Chapter 1

Introduction

1. Introduction

Polymer science is a field of applied chemistry that has a significant influence on the development of mankind throughout the past century. The macromolecular concept of polymeric materials in 1920s proved to be a vital turning point. The definition of a polymer was introduced by Hermann Staudinger, in 1924, who suggested that polymers were large molecules containing long sequences of chemical units linked by covalent bonds.[1] He was awarded Nobel Prize in chemistry the 1953 because of his initial pioneering work in the polymer science. P.J. Flory postulated several theories regarding the polymerization reaction, and properties of polymers which made polymer science a separate discipline to study.[2] Flory was awarded Nobel Prize in 1974 for his great contribution in the field of polymer science. Today polymeric materials have found applications in different household commodity and appliances used in our daily life. It has also found applications in a number of important areas of engineering involving mechanical, electrical, telecommunication, aerospace, chemical, biochemical, and biomedical applications. Polymers that are assigned to use in high-tech applications need to have tailor-made properties as well as they should have specialty groups.[3–5]

Specialty polymers possess, inherently, one or more special functional group which exerts special properties in the polymer. In many cases post-polymerization modification of these functional groups can lead to interesting materials which can be used in different critical applications where specific properties are necessary.[5] These polymers can be placed in different groups according to their properties and/or area of uses, such as high-temperature resistant and fire-resistant polymers, liquid crystal polymers, electroactive polymers, electrolytic polymers, photoresist polymers, ionic and ion-exchange polymers, polymers in optical information storage, polymeric sensors, polymer electrolyte membranes, biodegradable polymer scaffolds, hydrogels, smart polymers, dendritic polymers, shape memory polymers, micro-encapsulation polymers, polymer nanocomposites, self-healing polymers and polymers in paints, coating and adhesive applications.[6–7] The specialty polymers are difficult to prepare via conventional polymerization methods. Because these specialty functional groups either affect the polymerization reaction or are affected during the course of polymerization.[5]

1.1. Different types of polymerization

Staudinger [1] was the first to propose the concept of a chain polymerization. Addition polymers are produced in largest tonnages among industrial polymers. A kinetic chain reaction usually consists of three steps namely, initiation, propagation, and termination. The addition polymerization can be broadly classified into three types according to the nature of active species generated during the polymerization reactions.[8] They are; (i) Ionic (anionic and cationic) polymerization

(ii) Coordination polymerization

(iii) Free radical polymerization

1.1.1. Ionic Polymerization

Ionic polymerizations have several advantages. In 1954 Michael Szwarc [9] first reported anionic polymerization. This ionic polymerization does not have any formal termination process if it is carried out under stringent and restricted reaction condition. J. P. Kennedy reported cationic polymerization in 1970s.[10] However, this polymerization is applicable only few monomers like isobutylene etc. The great advantages of the ionic polymerizations are as follows; (i) It is possible to prepare to polymers with controlled molecular weights and narrow polydispersity index (PDI). (ii) Polymers with well-defined architecture and topology (like di, triblock copolymers, star polymer, and hyper branched polymer) can be prepared by ionic polymerization. There are very limited numbers of few monomers which can undergo ionic polymerization [9, 11–12] because of several limitations associated with the ionic polymerizations as compared to free radical polymerization. There are several disadvantages of the ionic polymerizations.

(1) Ionic polymerizations are quite sensitive to the impurities present in solvent, or in monomer or in different reagent.

(2) The kinetic study of the polymerizations is difficult and the results are sensitive to the particular reaction conditions.

(3) The ions are very unstable and cannot propagate at ambient temperature or at high temperature. Hence ionic polymerizations are mostly carried out at very low temperature. For example, butyl elastomers are commercially prepared at ~ -100 °C via cationic polymerization.[13]

(4) Some polar solvents, such as water and alcohols react with ionic initiators as well as ionic propagating species. Other polar solvents such as ketones prevent initiation because of the formation of stable complexes with the initiators. Ionic polymerizations are conducted in non-polar or moderately polar solvents such as hexane, and ethylene dichloride.

It is very difficult to use ionic polymerizations to polymerize the specialty monomers. The specialty functional group can react with the ionic initiators. The propagating ionic species may be destroyed by the reactive functional groups. [14]

1.1.2. Coordination Polymerization

Coordination polymerization was started by Ziegler and Natta in 1950s for which they were awarded Nobel Prize in 1963.[2] This coordination polymerization is mainly applicable to olefinic monomers (like ethylene, propylene) and diene monomers (like butadiene, isoprene etc.).[8, 13] The major limitation in the coordination polymerization is that the catalyst systems are very much sensitive to air and moisture. They are also intolerant to hetero atom-containing monomers like acrylates and acrylamides etc.[8, 13, 15] The specialty monomers are difficult to polymerize via coordination polymerization. Because the reactive functional groups can react with the coordination catalyst leading to several side reactions.[14]

1.1.3. Free radical polymerization (FRP)

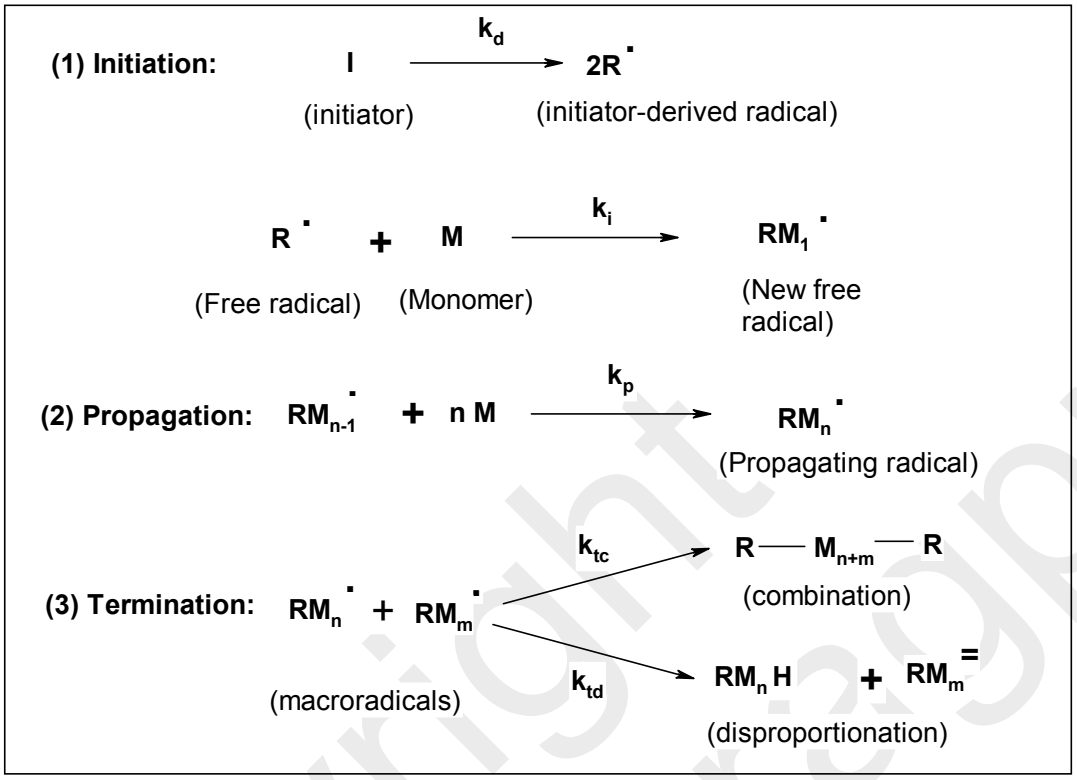
In recent years radical polymerization is the most widespread commercial process to produce different polymeric materials such as plastics, rubbers and fibers.[16, 17] In the United States alone, current production of all polymers prepared by free radical polymerization is around 37×10^6 metric tons of plastics, 4.5×10^6 metric tons of synthetic fibers, 2.4×10^6 metric tons of synthetic rubber, and 5×10^6 cubic meters of paints and coatings.[18]

Generally free-radical polymerization proceeds via a chain mechanism, which basically consists of three different types of reactions involving free radicals.[19–21] In 1937 Flory [22] showed conclusively that radical polymerization proceeds by the following steps.

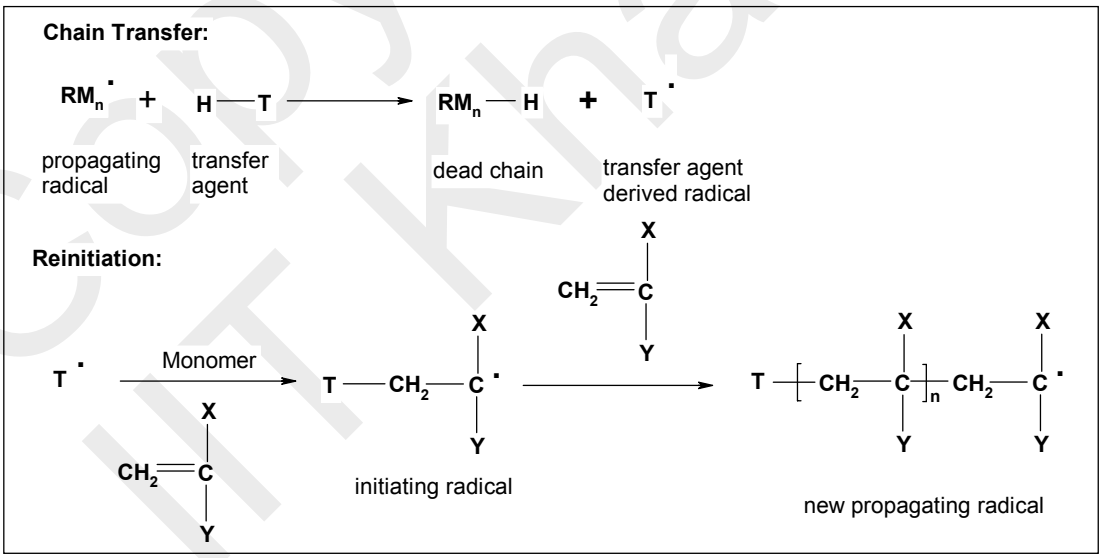
(i) Radical generation from nonradical species (initiation),

(ii) Radical addition to a substituted alkene (propagation),

(iii) Atom transfer and atom abstraction reactions (chain transfer and termination by disproportionation), and radical–radical recombination reactions (termination by combination). The different steps in FRP are shown in Scheme 1.1.



Scheme 1.1: Mechanism of Free Radical Polymerization



Scheme 1.2: Possible Chain Transfer Reaction during Free Radical Polymerization

Free radical polymerization is the most widely used method of polymerization of vinylic monomers.[8, 23] During the course of polymerization the reactivity of a

radical could be transferred to another species, which would be capable of continuing the chain transfer.[22] During this side reaction hydrogen or other species is transferred from a component of the reaction mixture, e.g. monomer, initiator or solvent to the growing radical (Scheme 1.2). The 'initiating radicals' are not only formed directly from initiator decomposition but also indirectly by transfer to monomer, solvent, transfer agent, or impurities.

1.1.4. Application and Advantages of Free radical chain polymerization

Free radical polymerization has been an important and widespread commercial method for the production of polymers during last seventy years. [23, 24] Because FRP has several advantages over other methods of addition polymerizations.

i) FRP can be carried out under simple and relatively undemanding experimental conditions unlike in ionic and coordination polymerizations.

ii) It can produce high molecular weight polymers without removal of stabilizers. The solvents, monomers and initiators need not be of very high purity.

iii) A large number of monomers can be polymerized via FRP.

iv) This polymerization can be carried out at wide range of reaction temperature.

v) Importantly, it is compatible with water and other protic solvents. Hence it can be applied to emulsion and suspension polymerization.

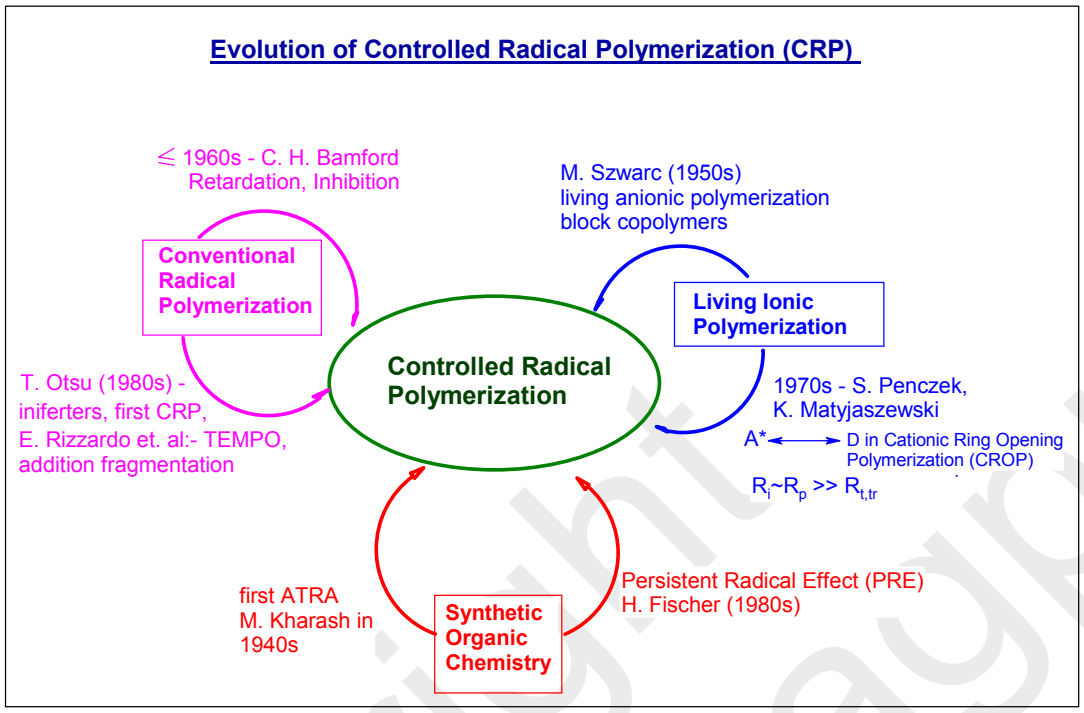
However, FRP has several disadvantages. They are as follows;

(i) It is very difficult or rather impossible to get precise control over the molecular weight and polydispersity index (PDI).

(ii) Due to slow initiation, fast propagation and succeeding chain transfer (or) termination, the resultant polymers have very high PDI.

(iii) It is difficult to control the end functionality in the polymers. It is very difficult to prepare polymers with well-defined architecture and topology like block copolymer, star polymers, hyperbranched polymers.

(iv) Polymerization of the functional polymers via conventional FRP undergoes gelation. For example, 3-ethyl-3(acryloyloxy)methyloxetane undergoes severe gelation during FRP. [25, 26]



Scheme 1.3: Development of CRP by Integration of Advances in Several Fields of Chemistry

In the past decade, the limitations of FRP have been overcome, as several procedures for controlled radical polymerization (CRP) have evolved. They are based on an understanding and integration of chemistry developed over the past 60 years in the fields of organic chemistry, conventional radical polymerization, and living ionic polymerizations (Scheme 1.3). [27–32] CRP provides finely tuned control of microstructure and the ability to synthesize a range of morphologies, including block, star, brush, and comb polymers.[33–34]

1.1.5. Controlled Radical Polymerization (CRP)

CRP methods are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. The position and dynamics of this equilibrium define the rate of polymerization and they also control the molecular weights and polydispersities of the polymer formed.[35–38] The important features of CRP are;

(i) It obeys the first order linear kinetic plot ($\ln([M]_0/[M]$ vs time, [M] = concentration of monomer and $[M]_0$ = initial concentration of monomer), with respect to the monomer concentration. Acceleration on such a plot may indicate slow initiation, whereas deceleration may indicate termination or deactivation of the catalyst (Figure 1.1a). Straight lines indicate a constant number of active sites during the course of polymerization.

(ii) In CRP there is gradual increase in molecular weight (MW) with conversion (Figure 1.1b). MW lower than the predicted ($\Delta[M]/[I]_0$, [I] = initiator concentration) one indicates transfer during the polymerization, whereas MW higher than the predicted ($\Delta[M]/[I]_0$) one indicates either inefficient initiation or chain coupling. MW twice higher than the predicted one can be formed by bimolecular radical coupling. Straight line indicates only a constant number of all chains (dead and growing) and cannot detect unimolecular termination (or termination by disproportionation) (Figure 1.1b).

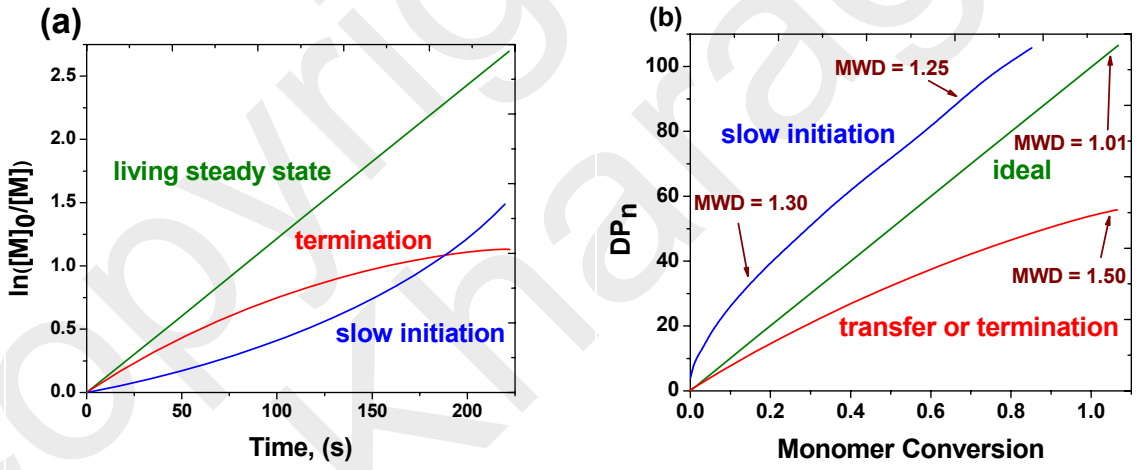


Figure 1.1: General Scheme Showing the Effect of Slow Initiation, Transfer and Termination on the Polymerization Kinetics (a) and on the Molecular Weight (b) during the Polymerization.[38]

(iii) Polydispersity (Mw/Mn) should decrease with increasing conversion in case of a system of slow initiation and slow exchange. Increase in polydispersity with increasing conversion indicates the significant contribution of chain breaking reactions during the polymerization.

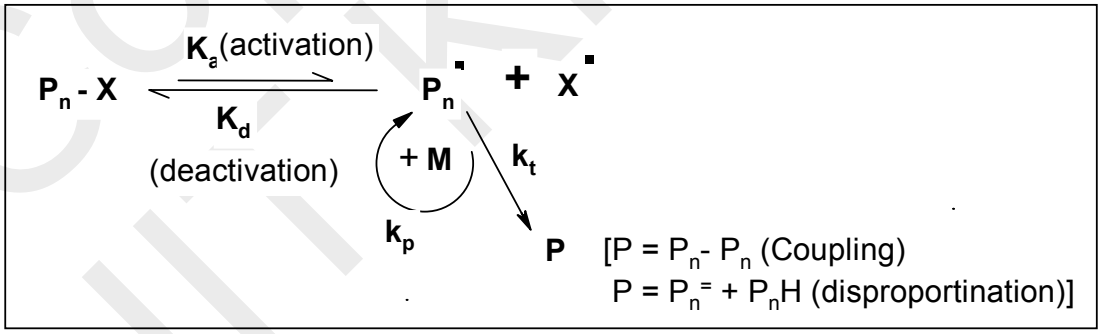
(iv) End-functionality is not affected by slow initiation and exchange but it is reduced when chain breaking reactions become important.[35–38]

CRP allows the synthesis of various types of functional polymeric materials and provides the capability of designing polymers with controlled molecular weight and molecular weight distribution (MWD), in addition to controlled chemical composition, chain-sequence distribution, site-specific functionality and predetermined topology.[39–40]

1.1.6. Different types of Controlled Radical Polymerization

In the past decade, a number of CRP methods have been developed. The three very promising CRP methods are: (1) stable free radical polymerization (SFRP) (also known as nitroxide-mediated polymerization (NMP),[41–43] (2) reversible addition-fragmentation chain transfer (RAFT) polymerization,[44–45] (3) atom transfer radical polymerization (ATRP) (also known as transition metal catalyzed radical polymerization).[46–47]

In all these cases dormant, non-propagating species are reversibly activated with the rate constant of activation (k_a) to form the active species P_n*, which reacts with monomers (M) with the propagation rate constant (k_p) (Scheme 1.4). The propagating radicals can be deactivated with the rate constant of deactivation (k_d) or it can terminate with other growing radicals with the termination rate constant (k_t). In all CRP methods the concentration of radicals is very low, so the termination process is almost absent.[36] It is important to note that while NMP and ATRP are subject to the persistent radical effect (PRE), [48–51] but chain transfer processes and RAFT do not conform to the PRE model because of the transfer-dominated nature of the reaction.



Scheme 1.4: General Scheme of Persistent Radical Effect (PRE)

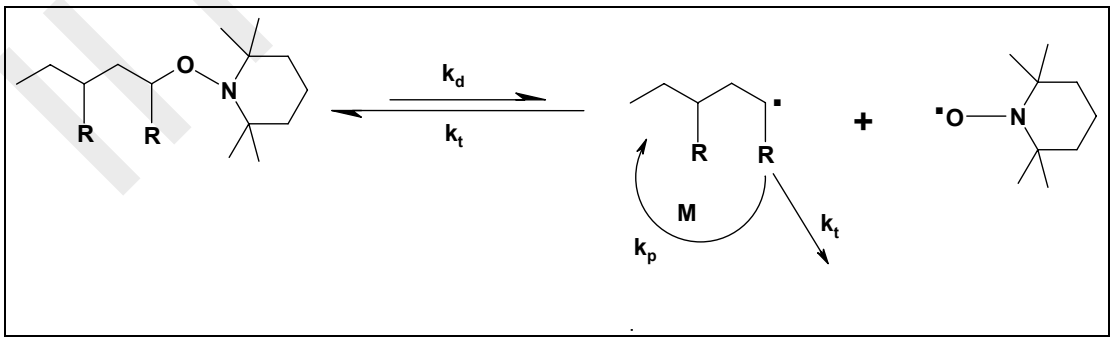
Persistent Radical Effect is widely accepted to describe the kinetics of ATRP and NMP. The model was originally developed by Fischer[48, 49] in order to explain the high selectivities observed in some radical reactions. In scheme 1.4, the persistent species (X) is an oxidized metal catalyst or a stable nitroxide (like TEMPO) in ATRP

or NMR respectively. In this case the cross-coupling between the active alkyl radical (P_n^*) and the deactivating species (X) is much faster than the homo-coupling between the two active radical species. It should be noted that RAFT polymerization does not follow the PRE kinetics, as this polymerization is a transfer dominated reaction.

1.1.6.1. Nitroxide Mediated Stable Free Radical Polymerization (SFRP)

Nitroxide-mediated radical polymerization (NMP), also referred as stable free radical polymerization (SFRP), is one of the versatile methods of the CRP. NMP is generally based on the use of stable nitroxyl radicals (nitroxides) or alkoxyamines. Solomon and Rizzardo,[52,53] and Moad and Rizzardo[54] first used alkoxyamines for the polymerization of various vinyl monomers. However, only low molecular weight polymers were obtained. Later Georges et al.[55] showed that high molecular weight polystyrene (Mn > 50,000) with low polydispersity (<1.5) could be prepared using benzoyl peroxide (BPO) and a nitroxyl radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).

The reversible deactivation equilibrium in nitroxide mediated CRP is shown in Scheme 1.5. In order to effectively mediate polymerization, TEMPO (and other stable free radicals) should neither react with itself nor with monomer to initiate the growth of new chains, and it should not participate in side reactions such as the abstraction of hydrogen atoms. These persistent radicals should also be relatively stable, although their slow decomposition may in some cases help to maintain appropriate polymerization rates. Nitroxide mediated CRP (NMP) has been used to polymerize various monomers. Styrenic-type monomers and its derivatives have been the most widely studied using NMP in the presence of TEMPO.[55–57] Alkyl methacrylates can also be polymerized via NMP strategy using NO/NO_2 mixtures.[58–59] Polymerization of dienes [60] and acrylic acid[61] have also been reported by using NMP method.

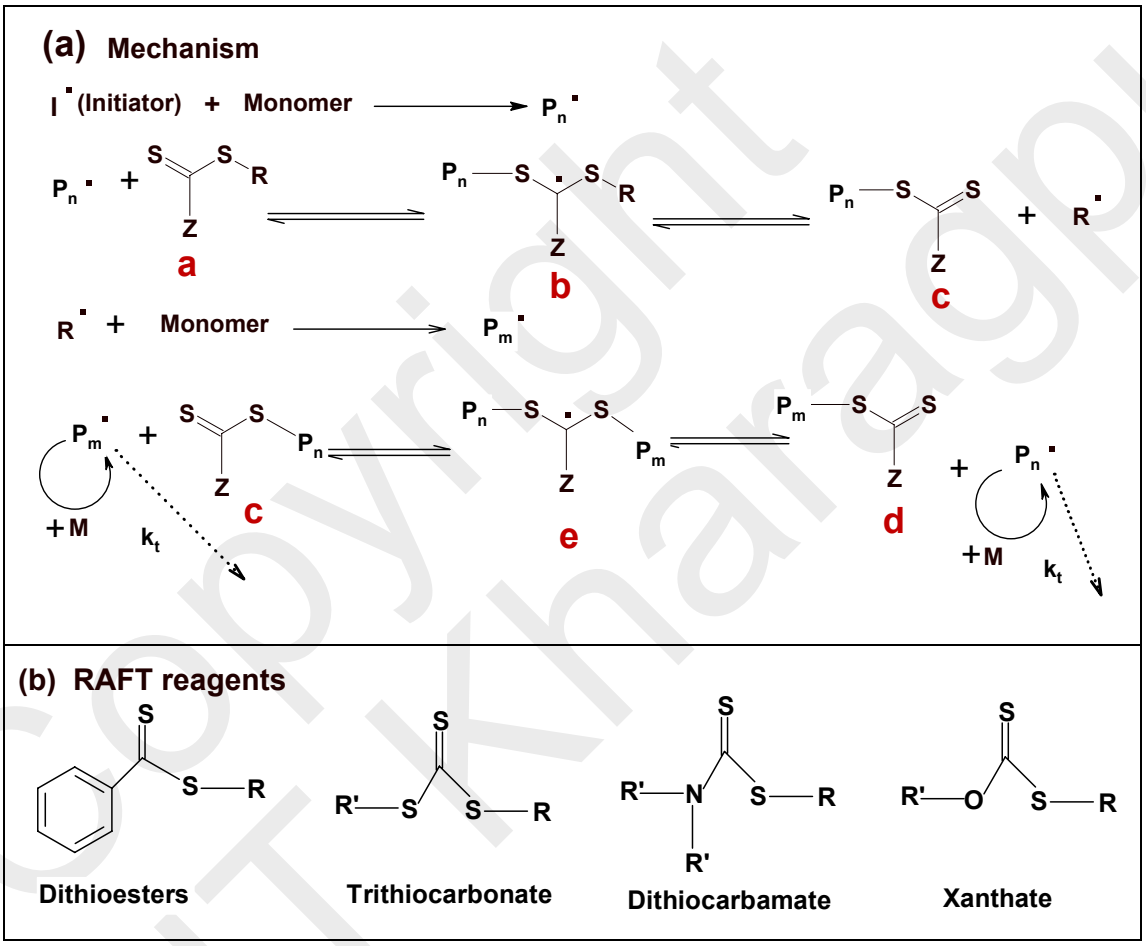


Scheme 1.5: Reversible Deactivation Equilibrium in Nitroxide Mediated CRP

Advantages of NMP over other CRP systems are that the metal catalyst is not necessary and no further purification after polymerization is required. However, major drawbacks of NMP are the long polymerization time, limit of the range of the monomers that can be polymerized, and the relatively high polymerization temperature. The synthesis of the new nitroxides leads to a wider range of monomers to be polymerized by NMP at lower temperatures in a shorter polymerization time.

1.1.6.2. Reversible Addition Fragmentation Transfer (RAFT)

The basic concept of this relatively new technique was first reported by Rizzardo et al. in 1998.[44,45] The general RAFT mechanism is shown in Scheme 1.6.



Scheme 1.6: (a) General Mechanism of RAFT; (b) Examples of Different RAFT Agents

The addition of propagating radical P_n* to the thiocarbonylthio compound 'a' gives the adduct radical 'b' which fragments to a polymeric thiocarbonylthio compound 'c' and a formation of new radical R*. The radical R* then re-initiates polymerization to give a new propagating radical P_m*. Subsequent addition fragmentation steps set up an equilibrium between the propagating radical Pn* and Pm* and a dormant polymeric thiocarbonylthio compound 'c' and 'd' by way of the

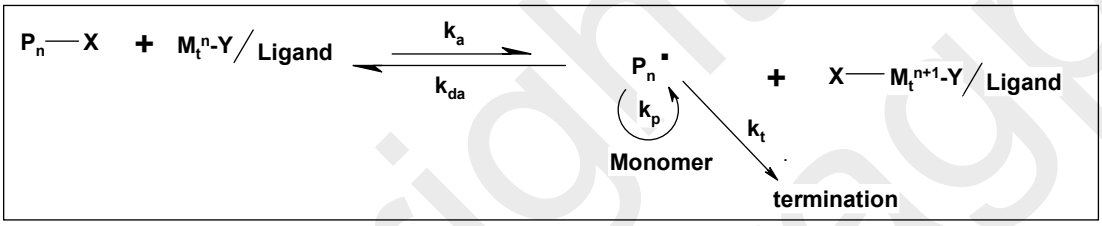
intermediate radical 'e'. Equilibrium of the growing chains gives rise to a narrow molecular weight distribution and throughout the polymerization the vast majority of the polymer chains are end capped by a thiocarbonylthio group (dormant chains). This polymerization is one of the most recent entrants and one of the most efficient methods in CRP. An important advantage of this method over NMP is its tolerance to a wide range of functionalities, namely -OH, -COOH, $CONR_2$, NR_2, SO_3Na, etc., in monomer and in solvent. This provides the possibility of performing the polymerization under a wide range of reaction conditions and polymerizing or copolymerizing a wide range of monomers in a controlled manner.

One of the major advantages of the RAFT polymerization is that the polymerization can be carried out at room temperature at relatively shorter reaction time. Radical generation by plasma treatment can also be used for the RAFT polymerization yielding polymers with narrow molecular weight distribution.[64] The γ-Ray-induced RAFT polymerization is also reported and appeared to be more effective than the corresponding UV-induced processes.[65, 66] The major disadvantages of the RAFT polymerization are; (i) the resultant polymers are colored. (ii) the RAFT reagents have obnoxious odour of sulphur compounds.

1.1.6.3 Atom Transfer Radical Polymerization (ATRP)

Metal catalyzed CRP mediated by Cu, Ru, Ni, and Fe complexes, is one of the most efficient methods to produce tailor-made polymers.[46, 47, 67–68] Transition metal catalyzed CRP is often called atom transfer radical polymerization (ATRP), as during the course of polymerization the atom transfer step is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP originates in atom transfer radical addition (ATRA) reactions, which target the formation of 1 : 1 adduct of alkyl halides and alkenes, which are also catalyzed by transition metal complexes.[69] ATRA is a modification of the Kharasch addition reaction, which usually occurs in the presence of light or conventional radical initiators.[70] Because of the involvement of transition metals in the activation and deactivation steps, chemo-, regio-, and stereoselectivities in ATRA and the Kharasch addition may be different. ATRP, which is the most versatile method of the controlled free-radical polymerization systems, uses a wide variety of monomers, catalysts, solvents, and reaction temperatures.

The general mechanism for ATRP is shown in Scheme 1.7. ATRP necessarily needs an activated alkyl halide as an initiator and a transition metal halide in combination with a suitable ligand as a catalyst. ATRP involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of Cu^1, in a redox process. Upon halogen abstraction, the free radical formed (the transient radical) can undergo propagation. However, the free radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are very rapid, and a dynamic equilibrium is established between the dormant species and active radical species. However, the dynamic equilibrium favors the dormant species as shown in Scheme 1.7. By this way, all chains can start growing at the same time, and the concentration of free radicals is quite low, resulting in a reduced amount of irreversible radical-radical termination.



Scheme 1.7: General Scheme of Transition-Metal-Catalyzed ATRP

The radicals, i.e., the propagating species P_n*, are generated through a reversible redox process catalyzed by a transition metal complex (activator, M_t^n –Y/ ligand, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, Pn–X. Radicals react reversibly with the oxidized metal complexes ($X–M_t^{n+1}$/ligand, the deactivator) to reform the dormant species and the activator. This process occurs with a rate constant of activation (k_a) and deactivation (k_{da}) respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation (k_p). This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages.[71] The equilibrium constant ($K_{eq} = k_a/k_d$) should be very low, so that concentration of active radicals will be low. Thus the irreversible chain breaking reactions will be very low. However, the K_{eq} must not be too low. This will result in very slow polymerization

rates.[50] The component reactions at equilibrium should be fast so that all the chains have equal probability of growing to the same extent leading to narrow PDI.

1.1.7. Kinetics of ATRP

According to Scheme 1.7, and assuming insignificant contribution of termination due to the persistent radical effect (PRE)[71, 72] the rate of polymerization and the polydispersity in ATRP can be derived, as given in equations 1.1 and 1.2 respectively.[7, 9, 11]

$$R_p = k_p.K_{eq}\frac{[R-X][M_t^{\,n}]}{[M_t^{\,n+1}]}[M] \text{ (or) } \ln\left[\frac{[M_0]}{[M]}\right] = \frac{k_p.k_a[R-X][M_t^{\,n}]}{k_d[M_t^{\,n+1}]}t = k_{app}t \quad \ldots(1.1)$$

$$\frac{M_w}{M_n} = 1 + \left[\frac{k_p[R-X]}{k_d[M_t^{\,n+1}]}\right]\left[\frac{2}{P}-1\right] = 1 + \frac{2}{k_a[M_t^{\,n}]t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.2)$$

Where [RX] = concentration of initiator; [M] = concentration of monomer; R_p = rate of polymerization; K_{eq} = equilibrium constant; $[M_t^n]$ = concentration of metal with oxidation state of 'n'.

From equation (1.1) the rate of polymerization (R_p) is directly proportional to the equilibrium constant (K_{eq}) as well as to the propagation rate constant. The equilibrium constant ($K_{eq} = k_a/k_d$) plays an important role in the rate of ATRP, because it determines the concentration of radicals and, therefore the rates of polymerization. Equilibrium constant must be low to maintain a low stationary concentration of radicals, so that the termination reaction is minimized. When k_a is much less than k_d ($k_a << k_d$) equilibrium is strongly shifted towards the dormant species and this phenomenon is known as persistent radical effect (PRE).[71,72] For the ATRP system, the rate of polymerization (R_p) is first order with respect to the concentration of monomer [M] as well as to the activator $[M_t^n]$. R_p increases with the concentration of activator, monomer, and initiator [R-X], but it decreases with the increasing deactivator $[M_t^{n+1}]$ concentration.

Equation (1.2) shows that lower polydispersities are obtained at higher conversion, and at higher monomer to initiator ratio, $[M]_0/[I]_0$. Equation 1.2 also indicates that higher concentration of deactivator $[M_t^{n+1}]$ and greater k_d in comparison to k_a lead to low polydispersity index. As a result, the effect of termination reaction on the overall kinetics of polymerization is excluded. Both Fischer [71] and Fukuda et

al.[73] have separately shown that under ideal conditions the persistent radical effect should result in apparent orders of reactants of less than unity for monomer, initiator, and activator. Termination reactions occur continuously throughout the polymerization. Thus, the concentration of the deactivator species increases and monomer consumption should not be simply first-order. Fischer has shown that the monomer consumption should follow Equation (1.3).[71]

$$\ln\left[\frac{[M_0]}{[M]}\right] = \frac{3}{2}k_p\left([RX]_0[M^t{}_n]_0\right)^{1/3}\left(\frac{k_a}{3k_d.2k_t}\right)^{1/2}t^{2/3} \quad \text{..... (1.3)}$$

However, great majority of the ATRP systems represent a linear semi logarithmic kinetic plot of monomer conversion versus time. Typically, a small fraction (~5%) of the total growing polymer chains terminate during the early stage of the polymerization, but the majority of the chains (>90%) continues to grow successfully. If a small amount of the deactivator (~10 mol% versus activator) is added initially to the polymerization, then the proportion of terminated chains can be greatly reduced.[74, 75] Wang and Matyjaszewski [47, 67] attributed this result to the decrease of k_t with increase in the degree of polymerization (DP). The theoretical number-average molecular weight of the polymer can be calculated as follows:

$$\text{DP = degree of polymerization} = \frac{\Delta[M]}{[I]} \quad \text{..... (1.4)}$$

Where [I] = concentration of initiator; $\Delta[M]$ = conversion of monomer at different polymerization time.

As in a typical controlled radical polymerization, the average molecular weight of the polymer can be predetermined by the ratio of consumed monomer and the initiator (DPn) while maintaining a relatively narrow molecular weight distribution (1.0 < Mw/ Mn < 1.5). This occurs in a well controlled ATRP; in addition, precise control over the chemistry and the structure of the initiator and active end group allow for the synthesis of end-functionalized polymers and block copolymers.[76–79]

Among all the CRP methods transition metal mediated ATRP appears to be the most versatile one because of its freedom on choice of monomers and tolerance over a wide range of functionality of monomer as well as solvent and initiating

species. This thesis outlines the synthesis of tailor-made polymers bearing specialty functional groups, their characterization and applications.

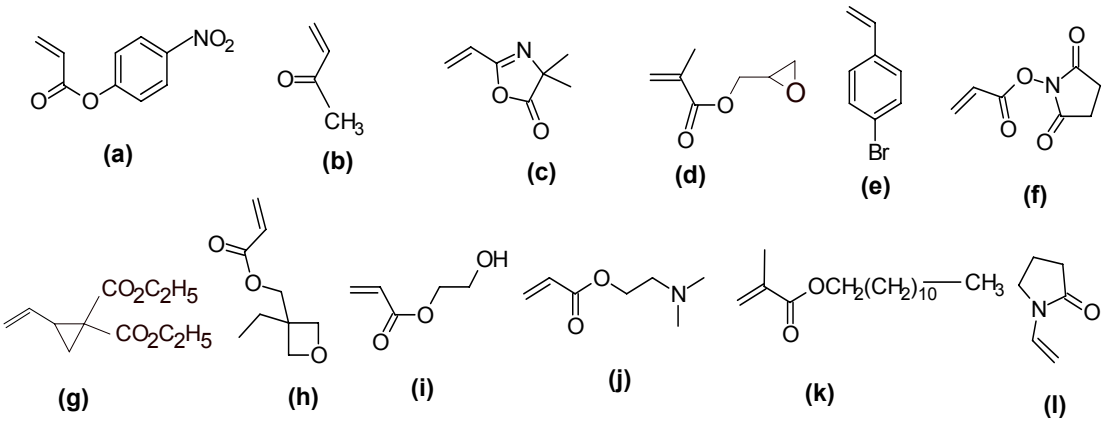
1.2. Literature Review

1.2.1. Specialty Monomers

Current advances in the field of polymer chemistry with its great importance in various fields like biological, microelectronics, and materials sciences etc have realized increasing needs for specialty polymeric materials with more sharply defined structures. However, the preparation of such polymeric materials with specialty functional groups imposes major synthetic challenges.[55] Many of the currently used processes to synthesize materials allow only crude control over the structure as well as functionality of the material as discussed earlier. For a synthetic organic concept to be applicable to the preparation of macromolecules with specialty functional group, the reactions must i) result in a stable linkage, ii) exhibit minimal cross-reactivity with other functional groups, iii) react to completion, iv) be free of appreciable amounts of side products, and v) proceed under various reaction conditions. Structural integrity of these specialty functional groups is absolutely necessary for making them suitable for different applications and post-polymerization modification like 'click reactions',[80] grafting, reversible coatings etc. As mentioned earlier conventional addition polymerizations like ionic polymerizations, coordination polymerizations cannot be used to these specialty monomers, as the specialty functional groups affect the polymerization reactions in many cases.

Since its discovery in 1995, ATRP has rapidly attracted growing interest of polymer chemists, because of its versatility in the synthesis of polymers with predictable molecular weights, low polydispersities, and specific functionalities.[76–79] In ATRP, monomers as well as initiators bearing functional groups are most often used to synthesize functional polymers.[46, 67, 81–84] ATRP has been used to polymerize different types of monomers to produce polymers with controlled molecular weight and narrow molecular weight distribution. These vinyl monomers include styrenes,[85] acrylates,[86–87] methacrylates,[88–90] acrylamides,[91] and acrylonitrile,[92–93] which possess substituents that can stabilize the propagating radicals. Each monomer has its own equilibrium constant, K_{eq}, which determines the polymerization rate in ATRP

according to equation (1.1). Scheme 1.8 shows the different functional monomers which have been polymerized by ATRP as well as by FRP.



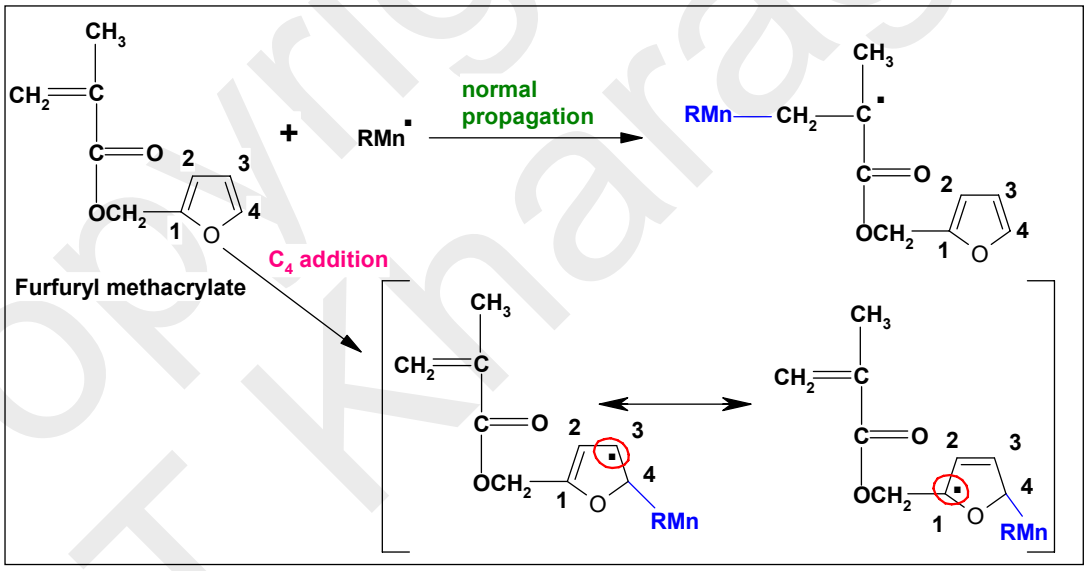
Scheme 1.8: Different Specialty Monomers Prepared via Conventional Radical Polymerization (FRP) and Atom Transfer Radical Polymerization (ATRP)

(a) p-Nitrophenyl acrylate – (FRP[94] & ATRP,[95]) (b) Methyl vinyl ketone – (FRP[96] & ATRP,[97]) (c) 2-Vinyl-4,4-dimethyl-5-oxazolone- (FRP[98] & ATRP,[99]) (d) Glycidyl methacrylate – (FRP[100] & ATRP,[101]) (e) Bromostyrene – (FRP[102] & ATRP,[103]) (f) N-Acryloxysuccinimide– (FRP[104] & ATRP,[105]) (g) 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane – (FRP[106] & ATRP,[107]) (h) 3-Ethyl-3-(acryloyloxy)methyloxetane – (FRP & ATRP,[25]) (i) 2-Hydroxyethyl acrylate – (FRP[108] & ATRP,[109]) (j) Dimethylaminoethyl acrylate – (FRP[110] & ATRP,[111]) (k) Lauryl methacrylate – (FRP[112] & ATRP,[113–114]) and (l) N-Vinylpyrrolidone- (FRP[115] & ATRP.[116])

FRP of these monomers leads to polymers with uncontrolled molecular weight and with broad polydispersity index. In many cases it leads to gelled polymers. Interestingly, ATRP of these monomers leads to polymers and copolymers with controlled molecular weight and narrow polydispersity index. It also leads to polymers with well-defined architecture and topology like block, graft, star and branched copolymers. Importantly, the functional groups in the polymers are not affected during ATRP. However, the literature survey reveals that the specialty monomer like furfuryl methacrylate, as well as acrylate bearing adamantyl derivatives (like amino-adamantyl group) has not been reported. This thesis describes the ATRP of these specialty monomers and the post-polymerization modifications of the tailor-made specialty polymers.

1.2.2. Furfuryl Methacrylate (FMA)

FMA is a very interesting monomer because of the presence of reactive furfuryl (a diene) functionality in its pendant group. It is synthesized by the transesterification reaction between MMA and furfuryl alcohol in presence of Na_2CO_3 as catalyst.[117] FMA is used in clinical applications as biomaterials (bone cement) due to its low polymerization shrinkage and its lower heat of polymerization than MMA.[118] Gandini et al.[119] reported the conventional radical copolymerization of styrene and FMA using AIBN as initiator and they observed that the final polymer was gelled because of the undesirable side reactions involving the reactive pendant diene (furfuryl) moieties. Other literatures[120–123] also reported the polymerization of monomers bearing furfuryl functionality via conventional free radical polymerization (FRP). In these cases the polymers had uncontrolled molecular weight and high polydispersity index (PDI). In many cases it leads to gelation in the polymer. This gel formation is due to the participation of the C-4 position of the furan ring (Scheme 1.9) as radical trapping.[124]



Scheme 1.9: Molecular Structure of the Species that Participate in the Mechanism of the Polymerization of Furfuryl Methacrylate

Mihajlov and Boudevska [125] studied the polymerization of FMA and the carbomethoxyfurfuryl methacrylate (CMFM) by using AIBN as initiator. They reported faster rate of polymerization of CMFM than that of FMA. It was attributed due to the formation of more stable complex between the polymeric radicals and the furan ring. However, the interaction of radicals with the furan ring has been shown to occur through the addition of the radical to the C-4 position of the furan ring

(Scheme 1.9) with the formation of a stabilized allylic-type radical.[118, 124] This leads to a so-called degradative transfer process of the chain in the case of the polymerization of acryl-furanic compounds.[118] The retardation effect of furan compounds on the free radical polymerization of vinyl monomers has been widely reported in the literature.[124–126] The reactive furfuryl functionality of the homo and copolymers of FMA can be used to carry out Diels Alder (DA) reaction, an important 'Click Reaction' in presence of a suitable dienophile like bismaleimide. However, the DA reaction is difficult to study in the polymers of FMA prepared via FRP, as these polymers are severely crosslinked. There is no report on the ATRP of FMA.

1.2.3. Acrylate bearing adamantyl group

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a colourless, crystalline compound (Figure 1.2) with a camphor-like odour. It is thermodynamically stable and highly symmetrical tricyclic hydrocarbon with a formula $C_{10}H_{16}$, which consists of fused chair-form cyclohexane rings with the same structure as a diamond lattice.[127–135] It was discovered in petroleum in 1933. Its name is derived from the Greek word adamantinos which relates to steel or diamond. Adamantane is the most stable isomer of $C_{10}H_{16}$. It was first synthesized by Prelog in 1941.[136] In 1957 Schleyer et al. reported a more convenient method of preparation of adamantane from dicyclopentadiene by hydrogenation followed by acid-catalyzed skeletal rearrangement.[137–138]

Polymers bearing adamantyl group have very good thermal and oxidation stability, low surface energy, high density, and hydrophobicity.[139–141] Polyadamantanes have excellent thermal stability and do not decompose below ~ 400 °C.[142] In solid-state NMR spectroscopy, adamantane is a common standard for chemical shift referencing.[143] Adamantane derivatives are useful in medicines, e.g. amantadine, memantine and rimantadine (Figure 1.2). Memantine (1-amino-3,5-dimethyladamantane) is used in a novel class of Alzheimer's disease medications acting on the glutamatergic system by blocking N-methyl-D-aspartate (NMDA) glutamate receptors.[144] It is marketed under the brands of Axura and Akatinol. Amantadine and Rimantadine have been well-known because of their antiviral activity (Figure 1.2). The main application of these drugs is in prophylaxis and treatment of influenza A viral infections. They are also used in the treatment of

Parkinsonism and inhibition of hepatitis C virus (HCV).[145] There are some successful instances of amino-adamantyl moiety application for brain delivery drugs.[146–147]

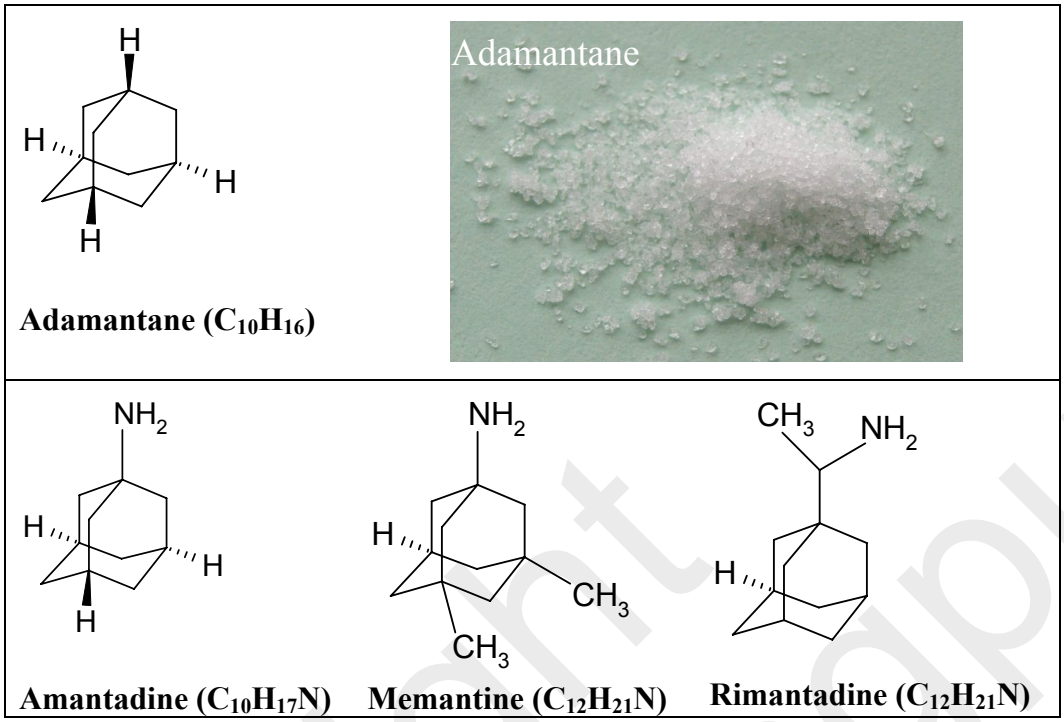


Figure 1.2: Structure of Adamantane and its Derivatives

Choi, S. K., et al.[148] synthesized poly(acrylic acid) bearing amantadine or rimantadine via conventional radical polymerization. These polymers are mostly applicable for the polymeric modulators involved in a range of biological processes including pathogen-cell interaction, tumor metastasis, immunomodulation, cell migration and adhesion. Ritter, et al. [149] synthesized thermo-responsible copolymer of adamantyl containing N-isopropylacrylamide copolymers via conventional radical polymerization. These polymers are good example for an analytical system based on supramolecular recognition. The new adamantyl-derivatized copolymer is an interesting polymer probe that reacts with β-cyclodextrins.

There are literature reports on the preparation of polymers bearing adamantyl group via conventional radical polymerization, which leads to uncontrolled molecular weights and very broad polydispersity indexes.[150–153] Huang et al. [154] synthesized a series of multifunctional initiators derived from adamantane-based derivatives which they used in the syntheses of various styrenic and (meth)acrylic star polymers by ATRP. The literature survey reveals that there is no detailed study on the synthesis of the monomers bearing adamantyl group or amino-adamantyl derivatives and on the polymerization of these monomers via ATRP.

1.2.4. Applications of these tailor-made specialty polymers prepared by ATRP

Specialty polymers have specific functional groups which can lead to several applications such as in adhesives, paints and coatings, textiles, non-woven fabrics, personal care products, specialty additives, thermoreversible coatings, biomaterial and high temperature resistant materials. Importantly, these specialty functional groups can be modified with some specific reagents to make them suitable for several applications like in smart materials, self-healing material, supramolecular materials. ATRP is applied to prepare polymers with controlled molecular weight, narrow polydispersity and with well-defined architectures like block copolymer, gradient copolymer, star polymers and hyper branched materials. Application of ATRP can be classified mainly into two categories; i) preparation of tailor-made polymers having well-defined end group, and well-designed architectures and topology which have direct applications in many different areas. ii) post-polymerization modification of the tailor-made polymers bearing specialty functional groups using suitable reagents like e.g Diels Alder reaction can be carried out if the tailor-made polymers have reactive diene functionality.

1.2.4.1. Polymers with controlled end-functionality

Since mid-1990s ATRP has been one of the most powerful controlled radical polymerization and a very versatile tool for the preparation of polymers with well-defined end functionality. Importantly, the end-functionality should be quantitative with all chains carrying both an initiator derived one end (α – end) and terminated with other end (ω – end group) (Figure 1.3).

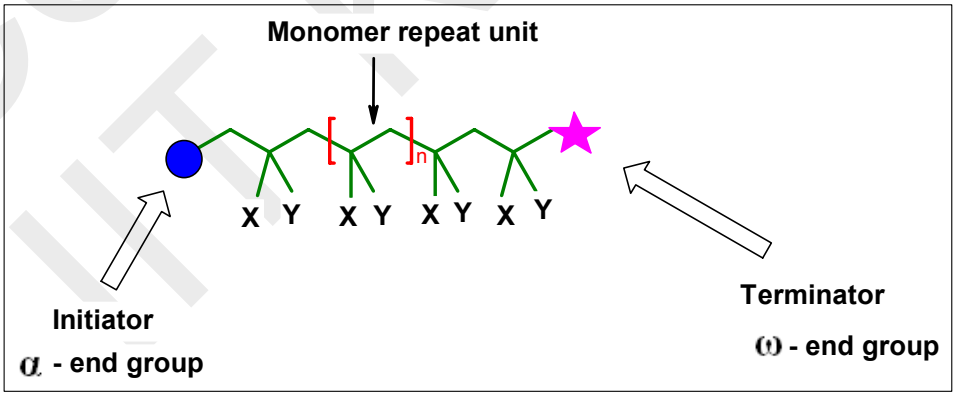


Figure 1.3: Structural Features of an Ideal Atom Transfer Radical Polymerized Polymer showing α and ω Functionalities

The α- end functionalization approach can be performed using ATRP by the use of functional initiator such as alkyl halide as initiator. The ω– end functionalization is possible to introduce into the polymer chain via ATRP by chemical transformation of the halo-end of a dormant polymer chain. Under specific conditions, functionality can also be divided into various categories, which can be placed in other key parts of the polymer chain (figure 1.4).

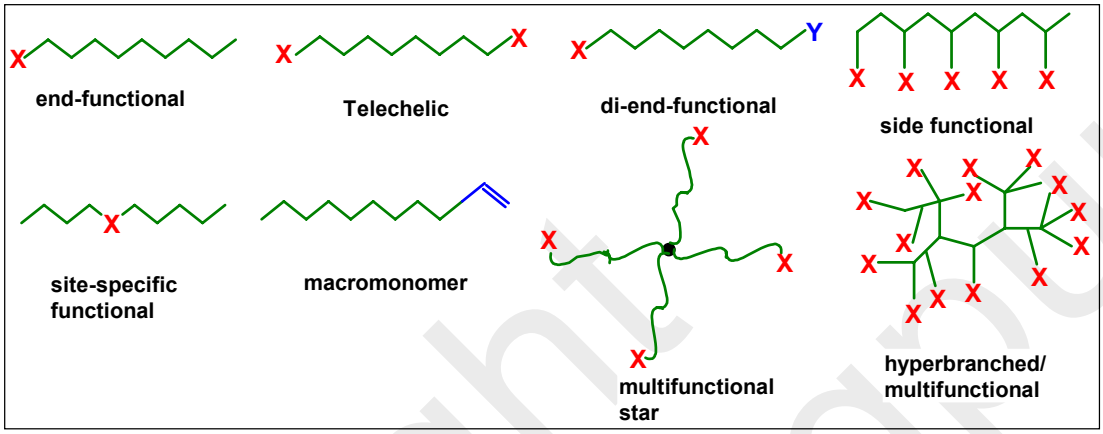


Figure 1.4: End-Functional Polymers Synthesized by ATRP

End-functional groups increase the utility of polymers and are fundamental to the development of many aspects of structure-property relationships.[155–156] The loss of end functionality may be due to the termination by disproportionation and radical-radical coupling. ATRP allows the control over formation of block copolymers at the living ω – end group.[157–159] The halide end-functionality, frequently present on the active chain end(s) of polymers prepared by ATRP, particularly polystyrenes or polyacrylates, can participate in nucleophilic substitution reactions.[160] This strategy has been used for the synthesis of a plethora of end-functional well-defined polymeric materials. The advantages are that one can incorporate functionality incompatible with the polymerization process, and if desired the material can be characterized prior to further functionalization. This procedure allows the preparation of ω and α, ω-telechelic polymers and the selection of functionality suitable for further specific reactions such as attachment to bio-materials or materials that can be immobilized to surfaces, etc.[155–160]

1.2.4.2. Polymers with well-defined architecture

The living ω – end group in the tailor-made polymer can further chain extend, thereby allowing the formation of block, star, graft and hyperbranched materials.[161–162] Control over the synthesis of blocks, grafts and other polymer architectures (figure

1.5) has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and polymer self-assembly.[163, 164] This category of materials can actually be distinguished, depending upon the feature considered: functionality, composition, and topology (Figure 1.5). ATRP is very well suited for the preparation of copolymers with controlled topologies, including star- and comb-like polymers as well as branched, hyperbranched, dendritic, network, and cyclic type structures.

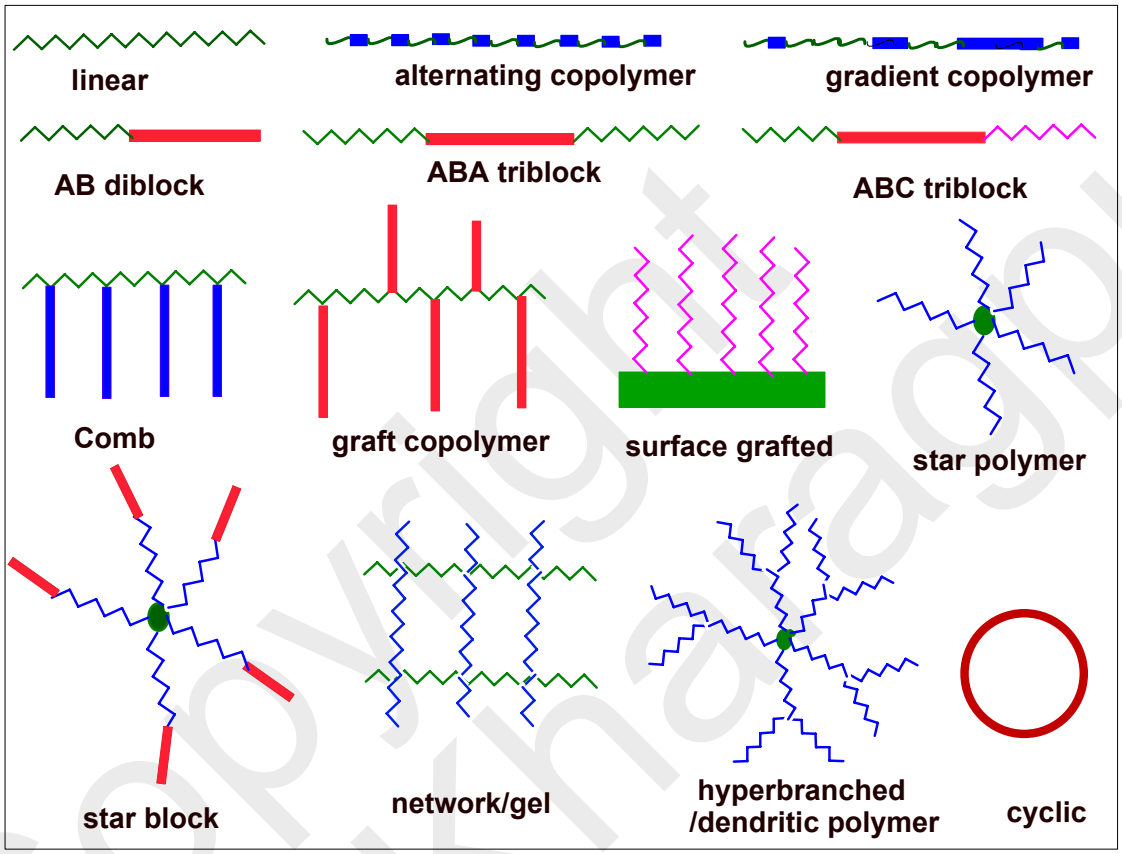


Figure 1.5: A Variety of Polymer Architectures Prepared by ATRP

Block copolymerization has been conducted with a combination of methods through site transformation of the polymer end groups. However, ATRP has been used to make AB, ABA or ABC block copolymers using sequential polymerization techniques. ABA triblock copolymers whose central B blocks are soft, (with a low glass transition temperature (Tg)) e.g., hexyl acrylate, n-butyl acrylate, methyl acrylate, 2-ethylhexyl acrylate) and outer B blocks are hard (high Tg); e.g., styrene, methyl methacrylate, acrylonitrile) attract interest because of their potential applications as thermoplastic elastomers.[165] Similar strategies were also applied to the synthesis of various block copolymers,[166] star polymers,[167] H-shaped terpolymers,[168]

miktoarm stars and mikto dendritic copolymers,[169] and well-defined macromonomers[170] from building blocks prepared by ATRP. There are a large number of literatures on block copolymer synthesis, only few examples are described here.

Wang and Matyjaszewski [47] described the synthesis of block copolymers based on styrene and methyl acrylate units that were obtained by sequential polymerization. Granel et al. [171] and Kotani et al.[172] synthesized poly(methyl methacrylate)-b-poly(n-butyl methacrylate) (PMMA-b-PBMA) diblock copolymers as well as PMMA-b-PBMA-b-PMMA triblock copolymers by various catalytic systems. It is always desirable that during the preparation of well-defined block copolymers, the polymers should be free from any homopolymer contaminants. For monomers that belong to the same family, their order of polymerization is less critical.[163, 171–172]

In the preparation of block copolymer usually halogen exchange approach is used to prepare well-defined block copolymer.[165] In this method the macroinitiator is prepared in the Br ended form and the catalyst for the second stage polymerization is taken as CuCl. Because the C-Cl bond is much stronger than C-Br, the initiation rate is vastly increased leading to efficient initiation which becomes faster than propagation. Block copolymerization becomes successful following this approach.[82, 173] The ‘‘halogen exchange’’ technique has been used by several researchers for the synthesis of narrow distributed different ‘all acrylate’ triblock copolymers.[162–164, 174, 175]

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) containing glassy hard domains (often polystyrene).[165] Block copolymers, behave as a rubber at ambient conditions, but can be moulded at high temperatures due to the presence of the glassy domains that act as physical crosslinks. However, they can also be used for much more sophisticated applications such as specialized chromatographic packing[176] or controlled drug-release in cardiovascular stents.[177] In solution, attachment of a water soluble polymer to an insoluble polymer leads to the formation of micelles in amphiphilic block copolymers. The presence of micelle leads to structural and flow characteristics of the

polymer in solution that differ from both the parent polymers.[178–180] Segmented copolymers with nanostructured morphologies are promising materials in microelectronic devices.[181, 182] Graft copolymers have been used as compatibilizers for polymer blends and may be used in many applications described for block copolymers.[183, 184] Gradient copolymers hold great promise in applications ranging from surfactants to noise and vibration dampening materials.[185]

End functional polyacrylates are excellent components of sealants for out-door and automotive applications. These functionalities can also be used for reactive blending. Well-defined polymers prepared by ATRP are very well-suited for biomedical applications such as components of tissue and bone engineering, controlled drug release and drug targeting, steering enzyme activity,[186, 187] antimicrobial surfaces.[188] The other potential applications include microelectronics, specialty membranes, soft lithography, optoelectronics, sensors and components for micro fluidics.

1.2.4.3. Post-polymerization modification of the functional group in the tailor-made polymers

The functional group in the tailor-made polymers can be modified by using suitable reagents. Post-polymerization modification [80] is an important route to modify the polymer to make it suitable for several applications. For example, if the polymer has diene functionality in their pendant group, it can be modified by Diels Alder reaction (DA), a click reaction by using a suitable maleimide as a dienophile. Since its introduction in 2001 by K. Barry Sharpless '**Click Chemistry**' has been an important synthetic tool in the organic chemistry. He was awarded Nobel Prize in 2001 for his contribution in this field.[189] Diels Alder reaction (DA) ([4+2]-cycloaddition), alkyn-azide reaction (1, 3-dipolar cycloaddition), nucleophilic substitution/ring-opening reactions, carbonyl reactions of the non-aldol type and addition to carbon–carbon multiple bonds are examples of click reaction.[189] The click reactions have important characteristics; (i) they occur in very high conversion (in many cases ~100% yield). (ii) they can occur in no solvent or in a benign solvent which can be easily removed, (iii) they need very mild conditions and (iv) they can be carried in simple reaction set up. [80, 189]

Some of the click reactions can be reversible. For example, DA reaction can be reversible via retro-DA reaction. In recent years click reactions are being used in polymer chemistry and material science to prepare new materials. These materials are used in smart materials, self-healing materials, microelectronics and in biomaterials etc. [190]

Devaraj et al.[191] used the 1,3-dipolar cycloaddition reaction to develop a selective procedure for creating well-defined surface arrays of acetylene-containing oligonucleotides onto azide functionalized self-assembled monolayers (SAMs) on gold. McElhanon and Wheeler[192] prepared dendrons and dendrimers that had thermoresponsive properties, owing to the reversibility of the DA reaction. Triblock copolymers of poly(ethylene glycol), polystyrene, and poly(methyl methacrylate) were synthesized in a one-pot method via a combination of DA cycloaddition.[193] Using click chemistry various functional groups, such as carboxyl, olefin, and amine were attached to the ends of polymers prepared by ATRP.[194–196]

Wudl, et al.[197] demonstrated that thermally reversible DA polymerization of multidienes and -dienophiles can lead to highly crosslinked, thermally controlled polymeric networks with mechanical properties comparable to those of commercial thermoplastics. One of the most relevant aspects of the DA reaction for re-mendable polymers is its thermal reversibility, a process known as the retro-Diels Alder (RDA) reaction. While a substantial amount of work has been published concerning fabrication of reversible DA-based polymers, only recently the healing ability of such polymers has been demonstrated.[198]

The earliest report of incorporation of furan–maleimide moieties into polymers for the purpose of achieving thermal reversibility was reported in 1969 by Craven.[199] The work of McElhanon et al.[200–201] who have successfully exploited furan–maleimide reversible DA chemistry for the design of debondable epoxy resins. The built-in reversibility of the material enabled debonding at 90 °C. Since then several reports of furan–maleimide based polymers have been published, all regarding the fabrication of a thermally reversible polymer network bearing DA-reactive furan and maleimide units, either as pendant groups (for reversible crosslinking).[121, 124, 202–207] Liu and Chen [208] designed polyamides containing various amounts of maleimide and furan pendant groups that exhibited thermally reversible crosslinking behavior via DA and RDA reactions. Films of these polymers were cut and then subjected to

thermal mending. For these polymers, only partial healing was observed. Watanabe and Yoshie [209] reported the synthesis and recycling of polymers made up of bis-furan terminated poly(ethylene adipate) (PEA2F) and multi-maleimide linkers (3M and 2M). The polymer exhibited thermal re-mendability and removability through DA and retro-DA reactions. These materials were shown to be applicable as advanced encapsulants and structural materials.

Despite these and several later reports, [210–211] where dicyclopentadienyldiethoxy (DCP)-based systems were employed to obtain reversible crosslinking. Few reports have appeared in the literature concerning thermally reversible polymers based on anthracene-maleimide DA chemistry.[212–213] The literatures reported other types of self-healing polymers like, supramolecular polymers,[214] externally mendable polymer system,[215] and autonomous repair by chemical catalysis.[216] There are also reports of using 1, 3 dipolar cycloaddition click reaction to prepare star polymers. In this case polyacrylates were prepared via ATRP and these polymers were modified via click reaction between azide and propargyl group to obtain star polymer. [217]

1.3. Scope and objectives

The literature review explained in section 1.2 reveals that different specialty monomers are polymerized by ATRP to produce polymer with controlled molecular weight, narrow molecular weight distribution, well-defined compositions, architectures, and chain topology and specific functionalities. However, ATRP of the specialty monomers, like (meth)acrylates bearing reactive functional groups like furfuryl group, amino-adamantyl group ($C_{10}H_{15}NH_2$) is not reported. The polymerization of these specialty monomers without affecting the functionality is very challenging. Because the polymerization of these specialty monomers prepared via FRP affects the functional groups leading to gelled polymers with uncontrolled molecular weights, molecular weight distribution and minimized the application. The impetus of the present research is to overcome the above mentioned limitations and to introduce those specialty monomers in the field of ATRP.

FMA is an interesting specialty monomer mainly used in the clinical application in biomaterial as bone cement, coatings, and adhesive applications because of its low polymerization shrinkage. There is a scope of carrying out the post-

polymerization modification like (4+2) cycloaddition, a click reaction using this diene functionality present in the pendant group of FMA. However, there is no literature on the preparation of tailor-made poly (furfuryl Methacrylate) (PFMA) using ATRP.

Literature survey also indicates that there is no reports on the ATRP of different (meth)acrylates bearing adamantyl group and its derivatives. Adamantane and its derivatives have interesting physical properties like excellent thermal and oxidation stability, low surface energy and very good rigidity etc. Amino derivatives of adamantane e.g. amantadine and rimantadine etc are used in different drugs for the treatment of various diseases like Alzheimer's disease, influenza A viral infections etc. It can be mentioned that polymers bearing drug molecules are being used in different medical applications.[144] Amine ($-NH_2$) group of the tailor-made polymer bearing amino-adamantyl group can be used to react with epoxy group of other polymer.

As explained in section 1.2 it is very challenging to polymerize these functional monomers bearing specialty functional group via convention polymerization like FRP, ionic polymerization or via coordination polymerization. ATRP is a very promising method of CRP which has good tolerance to the different functionality present in the monomers or in the initiators. Importantly, ATRP can be carried out at a wide range of temperature and relatively at undemanding reaction conditions without affecting the functional groups in the monomers and in the initiators. Interestingly, these tailor-made specialty polymers can be modified via DA reactions etc. Also, there is a scope to explore the ATRP of these specialty monomers with well-defined molecular weights, molecular weight distribution, and without affecting the functionality in the monomer. After polymerization the well-defined specialty polymers can undergo post-polymerization modification leading to different applications.

The objectives of the present thesis are as follows:

a. To study the homo-polymerization of FMA by ATRP and the application of Diels Alder (DA) reaction, a ‘Click Reaction’ to the reactive furfuryl group in the tailor-made polymer.

b. To study the copolymerization of these specialty monomers with a conventional monomer like methyl methacrylate (MMA) via ATRP and to determine the reactivity ratio of copolymerization by using different models.

c. Preparation of 'all acrylate' ABA triblock copolymers based on FMA (as a hard block) and 2-ethyl hexyl acrylate (EHA) (as soft block) with different block length and to study the thermo-mechanical properties of these block copolymer.

d. To study the DA reaction, a 'click reaction' using the diene functionality of the tailor-made homo, co- and block copolymer of FMA and a bismaleimide as a dienophile (Scheme 1.10a). In this case the reversibility of DA reaction and retro-DA reaction will also be studied at different temperature.

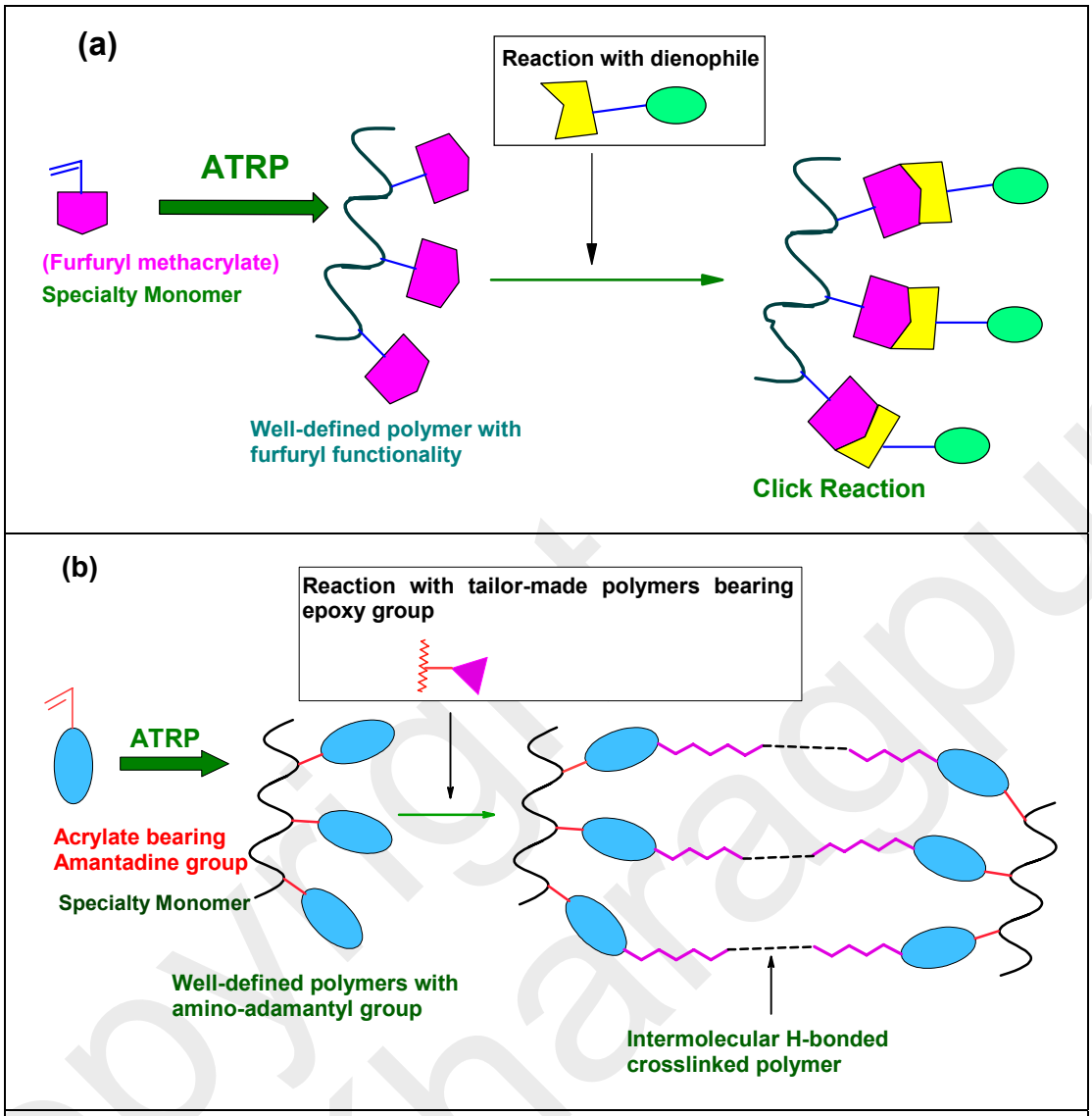
e. To study the self-healing properties, thermoreversible properties, mechanical properties of the PFMA-BM adduct (DA polymers).

f. To prepare the initiators and the monomers bearing adamantyl as well as amino-adamantyl group via protection and deprotection synthon of the organic chemistry.

g. To study the ATRP using the initiators as well as the monomers bearing adamantyl functionality and its amine ($-NH_2$) derivatives.

h. To carry out the post-polymerization reaction between $-NH_2$ in the tailor-made polymer and the epoxy group in another tailor-made polymer (Scheme 1.10b).

In all the cases the functional monomers, functional initiators and the tailor-made polymers will be characterized by using ^{1}HNMR, ^{13}CNMR, FT-IR, GPC, MALDI-TOF-MS analysis and UV analysis. The self-healing properties, thermoreversible mechanical properties and thermal properties will be characterized by using FT-IR, SEM, DSC, TGA and UTM.



Scheme 1.10 General Representation of the Specialty Monomers and its Post-Polymerization Modification Reported in this Thesis