Chapter 1: Introduction

1. Introduction:

The word polymer was derived from Greek, where “poly” means many and “meros” means parts. Today polymer has become a major component of our daily life. It is used in almost everywhere and therefore may be called the current age as the age of polymer. The word polymer was first introduced by Jons Jacob Berzelius in 1833.[1] Hermann Staudinger forwarded the concept of polymer (as macromolecule) in his published work entitled “Über Polymerisation” in 1920. According to him, the polymers are formed by joining small repeating units.[2, 3] After this discovery, the development in this field of has been extremely rapid and as a result of that we are now surrounded by materials consisting of either polymers or polymeric materials.

Depending upon the origin, polymers may be classified into two categories: (i) natural or biopolymer and (ii) synthetic or man-made polymer. The developments in both the classes are found to be very rapid. They also find wide applications in different fields like construction, transportation, medical, consumer products, electronics, etc.[4] Now days, synthetic polymers are produced in large quantity e.g., US alone produces around 45 million tons of synthetic polymers every year.[2]

Biopolymers have poor water resistance, poor physical and mechanical properties. But scientists are trying to improve their properties via modification such that they may substitute the synthetic polymers from their traditional hold. Now biopolymer modified with synthetic polymer finds a number of applications in fields like agriculture, medical, consumer products, etc.[5] For all these reasons, researchers are engaged themselves to explore more in this field either to develop new polymeric materials or to modify the existing one with specific properties.

1.1. Methods of polymerization:

Polymer can be prepared by different methods of polymerization: free radical polymerization (FRP), ionic polymerization, coordination polymerization etc. These methods differ from each other by the polymerization mechanism, reagents used and the nature of polymers obtained.

1.1.a). Free radical polymerization:

Free radical polymerization is a rapid polymerization process initiated by a free radical. It proceeds via chain reactions and follows the three characteristics steps: i) initiation (generation of radical from non-radical species), ii) propagation (addition of radical to a substituted alkene) and iii) termination (either by disproportionation and chain transfer or by recombination) of a chain reaction. The first step is initiation, where a free radical is generated from an active species present in the system. A weak covalent bond of the species is targeted to break down homolytically by the application of light, heat, electricity or using a redox reagent to generate such free radicals for the polymerization. In the propagation step, the polymer chain grows with successive addition of monomer units to the growing chains. In the third and final step, termination of radical chains occurs by means of disproportionation or combination and results the polymer.

Free radical polymerization has earned a significant interest of industries and scientists due to its numerous advantages. The advantages of FRP over other methods are: i) it can be carried out in wide range of temperatures, ii) almost all vinyl monomers can be polymerized, iii) simple method and very compatible with the polymerization system and iv) also tolerant to impurity and functionality present in the polymerization system. However, along with these advantages, it has got some disadvantages too. These are: i) poor control over molecular weights and its distribution,[6] ii) difficult to obtain well-defined polymer with complex architecture,[7] etc. These drawbacks limit the application of FRP. However, reversible-deactivation radical polymerization (RDRP), a modified version of FRP may be employed to overcome all these difficulties faced by FRP.

1.1.b). Ionic polymerization:

Ionic polymerization is a chain growth living polymerization in which neither termination nor transfer takes place. In this polymerization process, the growth of the polymer chains is induced by a single active initiating species which may be a cation (cationic polymerization) or an anion (anionic polymerization).[2] It is one of the best technique to obtain well-defined polymer with good control over molecular weights, their architecture and end-groups.[9, 10] However, this polymerization method also has some drawbacks which limit its wider application in industry. These are: i) requirement of very stringent reaction conditions,[7] ii) functional monomers are difficult to polymerize without affecting their functional groups,[11] iii) requirement of high-purity monomers, initiators, solvents, iv) anhydrous conditions[12] etc.

1.1.b).i. Anionic polymerization:

Anionic polymerization is an attractive technique which allows the synthesis of tailor-made functional polymers with control molecular weight and well-defined structures such as block, star, graft copolymers etc.[13-16] In anionic polymerization, the monomers with electron-withdrawing group such as styrene, acrylonitrile, butadiene, methacrylates, acrylates, ethylene oxide, and lactones are readily polymerized. Anionic polymerizations are also conducted in solvent but the choice of solvent is limited to aprotic polar solvents like esters, ketones etc. only. However, halogenated solvents are excluded due to its reaction with the carbanions. In anionic polymerization, carbanions are formed in the initiation step by the addition of the initiator to the double bond. These carbanions propagate the polymer chains by attacking fresh monomers.[2] Lastly, though formal termination step is absent in anionic polymerization but it may occur by the transfer of a positive fragment from the trace amount of impurities if present in the system. Baeman first reported the anionic chain polymerization of methacrylonitrile by sodium in liquid ammonia at -75 ºC in 1948. Then Szwarc reported the homogenous anionic polymerization of styrene by the use of naphthalene-sodium initiator system in 1956.[17 i)] In early days, alkali metals in liquid ammonia were used as an initiator but later the metal alkyls such as n-butyl lithium replaces them.

1.1.b).ii. Cationic polymerization:

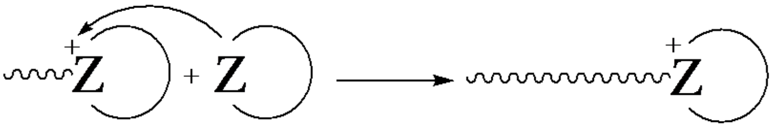
In 1988, Higashimura et. al. first demonstrated the living cationic polymerization of vinyl ethers and related vinyl monomers using hydrogen iodide/zinc iodide or diphenyl phosphate/zinc iodide initiating systems.[17b)] Kennedy et. al also demonstrated separately the cationic living polymerization of isobutylene using methyl ether and boron trichloride system.[17c)] This organic esters with lewis acids cationic initiator systems readily polymerizes vinyl monomers such as isobutylene, p-methoxystyrene, vinyl ethers, indene, N-vinylcarbazole, etc. The cationic initiator systems includes lewis acid like boron trifluoride (BF_3) or Friedel–Crafts catalysts like $AlCl_3$ with a lewis base or a proton source like water as a co-catalyst. In the initiation step of a cationic living polymerization, a carbonium ion is formed by the addition of proton to the monomer that remains in association with the counterion species.[2] The active positively charged species or carbonium ions then propagate the polymer chains. This polymer chain with active positively charged species at the growing end attacks more and more fresh monomers and successive addition of such monomers results a longer polymer chain. In cationic polymerization, termination occurs by rearrangement forming a polymer with the original complex and an unsaturated terminal unit or by chain transfer to a monomer and possibly to the polymer or solvent molecule.

The cationic polymerization is generally carried out in solvents at very low temperatures –80 to –100 ºC. The polymerization rate generally increases at low temperatures. But the solvent selection is very important for this kind of polymerization. Because with the increase in solvent dielectric strength, the polymer chain length increases as well as the reaction rate also increases exponentially.[18]

1.1.c). Ring Opening Polymerization (ROP):

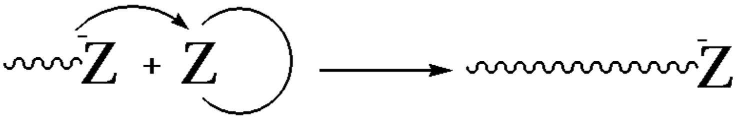
ROP is a process by which cyclic monomers undergo polymerization to obtain a straight chain polymer via ring opening of the monomers. A wide variety of cyclic monomers may be polymerized via this ROP. These are: cyclic amines, sulfides, olefins, cyclotriphosphazenes, N-carboxy-a-amino acid anhydrides, cyclic ethers, acetals, amides (lactams), esters (lactones), siloxanes etc. The ease of polymerization of these monomers depends on two factors: thermodynamic factor and kinetic factor. The resulting polymer obtained from ring-opening polymerization finds variety of applications such as in coatings, fibers, elastomers, adhesives, thermoplastics, thermoset-based composite systems etc. In general, ROP is initiated by the same initiators used in ionic polymerization.

Cationic ring-opening polymerizations may be represented schematically as (Scheme 1.1). Where Z is O, NH, Si-O, CO-O or CO-NH groups present in ether, amine, siloxane, ester and amide respectively



Scheme 1.1: Cationic ROP

For anionic ring-opening polymerizations, anionic center is formed as the propagating species. The polymerization proceeds by a nucleophilic attack of the propagating species on the monomer. Anionic ring-opening polymerizations may be represented schematically as (Scheme 1.2), where Z is an anionic propagating center of alkoxide or carboxylate type.



Scheme 1.2: Anionic ROP

1.1.d). Coordination polymerization:

Coordination polymerization is also a chain growth polymerization process which is catalyzed by transition metal complexes and salts. It was first discovered by Karl Ziegler and Giulio Natta in 1950 with the introduction of titanium-based catalysts ($TiCl_4$ & $Al(C_2H_5)_2Cl$) which was later named as Zeigler-Natta catalyst. They used the catalyst for polymerization of ethylene, propylene and α-olefins. The most important nature of Ziegler-Natta catalysts is that it can control polymer stereoregularity. Natta polymerized propylene and characterized separately the three stereoisomers of polypropylene i.e., isotactic, syndiotactic, and atactic. Ziegler-Natta catalyst can be used to prepare a polymer with high density, high molecular weight and different stereochemistry like high density polyethylene (HDPE), isotactic polypropylene (iPP), higher α-olefin copolymers, cis- and trans-polydienes, ethylene-propylene-diene rubber (EPDM) and ethylene propylene elastomer (EPR). Thus, the technique gains a lot of attention from both industry and academia for its unique character. But one of the major disadvantages of this technique is the requirement of oxygen and moisture free system to carry out the polymerization as the catalyst is very sensitive to moisture, impurities and oxygen. It is also classified as ionic polymerization due to the nature of the active species generated during the growth of the polymer chain. The reaction is initiated by the reaction between catalyst and cocatalyst which produces an ionic species. This species then continues the growth of the polymer chain by continuous addition of monomer in the form of reaction cycle also known as the Cossee–Arlman mechanism. Further, the termination takes place by different reactions like β-hydride elimination depending on the structure of the polymer.[8]

1.1.e). Metallocene polymerization:

Natta and Breslow in mid 1950s, reported another new homogeneous catalyst based on bis-cyclopentadienyltitanium dichloride complexes (Cp_2TiCl_2) (titanocenes) activated with alkyl or alkyl chloride aluminum compounds. But the catalyst did not gain much attention as it was found to be inactive for propylene polymerization and nearly inactive towards ethylene polymerization. Later in the early 1980s, Kaminsky and Sinn reported the use of methyl aluminoxane (MAO) as an effective way to activate homogeneous metallocene catalysts. The activation of Titanocene and Zirconocene complexes with MAO increased the activity for ethylene polymerization but was less active for propylene polymerization and formed only atactic polypropylene.[8] But since then different metallocene catalysts were developed. The catalyst developed from the activation of group 4 metallocene with MAO was found to be more active than heterogeneous Ziegler–Natta complexes.

The direct activation of group 4 metallocenes with MAO gave catalysts that were more active for ethylene polymerization than the heterogeneous Ziegler–Natta complexes and also showed high activity towards the polymerization of propylene and α-olefin.

In 1991 metallocene catalysts, Zirconocene were commercialized for the industrial production of ethylene propylene (EP) elastomers in solution polymerization. The metallocene catalyst gains more attention as it is possible to produce novel polymers which were not possible with traditional Ziegler–Natta catalysts such as ethylene-styrene copolymers, syndiotactic polystyrene etc. There are also other advantages of metallocene catalyst over traditional Ziegler–Natta catalyst. The metallocene initiators are single-site initiator unlike the traditional Ziegler–Natta initiators therefore polymer with narrower molecular weight distributions, regiochemistry, and stereochemistry can be produced.

1.1.f). Reversible-deactivation radical polymerization (RDRP):

Over the past few years, reversible deactivation radical polymerization (RDRP) has become one of the mostly followed method to prepare polymer with well-defined compositions (homo, block, random, gradient and graft), topologies (linear, hyperbranched, comb and star), specific functionalities such as side groups and end groups, narrow molecular weight distribution and targeted number average molecular mass.[11, 19] The development of the RDRP method has allowed the scientists to prepare synthetic novel polymer with desired properties. This RDRP is established based on the equilibration between a large majority of growing free radicals and the dormant species.[20] They are further classified into three methods: 1) atom transfer radical polymerization (ATRP) or degenerative transfer polymerization, where alkyl halides are dormant species 2) stable free radical polymerization (SFRP) or nitroxide mediated polymerization, where alkoxyamines and thioesters are dormant species and 3) reversible addition-fragmentation chain transfer polymerization (RAFT).[19]

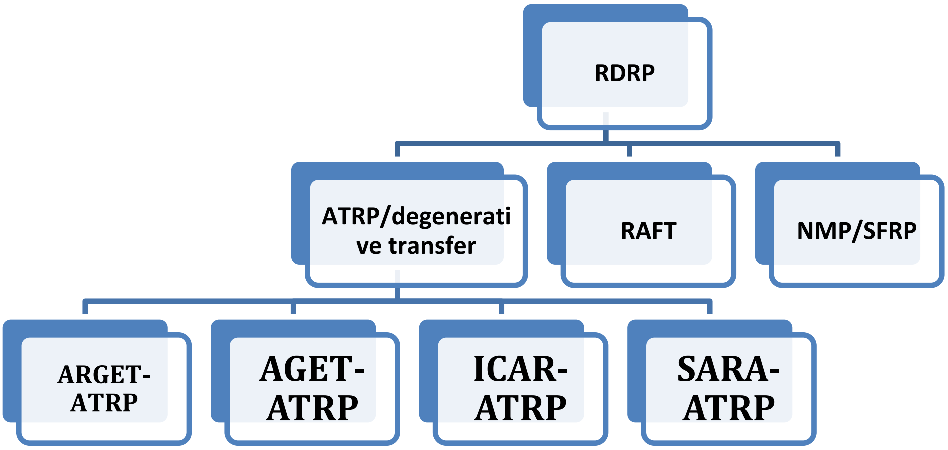
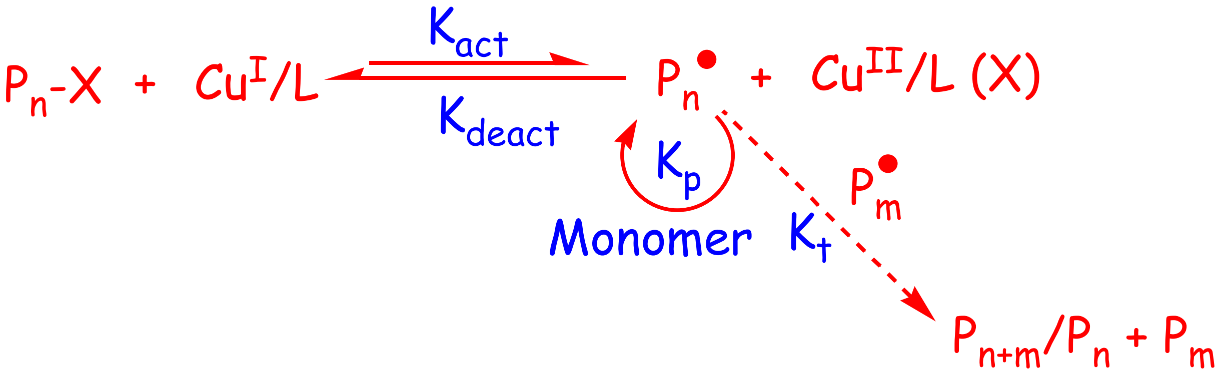


Figure1.1: Classification of RDRP

1.1.f).i. Atom transfer radical polymerization (ATRP):

Among the different methods of RDRP, atom transfer radical polymerization (ATRP) is found to be one of the most successful and versatile method to prepare polymer with controlled and varied chain architectures which include liquid-crystalline polymers, block-, star-, graft-, comb-, dendrimer- and hyperbranched co-polymers.[21, 9, 22-25, 26-31] This method proved to be an effective method to develop new polymeric materials with new designs and structure.[9] It is possible to polymerize a wide number of monomers such as styrene,(meth) acrylates, acrylamides, vinylpyridines, and acrylonitrile via ATRP.[32-36, 37-43] This method employs a wide range of transition metal such as Cu, Fe, Ni, Ru, and Os etc., as catalysts,[44, 21] an active alkyl halide (RX) as an initiator (where X is Cl or Br),[44] and a nitrogen or phosphine based ligand.[45] In ATRP, nonpolar solvent is preferred over polar solvent.[46] Ligand is another important ingredient in ATRP that influences the reactivity of the catalyst.[32, 47] It solubilizes the metal salts and adjusts the redox potential of the metal center.[48, 49] In ATRP, multidentateamine based ligands give best result thanmonodentate ligand in controlling the molecular weights and polydispersities.[32] Different amine based multidentate ligands used in ATRP are N,N,N′,N′,N′′-pentamethyldiethylenetriamine (PMDETA), diethylenetriamine (DETA), tris(2-aminoethyl)amine (TREN), 1,4,7-trimethyldiethylenetriamine (Me3DETA), tris[2-(methylamino)ethyl]amine (Me_3TREN), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) etc.[50]Other ligands such as unsubstituted terpyridine and its derivatives, alkyl pyridylmethanimine, N-pentyl-2-pyridylmethanimin, (PPh_3), 2-(2′-pyridyl)-4,5-dihydrooxazole, 2,2′-bipyridine (bpy), 4,4′-dinonyl-2,2′bipyridine (dNbpy)[51-55, 56-58] are also used.

After the first independent report of catalyst systems in 1995 by Matyjaszewski[59] and Sawamoto,[60] number of different and successful report of catalyst system were reported including systems based on Co,[36] Fe,[32] Cu,[61] Ru,[62] Ni,[63] and Mo.[64] The transition-metal complex includes the metal possessing two oxidation states which are separated by a single electron and are capable of reversibility between the oxidized and the reduced state.[36] The catalyst system controls the rate of polymerization, growth of polymer chains and the polydispersities. The mechanism of ATRP may be best described by a scheme as shown below (Scheme 1.3). A dynamic reversible equilibrium is established with k_{act} (rate constant of activation) and k_{deact} (rate constant of deactivation) between the growing radical chains and dormant species as shown in Scheme 1.3. The concentration of the growing radicals propagating with the rate constant of propagation k_p, is kept low to reduce the radical-radical termination with rate constant k_t.[7]

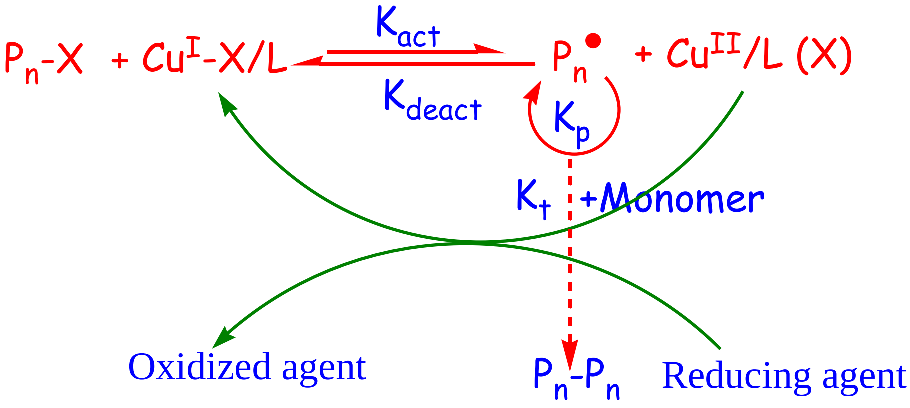


Scheme 1.3: Mechanism of ATRP[7]

But the use of the catalyst led to another challenge for polymer chemist. Although the chemists were able to prepare materials of pre-decided architectures in a controlled manner by this method, the removal of the catalyst became a major problem. The method requires high concentration of catalyst which co-precipitated with the product, thus the purity of the product is lost. These lead to an additional as well as challenging step of removal of catalyst residue from the final product.[65] Different techniques such as passing polymer-catalyst solution through column packed with silica gel or alumina, catalyst extraction and adsorption using catalyst-soluble solvents and ion-exchange resins were employed in lab to obtain the pure polymer.[66, 67] But this additional step results the loss of polymer as well as high cost, scale-up difficulty and complete separation of catalyst have made this method more problematic.[61] Therefore, scientists developed different methods with the aim either to use higher oxidation state air-stable catalyst or to reduce the concentration of catalyst under ATRP which are more environments friendly and less expensive.[21] Few such modified methods are: i) activators generated by electron transfer (AGET-ATRP),[47-72] ii) activator regenerated by electron transfer (ARGET-ATRP) [20], iii) initiators for continuous activator regeneration (ICAR-ATRP),[73-74(i)] iv) supplemental activators and reducing agents (SARA-ATRP).[74(ii)]

1.1.f).i.i. Activators regenerated by electron transfer (ARGET) ATRP:

Activator regenerated by electron transfer (ARGET) ATRP is one of the methods of ATRP which uses transition-metal catalyst in *ppm* level which is some 10^3 times less than the conventional ATRP and an excess amount of reducing agent. Another more important advantage of this method is that the presence of excess amount reducing agent eliminates the oxygenating species.[75] In this technique various reducing agent such as ascorbic acid,[20] tin(II) 2-ethylhexanoate [Sn(EH)2],[76, 77] 2-(8heptadecenyl)-4,5-dihydro-1H-Imidazole-1-ethylamine[78] are used which regenerate the activator state continuously by reducing the Cu(II).[21, 79] The use of catalyst even in low concentration gives graft-,[80, 81] block-,[82] star-[83] copolymers with preserved chain-end functionalities, high molecular weight (HMW), and narrow molecular weight distributions.[84, 79] It can be used to polymerize wide range of non-polar monomers such as acrylonitrile,[85] methyl methacrylate,[86] styrene,[87] and acrylate,[87, 75] and there are also few report of polymerization of monomers containing amido or amino groups.[88, 89] The technique ARGET ATRP is mostly being used to polymerize nonpolar monomers not the polar one as the polar group of monomer competes with the ligand (which is present in low concentration)for complex formation and lower its activity and hamper the polymerization.[75]



Scheme 1.4: Mechanism of ARGET-ATRP[83]

1.1.f).ii. Nitroxide mediated polymerization (NMP):

Nitroxide mediated polymerization is one of the class of living radical polymerization in which a stable free radical, such as a nitroxide is used to control the polymerization and thus also known as stable free radical polymerizations (SFRP). NMP gives polymers with control molecular weight and narrow polydispersities. The polymerization is carried out at temperatures where initiation takes place rapidly with the formation of all chains at the same time. The key step in the process of NMP is the activation/deactivation process which includes the reversible combination between nitroxide free radicals and propagating radicals.[90] There are numerous nitroxides which are designed to use in NMP among which 2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO) is commonly reported[92] as well as styrene and its derivative is one of the most reported monomer.[92, 93] The process also allows the synthesis of block copolymers.[94]

1.1.f).iii. Reversible addition-fragmentation chain transfer polymerization (RAFT):

Among the different methods of control/living radical polymerization, Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization has become one of the versatile methods that allow polymerization of wide range of monomer at room temperature with control molecular weight and narrow polydispersities.[95] In 1998, Chiefari et. Al., for the first time developed the method RAFT and discussed its mechanism.[96] It employs a sulfur-based organic reagent, chain transfer agent (CTA) known as RAFT reagent[97] (Figure 1.). Different types of RAFT reagents can be designed choosing deferent types of Z-groups. RAFT agents are generally very much monomer specific and therefore selection of RAFT agent is very much important for successful polymerization.[98] The thiocarbonylthio compound includes xanthate, where Z = O-alkyl, the compound is also known as MADIX (macromolecular design by interchange of xanthate),[99] dithioesters (Z = alkyl or aryl), trithiocarbonates (Z = SR′) and dithiocarbamates (Z = NR′R″).[100] Also, the R-group with respect to the propagating radical should be a good homolytic leaving group.[99] The RAFT mechanism is based on the reversible reaction between the propagating species and the CTR as shown in Scheme 1.5.[101]

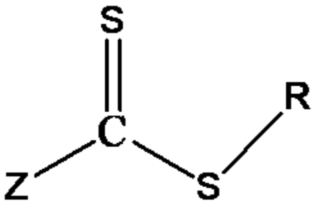
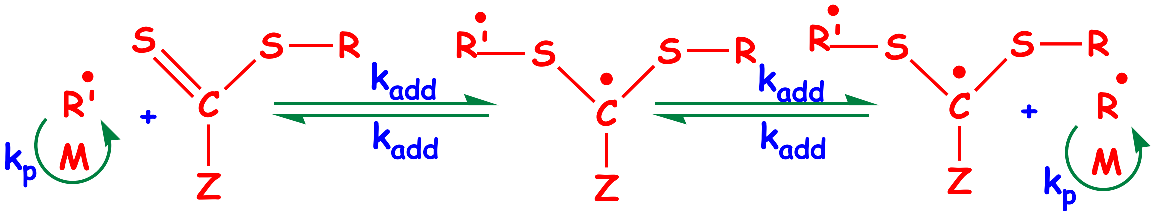


Figure 1.2: Structure of RAFT agent



Scheme 1.5: Mechanism for reversible addition-fragmentation chain transfer (RAFT)

1.2. Preparation Techniques:

There are four different types of polymerization techniques in which different methods of polymerization can be used to prepare polymer. All the methods vary from each other in reaction mechanism, and the reagents used.

1.2.a). Bulk polymerization:

In bulk polymerization, pure form of polymer is prepared by adding a radical initiator soluble in monomer in absence of solvent or any dispersant. The reaction is generally exothermic and is initiated radically either by exposing to radiation or heating. This technique is simple and it is possible to prepare pure polymer with high optical clarity. But along with the advantages there are also some disadvantages such as very high molecular weight along with broad molecular weight distribution polymers are obtained due to high viscosity.

1.2.b). Solution polymerization:

Solution polymerization is a technique which is followed industrially for the preparation of polymer. In this method, the polymer is prepared by adding monomer to a non-reactive solvent in presence of initiator or catalyst and the resultant polymer is soluble in the respective solvent chosen for the polymerization. This technique finds a wide application in the field of industrial as the method allows the preparation of polymer in a desired solvent. The reaction is not exothermic as the heat released during the polymerization reaction is absorbed by the solvent used. But this method also has disadvantages, the concentration of monomer and initiator decreases and hence reduces the reaction rate. The major drawback of this method is the complete removal of the solvent to obtain the pure polymer. The use of solvent also leads to additional cost of polymer production like solvent recycling, toxicity, environment effect due to the use of organic solvents.

1.2.c). Emulsion polymerization:

Emulsion is a useful commercial technique largely followed for the preparation of high molecular weight polymer with continuous rapid rate of reaction. The polymer latices formed via emulsion polymerization finds a wide range of applications in different fields.[102-104] In emulsion, the progress of polymerization is mainly influenced by the number of polymer particles formed during the course of reaction.[105] Emulsion polymerization is a heterogeneous reaction which makes use of a surfactant as emulsifier and water as a solvent to produce nearly monodisperse polymer latex.[102, 105-107] The use of water as a solvent instead of volatile organic solvents makes this process green, which is one of the major advantages of this process. The latex which is produced at the end of this polymerization method finds a variety of applications like in paints, adhesives, protective coatings, binders, paper sizing, textile products, etc.[103, 106, 108] In recent years, based on the polymerization strategies and the starting materials used for polymerization, a few synthetic emulsion techniques have derived. These are now, known as macro, micro and mini emulsion. These techniques differ from each other by the size of the monomer droplets formed and the polymerization mechanism followed.[109, 110]

1.2.d). Suspension polymerization:

It is a heterogeneous radical polymerization process, where mixtures of monomers or monomer are polymerized by mixing with a mechanical agitator in a liquid phase. The polymerization system consists of monomer(s), a liquid medium, stabilizing agent and an initiator soluble in monomer. Generally, the liquid with greater thermal conductivity, low viscosity and less temperature variation of viscosity are preferred as liquid phase. In this technique the polymer forms spheres and remains suspended in the liquid phase.One of the major advantages of this polymerization technique is that polymer with high degree of polymerization are obtained without monomer boil-off. But in this method an additional agent is required, protective colloid to avoid the creaming of the monomer droplets in this solution or do a careful mixing of the solution.

1.3. Literature review:

1.3.a). Methyl methacrylate (MMA):

Methyl methacrylate (MMA) is most commercially used monomer among the different acrylate monomers. It undergoes polymerization by different techniques such as free radical, reversible-deactivation radical, anionic, and group transfer. The resultant homopolymer, poly(methyl methacrylate) (PMMA) finds application in various fields such as in medical field for different purpose due to its transparency, biostability, processing ability, very good weather resistance and good mechanical properties.[111, 112, 20] Among the various grafting monomers and polymers, MMA and PMMA is one of the extensively used for surface modification of different fillers such as cellulose and starch incorporated onto it. The acrylic monomers and their corresponding methacrylates are preferred for grafting onto starch, since it is non-toxic, cheap and has excellent physical and chemical properties such as clear, colorless with a range of transition temperature (T_g), and most importantly its reactivity, and the ease of modification that allows easy grafting/crosslinking with other materials.[20, 113-115] Further, the resultant graft copolymer of starch and PMMA also finds application in various fields especially in agriculture and medical field.[116]

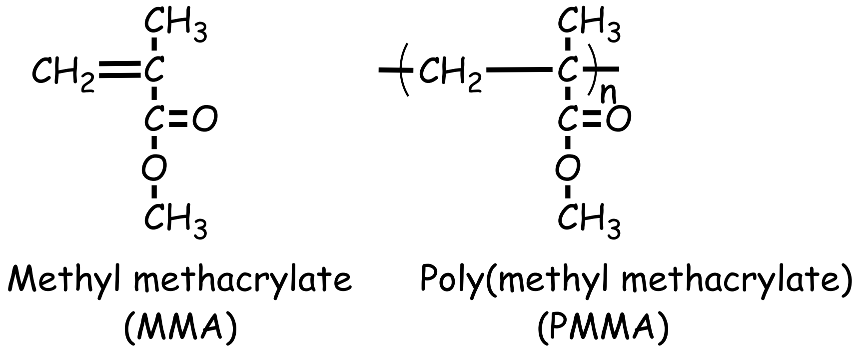


Figure 1.3: Structure of MMA and PMMA

1.3.b). Polyethylene glycol (PEG):

Polyethylene glycol has become one of the most interesting polymer due to its unique characteristic nature like biocompatibility, lack of toxicity, ease of excretion out of the living body[117] and favorable chemical properties like soluble in almost every solvent as well as water.[118] The polymer as well as its derivative has found a wide application especially in the field of medical for different activities as drug delivery matrices and systems, tissue engineering, etc. But along with so much of advantages there is also a disadvantage; the polymer has no reactive group in the units of ethylene oxide.[117] Thus, preparation of PEG with reactive group is of great interest. Different researchers are trying to prepare block copolymer of PEG with other monomer to align its property with other monomer[119, 120, 121, 122, 123] which finds variety of application as hydrogel nanoparticles,[119] in the field of DNA delivery,[123] thermoresponsive hydrogel.[124]

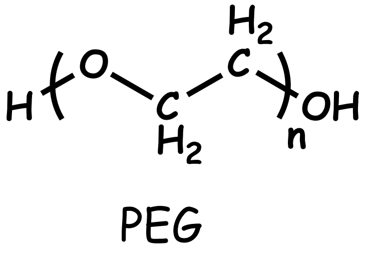


Figure 1.4: Structure of PEG

1.3.b).i. Graft copolymer prepared by ATRP:PEG-g-PMMA:

Nguyen et. Al., reported the synthesis of Poly(ethylene glycol)- polystyrene (PEG-b-PS) block polymer by the atom transfer radical polymerization using PEG-Br as the macroinitiator in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]).[125] Yang et. Al., reported the Poly(p-dioxanone)–poly(ethylene glycol)–poly (p-dioxanone) ABA triblock copolymer using poly(ethylene glycol) (PEG) as the macroinitiator by ring-opening polymerization.[126] Kawalec et. Al., also prepared Poly[(R,S)-3-hydroxybutyrate-block-ethylene glycol-block-(R,S)-3-hydroxybutyrate], a-PHB/PEG/a-PHB triblock copolymer using PEG macroinitiators by Anionic ROP of ß-butyrolactone.[127] Garcia et. Al., reported triblock and pentablock copolymer of methacryloyl uridine, methacryloyl adenosine and polyethylene glycol prepared using PEG as macroinitiator by copper-mediated living radical polymerization.[128]

1.3.c). Starch:

Among all the naturally occurring biopolymers, starch is the second most abundant,[129] renewable and cheap raw biomaterial.[130-132] It is a polysaccharide with general formula $(C_6H_{10}O_5)_n$.[133] It consists of a mixture of two polyglucans,[134] amylose [linear poly(1,4-α-D-glucopyranose)] and amylopectin [poly(1,4-α-D-glucopyranose) with (1,6-α-D-glucopyranose) as branching chains] (Figure 1.5).[135, 136] The shape of starch granules can be spherical, oval, polygonal, dome-shaped, elongated-rod and their diameters vary from submicron to few 100 microns (Table1.1). Based on the chain length of amylopectin, the crystallinity of starch granules varies and they exhibit A-, B- and C-type of X-ray pattern.[137] The crystallinity of the native starch varies in the range of 15% to 45%, implying that on an average 70% starch is an amorphous material.[138] Botanical originality of the starch granules also defines its crystallinity, morphology, susceptibility to both chemical and enzymatic reactions. It is found that the variation of such properties as well structure is due to the variation in structure of amylose and amylopectin which are synthesized by different plants in different organs and at different stages of their development.[139]Native starch exists in granular form having microscopic diameter ranging from 2-100 µm,[140] comprising of macromolecules arranged in polycrystalline form.[141, 142, 143]

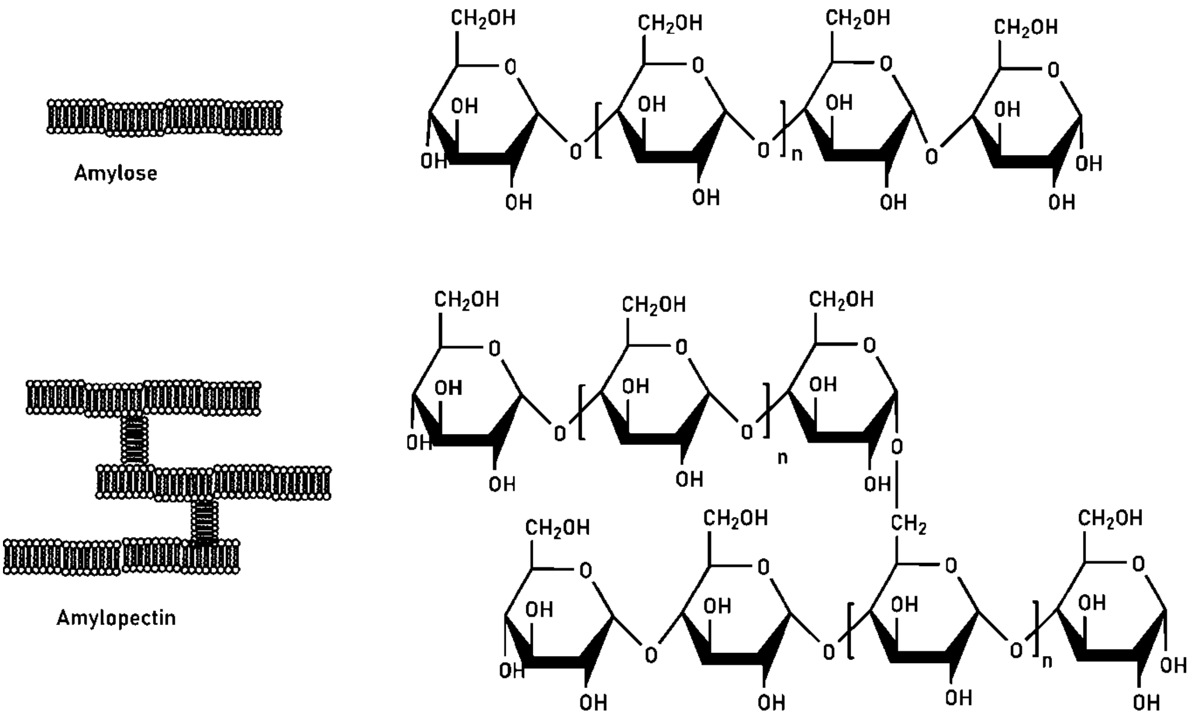


Figure 1.5: Structure of Starch

However, native starch does not find much application due to its poor physico-mechanical property, poor water-resistance property, poor solubility and poor dimensional stability.[159, 160, 161] Therefore, attempts have been made to modify starch enzymatically, physically or chemically to enhance the scope of its applicability.[159, 133] Among the various ways of chemical modifications, grafting, cross-linking, esterification, etherification, oxidation are the few used very frequently for the modification of starch.[162] It is also possible to alter the physiochemical properties like biodegradability, biocompatibility, non-toxicity etc. via chemical modification.[163] The hydroxyl groups present in the starch molecule may be used for this purpose.[129, 164] Cereal grains, vegetables and fruits are considered as the major sources of starch.[165, 166] Being biodegradable, biocompatible and non-toxic in nature, starch has gained a lot of attention from the researchers.[167] Starch can be treated with plasticizers to avoid the brittleness in the films and make it shatter resistant.[133, 167]

Table 1.1: Size and shape of starch granules with the amylose contents (%)

Starch	Diameter (μm)	Shapes	Amylose (%)
large canna starch[144-146]	62 – 94	B-type, oval-shaped granules	38.7
medium canna starch[144-146]	--------	oval and elliptical	--------
small canna starch[144-146]	14-35	round and polygonal	29.2
small wheat starch[147-149]	2–8	bimodal spherical shaped B-granules	23.0
large wheat starch[147-149]	12-20	bimodal disc shaped A-granule	30.0
small potato granules[150, 151]	5–20	spherical or ellipsoidal	212.5
medium potato granules[150, 151]	25–40	ellipsoidal to irregular	250.8
large potato granules[150, 151]	40–85	cuboidal	274.6
rice granules[144,152]	4.46-7.2	polygonal	29.7
blackgram[153,154]	12.8-14.4	Round, elliptical, oval shaped	32.9-34.3
kidney bean[153,154]	15.5–60.5	Kidney shaped	35.9
large chick pea[153, 154]	17 - 29	Spherical, oval shaped	30.2
small chick pea[155, 156]	6 - 7	oval shaped	25.6
large maize granules[157]	5–20	spherical shaped	26.4
small maize granules[157]	>5	Angular-shaped	21.7
large barley starch[148, 158]	15-32	bimodal with large disk-shaped	24~29
small barley starch[148, 158]	2-3	bimodal	23 ~ 25

However, the presence of plasticizer is not sufficient enough for application in packaging as starch is hydrophilic in nature, therefore it is very much necessary to incorporate a hydrophobic group into it.[168-169] Microorganisms such as fungi and bacteria consume starch allowing easy degradation starch-based polymer.[170]

1.3.c).i. Chemical Modification of Starch:

1.5.c).i.i. Grafting via reversible-deactivation radical polymerization (RDRP):

Grafting is an efficient tool to improve properties of starch.[171] Grafting has mostly been employed to increase the hydrophobicity of starch[172] and is done three different ways: grafting to, grafting through, and grafting from.[173] Starch can be modified physically, chemically or enzymatically depending on the requirement as well as the end use. Chemical modification enables the addition of a functional group in the starch moiety replacing its hydroxyl group.

Due to this, starch becomes an important material in industries.[174] Chemically it can be modified by different chemical reactions such as esterification, etherification and oxidation.[160] However, during modification of starch, its granule form is maintained and only few hydroxyl groups are transformed to yield its ethers or esters.[175] These hydroxyl groups of starch can be modified to incorporate an initiating site for RDRP. For example, hydroxyl groups of starch may be converted to groups containing an active halide bond which eventually may be used for grafting of monomers via atom transfer radical polymerization. In this case, the resulted modified starch may be termed as macroinitiator. There have been several reports on the modification of starch as a macroinitiator for a further modification or grafting process. The different chemical reagents used and the degree of substitution reported in this process are tabulated in Table 1.2.

Table 1.2: Synthesis of starch macroinitiator and polymerization by different techniques of ATRP

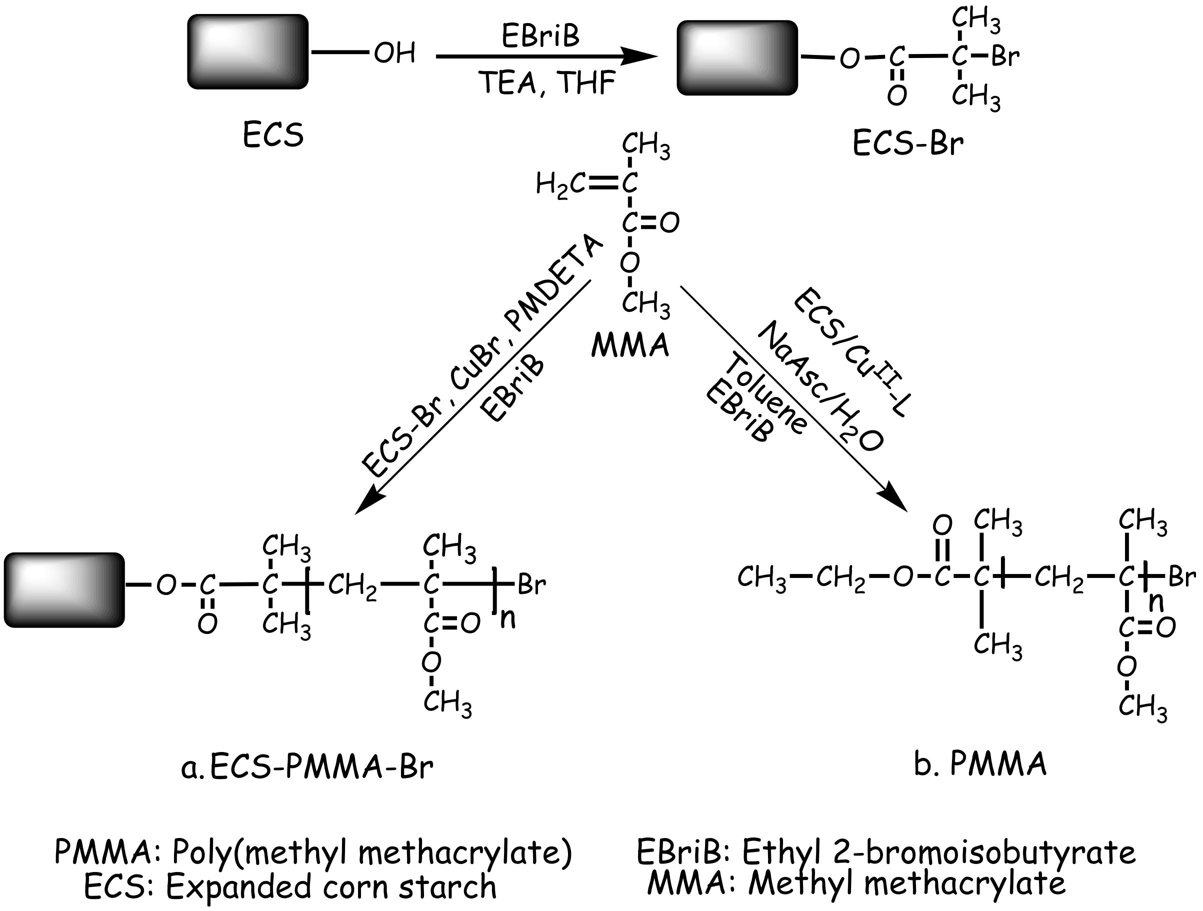
Preparation of macroinitiator					Polymerization condition	
Type of Starch	Reagents	Mole ratio in the Reaction[a]	Degree of substitution[b] (macroinitiator)	Technique	Temperature of reaction (°C)	Technique
Acetylated Starch[176]	2-bromoisobutyryl bromide	0.02 0.09 0.76	0.3 1.0 3.9	Substitution of hydroxyl group	70	ATRP
Expanded corn Starch[177]	Ethyl 2-bromoisobutyrate	-------------	0.06	Substitution of hydroxyl group	70	SI-ATRP AGET-ATRP
Corn Starch[160]	2-Bromoisobutyryl bromide	1.1 1.3 1.5 1.7 1.9 1.5 1.5 1.5 1.5 1.5 1.5 1.5	0.56 0.72 0.83 1.11 1.22 1.06 1.20 1.53 0.12 0.83 0.93 1.36	Esterification	70 & 80	ATRP
Amylopectin[118]	Tert-butyl α -bromoisobutyrate	1:3 1:3 1:3	1.04 1.08 0.98	Substitution of hydroxyl group	20	ATRP

[a]Mole ratio of reagent/OH groups in reaction mixture

[b]The amount of reagent groups/anhydroglucose unit

1.3.c).ii. Modification of Starch via ATRP:

In recent years, there are several reports on the starch-initiated polymerization of different monomers by different reversible-deactivation radical polymerizations (RDRP) among which atom transfer radical polymerization (ATRP) is mostly employed.[20]



Scheme 1.6: Synthesis of ATRP macroinitiator and graft copolymerization of PMMA via SI-ATRP

ATRP is a well-controlled radical polymerization which allows copolymerization with controlled architecture.[160] Bansal et al prepared copolymers of MMA and styrene by SI-ATRP and AGET-ATRP using expanded corn starch (ECS) as a support.[177] They first converted the corn starch into expanded corn starch (ECS) then carried out SI-ATRP of

MMA from the starch surface. For this, starch was modified as a macro-initiator (ECS-Br) by reacting few of its -OH groups with 2-bromoisobutyryl bromide (BiBB). This ECS-Br was used for activator generated by electron transfer (AGET-ATRP) of MMA. ECS-Br was also used to prepare copolymers of MMA and styrene via SI-ATRP. They further determined the degree of substitution by NMR spectroscopy and found to be 0.06 and also characterized the polymers by SEM, FT-IR and^{1}H NMR analyses. Wang et al reported the synthesis of starch-based copolymers (Starch-*g*-PS and Starch-*g*-PMMA) with styrene and MMA via ATRP.[160] Starch was used as a macroinitiator in this grafting reaction as shown in Scheme 1.6.

The starch macroinitiator was prepared by esterification reaction with 2-bromoisobutyryl bromide (BiBB) in a solution of ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) and DMF. They further studied the effects of molar ratio of monomer to solvent, ligand, initiator and temperature on the graft polymerization. The prepared macroinitiator and the grafted copolymers were characterized by ^{1}H NMR, FT-IR and TGA analyses. Similarly, Nurmi et al also reported the synthesis of starch grafted copolymer of MMA with acetylated starch via ATRP.[176] Starch was used as a macroinitiator with varying densities and lengths in a controlled manner. They prepared it with different degree of substitution by the reaction of 2-bromoisobutyryl groups with the hydroxyl group of acetylated starch. The graft polymerization was carried out in bulk as well as in THF using CuBr/BPy as catalyst system. Furthermore, they studied the hydrophobicity of the prepared copolymer using contact angle measurements.[176] In a similar vein, Handayani et al modified amylopectin using tert-butyl α-bromoisobutyrate (TBBiB) to yield an efficient macroinitiator, Ap-TBBiB. This initiator was used to prepare amylopectin-*g*-PMMA through ATRP. The grafted copolymers had well-defined structure, as evident by different characterization techniques.[178]

1.4. Scope and objectives:

Methyl methacrylate (MMA) is an interesting monomer, which can be polymerized via different methods of polymerization to form resins and polymers. MMA is the most used commercial methacrylate monomer. The homopolymer of MMA i.e., poly(methyl methacrylate) (PMMA) finds many applications in various fields e.g., in drug delivery, bone cement, tissue engineering as electrolytes for lithium batteries, in molecule separation, in conductive polymer matrix, in photonic devices, in solar devices etc.These diverse applications of PMMA is mainly due to its excellent optical transparency, biostability, processing ability, very good weather resistance and good mechanical property. Apart from these, MMA and PMMA are also used to modify surface of fillers like cellulose and starch via grafting reaction. Due to the excellent physical, chemical and optical properties of PMMA and more importantly due to the reactivity of MMA, grafting or cross-linking reactions may be carried out very easily with other materials. This resultant graft copolymer may find applications in agriculture and medical field. The microstructure has strong influence on both physical and chemical properties of a polymer. For example, the isotactic PMMA melts at 160 °C and syndiotactic PMMA at 200 °C. Similarly, isotactic polystyrene melts at 240 °C and syndiotactic polystyrene at 200 °C. In addition, the crystallinity of the polymers also varies with the degree of the tacticity. Hence, the study of micro structures and property relationship is very important to have a idea about the physicochemical properties of a polymer. The study of microstructure present in a polymer is possible via NMR analysis through the various type of chemical shifts arises from the different chain configuration. To elucidate the complete structure of the polymer, only ^{1}H NMR spectroscopy is not sufficient as major portion of the information remains unseen due to the presence of multiple peaks of broad range. Therefore, ^{13}C NMR spectra are also used along with ^{1}H NMR spectra to study the complete structure of polymer. The ^{13}CNMR spectrum of polymer with carbonyl carbons e.g. acrylic polymer gives detailed information about uneven distribution of configurational sequences. The microstructures present in a polymer also vary with the type of polymerization methods used. Free radical polymerization method mainly gives syndiotactic polymer whereas polymer prepared via anionic polymerization exhibits a range of tacticities. Similarly, group transfer polymerization of MMA mainly leads to syndiotactic PMMA. Therefore, microstructure and property relationship would be very important for the PMMA prepared via ARGET-ATRP.

Polyethylene glycol (PEG) is another interesting polymer due to its unique properties like biocompatibility, lack of toxicity, solubility in almost every solvents etc. PEG and its derivative are used in medical field for different activities such as in drug delivery, tissue engineering, etc. This PEG has several advantages, however it has no reactive groups in its ethylene oxide units which is noted as a disadvantage for this material. Block copolymerization is way to introduce such reactive groups in PEG. Block copolymers of PEG with other monomers has been attempted by researchers to align its property with the monomers. Thus this way prepared PEG based block copolymer may find applications in nanotechnology, hydrogel nanoparticles, DNA delivery, thermoresponsive hydrogel, etc. Therefore, preparation of polyethylene glycol based ABA type tri block copolymer with MMA via ARGET-ATRP with a series of good of properties would be very interesting.

Among all the naturally occurring biopolymers, starch is the second most abundant, renewable and cheap raw biomaterial. Native starch does not find much application due to its poor physico-mechanical property, poor water-resistance property, poor solubility and poor dimensional stability. Therefore, attempts have also been made to modify starch enzymatically, physically or chemically to enhance the scope of its applicability. Among the various ways of chemical modifications, grafting, cross-linking, esterification, etherification, oxidation are the few used very frequently for the modification of starch. It is also possible to alter the physiochemical properties like biodegradability, biocompatibility, non-toxicity etc. via chemical modification. The hydroxyl groups present in the starch molecule may be used for this purpose. Therefore, modification of starch via ARGET-ATRP of MMA would result a graft copolymer with many interesting properties.