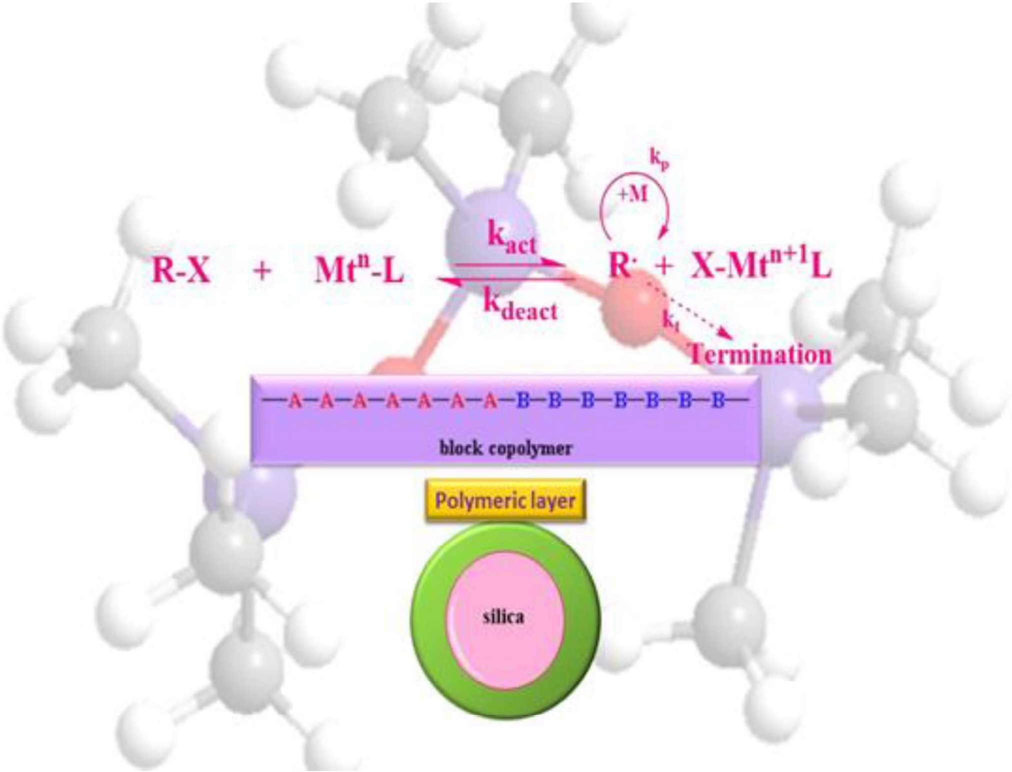
Chapter 1
General Introduction



1.1. Consequences of polymers

In the 1920s, German chemist Hermann Staudinger (1881–1965) introduced the modern view of polymers as chains of covalently-linked repeating units ("many parts")[1] called polymerization process. Polymers are a type of advanced material that can be found in a wide variety of everyday objects. The importance of polymers, which have been used for everything from simple purposes to advanced biopolymers and therapeutic polymers, has recently been brought to light[2]. In a variety of research and industrial domains, thermoplastic and thermosetting polymers both represent interesting and difficult applicants[3]. The applications of polymers depend on their architecture (form and size), functionality, physical characteristics of individuals, molecular weight, etc. Demonstrated vinyl monomer polymerization has huge industrial applications. Thermoplastic vinyl polymers have several uses. Free radical, ionic, and ionic coordinate polymerization produces several vinyl monomers. Radical polymerization improves ionic and coordination polymerization[4].

1.1.1. Brief Introduction and History

Polymer science studies plastics, synthetic and natural fibers, rubber, elastomers, coatings, adhesives, sealants, and other popular materials. They possessed distinct viscoelastic and flexible characteristics before polymers were discovered. In 1862 and 1866, Parkes and Hyatt discovered the first nitrocellulose-based plastic.[5]. Through the polycondensation of phenol and formaldehyde, Baekeland produced the first synthetic thermoset polymer called "*Bakelite*", in 1907[6]. In 1933, Ellis made the discovery of unsaturated "*polyesters*", which were first used commercially in 1942[7]. Even though Liebeg and Regnault mentioned Vinyl chloride (VC) in 1835, its polymerization potential was not fully understood at the time. Later, in 1878, Baumann looked into what happened when VC was exposed to sunlight and found that a white colour substance formed[2]. Since the 1930s, this monomer has been utilised in elastomeric co-polymers. Poly(Methyl Methacrylate) (PMMA) has been made since 1933, when it was first used to make aircraft windows. It is also used for a wide range of other things where transparency or good weather resistance are crucial[8]. In 1956, production of High density polyethylene (HDPE) resulting from this process began. One of the most common types of plastic at the moment is HDPE. Soon after (1953), Ziegler and Natta independently created a group of stereospecific transition-metal catalysts, which helped produce HDPE as well as polypropylene (PP), a major commodity plastic, in 1957[9, 10]. Metallic, mineral, and organic fibres are all possible. Almost all nonmetallic fibres are made of polymeric materials, which can be natural, artificial,or synthetic[11]. Organic fibres are made of carbon or heterochain polymers, while glass and asbestos are examples of macromolecular silicate fibres[6, 12]. Most organic synthetic fibres are thermoplastic, a few are elastomeric, and only a small number are thermoset. Carothers is known for making the first synthetic fibre, which is called "*nylon66*"[13]. Ziegler's finding of heterogeneous stereospecific catalysts led Natta to make crystalline PP in 1954. In 1957, people started making PP fibres and filaments for sale. Styrene-Butadiene (SBR) is a co-polymer of styrene and butadiene[14]. In the 1920s, emulsion polymerization led to high-molecular-weight polymers[15]. A desired amount of a polymer can be produced through polymerization using the right combination of monomers, catalyst, and polymerization technique[16, 17]. The polymerization process are given below.

1.1.2. Classifications of polymers

Polymers are classified by monomer form. (i) Homopolymers, formed of the same monomer; (ii) hetero/co-polymers, composed of two or more monomers. Random, blocking, and grafting copolymers are categorised by monomer structure. Characterizing polymerization included addition and condensation polymerization. The polymerization process follows the three main steps including: initiation, propogation and termination (chain transfer)[18, 19]. The route of classifications of polymers given in below Figure 1.1.

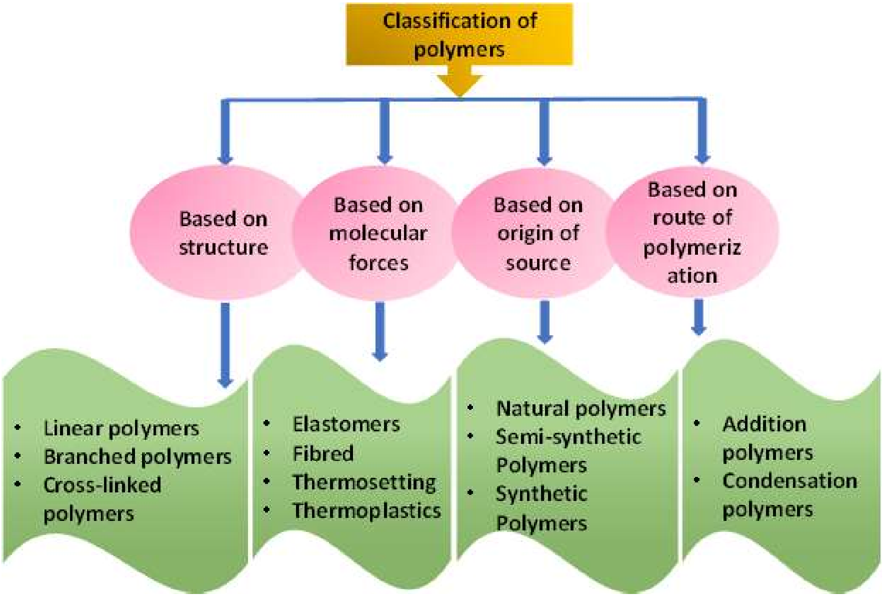


Figure 1.1 Classification of polymers.

1.2. Free Radical Polymerization (FRP) and its limitations

FRP is a chain growth polymerization process that involves sequential addition of monomer units[18, 20]. The Figure 1.2 represent the different polymerization process.

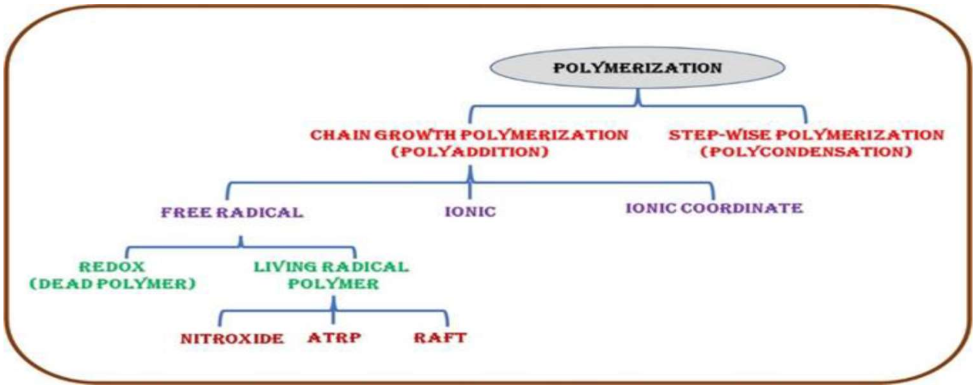


Figure 1.2 Different polymerization techniques.

FRP is a propogative radical generated by breaking the double bond of a monomeric unit. It is suitable for different techniques such as solution, bulk, emulsion and suspension polymerization due to its mild reaction conditions, rapid polymerization, and lack of complexity. It also offers a wide range of alternatives for monomers, allows to choose from a number of different processes, and takes much less time than step-growths. However, radical polymerization has some restrictions when it comes to molecular weight and polydispersities. Cationic and anionic ionic polymerization are useful for the synthesis of polymers with controlled molecular weight (MW) and low poly dispersity index (PDI)[4, 21]. The basics and limitations of FRP mentioned in given below in Figure 1.3.

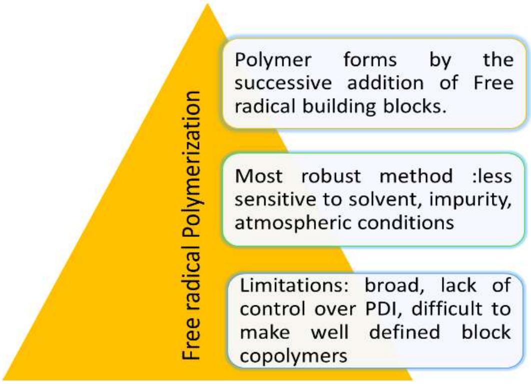


Figure 1.3 General information of FRP.

1.3. "Living"/Controlled Radical Polymerization (L/CRP)

The Limitations of FRP is further overcome by Living/Controlled Radical Polymerization (L/CRP) technique. The term "living polymers" was used for the first time by M. Szwarc and a coworker in a work they published in 1956[22]. After that, he discussed this concept in "*Nature*"[17] publication individually. It is completely dependent upon the pure reactions, so it prevents termination process during polymerization which is carried on by impurities. Termination steps will only occur when all the monomeric units get consume. As a result, adding more monomers will allow the polymerization to proceed, it is also known as "chain polymerization without chain breaking processes". The fundamentals of CRP tells that the initiation rate of polymerization process ia higher then propogation step. As a result of the irreversible addition of monomers to polymer chains, the range of the molecular weight distribution (MWD) becomes very small[24]. The concentrations of propagating and stable radicals are equal at the start, but there is a rapid and drastic change in concentration. The stable radical acts as a controlling agent because it is sufficiently reactive to couple rapidly with propagating chains to convert them reversibly into dormant, non propagating species.

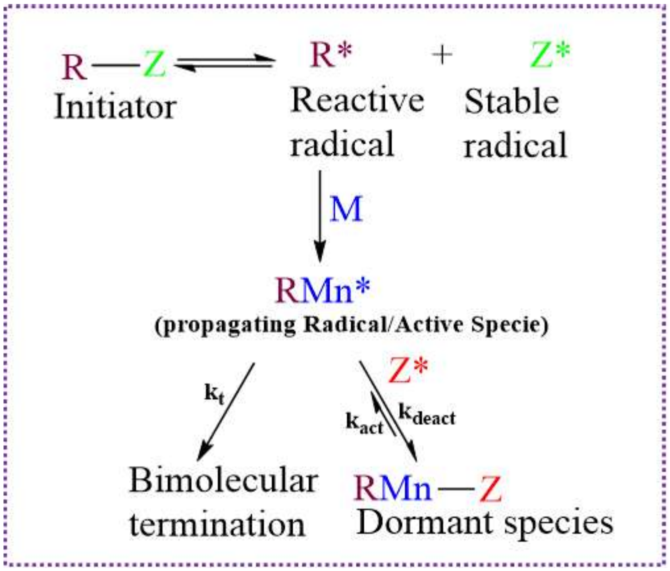


Figure 1.4 General mechanism of L/CRP, image modified from *ref*[23]

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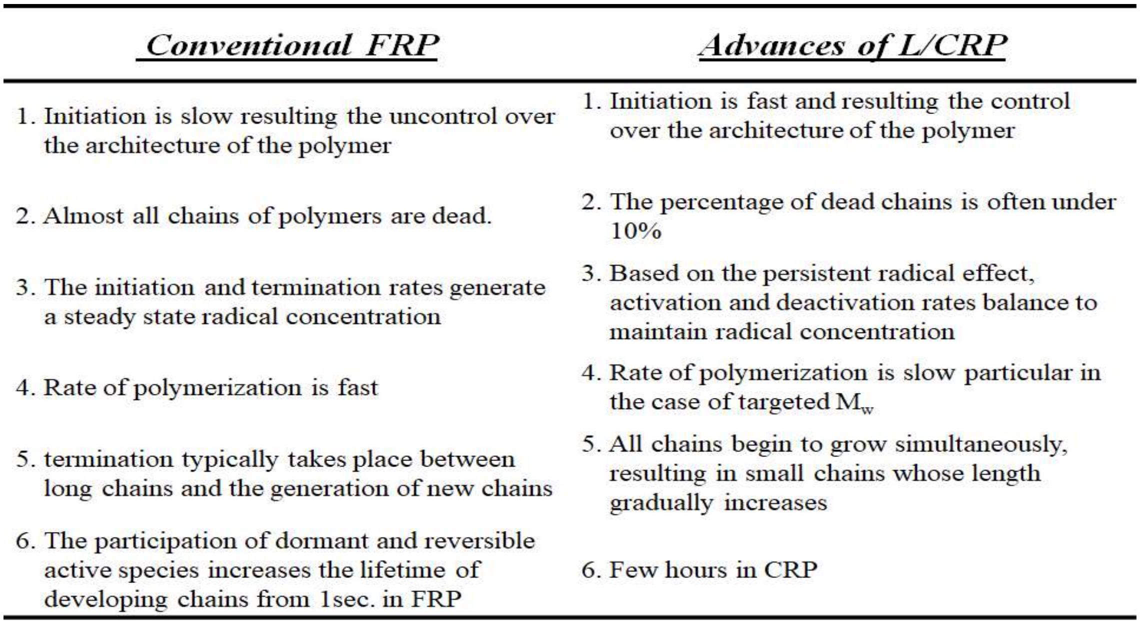
Table 1.1. Difference between Conventional FRP and Advances of L/CRP



Conventional FRP	*Advances of L/CRP*
1. Initiation is slow resulting the uncontrol over the architecture of the polymer	1. Initiation is fast and resulting the control over the architecture of the polymer
2. Almost all chains of polymers are dead.	2. The percentage of dead chains is often under 10%
3. The initiation and termination rates generate a steady state radical concentration	3. Based on the persistent radical effect, activation and deactivation rates balance to maintain radical concentration
4. Rate of polymerization is fast	4. Rate of polymerization is slow particular in the case of targeted M_w
5. termination typically takes place between long chains and the generation of new chains	5. All chains begin to grow simultaneously, resulting in small chains whose length gradually increases
6. The participation of dormant and reversible active species increases the lifetime of developing chains from 1sec. in FRP	6. Few hours in CRP

Living polymerization has evolved to include coordination/organometallic, cationic, and radical polymerization in the last 50-60 years[17, 25–29]. Living polymerization approaches are being developed to address the limitations of traditional FRP and provide technological accessibility for future polymer evolution[26, 30]. Considering that FRP is a popular technique because it doesn't need extreme conditions like cationic or anionic, it is the first one to be considered. The diffrence between Conventional FRP and Advances of L/CRP given in Table 1.1. The uncontrolled MW and polymeric structure obtained by the present termination of the growing monomeric chain. In term of Application perpose the polymer sould be in suitable architacture. Due to its commercial potential, several approaches of CRP technique have been established with greater control over the molecular structure and its weight. The most widely considered polymerization mechanism was Nitroxide Mediated Polymerization/ Stable Free Radical Polymerization (NMP/SFRP)[31], Atom Transfer Radical Polymerization (ATRP)[32–35] and Reversible Addition Fragmentation Chain Transfer (RAFT)[36]. CRP is used to prevent bimolecular termination by keeping low radical concentrations by reversible termination or reversible chain transfer. RAFT is the example of reversible transfer, while ATRP and SFRP are the examples of reversible termination. To control the MW, dithioesters, dithiocarbamates, and xanthates are used as transfer agents. The monomer that will be polymerized affects the RAFT agent, and polymers must be deodorised to eliminate the smell of agents[34, 36, 37]. The publications by Georges et al. in 1993 on the controlled radical polymerization of styrene employing TEMPO (2,2,6,6-tetramethyl-1-piperidynyl-N-oxy) as a mediating agent likely served as a guideline for the development of CRP techniques in the modern era[37, 38]. The dormant alkoxymines and actively propagating species are brought into dynamic equilibrium in order to maintain control in NMP. Figure 1.5 shows the overall history of living polymerization in a brief and silective timeline.

1.4. Generation of Atom Transfer Radical Polymerization (ATRP)

> "*Atom transfer radical polymerization involves an organic halide undergoing a reversible redox process catalyzed by transition metal compound*"

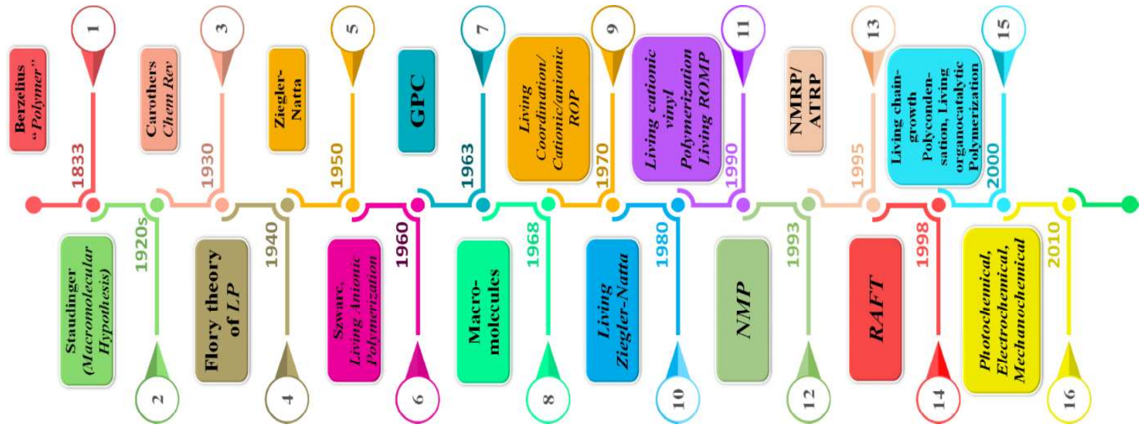


Figure 1.5 An overview of the history of living polymerization in a brief and silective timeline.

In the middle of the 1990s, two polymer scientists independently developed the ATRP. Kato et al. exhibited the use of a Ru(II)-metal complex for the polymerization of methyl methacrylate (MMA)[39], whereas Matyjaszewski et al. proved the use of copper for the polymerization of styrene[32]. ATRP is one of the most quickly growing areas of chemistry, with the publication in bulk , emulsion, solution, suspension, etc. number about doubling every year.

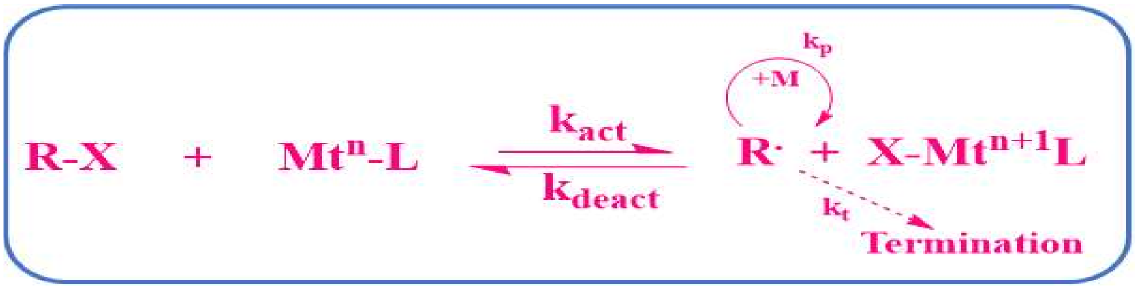


Figure 1.6 General mechanism of ATRP , image is represented from *ref*[34]

1.4.1. Mechanism of ATRP

As seen in Figure 6, Radicals that are propagating can be reversibly activated or deactivated by means of a dynamic equilibrium with a transition metal complex (Mtn-L). The rate of deactivation (kd) is significantly higher than the constant rate of activation (ka). The persistent radical effect (PRE) causes the radical concentration in ATRP to decrease and the equilibrium of ATRP to move towards dormant species (kd>>ka). The final termination (5% of rising radicals) will result in an increase in concentrations of deactivating species. An efficient ATRP will have minimal contribution of terminated chains, but consistent growth of all chains achieved by fast initiation and rapid reversible deactivation.

Components of ATRP

ATRP is a multicomponent system. The four main components of ATRP are the monomer, an initiator containing a movable (pseudo)halogen, ligand, and a catalyst which is composed of a transition metal species with suitable ligand. In ATRP temperature, solvent and reaction time are also the most important factors. ATRP technique is used to polymerize monomers with substituents that stabilize propagating radicals[34, 40, 41]. The primary function of an initiator in ATRP is to establish the total amount of polymer chains growing, and the concentration of developing chains remains constant with initiator concentration. The halide group, X, should quickly travel between the growing chain and the transition-metal complex to produce well-defined polymers. Alkyl halides have activating substituents on the R-carbon, and the R-X bond may break by heterolytic cleavage depending on the selection of transition metal catalysts[34, 42, 43]. Catalyst must contain two easily available oxidation states, possess a suitable affinity for halogens, and expand following oxidation.[32, 34]. ATRP ligands control metal center redox potential and a complex transition metal.[34]. ATRP is suitable for both homogeneous and heterogeneous systems, with solvents such as ethyl acetate, anisole, tetrahydro furan, chloroform, acetone, dimethyl formamide, toluene, benzene, alcohol, water, ethylene carbonate and many more. Temperature increases increase polymerization rate, but side reactions may occur.[44, 45].

1.4.2. Kinetics of ATRP

$$\mathrm{R_P} = k_p[\mathrm{M}][\mathrm{P}^*] = k_p[\mathrm{M}]\,\frac{k_a}{k_d}\,[\mathrm{R{-}X}]_0\,\frac{\mathrm{Cu^I}}{\mathrm{Cu^{II}X}} \text{ ....} \textit{equation 1.1}$$

ATRP requires fast initiation of polymer rate, controlled chain length, and rapid deactivation of developing chain to reduce radical termination. The reversible halogen transfer of transition metal complex ($\mathrm{Mt^n}$-L) and dormant species (R-X) are the functions of ATRP given in Figure 1.6. It formed the propagating radical (R*) and a metal complex goes to a higher oxidation state ($X\text{-}Mt^{n+1}\text{-}L$). In a deactivation reaction, radicals interact reversibly with oxidized metal complexes, $X\text{-}Mt^{n+1}\text{-}L$, to reconstruct the dormant species and the transition metal complex ($Mt^{n}\text{-}L$), which is the activator, in the lower oxidation state. The concentration of activation and deactivation variables in the ATRP equilibrium controls how quickly polymers are formed. Activation (kact), and deactivation (kdeact) are the rate constants for these processes, and polymer chains are created by adding monomers to radicals. Termination reactions (kt) occur via radical coupling and disproportionation[34].

1.4.3. Factors affecting ATRP

A. CRP process increases concentration of propagating radical in dynamic equilibrium with dormant species, leading to MWD narrowness and polymerization predicted by ratio of consumed monomer to dormant chains.

B. ATRP resembles traditional radical polymerization, but termination reactions can be avoided by reducing the concentration of growing radicals and establishing a rapid and reversible equilibrium. This reduces the proportion of termination in compared to propagation, resulting in narrow MW and PDI.

C. Low polydispersity polymers can only be produced if the transfer reaction between the developing radicals and the dormant species, Mn-X, is quick compared to propagation. The ratio of the deactivation rate to the propagation rate has a significant impact on the number of polymers in the reversibly deactivating system.

D. Alkyl chlorides are efficient initiators, but butyl chloride, C4H9Cl, and dichloromethane, CH2Cl2, are less effective, resulting in uncontrolled polymers with larger molecular weights than predicted and wider molecular weight ranges. Since the atom transfer process reflects the strength of bond breaking and formation in Mn-X, it is anticipated that the leaving group, X, will have a significant effect on the atom transfer radical polymerization. ATRP is faster when bromine is used as a ligand than chlorine.

The above given points represent the factors and its effects of ATRP[46].

1.4.4. Merits and Demerits of ATRP

ATRP is a robust macromolecular method for producing polymers with regulated molecular weights and low functionalities. It requires fewer strict experimental conditions, is tolerant to a wide variety of functional groups, and is compatible with both aqueous and organic media. It is the only catalytic RDRP procedure that requires only a few ppm of catalyst, which decreases the risk of catalyst contamination in the final product polymer. Re-initiation can be used to make linear and star-shaped block copolymers with complex architectures using end functionalized polymers as macro initiators. The polymer chain grows slowly and can be modified throughout the process to create a polymer with desired characteristics. The process requires transition metal catalyst, copper halides, and must be carried out in deoxygenated systems to prevent radical reactions with oxygen and the catalyst[34, 47–50].

1.5. Blocks/multiblock copolymers (BCPs)

ATRP enables the synthesis of materials with unique topologies, from blocks and block-copolymers to multi block copolymers with regulated topologies. Polymers have been produced in the form of stars using four different methods. ATRP can produce di-, tri-, or multiblock copolymers when an activated alkyl halide is present at a polymer chain end also can make the next block grow from an isolated macroinitiator or by adding a second monomer to a reaction that is almost done. The synthesis of PS-*b*-PMMA and PMMA-*b*-PS was the first reported for the block copolymers[32, 51]. Our group also synthesized the tri and pentablock copolymers by using styrene as a monomer make is as a macroinitiator and chain extended with methyl methacrylate and n-butyl methacrylate with the controlled PDI at 1.28 with high yield[52]. Another work from the same group demonstrated by Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET-ATRP) and synthesized triblock copolymer of PMMA-*b*-PS-I-PMMA had very accurate 1.05 PDI by using β-Cyclodextrin (β-CD) as a reducing agent[53]. Here, Figure 1.7 shows schematic representation of block copolymers (BCPs) and its topology, composition, functionality, and molecular composites.

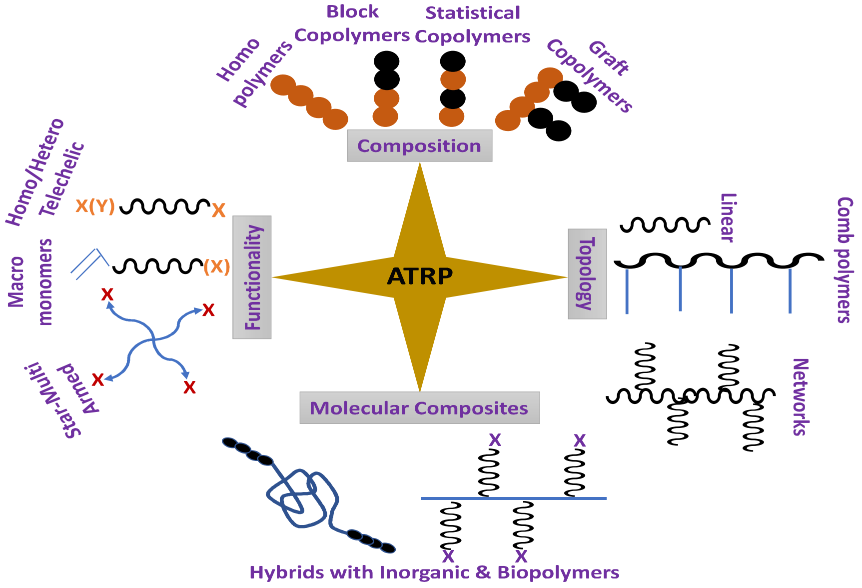


Figure 1.7 Schematic representation of BCPs and its topology, composition, functionality, and molecular composites.

Herein, the synthesis of multiblock (pentablock) copolymers[54] is performed by ATRP, in which three different monomers are used such as styrene, methyl methacrylate, and t-butyl acrylate (tBA). The reason behind the monomers are to gives excellent mechanism of ATRP and gives narrow MW with lower PDI. The applications in cosmetics as an additive and compatibilizers blending of structurally various polymers. Synthesis of such block copolymers using simple radical polymerization techniques resulting in copolymers with controlled segment length is interesting and challenging too. As the length of the polymeric chain increased the controllability of the overall MW and PDI is difficult because the additional monomeric segments are not same at a time it depend upon the overall condition that are maintained. The reaction should be followed the inert condition, reasonable Monomer:Initator (M:I) ratios which will give the predicted MW, the choice of catalyst and ligands and its capacity to formation of the radical through the initiators.

In the synthesis of multiblock copolymers copper catalyst is use amongst all other transition metals listed as Fe, Cr, Mn, Mo, Cu, Os, Ru, Re, Co, Ni, and Pd[34, 55]. When transition metals are used in ATRP, it is important to note that the metal center should have two oxidation states that are easily switchable by the electron transfer reaction, that transition metal compounds are typically soluble in organic solvents, which accounts for the solubility of both oxidized complexes of the metal core, and that another binding site for the incorporation of halogen from the initiator should be available at the metal center of the electron transfer reaction. The ideal catalyst for ATRP in the case of atom transfer should be extremely selective and should not take part in other reactions. To fulfil the fundamental requirement for monomers, it should have dispersion rate constants that deactivate very rapidly and have easily tunable activation rate constants. The most popular catalyst out of all of them is copper, though it has some drawbacks. The removal of unreacted copper content from the final mixture and unwanted colour of catalysts are the major disadvantages but still cannot ignore of the past research in this direction which was gave successful polymerization process.

In ATRP, ligands play an equally important role as initiators and catalysts. Their presence ensures the homogeneity of transition metal salts in organic media, helps to modify the reduction potential to give the metal center reactivity, and regulates ATRP equilibrium dynamics. There are a lot of different ligands that can be used, but the ones that contain nitrogen are the more common ones for the copper catalyzed ATRP reaction that has been studied in the given reference[56] Despite all odds, copper-mediated activity rises with the number of donor groups[57].

1.6. Silicon based polymers

Building polymers with an inorganic framework and organic or organometallic side groups using nanoscale building blocks is one of the most promising methods for creating innovative materials that combine the advantages of organic polymers and those of inorganic solids. In this regard, a lot of research has been done on inorganic polymers with backbones made of oxygen, nitrogen, silicon, or phosphorous atoms[58]. Organic/inorganic composite materials have been the subject of in-depth research for a very long time. Nanocomposites are organic/inorganic composites that contain nanosized inorganic phases. Most commonly, organic/inorganic nanocomposites are made of organic polymers and inorganic nanoscale building pieces. Novel polymer nanocomposites have been created as a result of the incorporation of inorganic modified agents with extraordinary properties into polymer matrices, such as silica dioxide, clay, fullerene, Carbon Nanotubes (CNTs), etc. Some of the most popular and significant examples include polysiloxane, polyphosphazene, and polysilanes. They have the benefits of both inorganic (such as rigidity and thermal stability) and organic polymer (e.g., Flexibility, dielectric, ductility and processability). Silicone structures offer a wide range of applications in materials science, optoelectronics, medicine, and environmental protection because of their physicochemical characteristics. The Si-H bond is polarized differently from carbon and its bonds, such as those with hydrogen, in that silicon has a positive character while hydrogen has a hydride character. Silanes therefore react heterolytically more readily than alkanes[59]. Compared to their carbon equivalents, Si-H and Si-Si bonds are weaker while Si-X bond is much stronger than C-X bond[60]. In addition, hydrosilicons are unstable compared to hydrocarbons, based on thermodynamic and kinetic studies. When the organic groups (Si-C) attached to silicon will increase the stability instead of attachment with hydrogen. The size of Si-O bond is longer then size of C-C bond (bond length are 1.64Å and 1.53 Å respectively) so, the bond angle of the Si-O-Si bond is around 143° and tetrahedral have bond angle is at ~110 which represent the flexibility of the Si-O-Si bond due to passing through the linear state (180°)[61]. Additionally, Si-O bonds have a far smaller torsional potential than C-C bonds. These characteristics make siloxanes flexible chains with great thermal stability[62]. Numerous potential applications for the silicon-containing polymers include surface coatings[63], optoelectronics[64], sensors[65], porous organic frameworks[66], and gas separation membranes[67], etc.

1.6.1. Vinyl terminated poly(dimethylsiloxane) in ATRP

Poly(dimethylsiloxane) (PDMS) is an example of the elastic polymer. It has interesting characteristics for biomedical applications, such as excellent biodegradation resistance, biocompatibility, physiological indifference, chemical stability, excellent optical transparency, insulating material, good mechanical properties, gas permeability[68–72]. The presence of $-CH_3$ group gives water contact angle of PDMS is ~180º±7º so it is hydrophobic polymer[73]. Since PDMS is hydrophobic, it can generate an anti-biofouling surface that inhibits bacterial attachment. As a result of its biocompatibility and hydrophobic properties, PDMS also has a significant impact on applications for medical implants[74]. The given below Figure 1.8 is the typical structure of PDMS, as the 3D model shows the flexible and elastic nature.

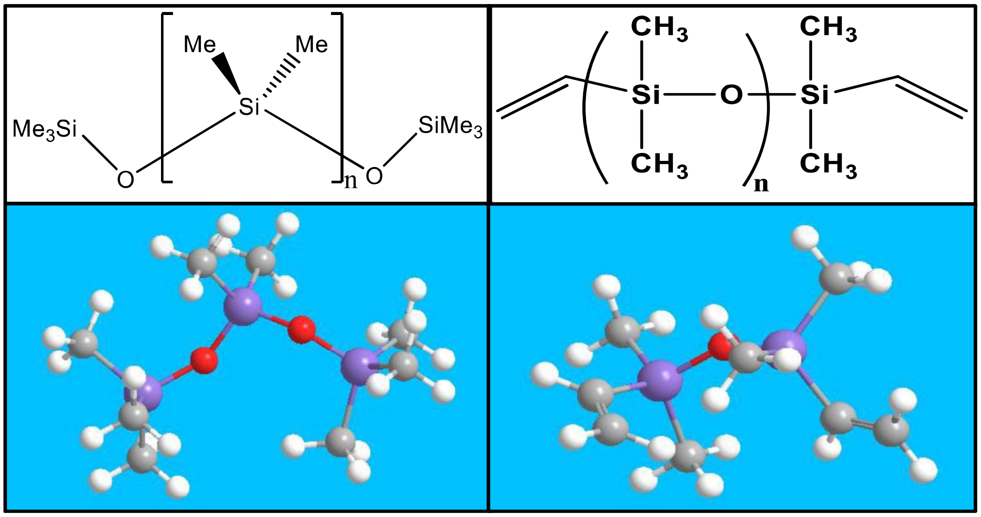


Figure 1.8 3D model of PDMS to show its complex structure.

With numerous functional groups like -OH, $-NH_2$, $-CH_2{=}CH_2$, and others, PDMS is one of them that is being employed extensively. PDMS has a high bond energy because of the methyl group and the siloxane backbone. PDMS possesses several remarkable features, including low surface tension, a low glass transition temperature, biocompatibility, and the ability to endure high temperatures, oxidation, moisture, and UV radiation. PDMS, on the other hand, has a low surface tension and is wettable[75].

1.7. Fumed silica and its grafting polymers

Fumed silica is a synthetic silicon dioxide product with a high degree of dispersion. Depending upon its production. It is categories in natural products, byproduct, or synthetic products. Quartz is an example of nature product while fly ash, silica fume and fused silica is the examples of their byproducts. Synthetic silicas derived from wet methods or heat pyrogenic reactions are generally amorphous silica with a surface area of 100 m^2g^{-1} or greater[76]. Flame pyrolysis of silanes, which yields the desired product is called fused silica and is by far the most significant thermal pyrogenic pathway[77, 78]. Fumed silica is a white powder with a bulk density of 20-50 g 1^{-1}. Fumed silica particle is amorphous silicon dioxide, thus its density is 2200 g 1^{-1}. The fact that the fumed silica particles have a nonporous, smooth surface is an exceptionally necessary property since it facilitates the interpretation of chemical surface reactions[79]. The surface silanol group and the presence of oxygen in silicon dioxide gives high surface energy hence it have hydrophilic nature and high surface area[76]. Various industrial applications make extensive use of fused silica. The two applications that account for more than two thirds of the market volume are thickening liquids as a rheological additive and reinforcing of elastomers as active fillers. Various industrial applications make extensive use of fused silica. The two applications that use as a rheological additive and reinforcing of elastomers as active fillers. Furthermore, it is used in anti-blocking, anti-foam agents, cable insulation, adsorbents, paper coating, cosmetics, catalysis, medicines, polishes, and other products. Fumed silica has two fundamental characteristics that come from its pyrogenic origin: a structure of finely distributed, aggregated particles, and a sizable surface area with high activity. All these applications take advantage of these characteristics[76, 80].

One of two techniques (Figure 1.9) for attaching a polymer to a surface are "grafting to" (attaching a resynthesized polymer to a surface/polymer backbone) and "grafting from" (growing polymers from a surface/polymer backbone having pendant functionality generated by RDRP). Another technique is "grafting through," which is based on the polymerization of a macro monomer (see below). In comparison to "grafting to" and "grafting through," the "grafting from" approach has the potential to simplify the synthesis of surface grafted polymers and has been used in conjunction with ATRP for tethering a polymer to a surface because only a small component needs to be coupled to the surface at first, after which the polymer component is grown in a stepwise fashion via the addition of small monomer molecules[30].

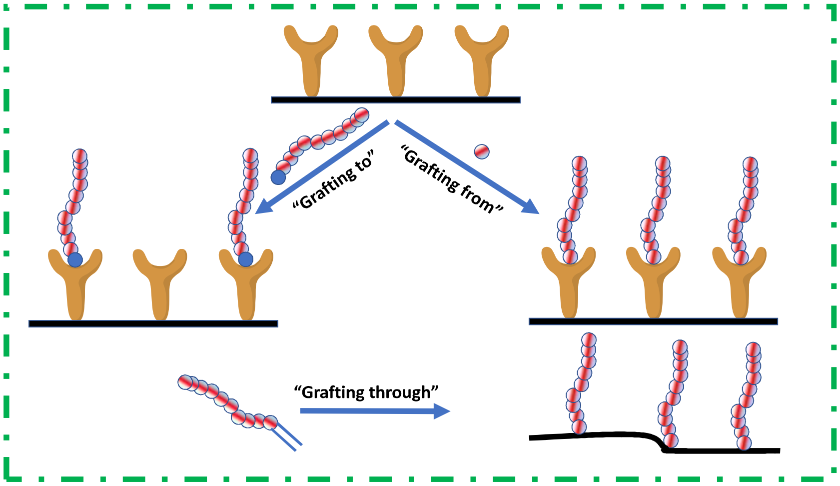


Figure 1.9 Different strategies for surface grafting with a polymer.

Organic-inorganic hybrid nanoparticles are critical functional components in a wide range of sophisticated applications, including nanomedicine, food packaging, and catalysis. Organic–inorganic hybrid materials can be tailor-made with an endless number of topologies and in a variety of physical forms based on the requirements of their eventual application, with the starting ingredients and synthesis and functionalization processes easily adjusted.

Core-brush particles, which are made by covalently grafting polymer chains onto an inorganic core, are gaining popularity because to their great particle size control, dispersibility, and usefulness. The features of the inorganic core and the organic polymer shell are merged in these hybrid nanomaterials, resulting in a novel class of materials that outperform their micro particle counterparts in terms of design and control of polymer and surface properties. Since their high surface area, cost-effective synthesis, and simple surface functionalization, biocompatibility, and cost-effective production, silica particles have garnered a lot of attention among the numerous inorganic oxides. Controlling the reactivity of silanol species (-SiOH) with organ silicon alkoxides in different media can be used to functionalize the silica surface in a simple manner[81]. The grafted organic moieties are important for the specific features of the resulting hybrid materials, such as chemical binding ability, surface charge, hydrophobicity, and colloidal stability, and can be derived with additional relevant functions. With the intent of modifying the nanoparticle surface, functional polymers have been effectively grafted to the surface from a large library of monomer species via controlled radical polymerization[82].

Silica–polymer hybrid materials are the most widely reported inorganic–organic hybrid materials among the several inorganic–organic hybrid materials. This is due to their widespread use and ease of particle creation. Paints, rubber goods, and plastic binders all employed silica nanoparticles as fillers. In the automotive, electronics, appliance, consumer goods, aerospace, and sensor industries, silica particles coated with organic modifiers are utilized in stationary chromatography phases, heterogeneous supported catalysts, and heterogeneous supported catalysts[83]. Core shell hybrid nanoparticles have sparked a lot of attention as nanocomposites, catalytic system components, and drug delivery system components. Inorganic particles having a grafted polymeric corona, known as nanocomposites, can be employed in bulk and have better compatibility with polymer matrices. The solid surface of the inorganic core can be covalently changed to prepare a well-defined nanocomposite by using the "grafting-onto," "grafting-from," or "grafting-through" approaches, as shown earlier in this section. The introduction of Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP) techniques has been a major driving force in the growth of this sector[84].

The fumed silica is used as a nanocomposite, so the target is to addition of different monomer with fumed silica by ATRP. SI-ATRP can produce polymers with a well-defined structure and a regulated molecular weight and molecular weight distribution made from inorganic nanoparticles. ATRP's controllability is dependent not only on a quick initiation phase, but also on a deactivation step that prevents free radicals from entering the chain transfer and termination step. The solubility and stability of a transition metal complex are determined by the ligand, which in turn controls the concentration of the activator and deactivator in the system, which has a significant impact on polymerization control. In addition, the molar ratio of monomer to initiator effects polymerization controllability because it affects the initiation and deactivation steps[85, 86]

1.8. References

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