polymers, in contrast, are often far easier to prepare under less drastic reaction conditions. Although they have less perfect branching structures than dendrimers, such systems retain high degrees of functionality, have improved solubility and low viscosity, and therefore provide a cheaper alternative to dendrimers for applications such as resin modification, encapsulation, polymeric liquid crystals, pharmaceutical use, catalysis, and electroluminescent devices. The creation and development of highly branched macromolecules with well-defined architectures take place via one-step processes.

Dendrimers contains a significant molecular weight between branch points. It has well-defined architectures, high numbers of functional groups on its surface, excellent solubility in a vast range of solvents, and

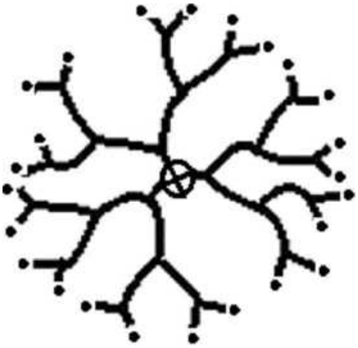

Figure 4. Structure of dendrimer

very low viscosity for a wide range of applications such as viscosity modifiers, catalyst supports, and drug carriers. It has unique chemical and physical properties. However, production of dendrimers requires multistep syntheses, with drastic purifications between each step, making it a costly and time-consuming process [39–41].

The synthesis of dendrimers requires several protection and deprotection steps as well as purification at each synthetic step.

The regular dendritic architecture possesses branching with radial symmetry. It possesses distinguishing architectural features, namely, core, interior layers, and an exterior or surface of terminal functionality attached to the outermost generation. Interior layers are repeating units radially attached to the core.

HYPERBRANCHED POLYMERS

Hyperbranched polymers (Figure 5) show similar properties to those of dendrimers, namely, low viscosity, high solubility in organic solvents, and lack of significant entanglement in the solid state [42–46]. They are synthesized readily by one-step polymerization. This is advantageous over the dendrimers because of the rapid production of large quantities [47].

Hyperbranched polymers have less perfect branching. They retain a high degree of functionality with improved solubility and low viscosity, and are cheaper and easier to prepare under less drastic reaction conditions. Applications of hyperbranched polymers are polymer modification, encapsulation, pharmaceutical uses, catalysis, electroluminescent devices, and so on. Their development and creation with well-defined architectures is through a one-step process.

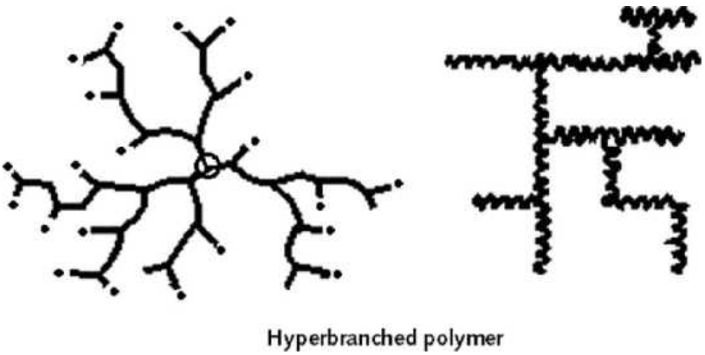

Figure 5. Structure of hyperbranched polymer

Most hyperbranched polymers are synthesized by step-growth polymerization via polycondensation of ABx monomers. Here, A and B are the two functionalities that can react with each other but not with themselves. Furthermore, as there is no control over size and structure, hyperbranched polymers show broad molar mass distributions. Moreover, facile routes to produce hyperbranched polymers via addition polymerization are very rare [48].

COMB POLYMER

Comb-shaped polymers (Figure 6) contain branches of generally equal length attached more or less equidistantly along the main chain. Comb polymers prepared by the homopolymerization of nonuniform macromonomers, even with narrow molecular weight distribution (MWD) values, should be comprised of polymacromonomer molecules with degree of polymerization (DP) distributions not only in the main chain but also in the side chains. Moreover, the polymacromonomer will involve a sequence distribution of macromonomer units with different DPs.

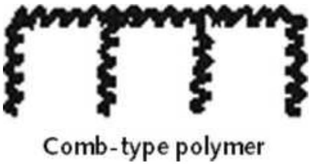

Figure 6. Structure of comb-type polymer

CYCLIC POLYMERS

Cyclic polymers are a broad spectrum of polymer architectures. They have no chain ends. They have aroused interest because of their special dilute solution, diffusion, and rheological properties. Cyclic polymers have unique properties that include lower hydrodynamic volume, lower melt viscosities, higher glass transition temperatures, and lower frictional coefficients in comparison with similar molecular weights of linear counterparts. Anionic polymerization has been utilized to synthesize well-defined cyclic polymers.

Cyclic polymers have novel properties that differ from those of their corresponding linear polymers [49–51]. Compared with other polymers with special architectures, such as star polymers, hyperbranched polymers, and dendrimes, the synthetic routes to cyclic polymers are less investigated. Cyclic oligomers have been known as minor byproducts in step-growth polymerizations due to ring-chain equilibrium reactions [52] and also in ring-opening polymerizations through backbiting reactions [53, 54].

INTERPENETRATING POLYMER NETWORKS (IPNS)

Interpenetrating polymer networks are formed by polymerization of one or more monomers. The networks can also occur with a monomer pair in the presence of a preformed cross-linked polymer. It is also possible by simultaneous but chemically independent formation of two or more cross-linked polymers. They are insoluble and exhibit little creep due to topological constraints imposed by the cross-links. Starting with one monomer using rapid polymerization reactions, phase separation is not as extensive as in blends of preformed homopolymers. However, immiscibility arises from the lack of entropy associated with combining two large molecules. IPNs involve the topological concepts of rotaxanes and catenanes in an intimate way.

IPNs are polymerized from a monomer and its cross-linker in the presence of another cross-linked polymer network with a different composition. They are a kind of polymer system that can be prepared sequentially, in which one network forms swollen in the second set of monomer reagent or prepared by reacting all of the constituents simultaneously [55,56]. They typically consist of flexible elastomers and one or more rigid, high modulus components.

IPNs may be divided into ideal, partly interpenetrating, and phase separated. IPNs have a tendency to show phase separation due to the low entropy of mixing. The extent of phase separation is restricted due to interpenetration, which plays a significant role in enhancing the intermixing of the polymer components through a physical interlocking. IPNs have proven to be economically, scientifically, and commercially important.

An ideal IPN is a system with a molecular level of mixing of constituent networks. It is impossible to obtain such an ideal system because of the thermodynamic incompatibility of components, similar to many other polymer–polymer systems. However, IPNs preparation requires most of the polymer couples derived from petroleum [57–60].

Poly(rotaxanes). Polyrotaxanes are two-component systems consisting of macrocycles threaded onto linear species such that there is no covalent bond between the linear and the cyclic components, one of which is polymeric.

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CHAPTER 3

POLYMERIZATION TECHNIQUES

Polymers are commercially important materials of long chains of short repeating molecular units linked by covalent bonds [1]. They differ in their physical properties from monomers, which are simple organic compounds. The number of polymers synthesized increases, even though molecular level of interactions is important.

Carothers classified polymers by types of compounds based on their capability to polymerize and types of polymerization. This classification is a commonly used strategy and is useful between different polymers produced by step-, chain-, or ring-opening polymerization. A large variety of modern polymerization techniques have been added such as metathesis, living, ionic, and radical polymerizations. However, they follow Carothers' classification.

POLYMERIZATION

Polymerization is the type of process in which monomers are combined into long-chain molecules called polymers. It is a chemical combination involving the operation of primary valence forces. It involves the formation of polyesters, polyamides, and others. Molecules can combine to form a polymer either by addition or condensation polymerization. Addition polymerization involves olefinic monomers, whereas condensation polymers undergo step-growth polymerization of difunctional or monomers of two different functional groups [2]. Chain length distribution of polymers provides direct evidence for the statistical nature of reactions.

Polymerization can generally be classified as addition polymerization and condensation polymerization. The majority of addition polymers involve olefinic monomers, whereas condensation polymers involve step and chain polymerizations of difunctional monomers or monomers of two different functional groups such as reaction of acid and alcohol [2].

Phenolformaldehyde is a step polymerization, and styrene reaction is a chain polymerization. Molecules of difunctional monomers such as X-R-Y where X and Y are mutually reactive functional groups. This difunctional monomer is polymerized through the elimination of small molecules as by-products of XY. Therefore, the product X-$(R)_n$-Y is formed. When an olefinic monomer such as $H_2C{=}CHR$ is polymerized, a vinyl polymer with a structure of $–H_2C\text{-}CH(R)_n$- is produced.

Difunctional and olefinic monomers have been the major sources of monomers, and their step and chain polymerization reactions have been the main synthetic routes to the conventional polymer. Single and double bonds of the monomer species are reacted. Therefore, new species of increased molecular weights are formed. The final destinies of chemical reactions are the formation of polymers with monomer repeat units connected by single bonds. Electronically saturated single bonds are electronically inactive. Traditional polymers are commercially used commodity materials [3]. Typical polymerizations are mentioned in the following figure:

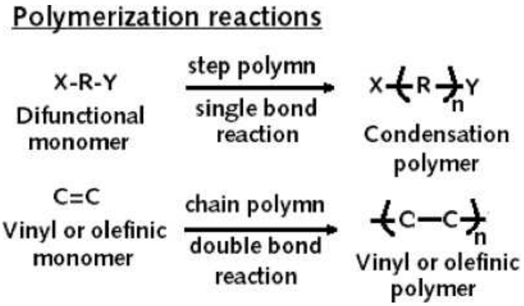


Figure [Reprint with permission from Liu, J., J.W.Y. Lam, and B.Z. Tang. 2009. *Chemical Reviews* 109, pp. 5799–67. All rights reserved].

In many polymerization processes, chemical reaction of the monomer occurs in a fluidized bed of catalyst and monomer. As polymerization proceeds, small pellets of polymer particles are formed, and after the reaction terminates, the residual monomer must be removed from these pellets. This is usually accomplished by devolatilizing the pellets in large purge towers. The fundamental mechanisms behind the impurity separation are complex, and proper design of purge towers requires fundamental properties of the polymer–solvent system. Of key importance are the diffusion coefficient and the solubility of the solvent in the polymer pellets.

3.1 ADDITION POLYMERIZATION

Many monomers are transformed into a long-chain polymer through an addition or chain reaction process. Addition polymerization is peculiar to unsaturated compounds in which the monomer undergoes polymerization in order to saturate them as a natural tendency. Addition polymerization is not limited to carbon–carbon bond polymerization. In addition polymerization, a large variety of unsaturated or cyclic compounds may be converted into polymers based on a variety of conditions. However, many other reactions are also possible to undergo polymerization, such as ethylene oxide, certain cyclic esters, and hydrides polymerize by self-addition. These reactions are in some respects radically different from polymers containing multiple linkages.

Addition polymerization is the double bond (–C=C–) polymerization [4,5]. Addition polymerization [6] proceeds by

1. Reactions—Chain reaction mechanism involves initiation, propagation, and termination. They have different rates and mechanisms. Many monomers are nonsymmetrical. Addition of monomer is without formation or loss of any other products. No monomer is lost, and no low molar mass species evolve during polymerization reaction. Polymers have the same composition as their monomers and result in linear structure.
2. Polymer growth—The growth reaction takes place by the addition of one unit at a time to the active end of the polymer chain. Monomer addition to the growing chain depends on the substituent group, stability of active center, and steric hindrance for placing the approaching monomer to the growing chain
3. Molecular weight—high-molecular-weight polymer formed immediately.
4. Monomer concentration—concentration of monomer decreases throughout the reaction.
5. Composition—composition of the polymerization reaction mixture contains only monomer, high-molecular-weight polymer, and growing chains after initiation and at the end of the polymerization. Hundred percent conversion of the monomer is usually not achieved.

Ethylene polymerizes less readily than most of its homologues and their derivatives Substituted ethylenes of the type CH_2=CH-R, in which R is a negative group, polymerize much more readily than does ethylene itself. Some of the monomers (Figure 1) that undergo addition polymerization are

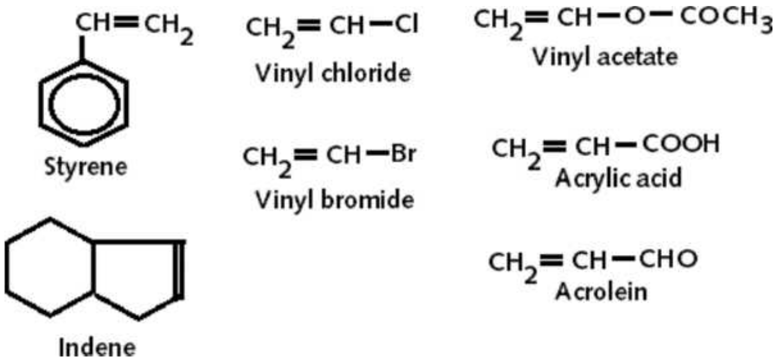


Figure 1. Monomers undergo addition polymerization

Addition polymerizations are practically polymerization of ethenic compounds of vinyl or alkene monomers. Polymerization involves the addition of monomer to an activated or initiated form of the monomer. Monomers may be converted to polymers by catalysts such as benzoyl peroxide or azobisisobutyronitrile. Chain polymerization must be either initiated or catalyzed. The active intermediates produced may be categorized as either radicals, anions, cations, or coordinated species. This polymerization (Figure 2) involves a change in the bonding from a sp^2 bond to a sp^3 type bond. Addition polymerization is interrupted even at an early stage. The polymer formed has its final high molecular weight is remaining in the reaction mixture with unreacted monomer. Transfer reactions play an important role in the kinetics of the reaction.

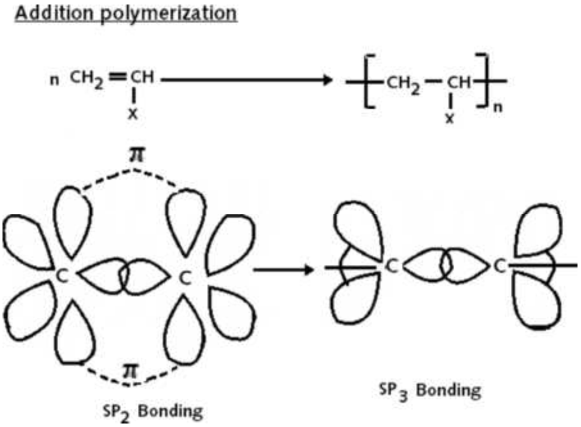


Figure 2. Addition polymerization and orbital hybridization

Catalysts are the most effective means of initiating polymerizations. The radical initiators will produce an active radical species capable of interacting with a monomer. Polymerization is accelerated by heat, pressure, UV light, and catalysts. Polymer synthesis is greatly facilitated by catalysts and their recovery and recycles.

Catalyst reuse increases the overall productivity and economy of chemical transformations while minimizing their environmental effect. In polymers, the criterion for the quality of a catalyst or initiator is its performance. High performance may be [7]

- High productivity—means rapid polymerizations and large quantities of polymers per molecule of catalyst.
- High molar masses should be accessible.
- Initiator or catalyst allows for tailor-making the molar masses
- Syntheses of block copolymers require narrow molar mass distribution is one of the desirable criteria.
- Various architectures such as random copolymers, block copolymers, and star-shaped polymers should be accessible.
- Side reactions should be suppressed.

In addition polymerization, the nature of propagation reaction allows variations in the mode of monomer addition to the growing chain, and variability in termination reactions results in great polydispersity of molecular weight. Variation in structure in addition polymerization happens due to

- Structural isomerism due to formation of branches in homopolymers and variation in the monomer distribution in copolymers.
- Asymmetric monomer units arise in sequence isomerism from variations in orientation.
- Stereoisomerism arises from differences in configuration of asymmetric carbon atoms in the chain.
- Geometric isomerism in dienes polymers (cis, trans).
- Possibility of sequence isomerism of the monomer units in head-to-tail, tail-to-tail, and head-to-head structures.

3.2 COMMERCIAL IMPORTANCE OF ADDITION POLYMERS

3.2.1 SIMPLE ADDITION

Some of the simple addition polymersare displayed in Figure 3:

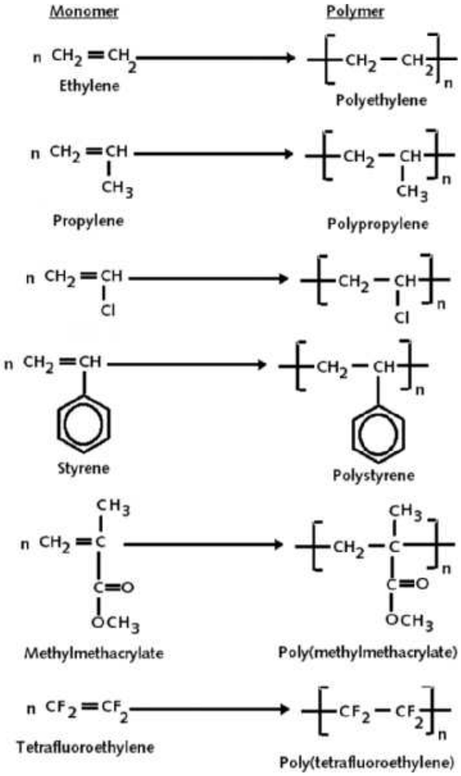


Figure 3. Addition polymerization of small molecules.

3.2.2 END GROUPS ADDITION

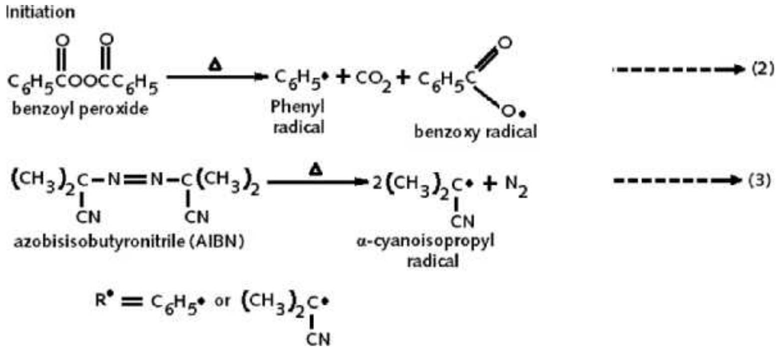
A type of addition polymerization reaction is that wherein the end groups on the reacting monomers add on to each other to produce quite new groups. An example is the reaction of an isocyanate with an alcohol to form a urethane (Eqs (1)), thus:

$$\mathrm{RNCO + HOR' \longrightarrow RNHCOOR'} \quad \dashrightarrow \quad (1)$$

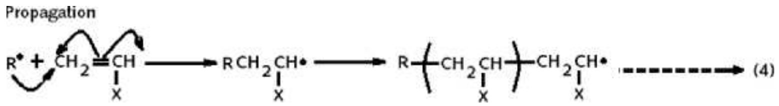
Substituents play a significant role in chain polymerization because polymerizability of a vinyl monomer by a radical, anionic, or cationic mechanism is dependent upon the steric and electronic properties of the substituents. The electronic effect of the substituent manifests itself by altering the electron density of the double bond through inductive and resonance effects and its ability to stabilize the active species, whether it is a radical, anion, or cation.

3.2.2.1 Reaction mechanism

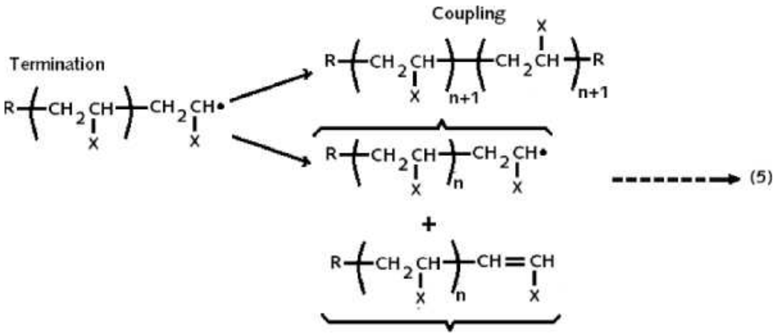
Reaction is initiated by an initiator, which generates free radical fragments that are incorporated as an endgroup in the polymer chain. The chain grows rapidly to its final molecular weight, and then the reaction is terminated. The purpose of a catalyst is to initiate the reaction by decomposing to generate reactive free radicals (Eqs (2) and (3)). Molecular weight of the polymer and the end-group content is useful to establish the ratio of termination. Two growing radicals present even in exceedingly small concentrations will find each other and react to give stable molecules by competing reaction either coupling or disproportionation as reaction termination. Coupling produces polymer with complete termination and disproportionation produces only one radical fragment per polymer molecule.



Radical (R^o) can rapidly attack the monomer. The product obtained must also be a radical, which can again in turn attack the monomer (Eq (4)).



Transfer reactions can be considered to be cessation reactions. They terminate the growth of any particular chain with no effect on the overall rate of polymerization because a new active nucleus is produced as each growing chain is terminated (Eq (5)).They may play an important role in the formation of branched chains. Polymers contain thousands of monomer units and may be completed within a few seconds. However, conversion of all monomersto polymers may require a long time:



3.2.3 FREE RADICAL OR LIVING POLYMERIZATION

Living polymerization proceeds with fast and usually quantitative initiation followed by polymer chain growth and, what is most important, no irreversible termination. Living polymerization works well not only for anionic polymerization of resonance-stabilized monomers such as styrene but also for other polar monomers if the reaction conditions are well controlled. It also works for certain cationic and radical polymerizations. Stereospecific living polymerizations that have recently been developed give stereoregular living polymers with narrow MWDs.

Free or living radical polymerizations [8–15] differ from other polymerizations in the following ways:

- Much of organic chemistry is not associated with polymerization.
- Most of the free radical polymerization reactions are of carbon–hydrogen bonds in aliphatic compounds and side chains in aromatic compounds.
- Involve most oxidation with oxygen, most halogenations and most degradation by oxygen, heat, or radiation.
- Formation of high-molecular-weight polymers even with low conversion of monomer.
- Propagation reaction in free radical polymerization is rapid [16, 17].

In a free radical reaction, the reacting radical with one electron less corresponds to a relatively stable positive ion, and the product radical with one electron corresponds to relatively stable negative ion or vice versa, then reaction is facilitated. Free radical polymerizations follow initiation, propagation, and termination process. Initiators of polymerization can be peroxides, persulfates, azo compounds, and others. Chain transfer occurs between the growing propagating radical with a nonradical substrate. Free radicals produce a polymer and a new radical capable of adding more monomers. Termination can occur while the propagating radical reacts with a primary radical.

Freeradical polymerization is one of the most important commercial processes leading to high-molecular-weight polymers, because a wide variety of monomers can be polymerized and copolymerized under relatively simple experimental conditions [16]. Free radical reactions in polymerization depend upon

- Resonance stabilization of reaction species. The more a reacting radical is stabilized by resonance, the less reactive it is, and vice versa. However, formation of species with more radicals from a substrate is stabilized by resonance, and then easier the substrate reacts.
- Polar effect in free radical reactions is interpreted as dipole or electrostatic effect or in terms of donor and acceptor properties, or as contributions of ionic resonance structures to the activated complex.

Free radical polymerization finds application in the synthesis of polymers that include methacrylates, styrene, chloroprene, acrylonitrile, ethylene, and many other copolymers of vinyl monomer. They are subjected to many complications. A high percentage of organic groups will promote organic solubility, which is important in certain types of polymerizations such as suspension reactions. Water-soluble initiator such as potassium persulfate, the potassium salt form, is quite soluble in aqueous media. Induced decomposition of peroxide molecule (Eq (6)) can be done by the use of additional compounds that can transfer an electron to an oxygen–oxygen bond and facilitate its decomposition into a mixture of anion, cation, and radical species. Metal salts are capable of transferring an electron, thus inducing decomposition of a hydroperoxide into a number of species including alkoxy-type radicals.

Free radical polymerization of styrene

Radical formation

$$\text{Initiator} \xrightarrow{\text{heat or light}} \underset{\text{radicals}}{2\,R\bullet} \quad \dashrightarrow (6)$$

Step I

Free radical addition to double or triple bond

Addition of free radical (Eq (7)) to styrene monomer and successive additions:

$$R\bullet + H_2C{=}CH\phi \longrightarrow R\left(H_2C-CH\phi\right)\bullet \quad \dashrightarrow (7)$$

The process of free radical addition that produces radical by adding monomer (Eq (8)) is

$$R\left(H_2C-CH\phi\right)^{\bullet}_{n} + H_2C{=}CH\phi \longrightarrow R\left(H_2C-CH\phi\right)^{\bullet}_{n+1} \quad \dashrightarrow (8)$$

Step II

Radical displacement reaction

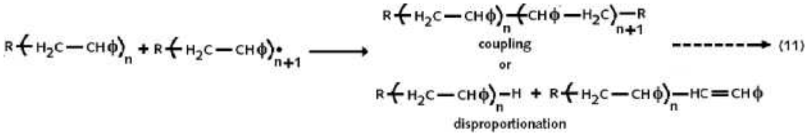
Abstraction of a univalent atom is from another molecule with formation of styrene radical with a free valence on a terminal styrene unit with carbontetrachloride (CCl_4) (Eq (9)). If a styrene radical has displaced a trichloromethyl radical from a chlorine atom, "chain transfer" occurs (Eq (10)). The activity (free valence) of one molecule has been transferred to another molecule. Halogen as well as hydrogen atoms are commonly transferred.

$$R\left(H_2C-CH\phi\right)^{\bullet}_{n} + CCl_4 \longrightarrow R\left(H_2C-CH\phi\right)_{n}-Cl + Cl_3C\bullet \quad \dashrightarrow (9)$$

$$Cl_3C\bullet + H_2C{=}CH\phi \longrightarrow Cl_3C-H_2C{=}CH\phi\bullet \quad \dashrightarrow (10)$$

Step III

Free radicals may react with other radicals only by coupling. Radicals may react with β-hydrogen atoms either by coupling or by disproportionation (Eq (11)):



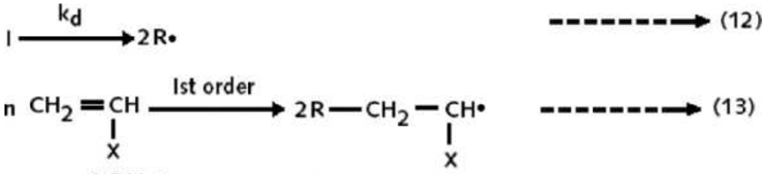
$$R\left(H_2C-CH\phi\right)_{n} + R\left(H_2C-CH\phi\right)^{\bullet}_{n+1} \longrightarrow \begin{cases} R\left(H_2C-CH\phi\right)_{n}\left(CH\phi-H_2C\right)_{n+1}-R & \text{coupling} \\ \text{or} \\ R\left(H_2C-CH\phi\right)_{n}-H + R\left(H_2C-CH\phi\right)_{n}-HC{=}CH\phi & \text{disproportionation} \end{cases} \quad \dashrightarrow (11)$$

While freeradical polymerizations require the absence of oxygen, they can be conducted using water as a solvent or additive. A significant drawback to these polymerizations, however, is that they yield polymers with uncontrolled molecular weights and high polydispersities, which precludes the synthesis of well-defined polymers with low polydispersities and complex architectures [18].

3.2.3.1 Reaction mechanism and kinetics of free radical polymerization

<u>Initiation step</u>

Initiation step involves the decomposition of an initiator such as peroxide or azo compound to yield two radicals per molecule of peroxide (Eq (12)). Each radical is capable of initiating one monomer molecule (Eq (13)):



$$I \xrightarrow{k_d} 2R\bullet \quad \dashrightarrow (12)$$

$$n\ CH_2{=}\underset{X}{\underset{|}{CH}} \xrightarrow{\text{Ist order}} 2R{-}CH_2{-}\underset{X}{\underset{|}{CH\bullet}} \quad \dashrightarrow (13)$$

$$R_i = d\frac{[\bullet RM\bullet]}{dt} = 2k_d\,[I]$$

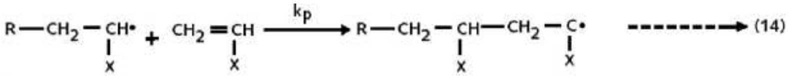
(two chains started)

<u>Propagation step</u>

Propagation involves the rapid addition of additional monomers to the initiated species.

Assumptions:

- All chains have the same reactivity.
- Initiation step only involves reaction of one monomer.
- Propagation involves addition of many monomers (Eq 14)).



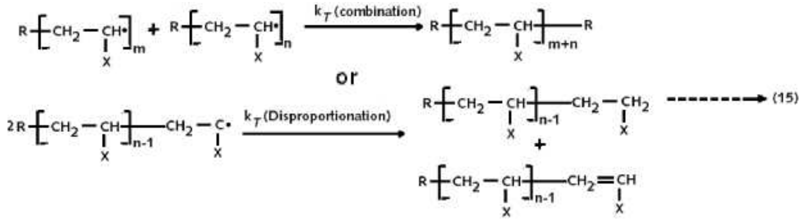
$$R{-}CH_2{-}\underset{X}{\underset{|}{CH\bullet}} + CH_2{=}\underset{X}{\underset{|}{CH}} \xrightarrow{k_p} R{-}CH_2{-}\underset{X}{\underset{|}{CH}}{-}CH_2{-}\underset{X}{\underset{|}{C\bullet}} \quad \dashrightarrow (14)$$

$$RM_n^\bullet + M \xrightarrow{k_p} RM_{n+1}^\bullet$$

$$\boxed{R_p = k_p[M]\,[M\bullet]}$$

Termination step

Termination of two growing radicals occurs by either combination or disproportionation (Eq (15)) to yield saturated polymer molecules:



$$\boxed{R_T = 2k_T[M\bullet][M\bullet]}$$

Steady state

$$\boxed{R_i = R_T \text{ or } [M\bullet] = \left(k_i/k_T\right)^{1/2}[I]^{1/2}}$$

Polymerization rate

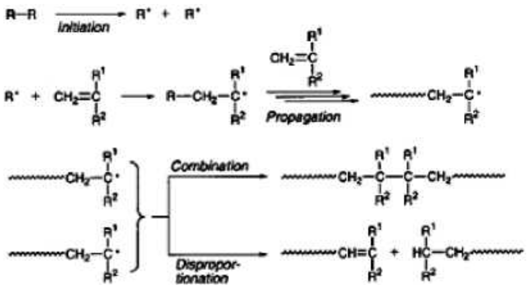
$$\boxed{R_{Po} = k_{P_o}\left(k_i/k_T\right)^{1/2}[M][I]^{1/2}}$$

Where R_i = rate of initiation, R_p = rate of propagation, R_{po} = rate of polymerization, R_T = rate of termination, k_i = rate constant = initiation, k_d = rate constant = dissociation, k_t=rate constant – termination, [M] = Monomer concentration, $[M\bullet]$= Monomer radical concentration, and [I] = initiator concentration

3.2.4 RADICAL POLYMERIZATION

In radical polymerization, growing radical species rapidly reacts with the C=C double bonds of the monomers, which significantly exist in the reaction media, to yield the polymers efficiently.

In the reaction, even radical chain (Eq (16)) presents at a very low concentration, the growing radical species react rapidly. During termination or hydrogen abstraction, the radical species are relatively slow abstraction from C-H bonds in the polymers or solvent to induce chain transfer reaction. The conventional mechanism of radical reaction is outlined in Eqs (17) and (18).



(16)

(17)

(18)

3.2.5 ATOM TRANSFER RADICAL POLYMERIZATION

Polymeric materials require complete control of physical, mechanical, and thermal properties. Therefore, it has the right characteristics appropriate for a wide variety of applications. Atom transfer radical polymerization provides a simple way to synthesize well-defined polymers with control molecular weights and narrow molecular weight distributions [19]. The catalyst plays a key role in an ATRP process. It is well-known that the ligand in the ATRP catalyst system provides appropriate solubility and an adjustable redox potential to the metal complexes. Therefore, the selection of ligand is extremely important to achieve high activity for the catalyst. As for the iron-mediated ATRP, these ligands such as organic acid, triphenylphosphine, and oniumsalts are usually used [20–22].

3.2.6 ANIONIC POLYMERIZATION

Anionic [23–28] polymerization is the best methodology to synthesize polymers with predictable molecular weights and narrow molecular weight distributions. It may ideally control molecular weight, molecular weight distribution, stereochemistry, chain-end functional groups, polymer architecture, and sequence distribution. Well-controlled block copolymers with precise molecular architectures can be prepared through this polymerization method [29–35].

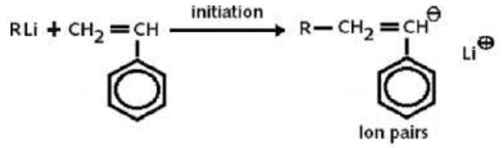
Polymers obtained through anionic polymerization are not homogeneous and have low molecular weights based on the catalyst used and experimental conditions. Critical catalyst concentrations are necessary to start polymerization, and activation energy is usually small. Copolymers composition control is very difficult by anionic mechanism [29–32].

Anionic polymerization differs from other polymerization in the following ways:

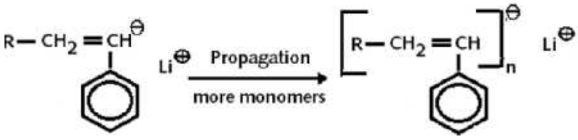
- Occurs with initiation and propagation steps
- No termination step presents in the strict absence of water, oxygen, and others.
- Sensitive to experimental conditions and difficult to control and reproduce. Polymers obtained are not homogeneous. It has low molecular weight that depends on the catalyst used and experimental conditions.
- Affected by the presence of foreign substances, which may act either as promoters or as retarders.
- Possible to predict molecular weight on the basis of ratio of monomer to the initiator concentration.
- Difficult to study the reaction mechanism.

Hydrocarbon monomers like styrene or butadiene, and hydrocarbon solvents like cyclohexane or benzene with initiators such as organolithium enhance stability of the carbanion relative to other chain intermediates such as radicals or even carbonium ions. Each initiator present may start one chain. Polymerization produces synthetic polymers that have a very narrow molecular weight distribution. Anionic chain end can have SP_3 type bonding associated with radicals or carbonium ions.

Styrene monomers are polymerized not only by anionic but also by free radical and cationic mechanisms. Styrene and other vinyl monomers are polymerized by butyl lithium (Eq (19) and (20)). Vinyl monomers such as acrylonitrile, acrylamide, and methylmethacrylate have electron-attracting groups attached to the vinyl group. The groups attached to vinyl make the double bond acidic and therefore more responsive to anionic catalysts. Methacrylonitrile will polymerize rapidly at low temperature on using sodium in liquid ammonia as catalyst.



--------→ (19)



--------→ (20)

3.2.7 CATIONIC POLYMERIZATION

In polymerization, catalytic methods are free radical and ionic mechanisms. In ionic polymerization, cationic polymerization is more preferred than anionic polymerization. Monomers (Figure 4) with suitable electron-releasing alkyl groups (Eq (23)) or ether bond will polymerize through cationic polymerization (Eqs (23), (24), and (25)) and the cationic chain end, also referred to as carbonium ion. The electron enrichment may occur by either inductive or resonance effects. Monomers that undergo cationic polymerization are

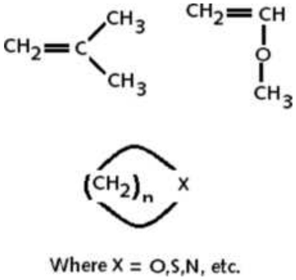


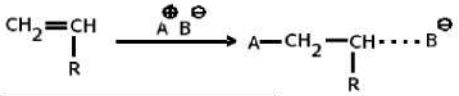
Figure 4. Some of the monomers—Cationic polymerization

In cationic polymerization,

- Chain growth end will have much Sp2 type hybridization in bonding (Eq (26)).
- Chain reactions have shorter lifetimes.
- Initiation by a variety of homogeneous or heterogeneous Lewis acids such as BF_3, $TiCl_4$, $AlCl_3$, and $Al(C_2H_5)Cl$.
- Reaction may require either a proton donor such as water or a cation donor.
- Carbonium ions can undergo many reactions such as alkylation and isomerization with lowering molecular weight.
- Temperature control is an important factor.
- Polymers are not stereoregular, and commercial utility has been quite limited.

Mechanism and kinetics of cationic polymerization

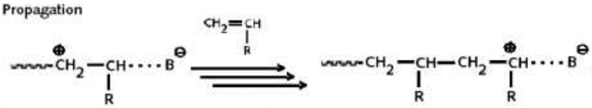
Initiation



(23)

$$\boxed{R_i = d[M+]/dt = k_i[I][M]}$$

Propagation



(24)

$$\boxed{R_p = -d[M]/dt = k_p[M+][M]}$$

Termination

(25)

$$\boxed{R_t = -d[M+]/dt = k_p[M+]}$$

Chain transfer or chain-breaking reactions can effectively compete with the chain growth step.

Chain transfer

(26)

Steady state

$$\boxed{R_i = R_T \text{ or } [M+] = \left(k_i/k_T\right)[I][M]}$$

Polymerization rate

$$\boxed{R_{P_o} = k_{p_o}\left(k_p k_i/k_T\right)[I][M]^2}$$

Where R_i = rate of initiation, R_p = rate of propagation, R_{po} = rate of polymerization, R_T = rate of termination, k_i = rate constant = initiation, k_d = rate constant = ionization, k_t = rate constant – termination, [M] = Monomer concentration, [M+]= Monomer ion concentration, and [I] = initiator concentration.

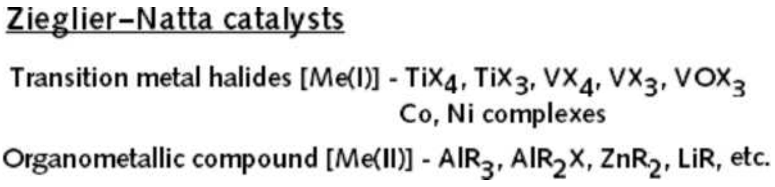
In styrene polymerization, propagation made by cation likely results in color formation. Cationic polymerization with a nonionic intermediate probably involves the perchlorate ester of polystyrene chain as the growing species rather than either the free ion or the corresponding ion pair. Either anhydrous perchloric acid or phenylethyl perchlorate added to an excess of styrene results in polymerwhich is occurred and the initiation likely across the styrene double bond. Cationic propagations are presumed to occur to form polystyrene.In the cation polymerization, the solution is colorless.Most of the styrene used up,a red color formation with increased rate of polymerization which results in rapid completion of polymerization[36].

3.2.8 COORDINATION POLYMERIZATION

Ziegler–Natta catalysis greatly expanded the idea that ionic polymerization can be stereochemically controlled through coordination of the growing chain end with its monomer and counter ion. In coordination polymerization, the catalysts used are similar and often identical to Ziegler–Natta polymerization, i.e., a transition metal compound along with an organometallic alkylating agent. Me(II) alkylates reduces Me(I) and alkylated Me(I) is responsible for chain growth is generally agreed. Some of the Ziegler–Natta catalysts are displayed in Figure 5.

METALLOCENE CATALYSTS

Metallocene catalysts are in many ways a more attractive industrial alternative to traditional Ziegler–Natta systems in view of their high degree of control over molecular weight, molecular weight distribution, and tacticity. Control of polymer properties through catalyst design is still in progress. Metallocene catalysts enable control over the whole range of molecular weights from oligomer to ultrahigh-molecular-weight polymers and microstructures with stereoregularity, regioregularity, and comonomer distribution of polyolefins in a very wide range. These catalysts are making possible the synthesis of improved and new polyolefin materials.



Zieglier–Natta catalysts

Transition metal halides [Me(I)] - TiX_4, TiX_3, VX_4, VX_3, VOX_3
Co, Ni complexes

Organometallic compound [Me(II)] - AlR_3, AlR_2X, ZnR_2, LiR, etc.

Figure 5. Organometallic compounds as Ziegler–Natta catalysts

Coordination polymerization (Figure 6) is

- Used to produce linear high-density polyethylene, linear low-density polyethylene, isotactic polypropylene, and various ethylene propylene co- and terpolymers.
- Catalysts may themselves be deposited on supports such as silica or alumina.
- Free radicals produced not involved in reactions.
- Availability and stability of coordination sites can be influenced by the metal alkyl.
- Coordinate species must undergo cisarrangement to both yield the stereoregular placement and produce a new vacancy in the transition metal structure. Therefore, it may coordinate with the next monomer unit as a propagation step (Figure 7).
- More consistent with an isotactic polymer during polymerization.
- Molecular control is required.

OLEFIN POLYMERIZATION

Olefin polymerization is a perfect example of the application of organometallic chemistry to homogeneous catalysis [37]. Metallocene-based catalysts are outstanding for scientific and technological development. Metallocenes are employed in the industrial and preindustrial production of several different ethane-based polymers. It is used in different processes from solution to slurry to gas-phase polymerization. Novel polyolefin structures such as random, stereoblock, and syndiotacticpolyolefins are made in the presence of titanium-based and chromium-based catalysts, with understanding of the catalyst structure/polymerization mechanism/polymer–structure relationships and, in part, as a consequence of it. Major part of research have been carried out in industrial laboratories, due to heavy investment is required.

Highly isotactic polypropylene is not as efficient until the feasibility of adapting metallocene catalysts to the production of propene-based materials such as isotactic and syndiotacticpropylenes. Only the benefit would come from the optimization of the catalyst stereoselectivity. Symmetry stereocontrol relationships offer opportunities and intrinsically interesting on catalyst [38]. The design of metallocene catalysts has led to a series of new polypropene microstructures, like highly syndiotactic materials, hemi-isotactic chains [39], and atactic-isotactic block structures [40,41].

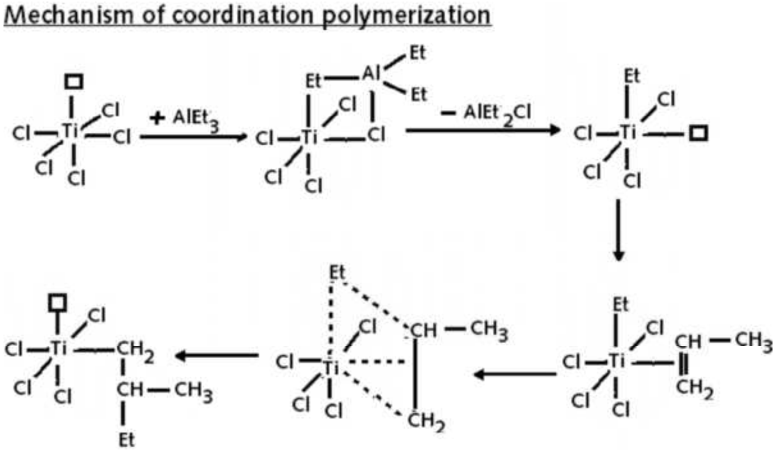

Mechanism of coordination polymerization

Figure 6. Coordination polymerization

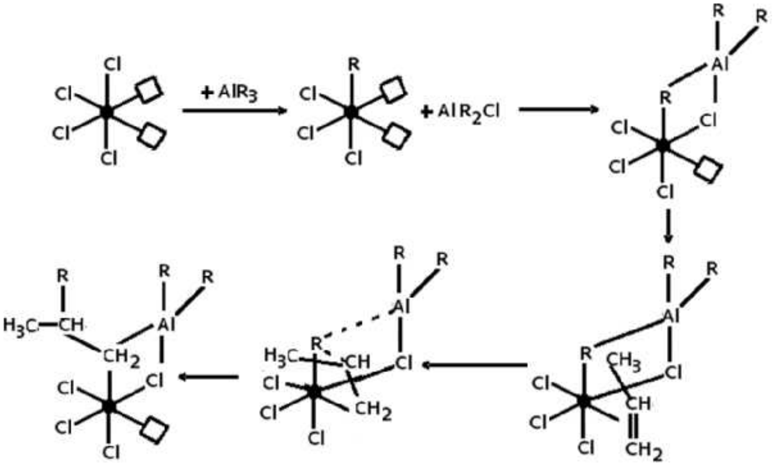


Figure 7. Coordinate species undergo cisarrangement

Metallocene complexes have initiated a renaissance in the field of catalytic olefin polymerization [37,42–44], which was established in the 1950s with the Ziegler–Natta and Philips catalysts.

Metallocene catalysts provide the following:

- Homogeneous nature provides active sites for every molecule in solution.
- Potential to polymerize prochiral olefins, such as propylene, to give stereospecific polymers. Metallocene catalysts (A, B, and C) (Figure 8) produce syndiotactic, hemitactic, and isotactic polymers.

- Ability to produce polyolefins with narrow molecular weight with single-site catalysts.
- To produce polyolefins with regularly distributed short- and long-chain branches.
- Heterogenization provides different active sites than those in solution and can have an enormous effect on the catalyst activity and the properties of the produced polyolefins in terms of molecular weight, branching, and stereospecificity.

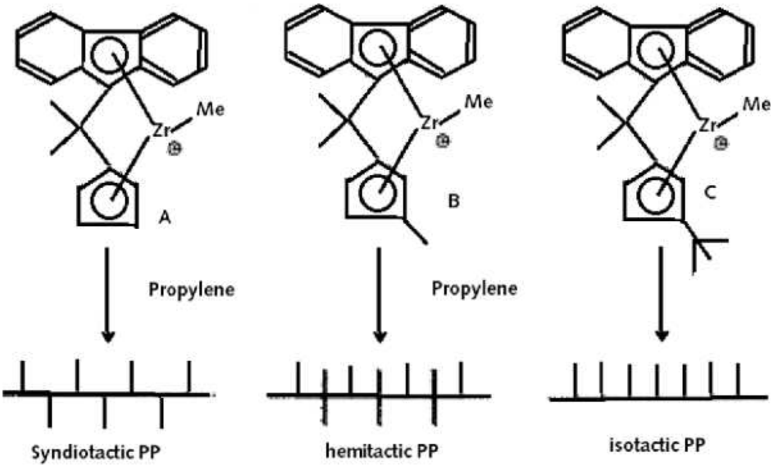


Figure 8. Syndiospecific, hemispecific, and isospecificmetallone catalysts

The insertion step consists of an alkyl migration to the olefin ligand, and a new free coordination site is generated at the vacant position of the former alkyl ligand. A smaller, less bulky substituent (B) leads to a catalyst precursor that produces hemitactic polypropylene, which exhibits a random configuration on every second monomer unit [45–47]. Also, the chain end of the growing polymer can control the stereochemistry of the polymerization as a catalyst produces isotactic polypropylene [48].

The polymerization of olefins to polymers with different microstructures and properties continues to be one of the most investigated areas for both industrial and academic laboratories in polymer science. The use of polyolefins is rapidly growing due to the fact that polyolefins are made from simple and easily available monomers [42]. New or improved properties are achieved by combining new monomers in copolymer systems, or by using new catalysts. Forty years after the discovery of the metallorganic catalyzed polymerization of olefins by Ziegler and the stereospecific polymerization of propene and a-olefins by Natta, the use of metallocene catalysts shows the way to expand the possibilities of olefin polymerization and the properties of the resulting polyolefin materials. One consequence of the development of new ‘‘tailor-made’’ polyolefins is the need for new and improved analytical techniques. In addition to monitoring the polymerization process, the molecular heterogeneity of the resulting products must be described by suitable methods. Information on molar mass distribution, chemical composition, tacticity, and branching is required to properly evaluate the polyolefin. Very frequently, polyolefins exhibit multiple distributions, e.g., long-chain branching and molar mass distribution in low-density polyethylene (LDPE) or chemical composition distribution and molar mass distribution in linear low-density polyethylene (LLDPE), copolymers, and polyolefin blends [49]

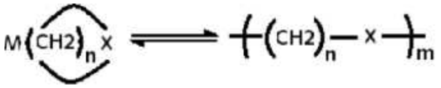
3.2.9 RING-OPENING POLYMERIZATION

Ring-opening polymerization can occur by addition or condensation. Addition polymerization involves repeated addition of a monomer to the chain end, which leads to an increase in the molecular weight. Syntheses of commercially important polymers are carried out by ring-opening polymerization (Eq (27)).Common polymers such as nylon6 (Eq (28)), polyoxyethylene (Eq (29)), polybutyleneoxide (Eq (30)), and polyethyleneimine (Eq (31)) are obtained by attack on the monomer either by chain ends or by internal group of the growing polymer. These competing reactions lead to a highly branched polymer structure. It is possible under this condition that rates of initiation and propagation are higher than termination and inter- and intra-chain reactions; there is exquisite control over the molecular weight, and distribution is possible [50]. The second class of addition polymerization reactions is one wherein a ring compound breaks and the individual units join together linearly.

Ring-opening polymerization is

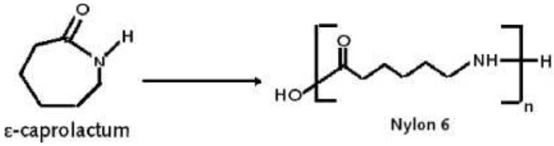
- The process of transforming a heteroatom containing ring to a linear chain.
- A process involving anionic, cationic, or coordination initiation (catalysis).
- Only in special situations have free radical initiators been successful.

Thermodynamics of ring-opening polymerization is driven by the enthalpy of the ring opening. The kinetics and selectivity of the ring-opening process are strongly influenced by the nature of the reactive chain ends, the monomers, and the presence of catalysts. Catalytic steps in a ring-opening polymerization must occur with the correct relative rates to yield a well-controlled reaction. Cyclic monomers that undergo ring-opening reactions are shown as

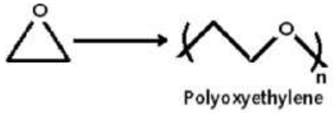


(27)

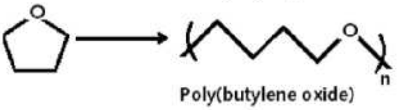
Polymerization of both aliphatic and semialiphaticpolymers with catalyst or initiators follows either ring-opening polymerization of cyclic esters, which includes cyclic carbonates and cyclic oligomers, or polycondensation of α,ω-dihydroxyalkanes with dicarboxylic acids or their di(m)ethyl esters [7]. Some of the monomers and their polymers by ring-opening polymerization are given as follows:



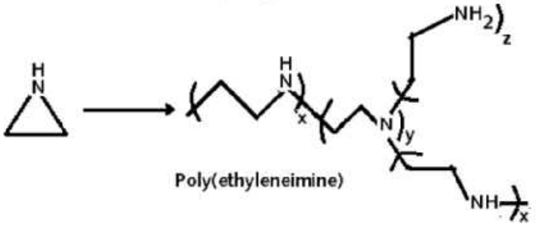
(28)



(29)



(30)



(31)

3.2.10 COORDINATION–INSERTION POLYMERIZATIONS

Coordination–insertion mechanism (Figure 9) consists of the coordination of the monomer to the Lewis acid metal center. Monomer subsequently inserts into one of the aluminum alkoxide via nucleophilic addition. Ring opening follows through acyl-oxygen cleavage, and hydrolysis of the active metal alkoxide bond leads to the formation of a hydroxyl end group.

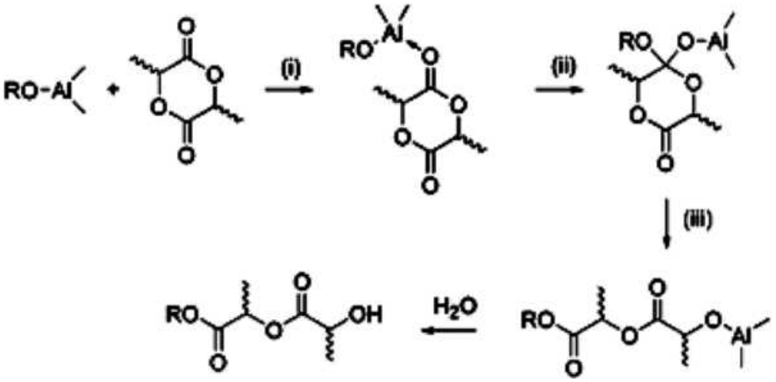


Figure 9. Coordination–insertion mechanism. [Reprint with permission from Dechy-Cabaret, O., B. Martin-Vaca, and D. Bourissou. 2004. *Chemical Reviews* 104, pp. 6147–76. Copyright © 2004, American Chemical Society. All rights reserved.]

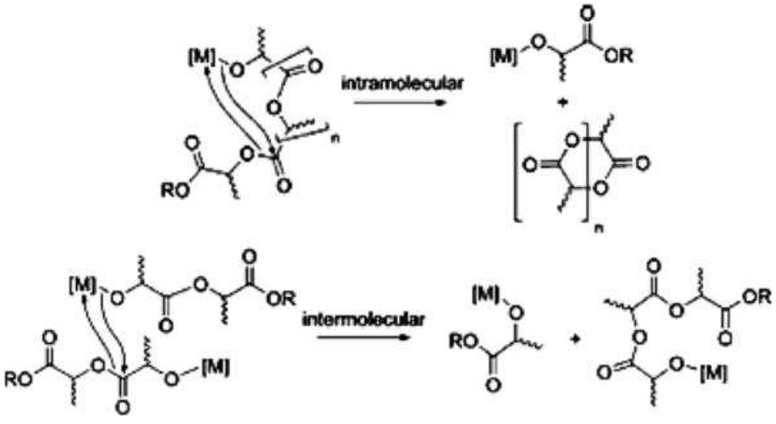


Figure 10. Side reactions (Intramolecular and Intermolecular transesterification)—Coordination–insertion polymerization. [Reprint with permission from Dechy-Cabaret, O., B. Martin-Vaca, and D. Bourissou. 2004. *Chemical Reviews* 104, pp. 6147–76. Copyright © 2004, American Chemical Society. All rights reserved.]

In coordination–insertion polymerizations,

- From the extent of transesterification side reaction, efficiency of the molecular weight control depends on the ratio $k_{propagation}/k_{initiation}$. These transesterification reactions can occur both intramolecularly (backbiting leading to macrocyclic structures and shorter chains) and intermolecularly (chain redistributions) (Figure 10) [51,52].
- Side reactions result in broader molecularweight distributions, sometimes making the molecular weights of the resulting polymers irreproducible.
- The extent of these undesirable transesterification reactions was found to depend strongly on the metallic initiator [53].

The occurrence of such a large amount of intramolecular backbiting is related to the higher stability of the cyclic moiety (Figure 11).

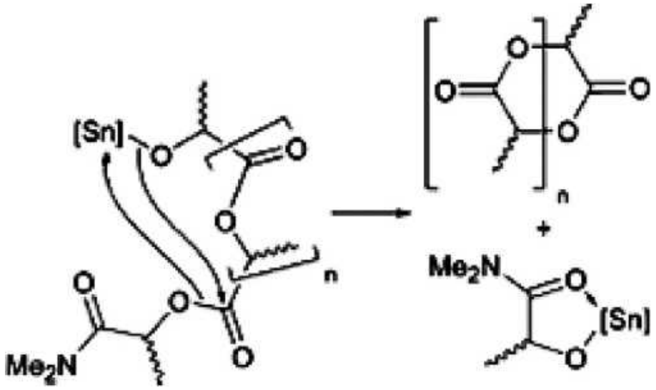


Figure 11. Intramolecular backbiting—Coordination insertion polymerization. [Reprint with permission from Dechy-Cabaret, O., B. Martin-Vaca, and D. Bourissou. 2004. *Chemical Reviews* 104, pp. 6147–76. Copyright © 2004, American Chemical Society. All rights reserved.]

3.2.11 METATHESIS POLYMERIZATION

Metathesis polymerization [54–56] differs from all other polymerizations (radical, cationic, anionic, or Ziegler–Natta). It is unique in that all the double bonds in the monomer remain in the polymer. Olefin metathesis is a metal-catalyzed reaction in which the alkylidene groups of olefins are scrambled. When the reaction is carried out with a cyclic olefin, the product is a linear ring-opened polymer with double bonds in the backbone. Acyclic olefins act as a chain transfer agent in the metathesis polymerization of cyclic olefins, and are frequently added to control the molecular weight. Since the alkylidene units of the acyclic olefin become the end groups of the polymer, this is a method of controlling the chain-end functionality.

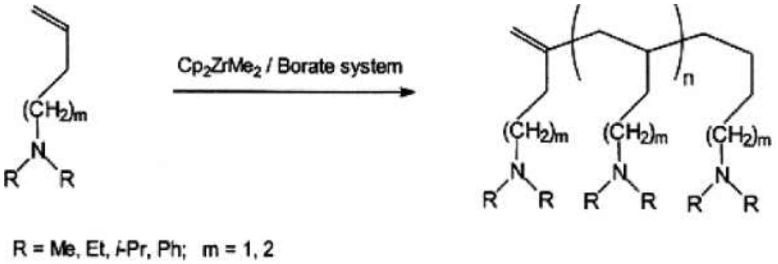


Figure 12. Homopolymerization of amino-functionalized -olefins [Reprint with permission from Stehling, U.M., K.M. Stein, M.R. Kesti, and R.M. Waymouth. 1998. *Macromolecules* 31, no. 7, pp. 2019–27. Copyright © 1998, American Chemical Society. All right reserved.].

3.3 CONDENSATION POLYMERIZATIONS

Condensation polymerizations (Eqs (32) and (33)) are often equilibrium reactions, and by-product must be removed to derive the reaction to completion. Only single-reaction sequence is involved in the synthesis of condensation polymers. Polar reaction results in bond formation. Each step in this polymerization is independent of the other, and there are no chain reactions.

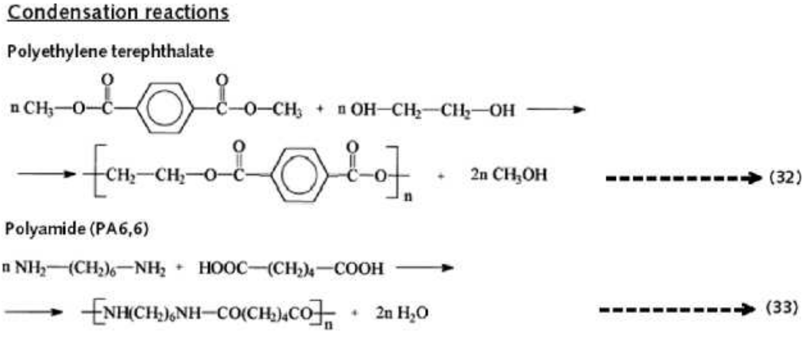
Condensation polymers are classified as those that are obtained by reacting two different functional groups that originate from different monomers. The first step is the polycondensation reactions. Condensation reactions involve the following:

1. Reactions—one reaction is responsible for polymer formation. Easy to control chain structural regularity during condensation reaction. Monomers react so as to eliminate small, stable molecules such as H_2O, HCl, or NH_3.
2. Polymer growth—any two molecular species present can react slowly with random growth. Involved in repetitive sequence of simple condensation reactions, and reactants are limited to only

two reactive groups per molecules. Resembled as linear addition polymers; however, mechanism and kinetics of the reaction are entirely different.

3. Molecular weight—rises steadily throughout the reaction. High conversion of monomers is required for high-molecular-weight polymer. Exhibit more narrow distribution of molecular weight compared with addition polymers and proceeds by individual reactions of the functional groups on the monomers. Produced polymers are high-molecular-weight species and difficult to control.
4. Monomer concentration—monomer disappears in the early stages of the polymerization.
5. Composition—Concerned reaction demands chemical purity and accurate control of quantities and composition of the polymerization reaction; relatively broad distribution of molecular species is present throughout the course of polymerization.

Reactions occur stepbystep as well as formation of polymer with increase in molecular weight as reaction proceeds in condensation polymerization. Reactions proceed with extremely high conversion in order to obtain high molecular weights. Premature growth of chains happens with exact balancing ratios of reactants, and to rigorously exclude monofunctional contaminants would terminate the reaction. Therefore, condensation polymerization [57] involves the industrial syntheses of polyamides (Nylon) and polyesters.



CONDUCTING POLYMERS

Electrically conducting polymers are a novel class of synthetic metals that combine the chemical and mechanical properties of polymers with the electric properties of metals and semiconductors.

Conducting polymers are a new class of electronic materials with the discovery of polyacetylene. It could be doped charge-transfer reactions with an oxidizing or reducing agent [58]. Doped polymers exhibit a dramatic increase in conductivity [59,60]. Organic conducting polymers exist in highly anisotropic quasi-one-dimensional structure charge-transfer salts. In the conducting state, both these types of materials are ionic. In conducting polymers, the chain-like structure leads to strong coupling of the electronic states to conformational excitations. Some of the conducting polymers are mentioned in the following figure:

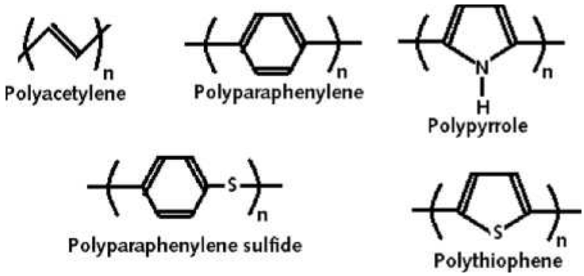


Figure 13. Conducting polymers

Conjugated polymers have many interesting electrical and optical properties and profound applicability in inherently transporting materials, light-emitting displays, rechargeable batteries, and electrochemical devices and sensors [61–64]. Electrochemical polymerization for the conjugated polymer is useful because it can be carried out at room temperature and homogeneous polymer films can be formed directly at the electrode surface so the film thickness is well controlled. One of the most attractive properties of the conjugated polymers is a so-called electrochromism, where the polymer changes in color upon an electrochemical reduction/oxidation (redox) [65,66]. Electrochromic polymers give switchable functions and controllable optical properties [67].

3.4 ELECTROPOLYMERIZATION

Electrochemical formation of conducting polymers is a unique process that is similar to electrodeposition of metals since it proceeds via a nucleation and phase-growth mechanism [68-70]. In electropolymerization, the charged species precursors of the deposited material (Figure 14) must be initially produced by oxidation of the neutral monomer at the electrode surface:

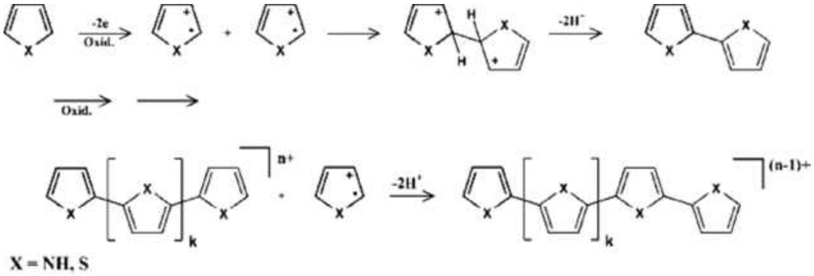


Figure 14. Electropolymerization—charged species precursors of the deposited material [Reprint with permission from Heinze, J., B.A. Frontana-Uribe, and S. Ludwigs. 2010. *Chemical Reviews*110, pp. 4724–71. All rights reserved. Copyright © 2010, American Chemical Society]

Electrochemical reactions (Figure 15) require an important overpotential to proceed at an appreciable rate. This is particularly true when the reaction does not merely consist of an outer sphere electron transfer between the electrode and a reactant but gives rise to bond breaking and bond formation, involving more than one reactant and one product, which may trigger the uptake or release of additional electrons [71]. Electropolymerization mechanism is a very complex problem. It has many experimental variables such as solvent, concentration of reagents, temperature, cell geometry, nature and shape of the electrodes, and applied electrical conditions.

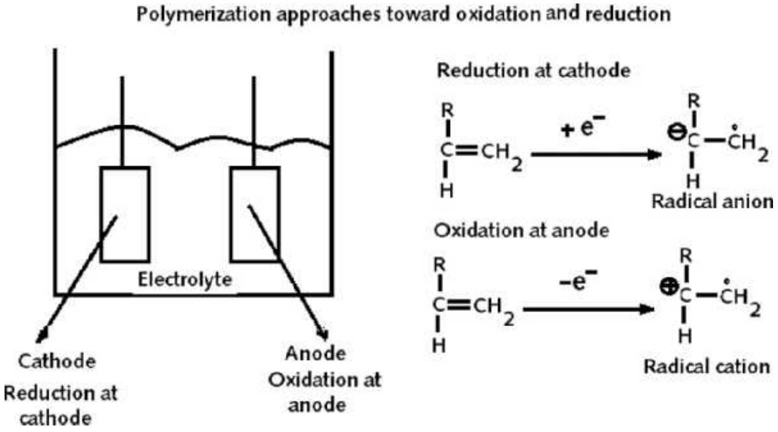


Figure 15. Electropolymerization technique

Electrosynthesis conditions determine, to a large extent, the structure and properties of the resulting polymer. Electrosynthesis conditions constitute a complex problem owing to the interdependence of experimental variables, the analysis of the effects of an individual parameter [72]. Electropolymerization of aromatic monomers is a straightforward route to conjugated polymers, which allows the formation of polymeric films directly on electrodes. In the field of electropolymerization, a variety of different polymers are easily accessible and usually obtained as films directly on the applied electrodes.

Electrochemical polymerization became a widely used procedure for quick generation of conducting polymers. The main reason is the high application potential of conducting polymers (CP) in chemical and biological sensors. Electrochemical polymerization uses an initial electrochemical step, generally oxidation via an applied potential to generate the radical ion.

One drawback of this synthesis route, however, is that mostly insoluble films are obtained that do not allow for an in-depth chemical characterization. In contrast to that, the chemical synthesis allows for control and characterization of the obtained structures, and material properties of the branched polymers have the inherent advantage of a higher number of end groups, which enables the facilevariation of material properties, e.g., solubility.

3.5 FUTURE TRENDS

Polymers can be used to synthesize new materials for biomedical and electronic applications [73].Polymer synthesis holds the potential to enable systematic methods for advanced polymer materials. In future, polymerization methods can be used systematically to control polymer properties and chemical identity of branches.

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CHAPTER 4

POLYMER SYNTHESIS

Polymer synthesis has been revolutionized by the introduction of polymerization techniques [1,2]. The development of polymeric materials critically relies on the synthesis of polymers. Polymer synthesis may involve a simple repetition of classical organic reactions such as esterification. An important factor in polymer synthesis is the permissible rise in temperature during polymerization of the monomer in the reactor. The key to generating the polymer is precise control over the spatial position to be occupied by chemical groups into polymer structures or perform complex functions to accommodate chemical groups.

Polymer synthesis starts with many monomers as starting material. Not only monomers but also their substituted derivatives undergo polymerization reactions to improve materials' properties. The discovery and development of new chemical reactions is the major focus of synthesis and research activity in polymer chemistry. Polymer synthesis has traditionally been the arena in which the utility of new reactions is critically evaluated. Therefore, new methods and creative strategies have arisen from the activity [3,4]. Hence, polymer synthesis constitutes a large proportion of commercially manufactured organic materials.

Carothers classified macromolecules by types of compounds that are capable of polymerizing and by the types of polymerization. Even today, this classification is a commonly used strategy and is extremely useful to clarify the difference between macromolecules made by step-, chain-, or ring-opening polymerizations. Many different polymers are made following these three mechanisms, and although large variety of modern polymerization techniques, such as metathesis, living ionic, and radical polymerizations, were added, they all follow Carothers' classification.

Different polymerization techniques result in polymers with different molecular architecture. Rheological and processing characteristics depend on the technique used. The number and size of the polymer molecules may be affected by the rate of polymerization, the solvent, and extraneous media involved in the technique. Molecular structure and characteristics have an impact on the properties of the polymers.

Polymer science and technology is to meet the effectiveness of the process in order to generate polymeric materials to meet product and market needs. An average property is no longer adequate in the development of polymer synthesis and their applications. In polymerization and end-use performance, structure, property, and morphology-processing relationships need to be established. The composition of polymer materials depends on polymerization kinetics, mechanism, and process conditions. Molecular parameters influence polymer properties and end-use performance.

4.1 MAJOR REQUIREMENTS

Synthesis of polymers has made significant progress through polymerization reactions. With all side reactions, polymer occurs, and termination of the reaction is suppressed. Polymer chain can be extended indefinitely by eliminating termination reactions. Polymerization demonstrates that various organic reactions involve different operating methods. Polymerization includes the effect of changes in structure during chemical reactivity, structure on physical properties, and role of catalysts in chemical reactions and the basic principles of polymerization.

Polymer production from polymerization has become one of the most important unit processes in chemical engineering. It has expanded rapidly in a correspondingly greater amount of research and synthesis until process becomes voluminous. Reactivity of monomers emphasizes the growing commercial importance of polymers. However, during polymerization, the polymer formed is relatively insensitive to temperature or forms at temperatures much below its reaction level, or a relatively large temperature rise can be tolerated.

In polymer synthesis, the major requirements are

1. Ease of preparation with controlled degree of polymerization
2. Compatibility with most organic reagents (monomers)
3. Stability with respect to chemical and mechanical properties
4. Inertness of the backbone of the polymer toward reactants and regents
5. Low cost and commercial availability of the monomer

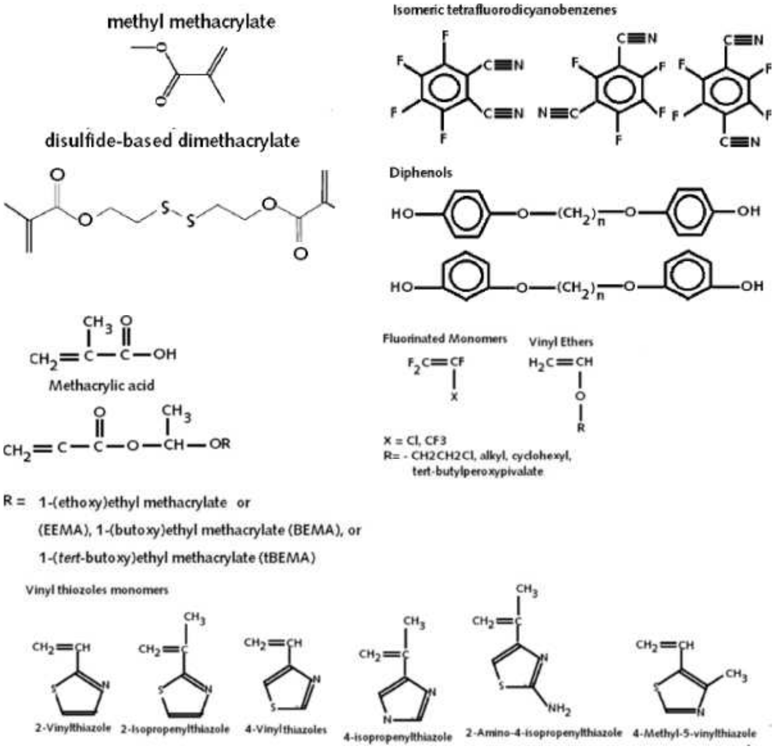
4.2 IMPORTANCE OF POLYMER SYNTHESIS

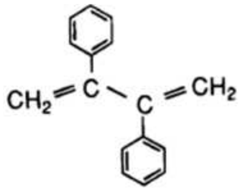
The important issues in polymer synthesis are as follows:

- Design and synthesis of new polymer for use in varied applications.
- Fundamental understanding of molecular architecture with control.
- Enables the design of complex polymers with range of applications.
- Discovery of small molecule reactions for equipping polymers.
- Provide composition, topology, and chemical functional group with a high degree of polymer chain uniformity [5–7].
- Increase control over polymer chain properties and produce architecturally complex polymers including star, comb, and hyperbranched topologies with controlled molecular weights and narrow molecular weight distributions [8–12].

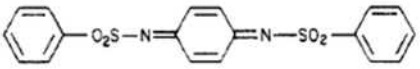
4.3 MONOMERS USEFUL FOR SYNTHESIS

Monomers useful for synthesis of polymer are as follows:

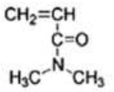




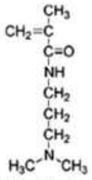
2,3-diphenyl-1,3-butadiene



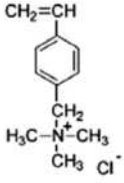
p-quinone bis(benzenesulfonimide)



*N,N*dimethylacrylamide



N-[3-(dimethylamino)propyl] methacrylamide



(aryl-vinylbenzyl) trimethylammonium chloride

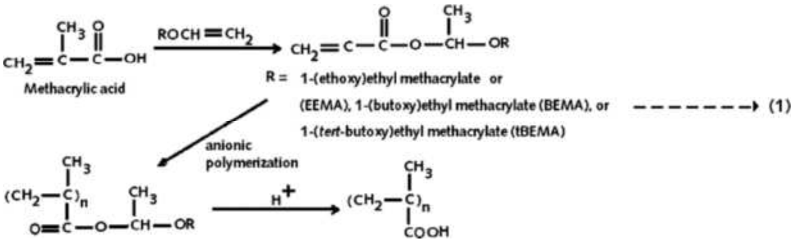
4.4 SYNTHESIS OF POLYMERS

Polymers are usually prepared by mechanisms involving random initiation and random termination. This is true for polycondensation, polyaddition, and chain polymerization. Both the chemical composition and interaction forces influence many technological processes and properties of polymeric materials.

4.4.1 MONOFUNCTIONAL COMPOUNDS

4.4.1.1 Poly(methacrylic acid)

Monomer is prepared through the addition reaction of methacrylic acid (MAA) and the corresponding alkyl vinyl ether, namely, ethyl, butyl, or *tert*-butyl vinyl ether, respectively. The anionic polymerization of these monomers under appropriate conditions generates polymers (Eqn (1))



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with controlled molecular weights and narrow molecular weight distributions. The protecting groups, 1-(ethoxy)ethyl, 1-(butoxy) ethyl, and 1-(*tert*-butoxy)ethyl, could be easily eliminated under mild acidic conditions to obtain a well-defined poly(MAA).

4.4.1.2 Acetylenic polymers

Polyacetylene (PA) is the archetypal conjugated polymer. The seminal discovery of the metallic conductivity of its doped form has triggered off research on synthetic metals. Structurally, polyacetylene is a linear polyene chain [-(HC-CH)n-] (Figure 1). The existence of two hydrogen atoms in its repeat unit offers ample opportunity to decorate the backbone with pendants.

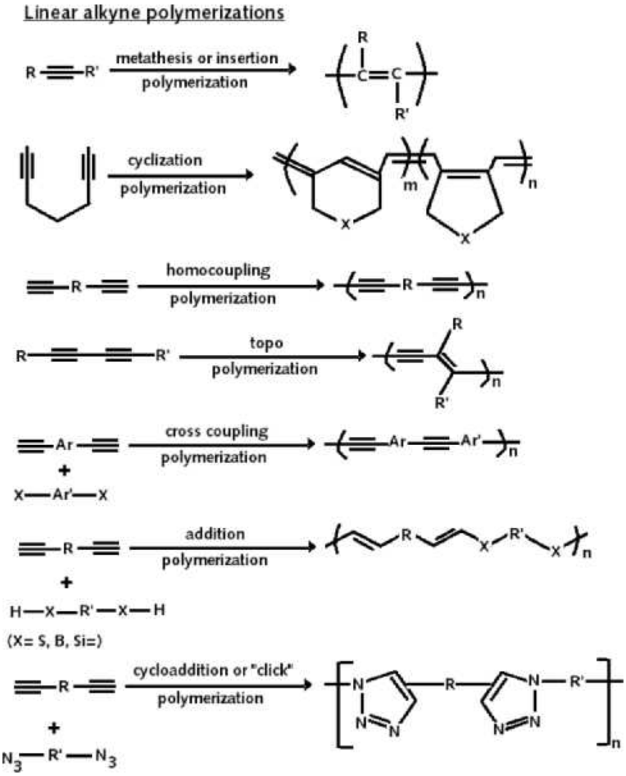

Figure 1. Linear alkyl polymerizations

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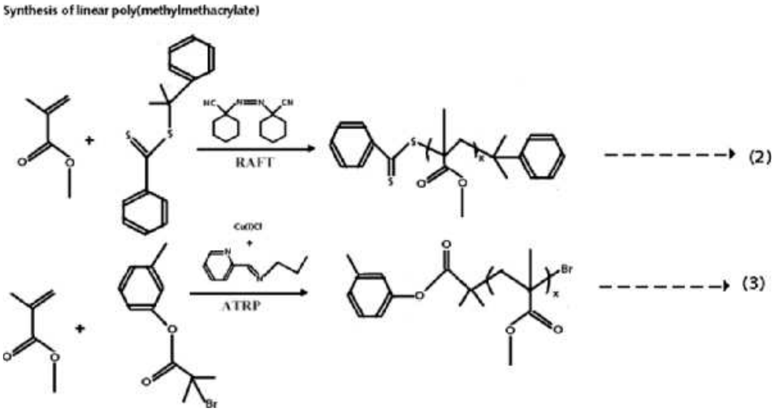
Effective polymerization of terminal and internal alkynes with one triple bond (monoynes) and two triple bonds (diynes) based on the reaction mechanisms of metathesis, insertion, cyclization, coupling, and addition has-been affording acetylenic polymers with linear and cyclic molecular structures such as polydiacetylene, poly(aryleneethynylene), poly(1,2,3, triazole), and their substituted derivatives.

4.4.1.3 Linear Poly(methyl methacrylate)

Linear Poly(methyl methacrylate) is synthesized by reversible addition-fragmentation chain transfer (RAFT) (Eqn (2)) polymerization using CumylDithiobenzoate (CDB) as Chain Transfer Agent and 1,10-Azobis-cyclohexanecarbonitrile (ACCN) Initiator, and atom transfer radical polymerization(ATRP) (Eqn (3)) using 3-Methylphenyl Bromoisobutyrate Initiator, Copper(I) Chloride Catalyst, and N-(n-Propyl)-2-pyridylmethanimine Ligand in Toluene. In particular, the effect of varying the initial monomer concentration difference can be attributed to the suppression of intramolecular cyclization in the RAFT and ATRP syntheses due to their much slower chain growth.



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4.4.1.4 Polyacrylamide

Free radical polymerization of acrylamide (Figure 2) is very sensitive to residual oxygen, which efficiently scavenges primary carbon radicals

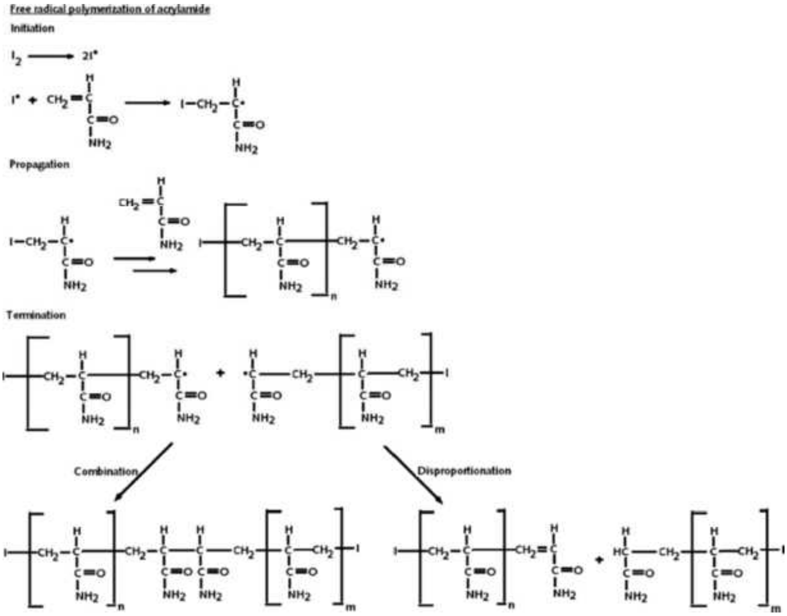

Figure 2. Free radical polymerization of acrylamide

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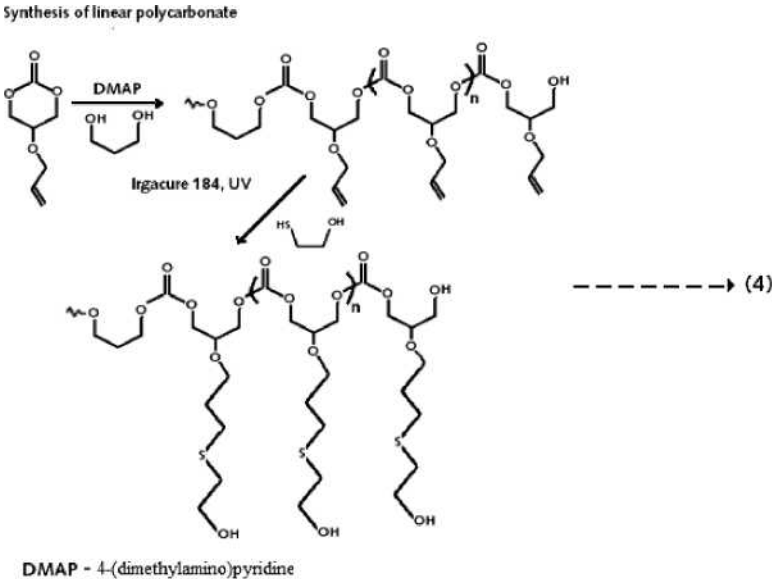
forming peroxide radicals [13]. These peroxide radicals can also participate in monomer addition, forming backbone O–O bonds. The industrial production of polyacrylamide leads to problems since the formation of high molecular weight in solution develops extremely high viscosities even at low polymer concentrations, in particular, inhomogeneous mixing and heat transfer.

4.4.1.5 Linear polycarbonate

The linear polycarbonate (Eqn (4)) with pendant SCH_2CH_2OH groups is obtained by the polymerization of compound 5-Allyloxy-1,3-dioxan-2-onein the presence of **DMAP – 4-(dimethylamino)pyridine and glycol,** followed by free radical addition of mercaptoethanol to the pendant allyl groups. In this structure, glycerol units are linked in the 1,3-positions by carbonate bonds. Secondary carbon atom of the glycerol structure is linked by an ether bond to an alkyl chain. Next to this carbon atom, there are two CH_2OR groups, where R can be a proton or a carbonate bond.



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4.4.1.6 Polypyrrole

The field of conducting polymers is to achieve a fundamental understanding of the relationship between the chemical structure of the monomer units and the electronic properties of the resulting conjugated polymer. Compared to other chemical and electrochemical syntheses of conducting heterocyclic polymers, electropolymerization of the monomer offers several distinct advantages such as absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for electrochemical applications), easy control of the film thickness by the deposition charge, and the possibility to perform a first in situ characterization of the growing process or of the polymer by electrochemical and/or spectroscopic techniques [14].

Pyrrole is electropolymerized (Figure 3) to give a black conducting powder. In doped form, it has better chemical and thermal stability. The polymerization of pyrrole can be carried out chemically or electrochemically. Chemically, it can be carried out both in solution and in gas phase. In neutral form, polypyrrole films are yellow/green and are sensitive to air and oxygen [15].

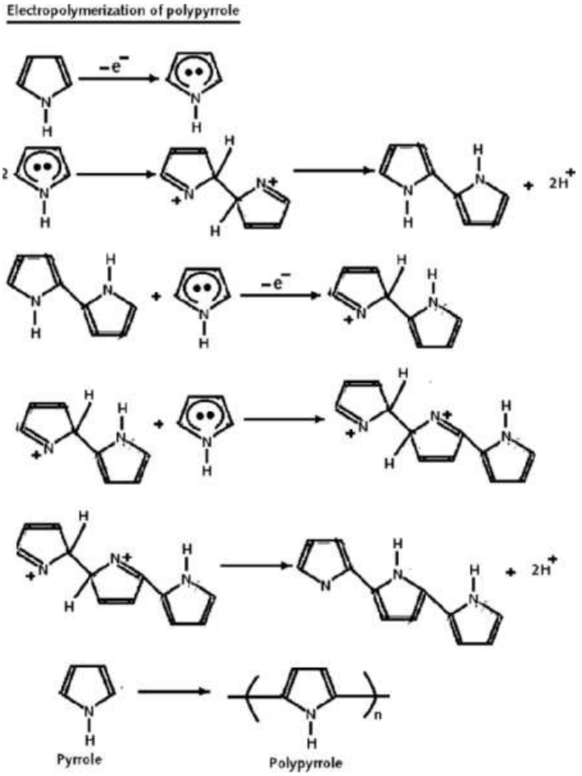
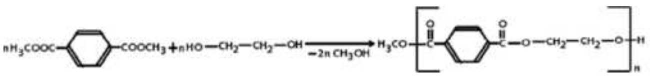


Figure 3. Electropolymerization of pyrrole

4.4.2 POLYFUNCTIONAL COMPOUNDS

4.4.2.1 Polyester formation

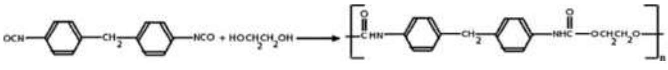
Functional groups involved in step-growth polymerization are carboxylic acid, ester or acid chloride, and hydroxyl such as 1,2 ethandiol (glycol), 1,2 propandiol, 1,2,3 propantriol (glycerol). Poly(ethylene terephthalate) (PET) (Eqn (5)) reactions occur between ethylene glycol and dimethyl terephthalate.



(5)

4.4.2.2 Polyurethane formation

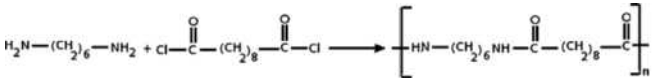
Polyurethanes (Eqn (6)) are synthesized by the reaction of an alcohol with an isocyanate either by themselves or as derivatives of alcohols. It is prepared by this fundamental reaction:



(6)

4.4.2.3 Nylon 6,10

Diacid chloride and a diamine react with release of HCl in interfacial polycondensation of nylon (Eqn (7)). High molecular weight can be executed with rapid stirring and also by adding the reactants.

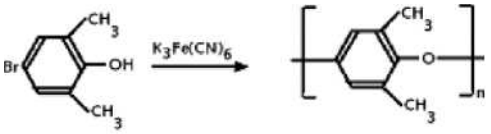


$$H_2N{-}(CH_2)_6{-}NH_2 + Cl{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow \left[HN{-}(CH_2)_6NH{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}} \right]_n$$

(7)

4.4.2.4 Poly(2,6-Dimethyl-p-phenylene ether)

Poly(2,6-dimethyl-p-phenylene ether) can be obtained either by oxidative bromine displacement from 4-bromo-2,6-dimethylphenol or oxidative coupling of 2,6, dimethylphenol.



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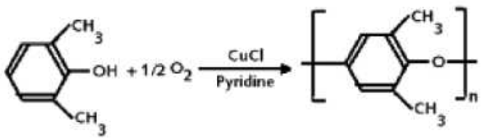
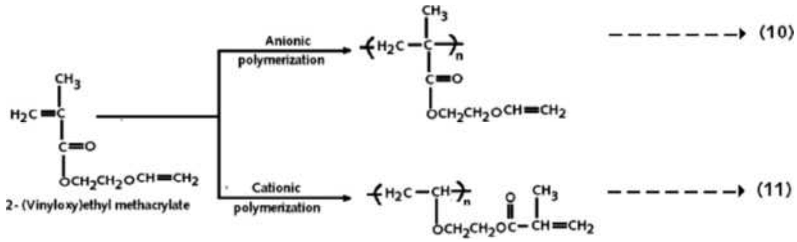


(9)

4.4.2.5 Polymers of 2- (Vinyloxy)ethyl methacrylate

2-(Vinyloxy)ethyl methacrylate is a bifunctional monomer possessing an anionically as well as a cationically polymerizable C=C double bond. The C=C double bond located in the R position of the carbonyl is expected to undergo anionic polymerization (Eqn (10)) and a functional polymer having a cationically polymerizable C=C double bond in each side chain, to be formed. On the other hand, the C=C double bond of the ester group of 2-(Vinyloxy)ethyl methacrylate is expected to undergo cationic polymerization (Eqn (11)) to generate another functional polymer with a reactive methacryloyl group in each repeating unit. Obviously, two different functional polymers can be obtained from the same monomer, by its selective anionic or cationic polymerization.



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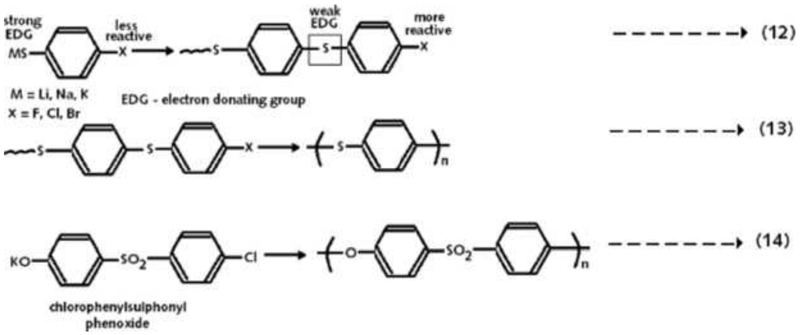
4.4.2.6 Poly(phenyl sulphonylphenoxide)

In the condensation polymerization of chlorophenylsulphonylphenoxide, increased reactivity of the polymer end group was demonstrated by the relation between conversion and reaction time. Furthermore, a comparison of the rate constants for the displacement of chlorine atoms (Eqn (12) and (13)) with hydroxide showed that a model of the polymer end group reacted



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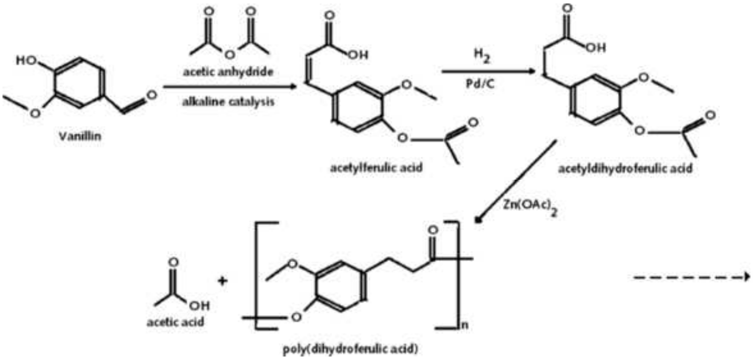
faster than the monomer. Thus, the electronic effects of a substituent in one ring are transmitted to the other via the sulfone linkage [16] into formation of polymer poly(phenyl sulphonylphenoxide) (Eqn (14)).

4.4.2.7 Poly(dihydroferulic acid)

Lignin-based vanillin and acetic anhydride are based on Perkin reaction followed by hydrogenation to produce acetyldihydroferulic acid. Polymerization of acetyldihydroferulic acid yieldspoly(dihydroferulic acid) (Eqn (15)). This polymer exhibits thermal properties functionally similar to polyethylene terephthalate (PET) [17].



(15)

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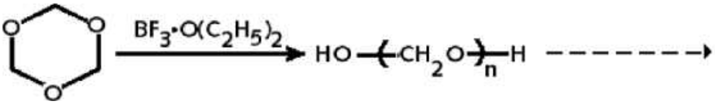
4.4.3 CYCLIC COMPOUNDS

4.4.3.1 Trioxane to Polyformaldehyde

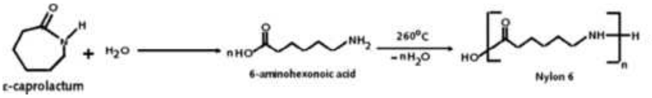
Polyformaldehyde (Eqn (16)) can be obtained by the polymerization of pure formaldehyde gas or by the polymerization of trioxane, the cyclic trimer of formaldehyde. Trioxane is more convenient and easier to purify and solids are easier to handle than handling a gas.



(16)

4.4.3.2 ε-caprolactum into Nylon 6

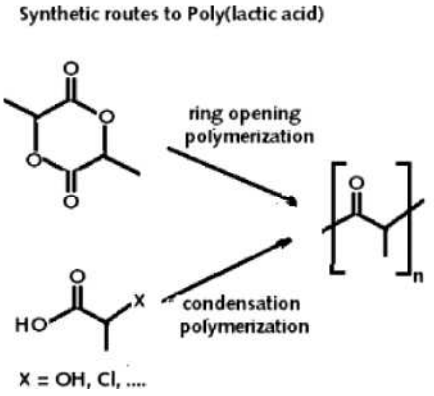
Polymerization of ring-opening reaction of cyclic monomers contains at least one heteroatom. The mechanism is a polyaddition type with a product that has a polycondensation-type character. Ethylene oxide and other cyclic esters can be polymerized into linear chains, and polymerization of ε-caprolactum into Nylon 6 (Eqn (17)) is undergoing this type of polymerization. Heating of 6-aminohexanoic acid from hydrolysis of ε-caprolactum to 260°C yields Nylon 6 (Eqn (17)).



(17)

4.4.3.3 Polylactic acid

Poly(lactic acid) (PLA), a biodegradable polymer made from renewable resources, can be made by either ring-opening addition polymerization of lactic acid or condensation polymerization of lactic acid or its derivatives [18]. The living ring-opening polymerization of lactic acid yields polymers with molecular weight control with a linear relationship between monomer conversion and poly(lactide) (Eqn (18)). The step-growth condensation polymerization limits the accessible range of molecular weights. Variant number of propagating chains in ring-opening polymerization (Eqn (19) and (20)) results in the generation of nearly monodisperse polymers at a high degree of polymerization [19]. Characteristics of a living chain-growth polymerization include the first-order kinetics (k_i and k_p) in monomer concentration and a linear relationship between molecular weight and monomer conversion.



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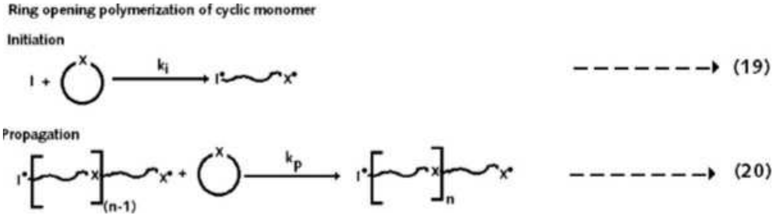

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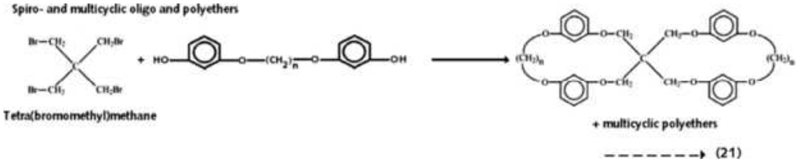
4.4.3.4 Spiro- and multicyclicoligo and polyethers (Multicyclicpolyethers)

Polycondensations (and other step-growth polymerizations) of difunctional monomers involve cyclization reactions at any concentration and at any stage of the polymerization, which also has consequences for three-dimensional polycondensations on multifunctional monomers. It is demonstrated that tree-shaped (hyperbranched) oligomers are gradually transformed into star-shaped polymers with a cyclic core when the conversion increases. Synthesis of spiro- and multicyclicoligo and polyethers (Eqn (21)) from Tetra(bromomethyl)methane:



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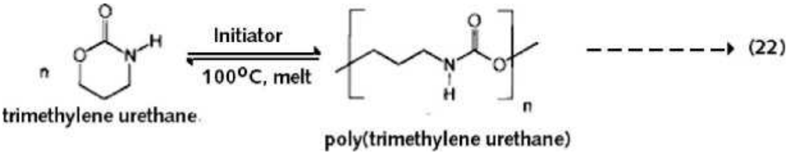
4.4.3.5 Poly(trimethylene urethane)

The polymerization of cyclic urethanes as a family of cyclic derivatives of carbonic acid. Six-membered trimethylene urethane (systematic name, tetrahydro-2H-1,3-oxazin-2-one) polymerizes in the presence of NaH and traces of N-acetyl-ε-caprolactam. The polymerization of trimethylene urethane can be carried out to yield poly(trimethylene urethane) with a uniform microstructure in a cationically initiated process.



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4.4.4 FUTURE TRENDS

Polymer synthesis has made progress with better understanding and brought a range of potential applications into consideration with respect to characteristics and structure–property correlations. With new syntheses, concepts, and architectures, both synthesis and characterization have developed to explore structure–property relationships and to establish applications.

The ultimate goal of polymer synthesis is to design, through a complementary and synergistic combination of covalent and supramolecular methods, synthetic polymers that approach the structural complexity and fidelity of biological macromolecules. These synthetic polymers would have to ultimately provide functions on demand with the aid of their precise primary structure. While these synthetic methods are in their early stages of development, traditional but more efficient synthetic methods for polymer synthesis continue to be elaborated.

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CHAPTER 5

POLYMER MODIFICATION

Successful polymer synthesis involves building and evolving conceptual process techniques from a rich collection of experiences and design. Such experience base generally includes extensive knowledge of available simple or complex synthesis methods, patterns, existing monomers, and some sense of chain of which synthesis problems to tackle, and in what order and level. Wealth of information is directly or modified as necessary to fit the synthesis methods. Generally, time and resource constraints limit the number of conceptual synthesis alternatives that may be generated and evaluated by the process. The key to research alternatives with superior economics is the judicious use of methods and tools together with information on synthesis methods.

Polymer chemistry and interfaces are important to many polymer material applications. Various synthetic routes can be employed to chemically modify polymer surfaces with substrates controllable surface chemical structures. There has been progress in modification of polymers with surface and chemical modifications. In polymer synthesis, a promising approach to the development of new polymeric material with high physico-mechanical characteristics, and good processability includes material properties based on polymer belonging to the same or different classes is possible. [1,2].

CHEMICAL MODIFICATION

Chemical modification may also improve enhanced properties [3]. It has emerged as an invaluable tool for the development of modified polymers. The use of chemical methods has provided a large toolbox. It allows the preparation of almost unlimited molecular constructs with either naturally or synthetically modified polymers [4].

For chemical modification, the commercial incentive in polymer synthesis of commodity polymers by grafting, chain scission, long-chain branching, and cross-linking is the enhancement of the physical and chemical properties of these polymers and polymer mixtures and/or the improvement of their processability. The chemical modification approach has a distinct advantage in that a wide range of narrowly defined chain lengths can be realized by the commercial availability of parent polymeric carboxylic acids [5].

The chemical modification of existing polymers can often lead to novel materials with interesting and desirable properties that are inaccessible by conventional polymerization techniques. The success of this approach to new polymers depends on the specificity of the derivatization reaction; competing side reactions cannot be tolerated if a uniform product is desired. This condition usually requires a parent polymer that undergoes facile chemical conversion so that forcing and harsh reaction conditions with increased probability of undesirable pathways can be avoided.

- The reactivity of the double bonds can be exploited in many addition reactions to modify the backbone of the polymer.
- Amine groups are useful as attachment sites along polymer chains or at chain ends because they are reactive and readily form covalent bonds with many types of groups. Amination of aromatic polymer chains is frequently achieved by a process of nitration followed by reduction.
- "Shear modification," "shear working," or "shear refining" causes a reversible modification of the rheological properties of melts of thermoplastics consisting of long-chain branched molecules [6–10]. There are also a number of reports on shear modification of linear polymers [11,12]. Whereas agreement exists on the susceptibility of long-chain branched materials to shear modification, the situation is less clear for linear molecules. The origin of the effect is probably of a different nature for branched and linear macromolecules.

Shear modification produces minor changes in the linear viscoelastic behavior of melts of branched polymers and in their steady-state shear viscosity. The elongational viscosity, on the other hand, is greatly reduced by a mechanical treatment. A lower elongational viscosity corresponds to a smaller degree of chain orientation due to the elongational component in the entrance flow and, therefore, to a smaller degree of recovery or extrudate swell after passage through the capillary [13].

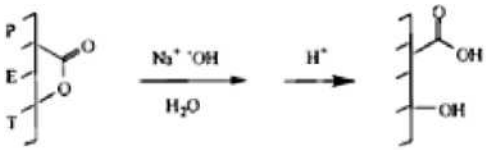
Another approach to improve the properties of a polymer system is neither by chemical modification nor by novel polymer architecture, but by blending with another polymer, resulting in a physical mixture of the polymers [14]. The blended polymers may be homopolymers or copolymers or a combination of both. In the last two decades, polymer blends have gained great importance since a wide variety of polymers can be utilized to make polymer blends of desired end-use properties. Further, the cost of developing such blend systems is much lower than that for new polymers or even to produce and commercialize a known polymer.

The properties of the blend such as Tg, Tm, modulus, crystallinity, and others depend on the nature and physical state of the original polymer; on the nature, physical state, and means of processing in the added polymer (or additive); on the interaction between polymers, the mixing ratio, and the processing steps to which they are subjected. Further, the properties derived from such blend systems also depend on the microstructure of the resulting blend, i.e., whether the blend is homogeneous (single phase, compatible) or heterogeneous (micro- or macrophase separated). Blends can be produced for a variety of reasons: to improve mechanical properties, processibility, heat resistance, thermomechanical properties, or otherwise to produce "high performance" materials. There are a variety of blend systems that are commercialized for uses ranging from high-impact strength thermoplastics to flame-proof materials. One of the major problems in the blend approach is the macrophase separation (large domain sizes) and nonmixing of the polymers [15]. Even with a knowledge of detailed structure–property relationships coupled with compatibilization and microstructural studies of polymers, polymer blends with significantly improved properties cannot be obtained from a wide variety of polymers at present.

SURFACE MODIFICATION

In many applications, the properties desired at a polymer surface, such as adhesion, wettability, gas impermeability, stain resistance, or biocompatibility, are often specific and distinct from the bulk properties of the material. Conventionally, control of surface properties is achieved by surface modification through various chemical or physical processes, such as plasma or flame treatment, chemical reaction, surface grafting, or metal coating [16,17]. Many of these kinetically governed reaction mechanisms allow relatively little control over the equilibrium surface composition and structure. Additionally, such processes may be expensive and difficult to model.

Polymer surfaces and interfaces are central to many polymer materials applications [18,19]. Chemically modifying polymer surfaces by preparing substrates with controllable surface chemical structures can rationally control macroscopic surface properties such as adsorption, adhesion, wettability, and friction. Reaction with thionyl chloride produces a surface mixture containing alkyl chloride (PET-Cl and sulfite (PET-$(O)_2SO$) functionality. Reactions with acid chlorides yield esters (PET-OC(O)R), and reactions with isocyanates yield urethanes (PET-OC(O)NHR). Reactions with diisocyanates produce surface mixtures containing diurethane and half urethane/half isocyanate functionality (PET-$(OC(O)NH)_2R$/-OC(O)-NHRNCO); the composition of these mixtures depends on both the method of PET-OH preparation and the diisocyanate structure. Functionality can be introduced to the surface of PET using reactions with thionyl chloride, acid chlorides, and isocyanates that cleave the PET chain as follows (eq) [20]:



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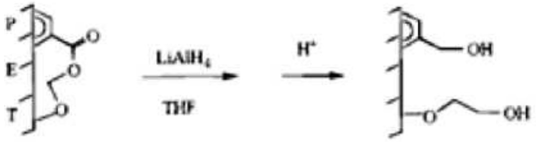

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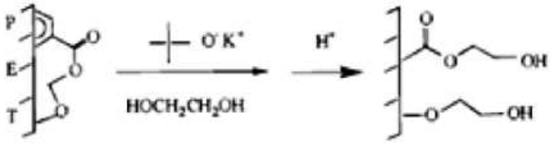

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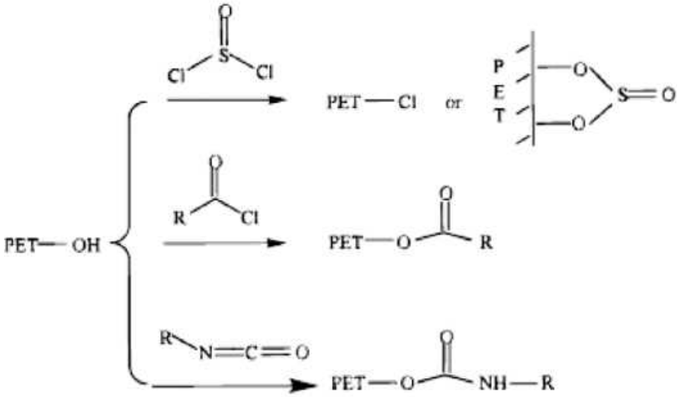

(5)

Modifications include acylation, methylation, phosphorylation, and sulfation that play a pivotal role. Consequently, reproducing such modification of polymers in a highly efficient and controlled way would provide an invaluable tool to their precise function. The possibility offered by the introduction and chemical modification makes site-selective modification of polymers a key tool [21].

Surface modification of polymers gives rise to new surface properties. It plays an important role in many polymer applications, and results in properties such as wettability, adhesion, and biocompatibility, which can be controlled. Polyethylene is one of the most interesting commodity polymers due to nonpolar nature, it requires tuning of its surface properties are highly desirable. The adhesion between PE surfaces and most matrixes is poor. This is due to their hydrophobicity and smoothness, which prevents chemical as well as mechanical bonding. Polyethylene has low surface energy. Surface modification can be made by chemical reaction [22–24] with a contacting solution [25], corona discharge treatment [26, 27], and surface grafting of hydrophilic monomers after photo irradiation [28–30].

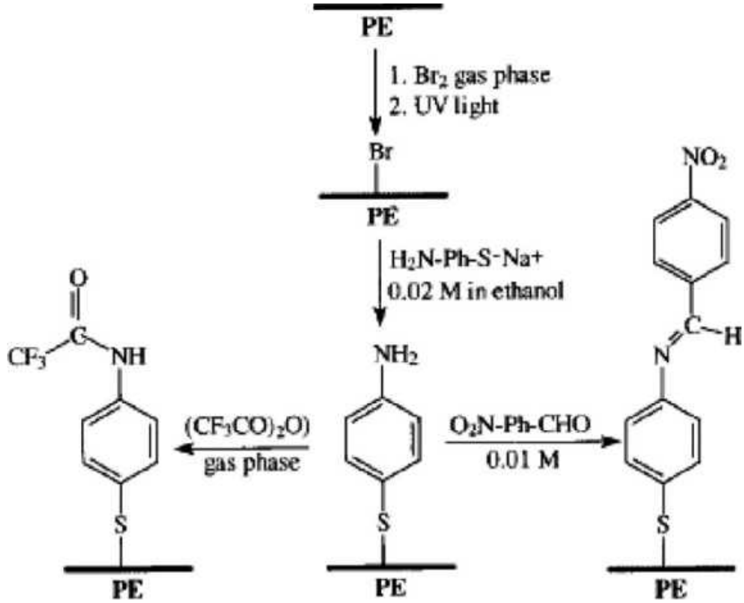

Figure 1. Reaction sequences in surface modification of PE films

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Surface bromination of low-density polyethylene (LDPE) was carried out by brief exposure of PE films to bromine followed by irradiation, which is considered as one cycle of bromination (Figure 1). A number of consecutive cycles are applied to the PE samples to increase the surface bromine concentration. The increase in hysteresis suggests an increase in surface inhomogeneity and roughness [31].

POLYMER MODIFICATION

Cross-linking is one means by which plastics can be effectively modified. Several properties of the original plastics can he altered substantially by cross-linking, e.g., solubility, creep behavior, and mechanical properties [32], without changing the chemical nature of the material significantly. Cross-linking of polyolefins can be initiated effectively by free radicals. Thermal decomposition of peroxides and high-energy irradiation is used for this purpose. If the macroradicals formed are sufficiently stable and the termination proceeds preferentially by recombination, the cross-linking efficiency reaches the theoretical value of 1.0 [33].

CHEMICAL MODIFICATION OF STYRENE-TYPE POLYMERS

The chemical modification of styrene-type polymers to introduce a range of functional groups, as well as their subsequent reactions and uses, is of both academic and industrial interest [34]. Significant advances have recently been made in functionalizing poly(4-methylstyrene) and 4-methylstyrene copolymers, especially with regard to avoiding side reactions on the aromatic ring or the backbone methine. Several approaches involve radical chlorination [35,36] and bromination [37,38] at the 4-methyl site. Recently, superbases have been successfully used to introduce electrophiles selectively into the 4-methyl positions of poly(4-methylstyrene) [39,40]. We have reported the cobalt-catalyzed air oxidation of poly(4-methylstyrene), converting up to 95 percent of the 4-methyl groups to aldehyde and carboxylic acid [41,42]. This reaction is related to the industrially important cobalt-catalyzed air oxidations of alkylbenzenes [43–45].

In all these modifications, the steric hindrance provided by the polymer backbone reduces the reactivity of the backbone methine and shifts the selectivities strongly toward the 4-methyl group. It appears that the transition state leading toward cleavage of a primary benzylic (methyl) carbon–hydrogen bond is more efficiently stabilized by the aromatic ring than the corresponding transition state leading to cleavage of a tertiary benzylic (methine) carbon–hydrogen bond.

CHLORINATED POLYMERS

Chlorinated polymers are widely used in the production of materials that have good mechanical and dielectric characteristics and are resistant to acids, oils, and gasoline [46]. Among the general methods for synthesis of chlorinated polymers is chemical modification by introduction of chlorine atoms into macromolecules at reactive bonds of finished polymers. Introduction of the chlorine atoms into macromolecules generally improves the adhesion properties of polymeric products.

OLEFIN POLYMERIZATION

Remarkable advances in olefin polymerization have been achieved over the past two decades, largely because of the development of homogeneous catalysts. Single-site catalysts are now available that polymerize R-olefins with unprecedented degrees of control over stereochemistry and polymer architecture [47–50]. A number of catalysts have recently been reported to polymerize olefins in a living fashion, allowing the synthesis of new polyolefin-based materials [51]. Despite these remarkable advances, synthesis of functional polyolefins using Ziegler–Natta catalysts remains a long-standing scientific challenge. The two strategies most commonly employed toward this goal are direct copolymerization of olefins with functional monomers [52] and post-polymerization modification [53]. Direct copolymerization has met with limited success owing to catalyst poisoning and interactions of the catalyst with Lewis basic monomers. However, recent developments in late transition metal catalysts have provided improved routes to functional polyolefins [54]. Despite recent advances in alkane C-H activation, modification of preformed polyolefins is also problematic because of the inert nature of the hydrocarbon polymer and lack of control over composition and microstructure.

A third approach that has received attention in recent years involves controlled incorporation of a reactive moiety that provides easy access to a wide range of functionalities through chemical modification. Along these lines, we present here a methodology for the synthesis of vinyl-functional polyolefin copolymers and block copolymers with narrow polydispersities through the insertion/isomerization polymerization of 1,5-hexadiene.

ELECTROACTIVE POLYMERS

Electroactive polymers comprise a new class of organic materials. Being exposed to certain electrolyte solutions, these materials exhibit both electronic and ionic conductivity. It is expected that the existence of electronic conductivity was first proven in the case of polyacetylene [55]. However, the intensive study of electroactive polymers was started after the discovery of electropolymerization of pyrrole [56] and aniline [57].

Electropolymerization is a powerful tool for development of modified electrodes, and its advantages include simplicity of targeting for selective modification of multielectrode arrays. In addition, the electropolymerized materials usually possess some unique properties that are not peculiar to the corresponding monomers.

The formation of electroactive polymers upon reduction or oxidation of different organic compounds has been studied. Among these compounds, the azines represent a group that has already found wide use as redox indicators and mediators in various branches of biochemistry and bioelectrochemistry. This group can be defined by the general formula shown in scheme 1 where X, N, S, O and R are halo, nitro, sulfur, oxygen and alkyl groups respectively present in phenazines, phenothiazines, and phenoxazines.

It was generally accepted that electropolymerization from acidic aqueous solutions was preferable for the formation of an electroactive polymer. Indeed, electrochemical synthesis of electroactive polyaniline occurs only in acidic solutions [58]. One can electropolymerize pyrrole from neutral solutions. However, the regular polymer growth in cyclic voltammetric conditions with a limited anodic switching potential requires acidic media [59].

This explains the attempts to achieve electropolymerization of different organic compounds in acidic solutions. However, in such conditions, thionine (Figure 1), the only representative of the azines, was successfully polymerized [60–62]. The possibility of electroactive polymer formation by other azines was not shown until Lyons et al. [63] demonstrated that both methylene blue and neutral red (Figure 1) could be polymerized by anodic oxidation from neutral aqueous media.

FUTURE TRENDS

The modification of polymers and methodologies for the synthesis of polymers is gaining importance in view of the increasing demand for the materials in various phases of modern technology. Industrial synthesis of polymers is presently underdeveloped and limited to chemical modifications. Developed idea in polymerization provides solution to outstanding problem of control of the polymer chain growth. A number of polymerization systems have been developed over the past years. The number of monomers amenable to use in modification has been gradually increasing year by year. It is possible to modify polymers more conveniently to make a variety of speciality polymers in the future with precise architectures at the molecular level. Modified polymers can be produced using polymerization techniques.

Polymer modification is to be considered from a technological viewpoint. The practical uses and applications of polymers synthesized by polymerization techniques results in variable in properties and can be made to suitable for the industrial and commercial applications. Some exciting advances in polymer modification will lead to further advances in research, and polymerization will thus maintain its importance both in industrial and academic research.

Polymers offer challenging opportunities for both research and applications development. An important advantage of polymers is their chain flexibility at the molecular and bulk levels. Chemical modification helps to tailor structural features and functionality. Using molecular engineering through chemical modification, it is possible to impart special characteristics to a polymer.

Polymer synthesis has tremendous potential in both research and application development. Polymer chemistry has shown intriguing prospects in new developments, and polymers have emerged from structural materials to functional materials. New properties that have come to light from research developments in the field of polymer synthesis have sparked interest in both the academic and the industrial communities.

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CHAPTER 6

FRONTIERS OF POLYMER SYNTHESIS

Polymer synthesis plays a significant role in the modern world. Many useful polymer materials are synthetically produced. The synthesis is intricate, involving forethought regarding sequence of polymerization, technical execution of experiments, polymer analysis of the outcomes, purification, and structural characterization. Polymer synthesis with desired properties is a challenging task, often involving considerable time and resources. Synthesis involves a trial-and-error approach with different monomers being tested in the laboratory.

The leading edge of polymer synthesis is to design through a complementary and synergistic combination of covalent and supramolecular methods. Therefore, polymer synthesis is an approach to form structural complexity and devotes macromolecules to the developing areas of medical, industrial and commercial areas. Synthetic polymers would have to ultimately provide functions on demand with the aid of their precise primary structure. These synthetic methods are in their early stages of development, traditional but more efficient synthetic methods for polymer synthesis continue to be elaborated toward the industrial level [1]. Industrial development of polymer materials has started intensively, and polymer synthesis is identified as an independent area of knowledge with its evident theoretical and practical challenges.

Polymer synthesis involves transformation of step condensation polymerization [2] reactions into chain polymerization, which is one of the most recent developments. These transformations are used in the generation of living condensation polymerization. Being condensation polymerization, polymers have variable monomers composition within limits and unorganized structures are obtained.

The synthesis of well-defined macromolecules with accurately controlled three-dimensional structure is becoming an increasingly important aspect of polymer science because of the continuing desire to prepare materials with new and/or improved physical properties [3,4].

POLYMERIZATION

Polymerization is exothermic, and restricted heat transfer is particularly important. Reactions during polymerization have unusual physical features that pose problems for reactor design. Monomer feeds usually have a relatively low viscosity, but the polymer-containing fluids produced in the reactors have high viscosities. Therefore, this imposes severe constraints on the choice of mixing pattern and limits the extent of heat transfer [5].

Physical properties of polymers affect all aspects of the polymer industry. It has many applications and covers all aspects of polymerization techniques as well as product lifecycle. It is the key input for the development of process. Good physical properties have been the main driving force in terms of reduced cost of manufacturing or increased production for the development of polymerization. In polymerization, industrial needs can often be related critical to success. Improved properties can help in the development of polymerization with economy.

Living polymerization techniques are useful not only to control molecular weights and molecular weight distributions of polymers but also to synthesize block copolymers and end-functionalized polymers [6]. In general, block copolymers are synthesized by ionic or coordination polymerization because of the living nature of the polymer chain end [3]. Free radical polymerization is the preferred chemistry for polymer manufacturing because it has the lowest cost and is the most versatile.

LIVING POLYMERIZATION

Living polymerizations and iterative synthesis are the two most advanced synthetic methods in the field of polymer synthesis. Anionic, cationic, and metathesis living polymerizations are methods of synthesis, through which monodisperse polymers with narrow molecular weight distribution, complex topology, and architecture are produced [7]. Living polymerization and other methods to produce well-defined polymers by radical reactions are currently being developed extensively in many laboratories.

Polymer synthesis techniques of “living” free radical procedures may (i) permit the synthesis of known polymers, such as random copolymers, with a significant increase in control over the macromolecular structure, (ii) permit the synthesis of complex macromolecular architectures, such as graft poly(styrene-*g*-methyl methacrylate) block copolymers, with a significant increase in synthetic ease and mild reaction conditions, (iii) allow the synthesis of unique macromolecular architectures, such as hybrid dendritic–linear block copolymers, which cannot be prepared by other synthetic techniques, and (iv) provide easy implementation due to the simplicity of the syntheses [8]. The field of "living" free radical polymerizations is a young, rapidly progressing area of research, and many of the difficulties or limitations associated with the general applicability of this technique are steadily, but surely, being overcome.

Useful and unique aspects of living polymerization are the ability to prepare chain-end functionalized polymers. Alkyllithium-initiated, living anionic polymerization has proven to be a useful method for the synthesis of well-defined, chain-end functionalized polymers. Polymers are formed with predictable molecular weights and narrow molecular weight distributions as long as initiation is competitive with propagation due to the absence of chain transfer or termination reactions. Living anionic chain ends produced after all of the monomer is consumed can react with electrophilic reagents to form well-defined, chain-end functionalized polymers.

Polyurethane-modified chitosan has become a new frontier [9,10]. Many interesting properties are expected, such as excellent mechanical property, good thermal stability, increasing anticoagulant, low hydrophilicity, and so on.

Polyacetylene with fairly long sequences of conjugated double bonds can be obtained by a thermal elimination of benzenesulfenic acid from poly(phenyl vinyl sulfoxide) (PPVS). In order to reduce the amount of sp3 defects of the chains, it is necessary to remove the side products as soon as they are formed; that is best achieved by a thermal treatment under dynamic vacuum.

PPVS is a potentially interesting new precursor route to the synthesis of polyacetylene. A color change from white to yellow, red, and finally black occurs on heating this polymer above room temperature. This indicates the formation of conjugated double bonds as a result of thermal elimination of benzene sulfenic acid from the PPVS. This thermal elimination reaction about the formation of polyenes can be found in the literature. Before trying to take advantage of the interesting potentiality of this new precursor route to polyacetylene, it is necessary to know more about the type of conjugated system generated by this elimination reaction [11,12].

BIOPOLYMERS

With growing environmental awareness throughout the world because of the imminent petroleum crisis, the design and use of environment-friendly materials based on renewable resources have attracted interest as frontier materials [13].

In many cases, polymer synthesis is very expensive and time consuming, with no guarantee that it will culminate in the selection of the desired polymer. In polymer synthesis, molecular design of polymers is the inverse problem of predicting the properties of a monomer given its structure [14].

Research focusing on homogeneous olefin polymerization catalysis has proliferated in recent years. In addition to metallocene type catalysts, transition metal active sites are now supported by ancillary ligand frameworks incorporating a wide variety of structural motifs [15–17]. Homogeneous catalyst systems offer both the option to use ligand geometry for precise control of polymer stereochemistry and the potential to use living catalysts to synthesize block copolymers. Many catalysts can generate highly isotactic polypropylene (iPP), and there are a number of living catalysts for propylene polymerization. Despite 50 years of intense research since Natta's synthesis of iPP, living isospecific propylene polymerization catalysts remain unreported. Such catalysts could be used to synthesize iPP block copolymers that have valuable applications as compatibilizers and thermoplastic elastomers.

The free volume is an intuitive theoretical concept [18–20] that has been proposed to explain the molecular properties and physical behavior of liquid and glassy states. Free volume is an open space that is freely moving in a medium. It is constituted of subnanometer-sized holes that appear in the medium owing to structural disorder. Because of thermal fluctuations, the free volume varies in both time and space [21,22].

Remarkable advances in olefin polymerization have been achieved over the past two decades, largely because of the development of homogeneous catalysts. Single-site catalysts are now available that polymerize R-olefins with unprecedented degrees of control over stereochemistry and polymer architecture [15, 16, 23, 24]. A number of catalysts have recently been reported to polymerize olefins in a living fashion, allowing the synthesis of new polyolefin-based materials [25]. Despite these remarkable advances, synthesis of functional polyolefins using Ziegler–Natta catalysts remains a long-standing scientific challenge. The two strategies most commonly employed toward this goal are direct copolymerization of olefins with functional monomers and postpolymerization modification. Direct copolymerization has met with limited success because of catalyst poisoning and interactions of the catalyst with Lewis basic monomers. However, recent developments in late transition metal catalysts have provided improved routes to functional polyolefins. Despite recent advances in alkane C-H activation, modification of preformed polyolefins is also problematic in view of the inert nature of the hydrocarbon polymer and lack of control over composition and microstructure [26]. A third approach that has received attention in recent years involves controlled incorporation of a reactive moiety that provides easy access to a wide range of functionalities through chemical modification. Along these lines, we present here a methodology for the synthesis of vinyl-functional polyolefin copolymers and block copolymers with narrow polydispersities through the insertion/isomerization polymerization of 1,5-hexadiene [27].

In recent times, research has been focusing on the development of solid supported catalysts, currently regarded as a viable tool to improve the efficiency of a catalytic process by allowing simple catalyst recovery and recycling [28,29]. In this context, the use of polymer-supported organic catalysts is attracting increasing attention [30], with the expression “organic catalyst” being used to define an organic compound (of relatively low molecular weight and simple structure and devoid of any metal) capable of promoting a given transformation in substoichiometric quantity [31]. In principle, metal-free catalysts are particularly suitable to anchoring on a support, because they are not affected by the problem of metal leaching that requires catalyst regeneration by metal replenishment before recycling. The use of metal-free catalysts for selective oxidations of organic substrates is very appealing [32].

HALOGENS INTO POLYOLEFINS

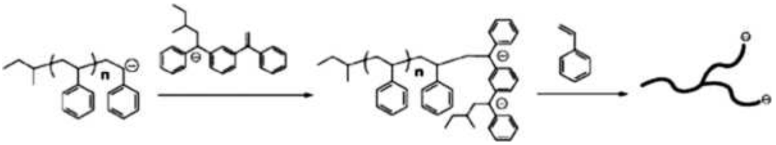
The incorporation of halogens into polyolefins influences many key polymer properties, including solvent resistance, barrier properties, gas permeability, adhesion, flammability, toughness, and thermal properties [33–38]. Halogenated polyolefins can be prepared by (i) radical copolymerization of ethylene and vinyl halides, which requires high pressure and produces branched LDPE-type materials [39–41]; (ii) halogenation of polyolefins, which generally gives a nonuniform distribution of halogens [42]; (iii) partial reduction of poly(vinyl halide)s using Bu_3SnH or other reagents [43];

and (iv) Ring Opening Metathesis Polymerization (ROMP) of halogen-substituted cyclooctenes or Acyclic diene metathesis (ADMET) of halogen-substituted dienes followed by hydrogenation [44,45], which provide exquisite control over polymer composition and structure but require special monomers and, in the latter case, feature poor atom economy. The direct copolymerization of olefins and vinyl halides to halogenated linear polyolefins by insertion chemistry would provide an attractive and long-sought alternative to these routes.

THE BRANCHING REACTION

The efficiency of branching reaction is investigated through a model reaction (Scheme 1). First, the addition of polystyryllithium to the inimer is performed in cyclohexane using a linear polystyryllithium (Mn, SEC = 1600 g/mol), resulting in a polystyryl α,α′-dianion (Mn, SEC = 2000 g/mol). MALDI−TOF MS spectrum of the product is shown in Figure 1, in which the main series is assignable to the inimer-capped species. For instance, the peak at m/z = 1963.9 is assigned to species with a degree of polymerization, DP = 14 (104.1 × 14 + 57.1 × 2 (two butyl) + 282.4 (MDDPE) + 107.8 (Ag) + 2.0 (two hydrogens) = 1963.8).

Second, the dianionic adduct is used to initiate the polymerization of styrene to form a star-like product.



Scheme 1 [Reprint with permission from Zhang, H., J. He, C. Zhang, Z. Ju, J. Li, and Y. Yang. 2012. *Macromolecules* 45, pp. 828−41.All rights reserved.]

Incorporation of multiple functionalities, covalent or noncovalent, into a polymer introduces the potential for increased structural complexity and versatility. In order to modify a polymer that contains two or more functionalities, the chemistries must be orthogonal, i.e., the transformations or binding events must not inhibit each other (Figure 2).

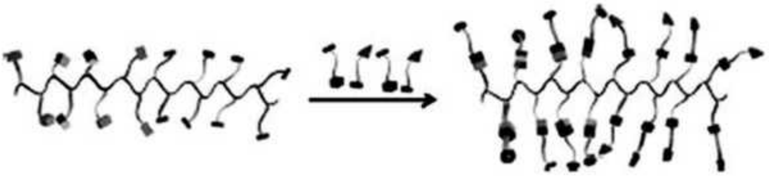


Figure 2. Block copolymer with two segments containing different functional side-chains that allow for orthogonal postpolymerization modicaiton.

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The future direction of much polymer research will be governed by efforts to better understand these properties and to improve on them. In reviewing what has been done, and what might be done in the future, emphasis will be placed on what can be achieved by the chemist by controlling the molecular architecture of polymers. There are other ways of changing properties, e.g., by adding plasticizers, stabilizers, and "reinforcing" agents, which are often the only practicable means of producing polymeric compositions (plastics) with processing characteristics and final properties to suit particular needs. However, on this occasion, attention will be focused on what the chemist can do.

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CHAPTER 7

POLYMER SYNTHESIS—APPLICATIONS

Systematic approaches to the invention of polymers have been of importance for front-end polymer engineering, especially conceptual design, product quality, health and safety, environmental impact, energy consumption, operability, capital and operating costs; and overall competitiveness has become important. A number of polymer synthesis frameworks, approaches, methods, and experiments have been developed to the point of industrial application. Polymer innovation process shows process synthesis fits into that structure and in turn influences the development of systematic synthesis process. A number of case studies show polymer synthesis has been successfully applied to the design of total process. Greater benefits are expected to be realized in developing polymer synthesis from the laboratory to industrial process using systematic process and methodologies.

The main activities of the polymer industry in the area of synthesis center on polymers. These polymers can be divided into two large groups: structural and functional materials. Structural materials are needed primarily in areas such as transportation, machines, and building materials. These materials require good mechanical, thermal, and chemical properties. Functional materials are needed in electronics, communications, information technology, and biotechnology, and have quite different properties, such as electrical, magnetic, and biological properties.

Polymers can be tailored to meet the needs of various applications through polymer synthesis. Therefore, polymeric materials are the choice in the fast-changing world from electronics to medical applications. Polymers are used in electronics, machinery, communication, transportations, pharmacy, and medicine as highly advanced materials [1] owing to light weight and ease of processing with mechanical properties. Moreover, most polymers are insulators with passive functions. Polymer use has expanded to functional areas such as light-emitting diodes, sensors, and solar cells.

Polymers offer many advantages that are encouraging their use by both consumers and industries. These include (a) low cost and high-speed production; (b) high mechanical performance; (c) good barrier properties; and (d) good heat sealability. For modern technologies, polymer leads to a permanent position in many sophisticated applications such as medical devices, human parts, etc. Effective utilization of polymers is related not only to advantages but also to properties that can fulfill specific applications. Polymers offer great potential to meet the requirements of other materials. They can be easily tailored by their structures at the synthesis level and also at different scales [2].

Polymers are being used for applications that range from leather cloths to gears, from lenses to signboards, and from control knobs to wire insulation. Polymers for each application must be carefully selected to meet component requirements at low cost. Synthesis and design aim to give proper function at lowest weight and cost. The use of polymers in automobiles is dependent not only on their inherent properties but also on meeting the conditions established by the adjacent materials. Cost reduction has undoubtedly been a prime motivation in the increased use of polymers, with steel and aluminum being more expensive. The current trend is for design synthesis to take full advantage of the properties and other physical characteristics of the material.

Chemical structure at the molecular level of polymers determines the essential properties and/or functionalities. Polymer synthesis provides new polymeric materials with dramatically different properties with a subtle manipulation of the chemical compositions, functional groups, and chain architectures.

SURFACE SCIENCE

Living polymer is challenging with increased synthetic polymer availability with unusual or unique macromolecules via “living” free radical procedures which will lead to advanced materials for a range of technological applications. Potential areas of application are surface science [3] adhesion [4,5], coating technologies, microelectronic applications [6], biotechnology, and others.

Polymer applications are widespread and are driven by their availability, processing ability, low density, and diversity of mechanical properties. They are ubiquitous in nature and are evolving into multifunctional systems with highly sophisticated behavior. They exhibit an extraordinary range of mechanical responses (Figure 1a) that depend on the chemical and physical nature of the polymer chains [7].

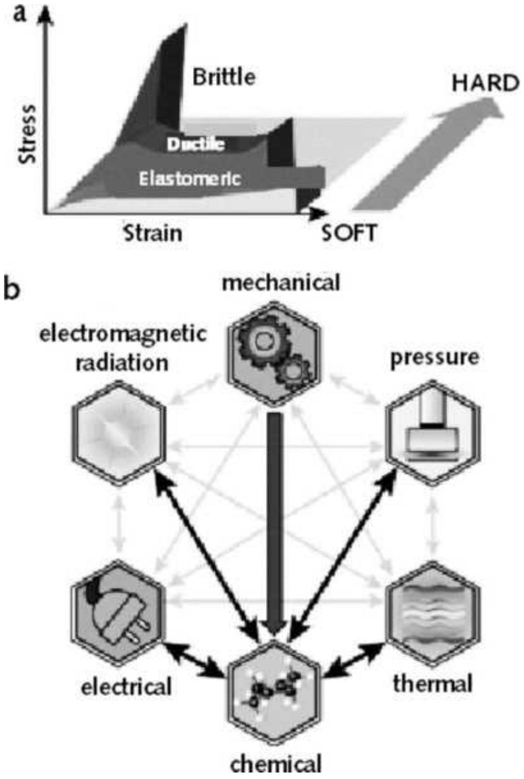

Figure 1. (a) Polymeric materials subjected to mechanical load (stress–strain curve) (b) Energy transduction pathways are the basis for the rational design of stimuli-responsive polymers

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Polymers consist of linear or branched chains. They can be amorphous or semicrystalline. Mechanical response of polymers (Figure 1b) in terms of thermoplastic polymers is highly influenced by the molecular mass, chain entanglement, chain alignment, and degree of crystallinity. Thermosetting polymers consist of highly cross-linked three-dimensional networks. The mechanical properties of these amorphous polymers depend on the molecular mass and cross-link density.

DRUG DISCOVERY PROCESS

The efficacy of high-throughput screening of compounds in biological assays has revolutionized the drug discovery process in automation equipment. A major outcome of new screening methods has been the easing of bottlenecks in the process of production of compounds for testing. Therefore, the demand for large numbers of new compounds has encouraged the search for ways to simplify and automate the process of small organic molecule synthesis.

Polymers are used as supports (Figure 2) for either substrate or reagent immobilization to synthesize small organic molecules. The primary advantages of attachment of one reaction component to a polymer are as follows:

- Substrate removal from the reaction mixture is easily accomplished.
- The bulk properties of the polymer carriers make them well suited for use with automation equipment.

Therefore, polymers can not only be used as platforms for organic synthesis, but they can also serve as reagent supports that allow for simple purification of solution-phase products [8].

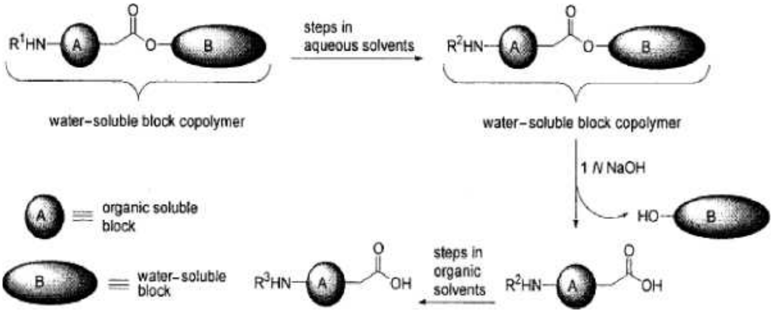

Figure. 2. Oscillating solubility of liquid-phase polymer supports

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APPLICATION IN MEDICINE

The application of polymer materials in medicine has some delicate features, calling for the creation of polymers with quite extraordinary physicochemical properties. If, for most other application areas, the polymers must be protected from unfavorable environmental effects (temperature, radiation, oxidants, etc.), then, in medicine, the environment should be protected from the harmful effect of polymers. This is especially true for polymers that are used for the manufacture of articles that contact blood, for example, prostheses of blood vessels, parts of artificial organs implanted into living beings, arteries of apparatuses of extracorporeal and assisted circulation, and containers for blood storage and transfusion. All of the currently used polymers are not truly thromboresistant. The contact of blood with any foreign materials, including polymers, results in clotting. This is the natural preventive reaction of a living body. The process of blood clotting on the polymer surface includes three main stages: the adsorption of plasma proteins and their partial denaturation; the adhesion and aggregation of platelets with the fracture of the cell membrane and the release of the intracellular content favoring further aggregation of platelets; and the activation of clotting factors accompanied by transformation of the soluble protein fibrinogen into insoluble fibrin that, along with the incorporated blood elements, forms a thrombus.

The most common and effective approach to the improvement of the thromboresistance of polymers is modification of their surface with biologically active compounds, influencing the final stage of thrombosis.

The most widely used compound of this type is heparin, a natural blood anticoagulant, which was first used as early as in 1963 [9]; however, up to now, this is practically a unique polymer modifier used in clinical practice.

As a rule, the surface of finished polymer articles is subjected to modification since the modification of the initial polymers results in degradation of modifiers during polymer processing and they lose their biological activity. In addition, among the main disadvantages of such an approach is the fact that substances immobilized on the article surface lose their biological activity under the action of blood components. For instance, human blood plasma contains more than 20 different proteins that can neutralize the anticoagulant activity of heparin.

The positive results of implantation of most polymer materials are achieved either owing to a relatively small size of implants (heart valves) or because, during intense blood flow, the products of thrombosis are constantly removed from the polymer surface and are hydrolyzed by fibrinolytic blood enzymes. In this case, the higher the blood flow rate, the smaller the amount of thrombosis products remaining on the polymer surface [10].

In the manifestation of thromboresistant properties of polymers, not only the amount and nature of adsorbed proteins but also changes in their native conformation that result from interaction with the polymer surface play an important (or even decisive) role.

CONDUCTING POLYMERS

Tremendous interest has been evinced in the synthesis of conducting polymers in view of their excellent electronic properties, with conductivities covering the whole range from insulator to metal while retaining lightweight, mechanical properties, and promising applications in nano devices [11,12]. Conducting polymers have also attracted interest because of their potential use as inexpensive and flexible organic (semi)conducting layers in various applications such as electronics, photovoltaic devices, and supercapacitors [13]. For practical applications, a conducting polymer must be cost effective to synthesize and purify, have good chemical and electrical stability, and be easily processable from either solution or the melt [14].

CONJUGATED POLYMERS

Electrochemical polymerization for the conjugated polymer is useful because it can be carried out at room temperature and homogeneous polymer films can be formed directly at the electrode surface, facilitating control of film thickness. One of the most attractive properties of conjugated polymers is a so-called electrochromism, where the polymer changes in color upon an electrochemical reduction–oxidation (redox). Conjugated polymers (CPs) are receiving much attention because of their unique optical, electrochemical, and electrical properties and their applications as optoelectronic devices [15–17]. They have profound applicability in inherently transporting materials, light-emitting displays, rechargeable batteries, and electrochemical devices and sensors [18–22]. The introduction of photoresponsive azobenzene groups into CPs can modulate the properties of CPs by light [23,24]

POLYACRYLAMIDE

The polyacrylamide family of polymers and copolymers is a highly versatile group used in a multitude of applications including clarification of drinking water [25–28], flocculants for wastewater treatment [29,30], oil recovery [31], soil conditioning [32–35], agriculture[36,37], and biomedical applications[38–41].

However, the neurotoxicity of the acrylamide monomer has led to some concerns and even reluctance to accept polyacrylamides as safe materials, particularly in situations where the polymer is in direct contact with bodily fluids (e.g., renal dialysis, blood filtration) or where the polymer is used in making therapeutic products. There are lingering concerns regarding the possibility that residual acrylamide is present in the polymeric materials and whether polyacrylamides can degrade back to the monomer.

Polymeric materials have been used for many decades in biomedical applications such as drug delivery, implants, contact lenses, vascular grafts, dental materials, and select artificial organs. Their useful and tunable mechanical properties have offered broad utility in the structural support or replacement of tissues or in controlled retention and release of drugs [42–44]. The development of polymers as bioactive pharmaceuticals in their own right has only more recently been exploited [45]. The introduction of the polymer–anticancer drug concept by Ringsdorf in 1975 marked the beginning of an era of fruitful research in this topic. Long thought to be too heterogeneous with respect to molecular weight (polydispersity), composition, and structure to be useful therapeutically, polymers are now known to offer many specific advantages critical to treating human disease and have recently entered into medical practice. Indeed, the early studies of Duncan, Kopecek, and Ringsdorf in the late 1970s resulted in the first polymer–drug conjugates to be used as medical treatment.

In the treatment of disease and injury, therapeutic molecules, regardless of their composition and physical form, must fulfill several basic requirements, including biocompatibility, stability under physiological conditions, specificity for the target, desired mechanical properties, and minimal adverse effects. The immunogenic responses and side effects of many drugs, especially protein drugs, are exacerbated by their hydrophobicity; therefore, drug toxicity can be reduced by increasing the drug solubility by conjugation of a hydrophilic polymer scaffold to the drug in question. With conjugation to a polymer, drugs can also be protected from degradation, resulting in improved efficacy due to increased drug circulation times. In addition to the environmental protection afforded by polymers, the tunable and responsive properties of many polymeric scaffolds have also permitted improved routes for targeted drug delivery. The controlled release of drugs from polymer–drug conjugates, by variations in pH, temperature, enzyme concentration, or attachment of targeting ligands, can increase drug efficacy by increasing local drug concentration at the desired site of therapeutic need [46–48]. In a different therapeutic approach, toxic small molecules can be eliminated selectively from the body via their sequestration in polymeric scaffolds [49]. Finally, polymers themselves can also offer special opportunities over small-molecule drugs in the manipulation of multivalent binding events, owing to not only their display of multiple pendant ligands but also the potential to vary polymer structure (and therefore biological activity) via living polymerization methods [50].

The synthesis of novel blood-compatible polymer-based biomaterials has been drawing great attention. Currently, much attention is being paid to the use of natural material for designing new biomaterial. Very large swelling characteristics along with its fast release of drug make pure chitosan unsuitable for many applications, especially in biomedical uses. Further, very low elongation at break or brittle nature of pure chitosan limits its use as a biomaterial.

Block copolymers are important materials because of their extensive technological applicability and as a result of their employment as model systems for the investigation of the structure and thermodynamics of multiconstituent polymers. Applications of block copolymers are based upon the elastomeric properties that result when a glassy component is linked to a second, incompatible component that is rubbery at the use temperature. Such a material exhibits thermoplastic behavior and can be readily processed by heating above the glass transition temperature of the glassy component.

More recently, a number of specialty applications have arisen for block copolymers in mixtures with, or as additives to, other materials. For example, certain block copolymers have been used as emulsifiers for incompatible homopolymers [51], as compatibilizers and adhesion promoters for immiscible homopolymer blend [52], as viscosity modifiers in lubricants [53], and as mechanical strength modifiers in composites [54,55].

In polymer synthesis, polymers with unique applications are being introduced. Polymer synthesis is a field that is coming into its own mainly because of its properties. Structural and functional polymer materials are attracting keen interest among researchers. The importance of polymer growth makes the interdisciplinary aspect of polymer synthesis research to industrial polymer research.

Polymers play a major role in all aspects of structural and functional processes. Advances in any technology depend critically on research. Fundamental information is better before synthesis for understanding of surface interactions and relationships between physical properties of polymers. The breadth of application of polymer synthesis is not generally recognized. Polymer is an active material that plays a central role with its range of properties, flexibility in processing, and potential for low cost.

Quality is an essential and challenging feature in polymer synthesis and is being demonstrated by polymers in an array of applications. Synthesis of polymer in many applications is just the beginning from the monomer selection. The importance of applications is a key factor in polymer synthesis. The following are some of the latest areas of polymer synthesis in terms of applications:

- Polymer dielectrics in electronics provide small circuits with high speed of operation.
- Conducting polymers—rechargeable batteries with high energy storage with less weight.
- Polymer sensors—thermal and acoustic radiation, temperature, pressure, humidity, ionizing radiation, and electric charge.
- High-density information storage.
- Optical fibers.

FUTURE TRENDS

Polymer synthesis is flourishing, and the future is bright. It is a vigorously emerging area from research to development to commercialization with respect to polymer applications, and competition in the field has assumed global dimensions.

Chemistry deals with molecules and makes it possible to organize them in ways that can generate new materials with the desired performance and functions to fulfill human needs. The polymer industry has helped to improve the standard of human life by mass production of commodity materials. Polymers are lighter and more functional, a property that contributes to the growth of the industry.

The basic concepts of polymer synthesis are:

- Expansion of business—new polymer commercialization
- Future commitment to production technology
- Unique technique and product derived from long-range basic research.
- Encouraging integration of new technologies and enhancement of new polymers.

Polymer synthesis should stand with harmonious industrial technology between human and without any pollution to the earth. Therefore, research can create global awareness to strengthen the basic research thinking in a better way. In the future, polymer synthesis is going to keep encouraging and challenging spirit to the centuries.

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CHAPTER 8

PROBLEMS OF POLYMER SYNTHESIS

Industry is now recognized as the major source of critical components for almost every space age activity. Many problems have been solved through the use of available polymers. The synthesis and development of new polymers or use of blends and other structural materials is assuring an important place for polymers in every progressive nation. Synthesis represents the source of new material. Recent advances in synthesis are based largely on experimental investigations. Theory is becoming more important and must take into account the optional value of the intermediate interaction of energy of reactants with catalysts, as well as porosity and physical properties.

ROLE OF POLYMERS

Polymers and their role in science and engineering are constantly being debated, especially considered in an industrial environment. Therefore, polymer synthesis is also misinterpreted instead of lack of understanding about the process as well as reluctance to systematic experiment. Polymers were originally developed for their durability and resistance to all forms of degradation, which includes biodegradation, and for their special performance characteristics achieved through control of molecular weight and functionality.

Polymer properties and interfaces are of paramount importance in many low- and high-tech applications. Surface appearance and properties play a major role in the selection of material. Also of considerable importance are polymer properties such as surface roughness, chemical surface composition, color and gloss, as well as softness, scratch resistance, or resistance against environmental attacks and their dedicated manipulation [1].

ROLE OF POLYMERIZATION

In each polymerization, the catalyst or initiator system undergoes the most important characteristics of polymerization and resulting polymers, namely [2],

- Reaction conditions—polymerization temperature, medium (solvent), pressure in the case of gaseous monomers.
- Polymerization activity—consumption of mole of catalyst (initiator) during polymerization.
- Polymerization tacticity—stereoregularity determines its thermal properties such as melting temperature and glass transition temperature.
- Stereocontrol mechanism—Active propagating center dictates the stereochemistry of monomer.
- Polymerization control—Reflects polymer molecular weight, molecular weight distribution, and initiator (catalyst) efficiency.

POLYMER WASTE

Polymers find wide acceptance for their properties, cost-effectiveness, and capacity to enhance the comfort and quality of life in modern industrial society. However, these same properties that make the polymers so useful have contributed to a problem with disposal, drawing huge media attention to polymer visibility in the environment as litter and their obvious contribution to landfill depletion. In view of their low density, polymers occupy a high volume fraction of buried waste despite their relatively low weight fraction [3].

POLYMER GROWTH

Polymer research in the laboratory during synthesis has been focused on the following problems:

- Fundamental research concerning the influence of monomers on synthesis or polymer modification.
- Procurement and preparation of starting materials.
- Development of synthesis technology.
- Side reactions, especially during polymer synthesis.

- Relationship between structure and characteristics of monomers that enables design of polymers with the desired performance properties.

The future growth of polymers, a versatile industry, will depend on new advances in basic polymer knowledge. Polymerization and polycondensation processes are an art of building polymers in molecular engineering. Molecular structure and performance characteristics enable better design of polymers with improved properties and economic advantages. The objective of polymer synthesis is to make polymers as strong as steel, clear as glass, light as a feather, resistant to heat, and thermally stable. Research and development continue to extend the availability of polymers and introduce new polymeric materials to promote the growth of the industry.

POLYMERIZATION PROBLEMS

- Emulsion polymerization research and development is devoted to determining particle size of the final emulsion and polydispersity. It involves loading a reactor with two crops of small seed particles, catalyst, surfactant, and so on, feeding the reactor with monomer(s), and observing the competitive growth rate of the two sets of particles.
- In suspension polymerization, the presence of suspending agents such as stabilizers hinders the coalescence of monomer droplets and adhesion of partially polymerized particles during the course of polymerization. Solid beads may be produced in the same spherical form in which the monomer is dispersed in the aqueous phase. The industry is continuously faced with problems in processes in controlling the particle size distribution, which shows that the main issues are still far from solved [4].
- Lower productivity of suspension polymerization for the same reactor capacity is used in bulk polymerization. There the reactor continue to be in problems of waste water with polymer buildup on the walls, baffles, agitators, and other surfaces with no continuous commercial operation. It is also in difficulty in producing homogeneous copolymer composition during batch suspension polymerization. Semibatch polymerization is more difficult with suspension versus emulsion polymerization because of lower interfacial area between particle and water [5].

POLYMER PRODUCTS

Polymer products are becoming more complex with precise quality requirement. Polymerization reactions require sensitive catalysts, control of monomer feed ratios, effective mixing, and precise temperature. High viscosity that is often encountered in polymerizing fluids not only inhibits mixing and impedes heat transfer but also affects the reaction kinetics [6].

The amorphous polymer separation from polymer solutions upon shear flow, deformation takes place.

This effect is of particular importance in technological polymer synthesis; under the action of deformation, the phase separation of reaction blend takes place. It exerts a harmful effect on the kinetics of the whole process [7,8].

During the past decades, increasing attention has been paid to a number of aliphatic polyesters owing to their biodegradability and biocompatibility. One of the most studied polyesters is polylactide, which is commonly prepared by ring-opening polymerization of lactide catalyzed by organometallic compounds. A variety of initiators and catalysts have been used in the ring-opening polymerization, including compounds of aluminum [9–11], lead [12], tin, 2,4-[13], zinc, [14,15], and bismuth [12]. The catalytically active metal is, for instance, in the reaction use of stannous octoate, covalently bound to the polymer chains as a result of polymerization mechanisms, and is, in most cases, difficult to remove completely from the polymer. This may affect the degradation environment in a harmful way and possibly even result in accumulation. These effects are particularly undesirable in medical applications, where both the polymer and the degradation products, including residues of the initiator, preferably should be nontoxic and resorbable. For this reason, salts and complexes of metals such as Al, Bi, Cd, Pb, Y, and Sn compounds should be avoided [16,17].

In many applications, the properties desired at a polymer surface, such as adhesion, wettability, gas impermeability, stain resistance, or biocompatibility, are often specific and distinct from the bulk properties of the material. Conventionally, control of surface properties is achieved by surface modification through various chemical or physical processes, such as plasma or flame treatment, chemical reaction, surface grafting, or metal coating [18,19]. Many of these kinetically governed reaction mechanisms allow relatively little control over the equilibrium surface composition and structure. Additionally, such processes may be expensive and difficult to model. Other techniques for controlling surface properties include the incorporation of small molecules or oligomeric additives that migrate to the polymer surface. Such additives may compromise the polymer's bulk physical properties, however, and, because they are not strongly bound to the polymeric matrix, may be removed by evaporation, dissolution, or wear. While technologically promising, surface control via chain end segregation may be prohibitively expensive in view of the relatively high cost of synthesizing end-functionalized polymers.

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CHAPTER 9

RESEARCH ON POLYMERS

Polymer research, traditionally being biased toward physical function and material, begins with synthesis [1]. Synthesis must be practical and provide sufficient quantities. In parallel, the side products and structural defects must be carefully investigated. In the face of increasing populations and diminishing supplies of basic raw materials, research continues to focus on maintaining and improving living standards.

9.1 PURE RESEARCH

Pure research requires skill, intelligence, and training in order to be successful and yield a profit. It is also measurably free of pressure, and organized and directed with growing appropriations for research. The effect of synthesis in research enhances the values derivable from monomers. The results from the laboratory have to establish the conditions governing the course of reactions. The difficulties anticipated or encountered are found by their number during the development into several stages. During polymer synthesis, experimental equipment is designed, setup, and operated. Material of construction, heat transfer study, development of system control, and balance of equipment proceed with design of semi-size operating plant. Commercial trials demonstrate output and costs, resolution of operating difficulties, and material production in sufficient quantity for commercial trials.

9.2 INDUSTRIAL RESEARCH

Industrial research requires motive and its immediate objective. It is always under pressure of time factor. With laboratory resources, it has been able to contribute to industrial progress in processes and many important industrial techniques. Industry research laboratory helps to improve the infant processes likely to be high. The difficulties during the processes lead from the laboratory to the plant.

Successful laboratory for industrial research is a plant of slow growth. Ultimate objectives of research may be its finding and developing exceptionally controlled imagination and are directed by a sense of relative values. Industrial research is commonly based upon the results of fundamental research. The quality and effectiveness of industrial research rises in proportion of fundamental fact and principle.

Emphasis on physical properties can well refer to established synthetic methods. Focus on polymer structures can design methods of synthesis; otherwise, it derives unknown target structure. Polymer research masters the details of the subject as far as laboratory methods allow to do so. Intricate study of synthesis does not accept any chemical explanation in simple terms.

9.3 PRINCIPLES OF POLYMER RESEARCH

Industrial applications of research are more notable in polymer synthesis. Many of the organic synthesis methods have never reached the industrial importance attained by the polymer. Research is the mother of industry and may lead to invention. Application of knowledge in research is the essence of invention.

Polymer research is supposed to be achievable by the classes of organic compounds as monomers. Renewed interest in polymer synthesis has been influenced by the following factors:

- Implementation of synthetic methods from organic and organometallic chemistry, and this interdisciplinary approach has largely increased the efficiency of polymer synthesis.
- The unique properties exhibited by polymers.

Industrial progress can be assured by the constant acquisition of new knowledge such as polymer synthesis. Through polymer synthesis, new raw materials, new products, better processes, and thereby new uses extend the market. The complex nature of polymer industry and the intense competition between countries consciously apply fundamental facts and principles. Polymer research has attained the standards of comfort and convenience by raising productive capacity. Research is nourished by complex outfit of machines and processes with multiplication of efficiency and product invention.

Polymer synthesis plays a role in the field of organic electronics, with potential applications in organic solar cells, organic light-emitting diodes, organic field-effect transistors, and electrochemical devices, attracting increasing research interest. The active materials in these devices are typically linear small molecules or polymers with a conjugated π-system being one of the most frequently used building materials [2]. Polymers with well-defined linear systems have been synthesized, and device preparation is performed with research innovation [3–5]. One of the research area of linear conjugated polymers can be the introduction of branching and two- or three-dimensional architectures. It has been proposed in terms of isotropic properties. Research activities are related to the generation-wise synthesis of well-defined polymers that exhibit properties based on polymer architectures. It is involved in comparison of solubility of increased in branched architectures with linear systems. Branching is an elegant tool in polymer synthesis to modify functional material properties such as energy levels and absorption properties [6, 7].

From the viewpoint of polymer synthesis, even structurally well-defined small molecules in combination with other functional groups are possible. Synthesis involves electropolymerization on electrodes, which allows modification of material properties, deposition parameters, and introduction of comonomers. With the help of chemical polymerization, it is possible to modify the polymers and their properties by the choice of polymerization techniques.

RESEARCH ON NATURAL OR BIOPOLYMERS

From both the social and environmental points of view, the worldwide interest in the replacement of petrochemical derivatives with renewable material in the production of valuable polymers is quite significant. The need is to reduce carbon footprints, shorten life cycles, and find alternative starting materials to synthesize new monomers and polymers with comparable properties. Therefore attraction of natural products performs pioneering research on polymer synthesis. Morphology and mechanical properties depend on reaction conditions and kinetics and phase behavior.

Significant progress has been made in fundamental and biomedical research on biopolymer synthesis and technology. Owing to their special characteristics such as nontoxicity, biodegradability, and biocompatibility, various biomaterials and their derivatives have been used in pharmaceuticals applications [8–11].

9.4 FUTURE REQUIREMENTS IN POLYMER SYNTHESIS

Understanding polymer synthesis in an industrial environment may be useful to know the research on polymer innovation. Invention is discovery, and new polymers may be invented. The chemistry of transforming monomers into polymer does not guarantee that the chemistry will be reduced to practice in an economical manner.

- Methods of synthesis should be designed to use and generate monomers that possess little or no toxicity to humans and the environment. Polymers should be synthesized such that it maximizes the incorporation of all materials used in the process into the final product and is also effective in their desired function.
- Synthesis should involve less hazardous materials and should be chosen to minimize the potential for chemical accidents, fires, and so on.
- Synthesis should be carried out at ambient temperature and pressure in order to conserve energy and avoid use of solvents, separating agents, and others unnecessarily.
- Economic impacts should be minimized. Therefore, raw material or feedstock should be renewable. Synthesis of polymers should be such that the polymer at the end of the use harmlessly degrades and does not present in the environment. Unnecessary steps should be minimized or avoided. These steps require additional regents that can generate waste and environmental pollution.
- It is better to prevent waste than to treat or clean up waste during synthesis. Catalytic reagents are superior to use in polymer synthesis. Analytical methods need to be further developed to allow for real or real-time, in-process monitoring and control prior to the formation of the polymer.

POLYMER SELECTION AND SYNTHESIS

The choice of polymer synthesis method and type of polymer for a specific application depends on several factors including polymer characteristics, cost, availability, and processing characteristics. For a given application, polymer synthesis leads to a selection process that can be tedious and expensive [12]. Polymer synthesis acts as the reservoir of one's knowledge about the monomer and the polymer. It contains knowledge that is transferable and extremely useful. They may reveal many factors such as process optimization, which varies simultaneously [13].

Polymer synthesis methods have received tremendous attention due to material versatility and improved mechanical, thermal, and processing properties; chemical stability; and possible structural modifications. The properties of synthesized polymers range from liquid and amorphous to solid and highly crystalline, depending on the polymer microstructure. The range of applications is as broad as their material properties. The development of novel polymerization techniques or advancement of existing ones as well as polymer synthesis of novel monomers enables the adjustment of properties of the materials, opening up further advanced applications. Owing to the increasing interest in materials for special applications, the research and development of polymer synthesis is a highly interesting field, whose importance will increase in future as novel improvements are made possible.

In polymer synthesis, increasing attention has to be given to biodegradability and biocompatibility. Studies are also commonly being done on biopolymers with a view to obtaining a high molar mass polymer with high monomer conversion. In polymer synthesis, polymerization is hardly controlled in terms of polymer yield, molecular weight, and its distribution due to inherent side reactions. Several modified polymerization systems have to be developed to prevent serious side reactions and to afford with well-defined polymer chain structures.

Successful strategies for polymer synthesis involve polymerization of substituted polymers with controlled molecular weights and narrow polydispersities. Polymer synthesis involves the chemical reaction of polymers. Interfacial polymer reactions are also important in polymer synthesis as a probe of polymer statics and dynamics at surfaces. Research is motivated principally by industrial applications of particular commercial relevance for the creation of new materials with enhanced properties.

The unique combination of high electrical conductivity, optical transparency, and stability of the conducting polymer has generated considerable research interest in relation to its use in a number of technological applications. The strong electron-donating properties of polymers and their excellent aptitude for electropolymerization have given rise to a rich chemistry focused on the research design of conjugated polymers [14, 15].

In polymer synthesis, task identification of monomers for reaction and isolate reaction products are associated with equipment with supporting utilities and other facilities. Each stage of synthesis follows with process implementation sense. Polymers can be made at one stage and are clearly limited by selections. Optimization is to be made among alternatives and may depend on costs associated with the stage of implementation. Decisions are made in earlier stages to have greater impact on the overall economic outcome of the entire polymer synthesis.

PROCESS OF POLYMER SYNTHESIS

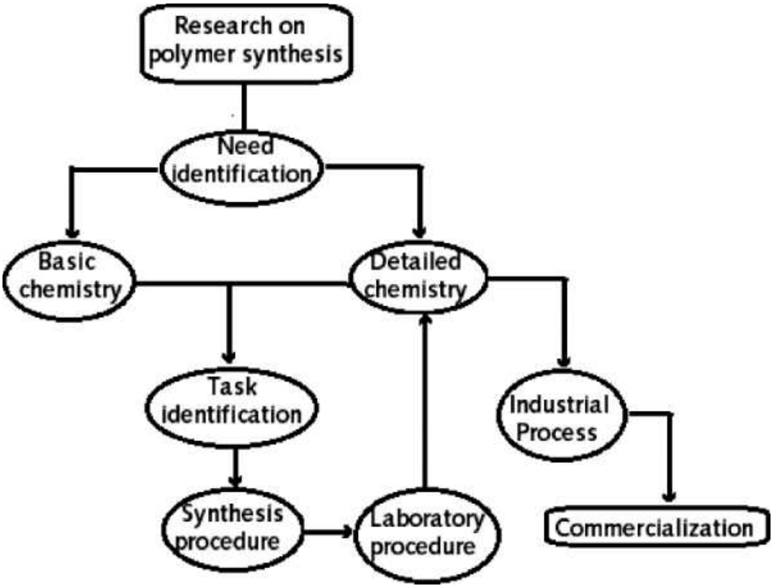
Polymer syntheses are innovative with the lowest level of detail at the first stage. The objective might be called target level. The rough indication is to be accomplished at the synthesis stage as well as made feasible in the process. Target polymers can give much information about what is technically and economically feasible with performance before synthesis. Each stage in the synthesis might be called the preliminary or conceptual level. Tentative solution is to be given to synthesis during problem is conceived. In the first stage of synthesis, the goal for the particular polymer is to be specified. Target level follows analysis, evaluation, and performance.

Polymer synthesis is going from target level to conceptual level to the refined level. Refined level accomplishes the synthesis process using a diagonal approach, with the conceptual level at one stage preceding the execution of the targeting level.

INNOVATION IN INDUSTRY

Innovation is an organized multistage goal-directed process in polymer synthesis. It leads from the identification of monomers to the production of polymers, which may be implemented in a variety of ways. The details and emphasis of the innovation process may differ depending on whether the objective is to synthesize a new polymer or improve an existing one. In general, in polymer synthesis, the need must be identified. The synthesis route must be found from available raw materials that produce the desired product. In the polymer synthesis process, the implementation in terms of chemical reactions must be conceived, designed, construed, started and synthesized.

In polymer synthesis, the conceptual process design is the stage of basic chemistry in which the fundamental reaction chemistry is involved with the support of chemical details of catalysis, solvents, and reactions conditions.



Polymer synthesis is generally the business of making polymers for research rather than making an industrial product [Flow diagram 9.1]. This is perceived needs and the materials offer needs in a valuable manner. Polymer synthesis involves more conversion and transformation. It is generally more capital-, labor-, and energy intensive. Synthesis facilities tend to be large and aggregated to take advantage of economies of scale. It also has a very long operating life and comes into existence through a series of actions called innovation process. The synthesis starts from the identification of the monomer.

The characteristics of polymer synthesis are fairly large manufacturing activities, very long operating lives, high initial capital costs, high operating costs, and potential environmental impacts, which place special importance on the implementation of the research process, in particular, on making good synthesis design.

All existing polymerization techniques were somehow invented. Some of them, in particular, are lower-volume products involving complex synthesis that has been implemented by a rather straightforward extrapolation of the laboratory procedure. Laboratory process is used to experimentally demonstrate the transformation of available monomers into the desired polymer. Large-volume polymers are more often implemented as a continuous process that bears little resemblance to either the procedure or the equipment used in the laboratory. Generally, there area very large number of combined alternative pieces of equipment and interconnections among the pieces of equipment that will feasibly implement the process of synthesis. Identifying better process alternatives is the key component of polymer synthesis.

Research issues are especially relevant for high-performance polymers for use in extreme environments. Long-term goals are as follows:

- Improvements in methods of synthesis, which leads to pure starting monomers.
- Prevention of weak bonds in polymers, which leads to an improvement in the properties of known polymers.
- Morphological improvements.
- Improved synthesis with new processing techniques.
- Polymers that adapt to change themselves with the changing conditions.
- Increase in activities to meet complex performance needs in a variety of environments.

Lack of reproducibility, difficult and expensive scale-up, and standardization of synthetic processes are the main hurdles to the industrial production of raw synthetic and semisynthetic polymers for (bio) pharmaceutical applications [16]. Time-and energy-consuming synthetic pathways that usually involve the use of volatile, flammable, or toxic organic solvents are apparently cost-viable and environment-friendly for synthesis on a laboratory scale. However, they are often not viable in industrial settings, especially on account of the impact they have on the product cost and the deleterious effect on the environment. Therefore, broad fundamental research and effective transformation of the results are required on application-oriented development. However, explosive growth of research on polymer synthesis is the primary reason for the great interest in polymeric materials which lies in the major research changes and can be achieved polymer properties. Still, some of the areas in polymer syntheses are in their infancy.

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Basics of Polymers

Materials and Synthesis

Muralisrinivasan Natamai Subramanian

Basics of Polymers: Materials and Synthesis is a major investigative tool in the design and synthesis of polymers in the modern academic and industrial fields. Materials and synthesis encompass a wide range of operations such as selection of monomer(s) and polymerization techniques for the synthesis of materials under various operating conditions. The design and synthesis of each process should therefore be based on specific features. This book highlights the diversity of approaches used in understanding polymer synthesis.

This book is designed to be used as study materials for students, professionals, and professors that support their wide use on material and synthesis. It emphasizes the value of each relevant synthesis method and polymerization type, rather than complex mechanisms or the history of its development. An area of considerable interest in this book is polymer synthesis in terms of the relationship between the structure and function of monomer(s). This book is also directed toward postgraduate students and practicing engineers who wish to develop polymer synthesis.

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