

LIVING RADICAL POLYMERIZATION: A REVIEW

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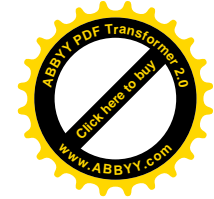
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1. Introduction

Free radical polymerization is one of the most widely employed polymerization techniques. This technique is applied to prepare latexes to be used in paints, high molecular weight poly (methyl methacrylate) for safety glass (Plexiglas[®]), or foamed poly (styrene) to be applied in coffee cups. Some advantages of radical polymerizations, with respect to other techniques, are the relative insensitivity to impurities, the moderate reaction temperatures and the multiple polymerization processes available, e.g., bulk, solution, precipitation or emulsion polymerization. Some disadvantages related to the mechanism of free radical polymerization is the poor control of the molecular weight and the molecular weight distribution, and the difficulty (or even impossibility) of preparing well-defined copolymers or polymers with a predetermined functionality.

To overcome these disadvantages new techniques were developed based on either reversible deactivation of polymer radicals or a degenerative transfer process, called 'living' or controlled radical polymerizations (CRP). It will be worthwhile to discuss the significance of the living radical polymerization process because of which it was selected for the present investigation. Controlled radical polymerizations, like atom transfer radical polymerizations (ATRP) [1], reversible addition-fragmentation chain transfer polymerization (RAFT) [2, 3], and nitroxide-mediated polymerizations (NMP) [4] represent key strategies for the preparation of polymers with narrow molecular weight distributions. To understand the living radical polymerization, firstly it is important to outline the significant of polymers.

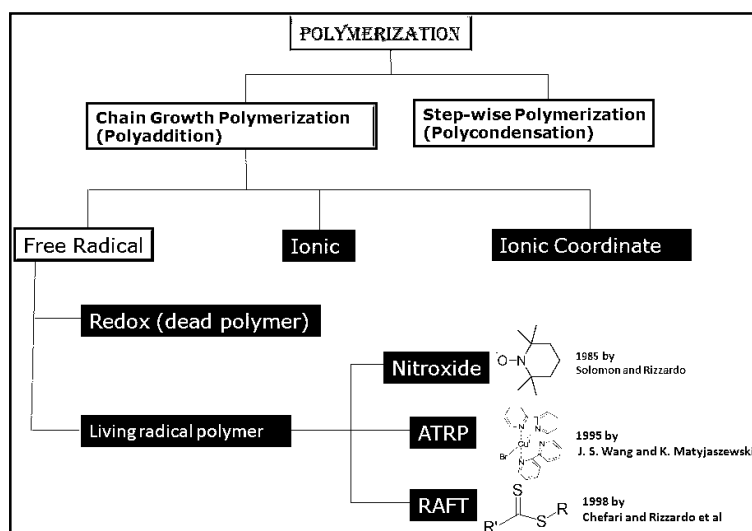
1.1 Significance of Polymers: Polymer constitutes an important material for meeting demand in specialized fields. In the present civilization, there is hardly any sphere of human life where polymers are not being used in one form or other. The human life would have been quite miserable without their applications. In fact, polymer forms the backbone of modern society. The idea is often expressed that we live in '*a plastic age*'. Synthetic polymers form the largest and most diverse class of biomaterials [5-6]. We are



familiar with range from the plastic bags and bottles used daily to the Kevlar and Mylar used to protect astronauts while they are in space.

Polymers [7] are large molecules built up by covalent linking of a large number of much smaller molecules. The term is derives from the Greek words: *polys* meaning *many* and *meros* meaning *parts*. A polymer may consist of hundreds, thousands, tens of thousands or more monomer molecules [8]. Hence, its molecular weight is very large, giving it interesting and useful mechanical and chemical properties. The volume of synthetic polymers produced worldwide is greater than the volume of steel. Polymer industry is a multi-billion dollar business, and still growing at a rate faster than most other industries. In the last decades, polymers have not only used as industrial bulk materials but also attracted great attention in high technology fields, *e.g.* nanotechnology, optics and biomaterials [9]. Therefore, the synthesis of tailor-made macromolecules with desired molecular design and understanding of the quantitative structure-property relationships (QSPR) have become main focus area for synthetic chemists. On the behalf of considerable demand of specialty requirements for specialty polymeric materials has arisen an increasing tendency to design “*intelligent polymers*” *i.e.* specialty polymers, which extend the scope of polymeric materials.

Figure 1
Route of the Polymerization



1.2 Background of present investigation: Polymerization of vinyl monomers [Fig. 1] shown earlier is of enormous industrial importance. These vinyl polymers are mostly thermoplastics and used in the wide variety of applications. Many vinyl monomers polymerized by free radical, ionic and ionic coordinate polymerization mechanism.



For several reasons, radical polymerization has significant advantages over ionic and coordination polymerizations. The reaction conditions are usually not as demanding, they exhibit a tolerance of trace impurities, and it is possible to polymerize a variety of monomers by radical polymerization. Because of these characteristics, it is possible to prepare high molecular weight polymers without removing the stabilizers present in commercial monomers, in the presence of trace amounts of oxygen. In solvents, they have not been rigorously dried, or even in aqueous media. Today free radical polymerization accounts for a large portion of mass-produced polymers.

1.2.1 Free radical polymerization: Free radical polymerization (FRP) is a type of chain growth polymerization, along with anionic, cationic and coordination polymerization. Free radical polymerization is one of the processes of polymer formation in which polymer grows by successive addition of the monomer units. It takes place via the breaking of a double bond of the monomer unit, converting it into an active propagating radical [10]. Despite its many benefits and wide spread use, the fast chain growth and the presence of the rapid irreversible termination impose some limitation with respect to the degree of control that can be asserted over polymer molecular weight distribution and polymer structure [11]. Furthermore, producing block copolymers, and polymers with complex structure via FRP is impractical.

In order to grow long chains in radical polymerization, the termination rate must be much slower than propagation rate. Since termination is a 2nd order reaction *w. r. t.* radical concentration while propagation rate is 1st order, the rate of termination becomes slower than that of propagation at very low radical concentrations [12]. Consequently, the radical concentration must be in the range of ppm or even ppb. Because the average life of a propagating chain is < 1s, which constitutes >1000s acts of propagation with a frequency ~1 ms, the life of a propagating chain is too short for any synthetic manipulation, end functionalization, or addition of a second monomer to make a block copolymer [12].

The overall kinetics can be described by eq. (1.1), where the rate of polymerization is a function of the efficiency of initiation (*f*) and the rate constants of radical initiator decomposition (*k_d*), propagation (*k_p*) and termination (*k_t*) according to

$$R_p = k_p [M] (fk_d [I]_0 / k_t)^{1/2} \quad (1.1)$$

The propagation rate scales with a square root of the radical initiator concentration and its efficiency of initiation (typically in the range of 50–80%). Molecular weights depend on the termination rate as well as the rate of transfer [12]. When the contribution of transfer neglected, the degree of polymerization depends reciprocally on the square root of radical initiator concentration, as shown in eq. (1.2)

$$DP_n = k_p [M] (fk_d [I]_0 k_t)^{-1/2} \quad (1.2)$$



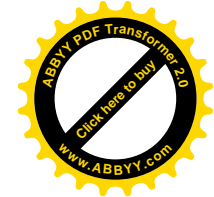
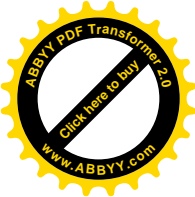
In conventional radical polymerization, solvents should not contain easily abstractable atoms or groups, unless low molecular weight polymers desired. The range of reaction temperatures is quite large (-100 to > 200°C). Monomers are sufficiently reactive when the generated radicals stabilized by resonance or polar effects [12]. Due to its lower reactivity, ethylene polymerization requires high temperatures.

However, it is accompanied by transfer under these conditions that leads to (hyper) branched polymers. Initiators are typically peroxides, diazenes, redox systems and high-energy sources, which slowly produce initiating radicals ($k_d \times 10^{-5} \text{s}^{-1}$).

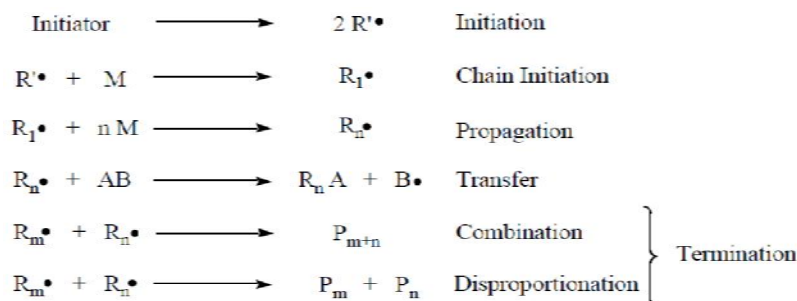
The industrial significance of conventional radical polymerization [13-15] is evident in the fact that it accounts for the production of ~50% of all commercial polymers. Low-density polyethylene, poly (vinyl chloride), polystyrene and its copolymers (with acrylonitrile, butadiene, etc.), polyacrylates, polyacrylamide, poly (vinyl acetate), poly (vinyl alcohol) and fluorinated polymers comprise the most important of these materials. However, no pure block copolymers and essentially no polymers with controlled architecture produced by conventional radical polymerization.

Many monomers capable of undergoing chain reactions are available in large quantities from the petrochemical sector [16]. Free radical mechanism is well understood and extension of the concepts to new monomers is generally straightforward. An advantage of free radical route is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is generally unnecessary while polymerization carried out either in the bulk phase or in solution. As chain reactions, free radical polymerizations proceed via four distinct processes:

- 1. Initiation:** In this first step, a reactive site formed, thereby “initiating” the polymerization.
- 2. Propagation:** Once an initiator activates the polymerization, monomer molecules added one by one to the active chain end in the propagation step. The reactive site regenerated after each addition of monomer.
- 3. Transfer:** occurs when an active site is transferred to an independent molecule such as monomer, initiator, polymer, or solvent. This process results in both a terminated molecule and a new active site that is capable of undergoing propagation.
- 4. Termination:** In this final step, eradication of active sites leads to “terminated,” or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation), the free radical chain process is demonstrated schematically below (Scheme 1):



Scheme 1
Free radical polymerization mechanism

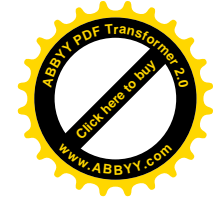
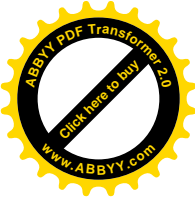


$R' \bullet$ represents a free radical capable of initiating propagation; M denotes a molecule of monomer; $R_m \bullet$ and $R_n \bullet$ refer to propagating radical chains with degree of polymerization of m and n , respectively; AB is a chain transfer agent; and $P_n + P_m$ represent terminated macromolecules. Because chain transfer may occur for every radical at any degrees of polymerization, the influence of chain transfer on the average degree of polymerization and on polydispersity carries enormous consequences. Furthermore, propagation is a first order reaction while termination is second order. Thus, the proportion of termination to propagation increases substantially with increasing free radical concentrations. Chain transfer and termination are impossible to control in classical free radical processes, a major downfall when control over polymerization is desired.

In the first quarter of the 20th century, Staudinger recognized the nature of free radical and put forward a correct interpretation for the mechanism of radical polymerization [17]. In 1937, Flory published a comprehensive paper on quantitative aspects of the kinetics and mechanism of the free-radical polymerization [18]. Subsequently free-radical polymerization has been studied and considerable progress has been made [19-23]. An important feature of free-radical polymerization is that the partially polymerized mixture mainly consists of high molar mass polymer molecules and unreacted monomer molecules.

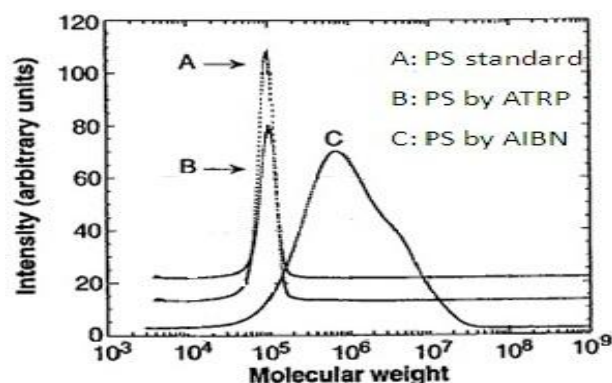
1.2.1.1 Limitations of the free radical polymerization:

- Due to diffusion-controlled termination reactions between growing radicals, little control over molar mass distribution (\bar{M}_n),
- Since, the typical life time of a propagating chain is very short, in the range of 1s, it is not possible to synthesize block copolymers or other chain topologies, and
- There is no control over the polymer tacticity.



1.2.2 Living/Controlled Radical Polymerization: This living/ controlled radical polymerization method relies on completely pure reactions so that no termination caused by impurities occurs. These polymerizations stop only when there is no more monomer and not when termination occurs. The polymerization can continue upon the addition of more monomer. Block copolymers can be made by this way. This type of polymerization can be stopped and restarted at anytime. This pioneering technology enables the synthesis of tailored polymers with unprecedented control over composition and architecture. Complete living radical polymerization allows for control of molecular weight and dispersity; however, this is very difficult to achieve and instead a pseudo-living radical polymerization occurs in which there is only partial control of molecular weight and dispersity [Fig. 2].

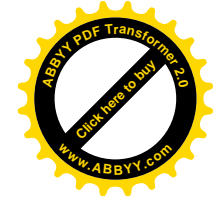
Figure 2
Specialty of living radical polymerization



This use of term “Living radical polymerization” was coined by Ostu, *et al.* during his work on the iniferter mechanism in 1982 [5]. In this article, they proposed calling the organic disulfide initiator with chain transfer and termination as *initiator-transfer agent-terminator* (iniferter). They used tetraethylthiuram disulfide in the thermal or photo polymerization of styrene and MMA, and obtained α , ω -functionalized polymers having initiator fragments and the chain termini. Later, they found that S-alkyl dithiocarbamate groups undergo reversible photo dissociation to a reactive alkyl radical and an inert dithiocarbamate radical [6]. They exploited this property of the dithiocarbamates in the formation of block and graft copolymer by irradiating a monomer in the presence of a suitable initiator.

However, the use of dithiocarbamates has the drawback of decomposition, which leads to a loss of the living nature of the chain end. For e.g., dithiocarbamate polymer chain ends can decompose to CS₂ and dialkyl amino radical, and this radical can initiate further polymerization at slow rate [24].

1.2.2.1 Fundamentals for Living Radical Polymerization: The basics for living radical polymerization can be summarized as follows,



- Fast initiation as compared to propagation since all chains should begin to grow essentially at the same time and retain functionality.
- Fast exchange between active and dormant species, so that majority of the growing chains are in the dormant state and only a small fraction is present as propagating free radicals.
- The propagation rate should not depend on the degree of polymerization.
- The polymerization reaction should be free of termination and transfer reactions.
- Concentration of the propagating radicals should be sufficiently low ($[P^*] < 10^{-7}$ M) to enable chain growth on one hand and reduce termination events on the other.
- A single type of propagating species must exist; if different propagating species are present, then their inter conversion should be very fast.
- The number average molecular weight of the polymer should have a linear relation with conversion.

1.2.2.2 Advances of living radical polymerization than conventional free radical polymerization: Living radical polymerization (LRP) and conventional free radical polymerization proceed via the same radical mechanism, exhibit similar chemo-, regio- and stereo-selectivities, and can polymerize a similar range of monomers. However, several important advances of living radical polymerization than conventional free radical polymerization exist as summarized below.

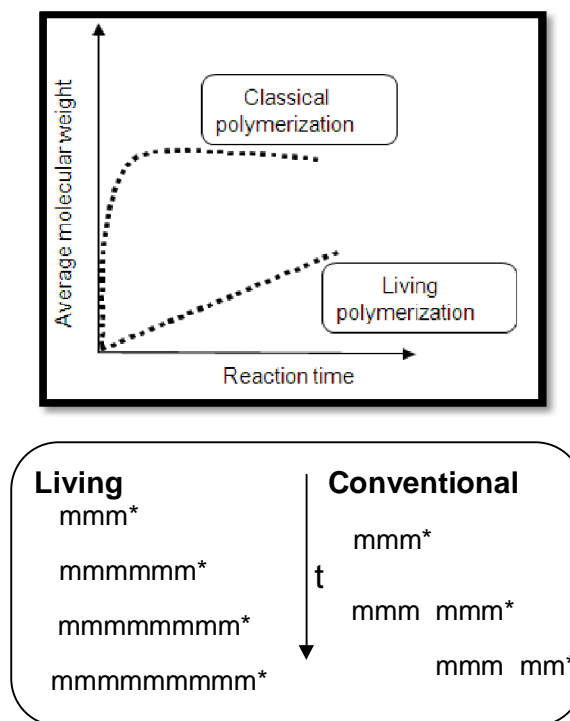
- The lifetime of growing chains is extended from <1 s in radical polymerization to more than 1h in controlled radical polymerization through the participation of dormant species and intermittent reversible activation.
- Initiation is slow and free radical initiator is often left unconsumed at the end of a conventional radical polymerization. In most CRP systems, initiation is very fast and near instantaneous growth of all chains can be achieved, which ultimately enables control over chain architecture.
- Nearly all chains are dead in radical polymerization, whereas in CRP the proportion of dead chains is usually < 10 %.
- Polymerization in CRP is often slower than in radical polymerization. However, the rates may be comparable in certain.
- A steady state radical concentration is established in radical polymerization with similar rates of initiation and termination, whereas in CRP systems based on the



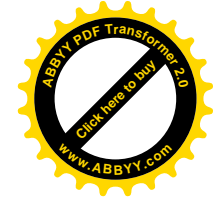
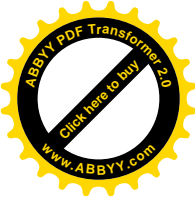
persistent radical effect, a steady radical concentration is reached by balancing the rates of activation and deactivation.

- Termination usually occurs between long chains and constantly generated new chains in radical polymerization [Fig. 3]. In CRP systems based on the persistent radical effect, all chains are short at the early stages of the reaction and become progressively longer; thus, the termination rate significantly decreases with time. In DT processes, new chains are constantly generated by a small amount of conventional initiator, and therefore termination is more likely throughout the reaction.

Figure 3
Living vs Conventional free radical polymerization processes



Controlled radical polymerization (CRP) techniques developed by Michael Szwarc in 1956 in the living anionic polymerization of styrene with an alkali metal/naphthalene system in THF, to retain the advantages of conventional free radical polymerization (FRP) and minimize its disadvantages. Accordingly, in living radical polymerization the rates of initiation, activation and deactivation are much larger than that of termination. The exchange between active and dormant chains also enables an extension of the lifetime of propagating chains from ~ 1 s in FRP to $\gg 1$ h in CRP. This enables synthesis of polymers with different chain topologies (e.g. block, graft).



1.2.2.3 Functionality of Living Radical Polymerization: Living\‘controlled’ radical polymerizations (LRP) have great potential for the production of polymers of lower molecular weight, but with high degrees of functionality [25]. Living radical polymerization of functional monomers is initiated by functional group containing initiators and transition metal complexes. The produced polymer contains different functional groups related to monomers and functional groups at the head and tail of living radical polymers. Precise control of the end groups is readily attained in controlled radical polymerizations; this methodology is ideally suited for preparing telechelic materials [26-33]. An example is the preparation of poly (butyl acrylate) with α , ω -hydroxyl groups that can be used as a replacement for poly (ethylene glycol) in polyurethane synthesis [34-36].

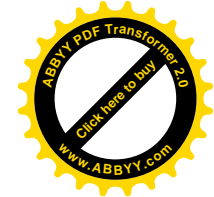
Currently, the three most effective methods of CRP include *nitroxide mediated polymerization* (NMP)[37-44], *atom transfer radical polymerization* (ATRP) [17, 25, 28, 29, 40, 45-101] and *reversible addition fragmentation chain transfer* (RAFT) *polymerization* [102-112]. In this section, a brief insight given for these techniques namely, NMP, ATRP and RAFT.

1.2.2.4 Nitroxide Mediated polymerization: With the advent of newly designed nitroxide radicals (others than the TEMPO radical) [113-118], nitroxide-mediated polymerizations have regained raising interest because of the growing number of monomers that nowadays can be polymerized in a controlled manner via this technique. However, the control over the polymerization often arises from equilibria that significantly decrease the reaction times.

In nitroxide-mediated polymerizations, control of the reaction is provided by reversible capping and de-capping of the growing (radical) polymer chain by a nitroxide radical. As a result, the concentration of the growing radical species is decreased and the speed of the polymerization is significantly decelerated. Consequently, the polymer chains grow with a (quasi) uniform speed, and side reactions, like the bimolecular termination, are kept at a minimum. Consequently, the polymers show relatively narrow molecular weight distributions. In order to gain optimum control over the radical polymerization, one-component species (decomposing into an initiating radical and a nitroxide radical) have shown to be superior to two-component mixtures, as the latter exhibit the disadvantage of inaccurately specified efficiencies of the initiating radical [119-120].

1.2.2.4.1 Basic mechanism: Reports by Georges in 1993 of a controlled polymerization of styrene in the presence of benzoyl peroxide and the mediating stable free radical TEMPO (2, 2, 6, 6-tetramethyl-1-piperidynyl-N-oxy) ushered in the dawn of modern CRP [119]. Despite earlier attempts, reported in the patent literature [121], this was the first example of a successful CRP utilizing a nitroxide-based system.

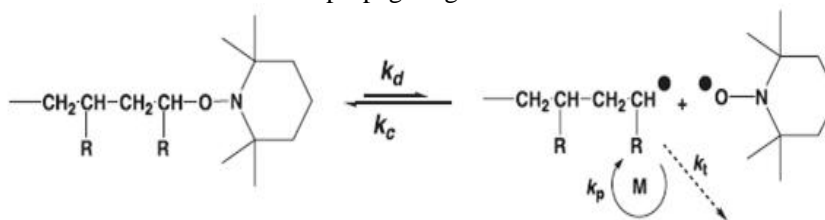
Control in NMP is achieved with dynamic equilibration between dormant alkoxyamines and actively propagating radicals (Scheme 2). In order to effectively



mediate polymerization, TEMPO (and other stable free radicals) should react neither 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 β -H atoms. These persistent radicals should also be relatively stable, although their slow decomposition may help maintain appropriate polymerization rates.

Scheme 2

Dynamic equilibration between dormant alkoxyamines and actively propagating radicals



TEMPO and its derivatives form a relatively strong covalent bond in alkoxyamines. The SFRP equilibrium constant (ratio of dissociation (k_d) to cross-coupling/association (k_c) rate constant) is generally very small. The values of K_{eq} are often so low that in the presence of excess TEMPO, the equilibrium become very strongly shifted towards the dormant species and significantly reduces the polymerization rate. While original TEMPO-based systems were successful at controlling the polymerization of styrene and some of its copolymers, they failed to mediate polymerization of acrylates and several other monomers for this reason.

Polymerization could in principle be accelerated (i.e., the concentration of growing radicals could be increased) if the concentration of TEMPO were reduced. This might be accomplished by the slow self-destruction of nitroxide by a reaction with additives or initiating radicals [122–124]. This occurs spontaneously in the polymerization of styrene due to thermal self-initiation at elevated temperatures.

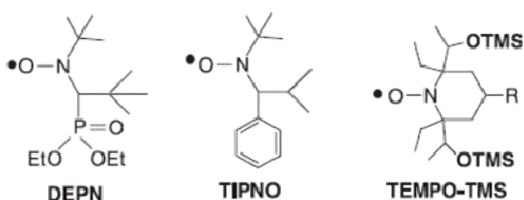
1.2.2.4.2. Mediating Species/Initiation Systems

1.2.2.4.2.1. Nitroxides as persistent radicals: TEMPO efficiently mediates styrene polymerization under the appropriate conditions but fails to mediate polymerization of other monomers with lower equilibrium constants. Other nitroxides were synthesized in an effort to provide more labile C–O bonds. Three exemplary nitroxide structures are illustrated in [Fig. 4].

Numerous derivatives of these structures have been successfully employed in NMP [44]. DEPN [124–125] and TIPNO [126] contain H atoms at the α -C. Such nitroxides were originally predicted to be very unstable and assumed to quickly decompose. However, they can both sufficiently mediate polymerization of styrene, as well as various other monomers. Bulkier nitroxides can decrease the bond dissociation energy of C–O

bonds formed during polymerization, which consequently increases the proportion of radicals during a polymerization and enables lower polymerization temperatures.

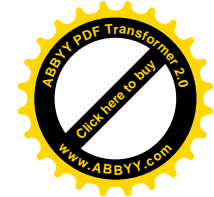
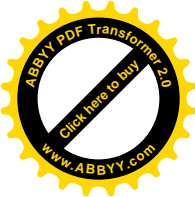
Figure 4
Structures of nitroxides commonly employed in NMP



Significant steric bulk was introduced to a TEMPO derivative at the 2, 2, 6, 6-substituents with trans-2, 6-diethyl-2, 6-bis (1-trimethylsilyloxyethyl)-1-(1-phenylethoxy) piperidine-N-oxyl (TEMPO-TMS) [127-128]. The steric effects of this bulk so effectively decrease the bond dissociation energy of the alkoxyamine that polymerization of butyl acrylate can be successfully mediated at temperatures as low as 70°C. However, further increasing steric hindrance by substituting the methyl group to the TMSO unit with an isopropyl group actually significantly reduces control, likely by slowing the rate of association too much [127]. Steric effects actually prevent the successful control of methacrylate polymerization mediated by nitroxides. Reactive nitroxides prefer to abstract β-H atoms rather than form alkoxyamines. Less reactive nitroxides do not cross-couple rapidly enough with growing chains to efficiently control methyl methacrylate (MMA) polymerization [129, 130]. One solution to this problem involves copolymerizing a small amount of styrene with MMA. Just 10 mol % styrene has been sufficient to control such copolymerizations [131]. However, further development of nitroxides stabilized by resonance and polar effects will be needed to achieve control in homopolymerizations of pure methacrylates.

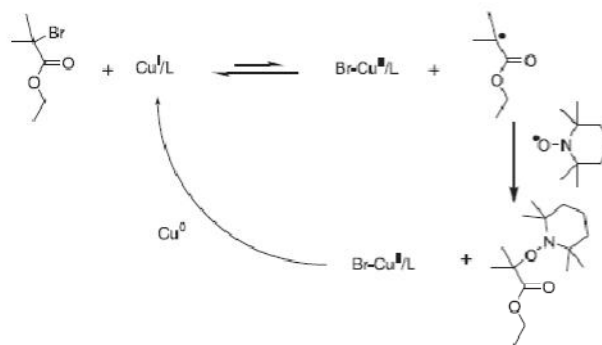
1.2.2.4.2.2. Alkoxyamine unimolecular initiators: SFRP systems can be initiated in two different ways. Conventional radical initiators can be used in the presence of persistent radicals. Alternatively, dormant species can be prepared in advance and used as unimolecular initiators [120, 132] or macro-initiators for block copolymerization. The structure of these species is based on the alkoxyamine functionality generated at the chain end during NMP. The thermally unstable C–O bond decomposes upon heating to give the initiating species. These well-defined unimolecular initiators permit much better control over polymer molecular weight and architecture than the aforementioned nitroxide persistent radicals used in conjunction with free radical initiators [37]. The exploitation of alkoxyamines was originally limited by a lack of efficient synthetic procedures for their preparation, procedures that often resulted in low yields and a wide range of byproducts [120, 133].

However, several versatile techniques have since been developed that involve the controlled generation and trapping of carbon centered radicals, including single electron



transfer reactions associated with ester enolates [134] and enolate anions [135]. Another simple method involves halogen abstraction from alkyl halides by a Cu catalyst via atom transfer radical addition, and subsequent trapping of the alkyl radical by an excess of nitroxide persistent radical (Scheme 3) [136].

Scheme 3
SFRP System Mechanism



1.2.2.5 Atom Transfer Radical Polymerization: In 1995, two research groups independently reported a similar controlled radical polymerization technique, the atom transfer radical polymerization (ATRP). They were based on catalytic systems used for the atom transfer radical addition reaction (ATRA), or the well-known Kharasch reaction, an efficient method of forming carbon-carbon bonds between organic halides and alkenes [137]. The first report by Sawamoto *et al.*, uses $\text{RuCl}_2(\text{PPh}_3)_3/\text{Al}(\text{O}-i\text{Pr})_3$ as a catalyst system in the polymerization of MMA initiated by CCl_4 [138].

The second system reported by Matyjaszewski, *et al.*, is the polymerization of styrene catalyzed by $\text{CuCl}/2, 2'$ -bipyridyl (bpy) in the presence of 1-phenylethyl chloride as an initiator [151]. Since these first reports, there have been many reports on ATRP of styrene, acrylates, methacrylates, and acrylonitrile by using various transition metal complexes, including nickel, iron, palladium, and rhodium. Compared to other controlled radical polymerization methods, ATRP is very versatile.

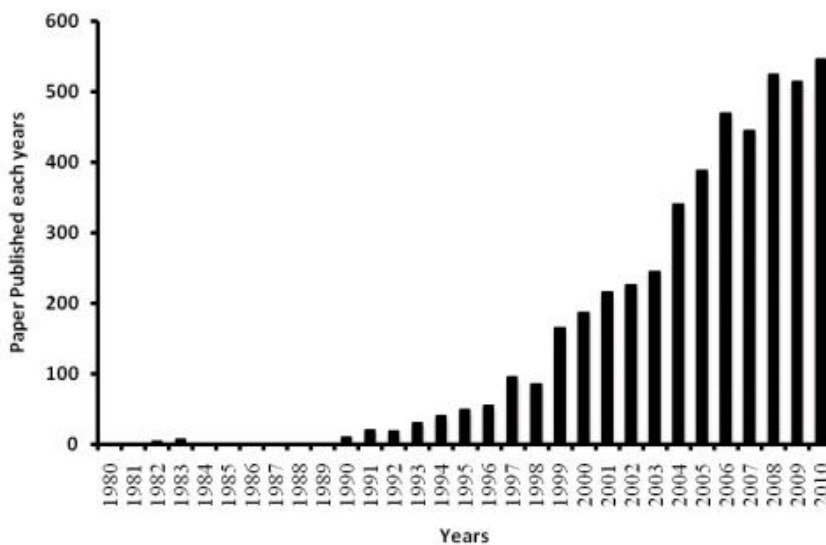
This method provides control in the polymerization of many different monomers under various reaction conditions and makes it possible to prepare polymers having a wide range of architectures including blocks, grafts, gradient copolymers, stars, combs, branched, and hyper-branched [50].

ATRP is among the most rapidly developing areas of chemistry, with the number of publications approximately doubling each year [38, 39-144]. According to Sci-Finder Scholar, 7 papers were published on ATRP in 1995, 27 in 1996, 49 in 1997, 78 in 1998, 150 in 1999, and more than 550 in 2010 [figure 1.3].

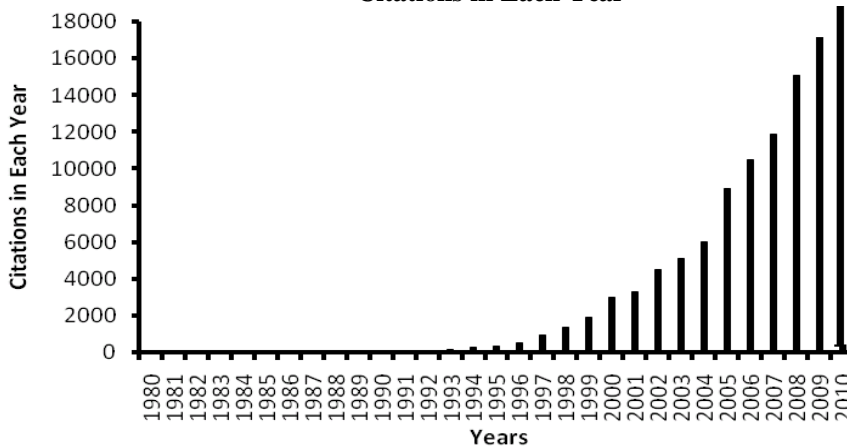


Figure 1.3
Atom Transfer Radical Polymerization publication and citations till 26 Dec, 2010, Fig 5

Published items in Each Year



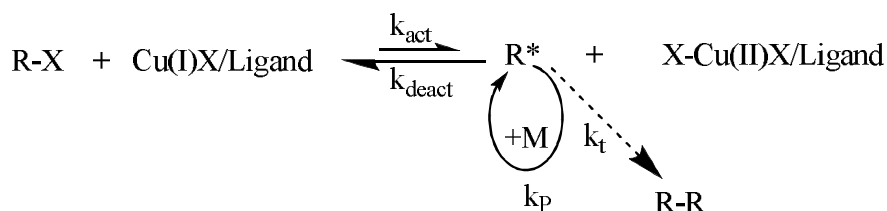
Citations in Each Year



The name ATRP comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of polymeric chains. ATRP originates in atom transfer radical addition (ATRA) reactions, which target the formation of 1:1 adducts of alkyl halides and alkenes, which are catalyzed by transition metal complexes [137]. In copper mediated ATRP, the carbon-halogen bond of an alkyl halide (RX) is

reversibly cleaved by a CuIX/ligand system resulting in a radical (R^*) and CuIIX₂/ligand. The radical will mainly either reversibly deactivate or irreversibly terminate [Fig. 6].

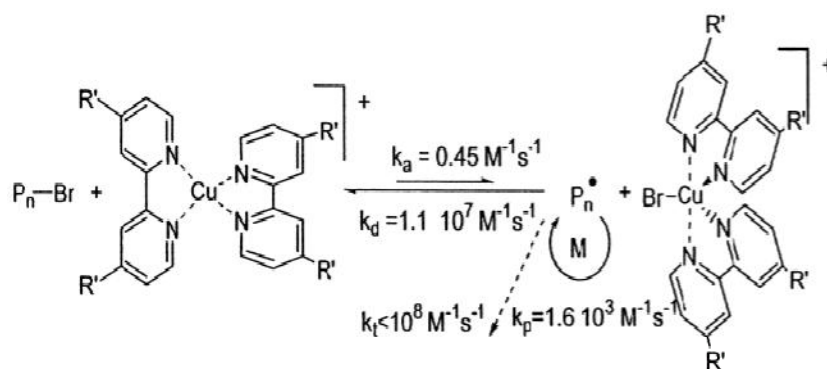
Figure 6
Simplified ATRP Mechanism

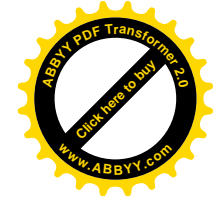


Atom transfer radical polymerization (ATRP) is based on the reversible transfer of halogen atoms, or pseudo-halogens, between a dormant species (P_n-X) and a transition metal catalyst (Mnt/L) by redox chemistry. The alkyl (pseudo)halides are reduced to active radicals and transition metals are oxidized via an inner sphere electron transfer process [1, 27, 97]. In the most studied system, the role of the activator is played by a copper (I) species complexed by two bipyridine ligands and the role of deactivator by the corresponding copper (II) species. Figure 7 shows such a system with the values of the rate constant for activation (k_a), deactivation (k_d), propagation (k_p) and termination (k_t) for a bulk styrene polymerization at 110°C [50]. The rate coefficients of termination decrease significantly with the progress of the polymerization reaction due to the increase in the chain length and increased viscosity of the system. In fact, the progressive reduction of k_t is one of the most important features of many controlled radical polymerizations [56, 93]. The role of the different ingredients like monomers, alkyl halide initiators, catalyst, ligand and solvent employed during ATRP is of paramount importance.

Figure 7

Values of the rate constant for activation (k_a), deactivation (k_d), propagation (k_p) and termination (k_t) for a bulk styrene polymerization at 110°C [72]





1.2.2.5.1 Mechanistic Understandings of Atom Transfer Radical Polymerization

1.2.2.5.1.1 Components: As a multicomponent system, ATRP is composed of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature must also be taken into consideration.

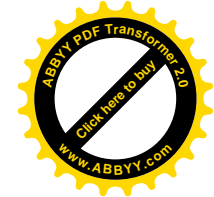
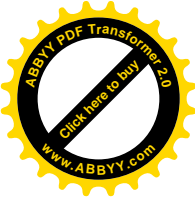
1.2.2.5.1.1.1 Monomers: A variety of monomers has been successfully polymerized using ATRP. The polar monomers used for the current study predominantly constitute of acrylates and methacrylates, which contain substituents that can stabilize the propagating radicals. ATR homopolymerization of α -olefins and allyl butyl ether was tried but without success. The reason is that, as there are no substituents present to stabilize the formed radicals, the propagating radicals are too reactive, leading to excessive termination as a result of side reactions. For each specific monomer, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain polymerization control.

Monomers often have a major effect on the ATRP reaction, several variables can account for the influence of the used monomer, including:

- The solubility parameters of the monomer and the effects in the copper-complex formation will affect the polymerization in a similar way as the solvent does.
- The k_p of the monomer will affect the polymerization rate. When a monomer with high polymerization rate is used, multiple monomer additions per activation/deactivation step can occur causing a broadening of the molecular weight distribution, especially at low conversion and low initiator efficiency.
- Each monomer used in a polymerization will result in an alkyl halide with a specific redox potential. This will influence the atom transfer equilibrium constant (K_{eq}), the (de)activation constant, and thereby change the radical concentration present in the system.
- Some halide containing polymer end-groups can have, beside halogen atom exchange, specific interactions with the copper species present in the reaction [70].

Each monomer has its own equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) for active and dormant species in ATRP even with the same catalyst and conditions. The product of KP and K_{eq} determines the polymerization rate.

Thus, the polymerization will occur very slowly if K_{eq} is too small. This could be the plausible reason why polymerization of less reactive monomers like olefins, halogenated alkenes and vinyl acetate are not yet successful. Because of this reason, optimal conditions for ATRP such as the catalyst type, ligand, solvent, temperature and additives are to be chosen carefully for each monomer.



1.2.2.5.1.1.2 Initiators: In ATRP, alkyl halides (RX) are typically used as initiators. Initiation should be fast and quantitative. The structure of the R group and halide atom X must be carefully selected depending on the monomer and catalyst/ligand employed.

In ATRP initiators can be chosen from a wide range of organic halogen containing compounds including alkyl halides with activated substituents on the α -carbon, arenesulfonyl chlorides [145-147] and polyhalogenated compounds. Macro-initiators can also be employed; including polymers prepared using ATRP, halogen containing polymers or halogen end functionalized polymers [71]. An effective control over the molecular weight and polydispersity index in ATRP is achieved if the contribution of side-reactions is low, the initiation rate exceeds, or at least equals, the observed propagation rate and if the initiation is quantitative.

Many factors can influence the initiation rate, including [83-84]:

- **The bond strength of the carbon-halide bond:** The bond strength of alkyl chlorides is generally higher than the one of alkyl bromides, thus lowering the activation coefficient (k_a) of alkyl chlorides.
- **The stability of the formed radicals:** The stability of the formed radical will generally increase with the number of alkyl side-groups on the radical center, and will form easier. Tertiary halides will be better initiators in that respect than secondary, which will be better than primary halides.
- **The possible formation of anions:** When the initiators form very electron deficient radicals, outer sphere electron transfer could occur during activation, leading to radical anions susceptible for side reactions.

Polyhalogenated compounds are established initiators for the use in ATRP [138, 139] also ATRP uses simple initiators, mainly alkyl halides R-X (X = Cl, Br) [25,27-29, 58-76, 148]. The number-average molecular weight (M_n) of polymers eq. (1.3) prepared by ATRP depends on the initial concentration ratio of monomer (M) to initiator as well as the monomer conversion:

$$M_n = \frac{[M]_0}{[RX]_0} \times \text{Conversion of monomer} \times \text{Molecular weight of Monomer (M)} \quad (1.3)$$

The alkyl halides used as initiators can contain one or more halogen atoms. Depending on the exact initiator structure and the number of halogen atoms, the architecture of the prepared polymers can be varied from linear (using alkyl halides with a single halogen atom), to star-like or brush-like (multiple halogen atoms in the initiator) [Fig. 8].

The alkyl halides used as initiators may also contain various functional groups. The main advantages of using functional initiators in the synthesis of polymers via ATRP are the following:

- Direct functionalization
- No post-polymerization modification required
- Yields α -telechelic polymers
- Multiple applicable functionalities (more than those attainable via nucleophilic substitution of ω -end halogen atom)

Figure 8
Examples of ATRP initiator

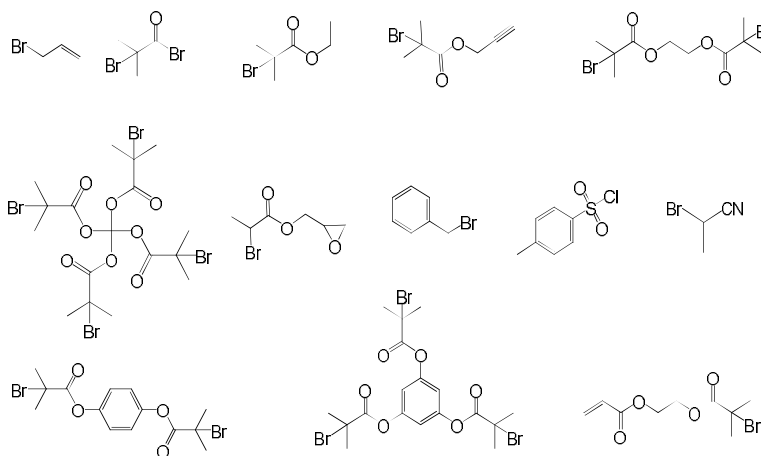
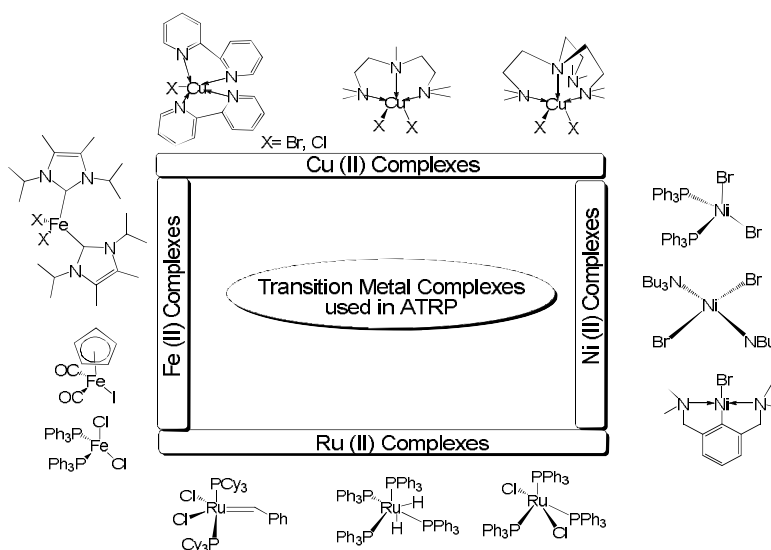
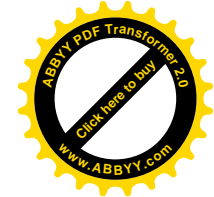


Figure 9
Transition Metal complexes used in the ATRP





1.2.2.5.1.1.3 Catalyst: One of the most important components of ATRP is the transition-metal complex *i.e.* catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The role of the transition metals (such as Cu(I)) is to abstract halogen atoms from the halogen-terminated inactive polymer chains and is oxidized to Cu(II) via a single electron transfer to generate a growing radical species[71]. The oxidized metal center returns back to the more stable lower oxidation state, by donating the halogen back to the radical growing species and deactivating the propagating polymer chains. In this way, it establishes an extremely low concentration of the radical species as well as a fast reversible reaction with halogen. Many transition-metal complexes used as catalysts for ATRP. Mostly used catalysts in ATRP [Fig. 9] are transition metal catalysts based on copper [25, 28, 67-76, 98, 149-154], nickel [155-156], iron [157-158] and ruthenium [138, 158-160].

The prerequisites for an efficient catalyst are:

- Two readily available oxidation states separated by one electron
- Reasonable affinity towards a halogen atom
- Relatively strong complexation with ligand and
- An expandable coordination sphere to accommodate a (pseudo) halogen.

The key to achieve the desired atom transfer equilibrium and the rate of exchange between dormant and active species is the appropriate choice of the catalyst/ligand combination. Some important prerequisites for a suitable catalyst are that the metal center should have reasonable affinity towards a halogen and the coordinating sphere around the metal should be expandable on oxidation to selectively accommodate the halide. The ligand, should strongly complex with the catalyst, solubilize the transition metal salt and adjust the redox potential of the metal center forming the complex. Various transition metals have been studied. In this research, for the ATRP reactions of acrylates, *copper (I) bromide* was employed, and for the methacrylate reactions, *copper (I) chloride* was used. Similarly, in literature, several ligands have been employed, the most extensive being 2,2'-bipyridine derivatives, 2-iminopyridine derivatives and some aliphatic polyamines. In the present case, N, N, N', N'', N'''-pentamethyl-diethylenetriamine (PMDETA) has been extensively employed.

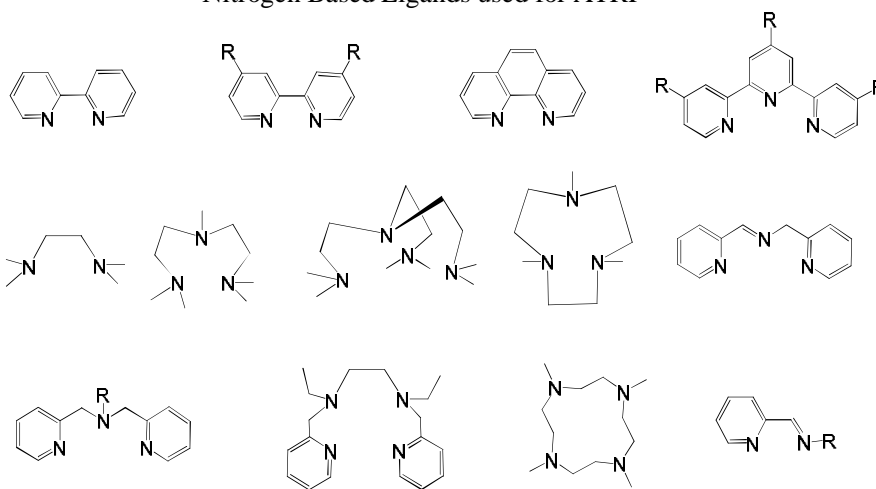
There are several guidelines for an efficient ATRP catalyst.

- Fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously.
- The equilibrium between the alkyl halide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized.

- Fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution.
- Relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate.

1.2.2.5.1.1.4 Ligand: Ligand plays a crucial role in ATRP by controlling the solubility of the complex in the reaction mixture and ensures stability of the complex in different monomers, solvents and temperatures. The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer. It adjusts the redox potential around the metal center, thus, affecting the reactivity and equilibrium dynamics of the atom transfer process [159]. They can fine tune the selectivities and force the complex to participate in a one-electron transfer process needed for ATRP. The ligands can also facilitate the removal and recycling of the catalyst allowing the immobilization of the catalyst.

Figure 10
Nitrogen Based Ligands used for ATRP



Various ligands based on nitrogen and phosphorous have been used in ATRP. Nitrogen based ligands [Fig. 10] have been particularly successful in copper and iron mediated ATRP [71] whereas phosphorous, sulfur, oxygen based ligands have been less effective. The electronic and steric effects of the ligands are important [71]. Catalytic activity is reduced when there is excessive steric hindrance around the metal center and also when the ligand used had strongly electron withdrawing substituents. It was also observed that the activity of N-based ligands in ATRP decreases with the number of coordinating sites *i.e.* $N_4 > N_3 > N_2 \gg N_1$ and with the increasing number of linking C Introduction atoms *i.e.* $C_2 > C_3 \gg C_4$. Activity is usually higher for bridged and cyclic

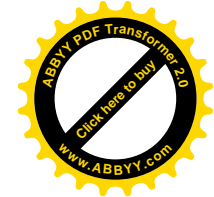
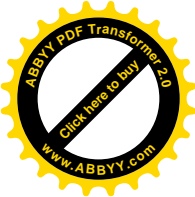


systems than for linear analogues. Another important consideration in choosing the ligand is the possible side reactions such as the reaction of amines (especially aliphatic) and phosphines with alkyl halides [161]. These side reactions are reduced when tertiary amines are used as ligands and minimum when the ligands are complexed to CuBr [29]. Phosphorous ligands have been used in ATRP in conjunction with most transition metals such as ruthenium [138, 162], rhodium [145-147, 163], rhenium [164], nickel [156-157], iron [158, 159, 165-166] and palladium [167]. Amongst the phosphorous based ligands (mostly PR₃ type), phosphines display a high catalytic activity and good control of the polymerization.

Recently, cyclopentadienyl, indenyl and 4-isopropyl toluene type ligands were used in ruthenium based ATRP and these ligands result in more reactive catalysts than the ones obtained with phosphorous [145, 158, 159, 162]. Oxygen based ligands such as phenols and carboxylic acids have also been considered as ligands in ATRP [67-77].

1.2.2.5.1.1.5 Solvents: The choice of the solvent is as important, since there is a possibility that the structure of the catalyst complex may change in different solvents, which in turn directly influences the atom transfer equilibrium and the polymerization reaction rate. Polar solvents are known to improve the solubility of the catalyst complex. The use of a solvent is sometimes necessary, especially when the polymers formed are not soluble in their monomers. Different solvents (benzene, toluene, xylene, diphenyl ether, ethyl acetate, DMF, ethylene carbonate, alcohol, water, and others) have been used for various monomers [67-77]. Several factors affect the solvent choice. Minimal chain transfer to solvent is one of the basic requirements for selecting a solvent. In addition, interactions between solvent and the catalyst or other components in the ATRP system should be considered. Catalyst poisoning by the solvent (*e.g.* carboxylic acids or phosphines in copper-based ATRP and solvent-assisted side reactions, which are more pronounced in a polar solvent [67-77]) should be minimized.

1.2.2.5.1.1.6 Reaction temperature and reaction time: In general increasing the temperature in an ATRP accelerates the polymerization due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. Furthermore, the solubility of the catalyst increases at higher temperatures. However, at high temperature the chain transfer and other side reactions, such as catalyst decomposition, become more pronounced [67-77, 156-157, 168-170]. Thus, the optimal temperature for the reaction should be pre-determined based on the particular ATRP system (monomer, catalyst and targeted molecular weight). The range of useful reaction temperatures is broad, from 20°C to 150°C. At high monomer conversions, the rate of propagation slows down considerably; however, the rate of side reactions does not change significantly, as most of them are monomer concentration independent. Prolonged reaction times leading to higher monomer conversion may not increase the polydispersity of the final polymer but will cause the obtained polymer to lose end groups, which are important for the subsequent synthesis of block copolymers. To avoid end group loss, it is suggested that the conversion should not exceed 95% [67-77].

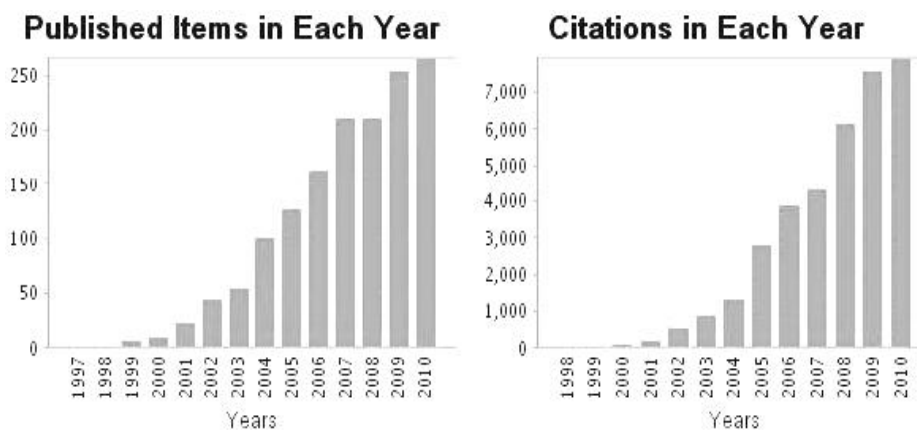


1.2.2.6 Reversible Addition-Fragmentation Chain Transfer (RAFT)

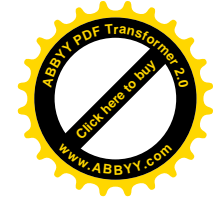
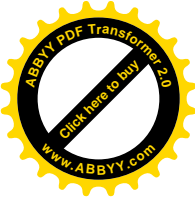
Polymerization: The reversible addition-fragmentation chain transfer process is certainly the most recent of the controlled radical systems. Even if the concept of atom/group transfer is well-known in organic chemistry[169], the first reports about the possibility of performing controlled radical polymerization using dithiocarbonyl compounds only appeared in 1998 [105-106,147]. There have been a number of publications ever since [10, 48, 50, 57, 96, 102, 104, 107-112, 171-172], clearly indicating the versatility of the RAFT systems using various monomers in both homogeneous and heterogeneous environments (figure 1.9). A recently published book on radical polymerization comprises a chapter, which deals with the work done in the RAFT field [105-106]. The interest in developing new radical processes with living character for the synthesis of well-defined architectures has allowed an unbelievable growth of this reversible chain transfer mediated process, as shown by the increasing number of publications on the subject.

The first RAFT polymerization using thiocarbonylthio compounds was reported by the Commonwealth Scientific and Industrial Research Organization (CSIRO) in 1998 [106].

Figure 11
RAFT polymerization citation and publications till 26 Dec., 2010



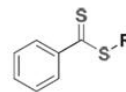
Subsequently, another group reported a similar mechanism using xanthate RAFT agents; they named this technique as MADIX [173-174]. The RAFT polymerization has several advantages over other CRP techniques. The most significant advantage is the compatibility of the technique with a wide range of monomers, such as styrene, acrylates, methacrylates and derivatives. This large number of monomers provides the opportunity of creating well-defined polymer libraries by the combination of different monomeric units. RAFT is among the most rapidly developing areas of polymer chemistry, with the number of publications approximately multiplying each year [Fig. 11].



1.2.2.6.1 Classes of RAFT Agents: Solubility and reactivity of a RAFT agent depend on the R and Z groups; as a result, different RAFT agents are more suitable for specific classes of monomers. The main classes of RAFT agents are:

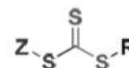
Dithiobenzoates

- Very high transfer constants
- Prone to hydrolysis
- May cause retardation under high concentrations



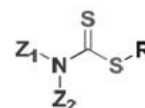
Trithiocarbonates

- High transfer constants
- More hydrolytically stable (than dithiobenzoate)
- Cause less retardation



Dithiocarbamates

- Activity determined by substituents on N
- Effective with electron-rich monomers

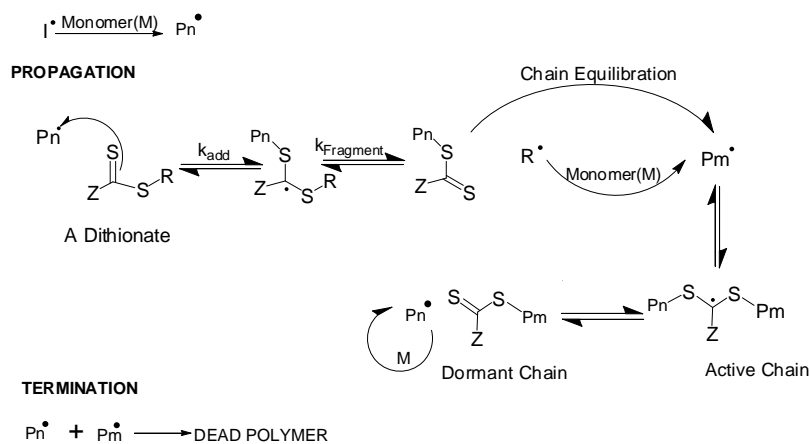


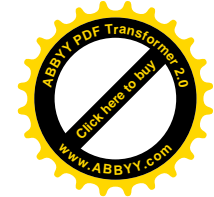
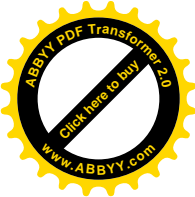
In a RAFT system, the important parameters are,

- Choice of the RAFT agent depending upon the monomer to be polymerized,
- A high ratio of RAFT agent to initiator consumed, and
- A low radical flux during the polymerization.

1.2.2.6.2 Mechanism of RAFT: In a RAFT mechanism, initiation occurs via the decomposition of the free radical initiator leading to formation of propagating chains. This is followed by addition of the propagating radical to the RAFT chain transfer agent. Further, the fragmentation of the intermediate radical occurs, giving rise to a polymeric RAFT agent and a new radical.

Figure 12
Central RAFT Equilibrium



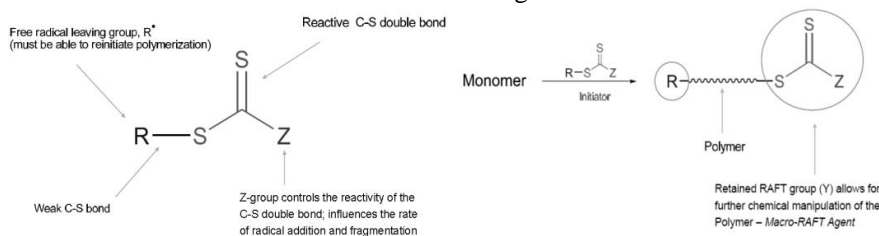


This radical reinitiates the polymerization to form new propagating radicals. The RAFT process relies on this rapid central addition fragmentation equilibrium between propagating and intermediate radicals, and chain activity and dormancy as shown in Fig. 12, shown earlier.

1.2.2.6.3 Choice of RAFT agent: The RAFT agent must be chosen such that its chain transfer activity is appropriate to the monomer to be polymerized. The electronic properties of the activating (Z) group and the stereo electronic properties of the leaving (R) group determine the chain transfer activity of the RAFT agent [Fig. 13]. The Z group in the RAFT agent must be chosen such that it activates the double bond towards radical addition, but at the same time not provides a too great stabilization influence on the intermediate radical. The R group should be a good leaving group, relative to the radical of the propagating species, and should also preferentially reinitiate the polymerizations [2, 105-106].

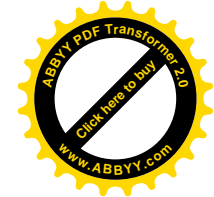
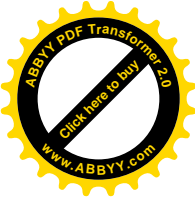
1.2.2.6.4 Choice of Initiator: The choice of the thermal initiator is also an important factor in obtaining control over RAFT polymerization. High ratios of the RAFT agent to initiator should be employed, so as to maintain a low radical flux. The choice of the initiator is dependent on its half-life at the desired reaction temperature and its initiation ability relative to the monomer employed. The longer the half-life of the initiator at the desired temperature, the longer is the duration of radical production and thereby, the RAFT polymerization is kept active for a longer time. The areas of immense interest, research and debate are focused to the initial stages of the RAFT polymerization (inhibition or initialization) and the retardation effects observed during the RAFT polymerization, which is related to the fate of the intermediate radical.

Figure 13
Choice of RAFT agent



1.2.3 Applications of Living Radical Polymerization

Applications discussed in the literature for materials prepared through living radical polymerization range from replacement of existing products in existing markets to novel material concepts, creating new applications such as some very novel approaches to drug delivery through the synthesis of well-defined diblock copolymers by ATRP. The block copolymers with a short hydrophobic block ($5 < DP_n < 9$) were explored in detail for the development of new colloidal carriers for the delivery of electro statically charged compounds (e.g., DNA), through the formation of polyion complex micelles [175]. A

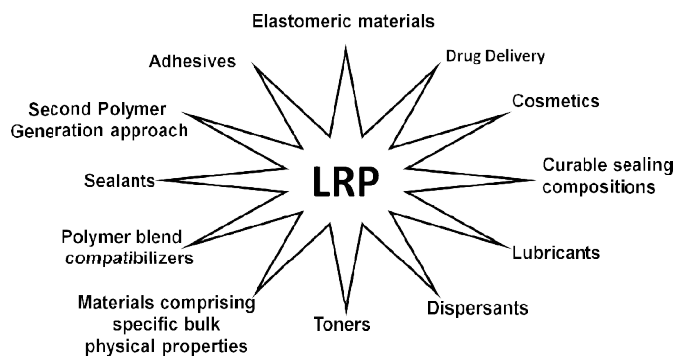


similar approach has been taken in electronics manufacture [176] where the self-organizing ability of materials prepared by living radical polymerization is being exploited.

Some existing markets targeted by materials prepared by living radical polymerization process [Fig. 14] are: Adhesives [177-191]; Sealants [34-36]; Emulsifiers [192]; Polymer blend compatibilizers [193-194]; Coatings [195-207]; Toners [208-213]; Dispersants [165, 166, 200-202, 214-220]; Lubricants [221-227]; Curable sealing compositions [177-183]; Elastomeric materials [228-229], Drug delivery [230-231], Cosmetics [232-234], Materials comprising specific bulk physical properties [235-237].

The above references have focused on applications identified by corporate research, in patents and patent applications. Academic workers [238-239] are also disclosing some new applications. Although this has been but a brief review of novel materials prepared using controlled radical polymerizations, one can easily see that, regardless of the type of controlled radical polymerization employed, these methodologies open the door to a wide range of novel polymers with unique properties.

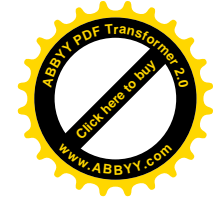
Figure 14
Applications of Living radical polymerization



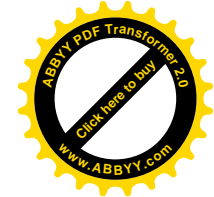
Indeed control over polymer sequence distributions continuously expanding and recently multi-block heteropolymer chains with upto 100 blocks in an ordered sequence and controllable block lengths have been reported [240]. CRP is among the most rapidly developing areas of chemistry, with the number of publications approximately doubling each year.

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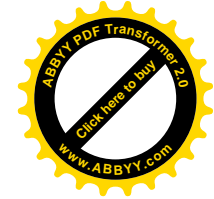
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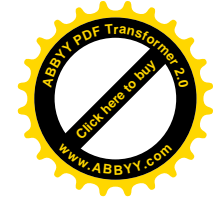
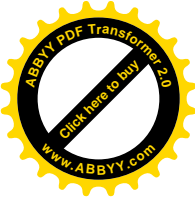
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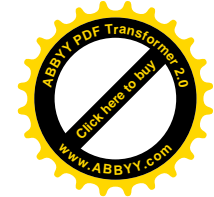
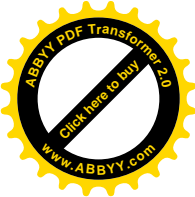
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