CHAPTER I

General Introduction

1.1. Introduction

Macromolecular science has had a major impact on the way we live. It is difficult to find an aspect of our lives that is not affected by polymers. The need for sophisticated polymeric materials has increased in parallel to the development of science. In the last two decades, it has been figured out that mankind can be benefited by polymers also for more complicated tasks. They can be employed in the production of high-tech electronic devices like chip production, flexible electronics, solar-cell, fuel-cells catalysis, ion-exchange, sensors, coatings, textiles, nanotechnology. Polymers are also used for biomedical applications such as for the replacement of some body parts like bones, artificial organs for intelligent drug carrier, or gene delivery etc. But all these above mentioned applications need specially designed polymers. Polymers with desired electrical, optical, interfacial and other properties have to be produced according to the particular needs. This can be achieved via the synthesis of polymers by making new building blocks, e.g. new monomers with new backbones, or by arranging established building blocks in new ways, e.g. varying the topology of (linear, branched, hyper branched, stars etc.) or the internal composition of polymeric chains (statistical/gradient copolymers, block). The latter approach is particularly economical. It implies the need for well-defined polymers, which can be synthesized by powerful, well controlled polymerization methods.

It was famously remarked at the end of the 19th century that there was nothing left to discover in physics. In recent times many chemists have had the same dismissive attitude towards free radical polymerization (FRP). Just as with the physics forecast, so this attitude towards FRP is proving to be highly mistaken, in two major ways. Firstly, it confuses invention with scientific discovery. For example, commercial production of polystyrene began a full eight years before people recognized that the process had a free radical mechanism.[1] Even today the underlying science behind many market products of free-radical polymerization is not well understood. So even about conventional free radical polymerization there remains much fundamental science to be unearthed. Secondly, and still more importantly, far from FRP being a completely explored landscape, much new and inventive FRP chemistry has emerged over the last two

decades.[2,3] In particular, Living-free radical polymerization (LFRP) has been developed,[2-4] and it promises to revolutionize polymer production. The following outlines the story of LFRP to date.

1.1.1 Background

Today many commercial polymers are prepared by conventional free-radical polymerization (CFRP). The method's popularity is high as a wide range of monomers can be used under mild reaction conditions. For these advantages one sacrifices a large degree of control over the polymer product. This can be explained using Figure 1.1, which shows a conceptual outline of CFRP. Radicals are continuously formed from initiator, and as a radical forms it quickly adds to monomer, a process which is repeated many times until at some stage a (macro) radical is converted into a *'dead'* polymer chain by participating in either combination, disproportionation (together called *termination*) or chain transfer.

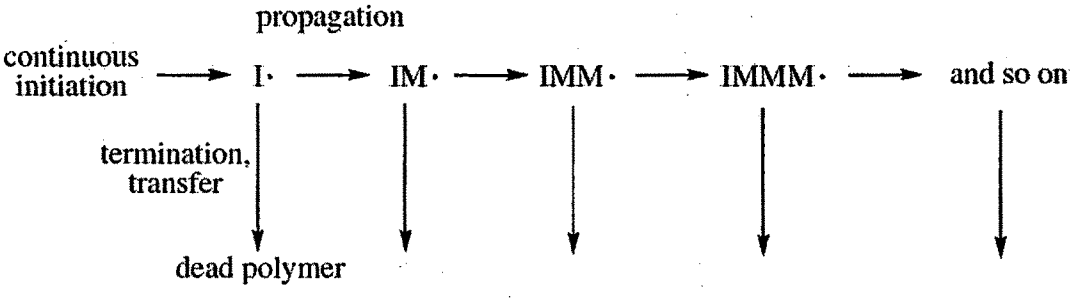


Figure 1.1. Conceptual representation of the process of conventional free-radical polymerization, where I denotes the initiating species, M monomer, and the arrows a reaction (as indicated).

Human populations are a good analogy for this: babies are born at all times (akin to initiation), people inexorably age (propagation), and at some time they die (termination and transfer). Just as human death can occur at any age, resulting in a *distribution* of ages at death, so too the dead-chain-forming reactions of FRP can occur at any stage of a radical's life. For CFRP carried out over constant conditions, one typically obtains an exponential-like distribution of molecular weights, as shown in Figure 1.2.

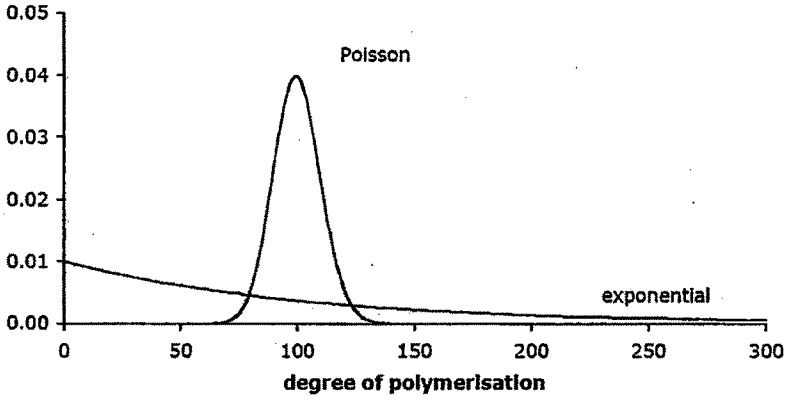


Figure 1.2. An exponential distribution of chain sizes, as typically obtained from conventional free-radical polymerization carried out over constant conditions, and a Poisson distribution of chain sizes, as obtained from ideal living polymerization. Both the shown distributions are normalized and have number-average degree of polymerization of 100.

Although *average* size can be controlled through choice of reaction conditions, nothing can be done to eradicate the *polydisperse* nature of the polymer product. The dead chains have a wide variety of sizes, even if they are otherwise chemically identical. An even more important way in which CFRP is lacking is shown in Figure 1.1. Once a dead chain has been formed, there is no easy way for its growth to be reinitiated.There is no easy way of forming *block copolymers* by CFRP, i.e., polymers that consist of a long block of residues of one monomer followed by a long block of residues of another monomer. Such polymers are unique, because they possess properties of both the corresponding homopolymers. For example, poly(styrene-*block*-isoprene-*block*-styrene) is a 'thermoplastic elastomer' because it behaves like both a plastic (due to the styrene) and a rubber (due to the isoprene). However there is no easy way of making such polymers by CFRP. Hence they must be made by other, more difficult means, and so they are expensive. With the above in mind one can prevailed the impetus for the development of *'living polymerization'* (LP). This term was defined in the 1950s to describe a chain-growth process that proceeds in the absence of irreversible chain-termination and chain-transfer steps:[5] there are no dead chains, and thus all chains are *living*. So once initiation occurs, chains grow in a continuous manner until the supply of monomer is depleted, as is conceptually illustrated in Figure 1.3.

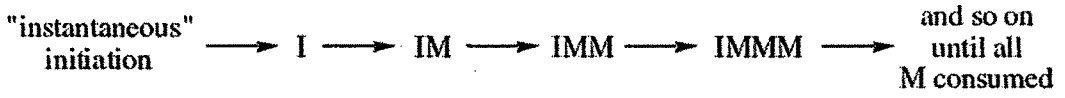


Figure 1.3. Conceptual representation of the process of (ideal) living polymerization, where I denotes the initiating species, M monomer, and the arrows a reaction.

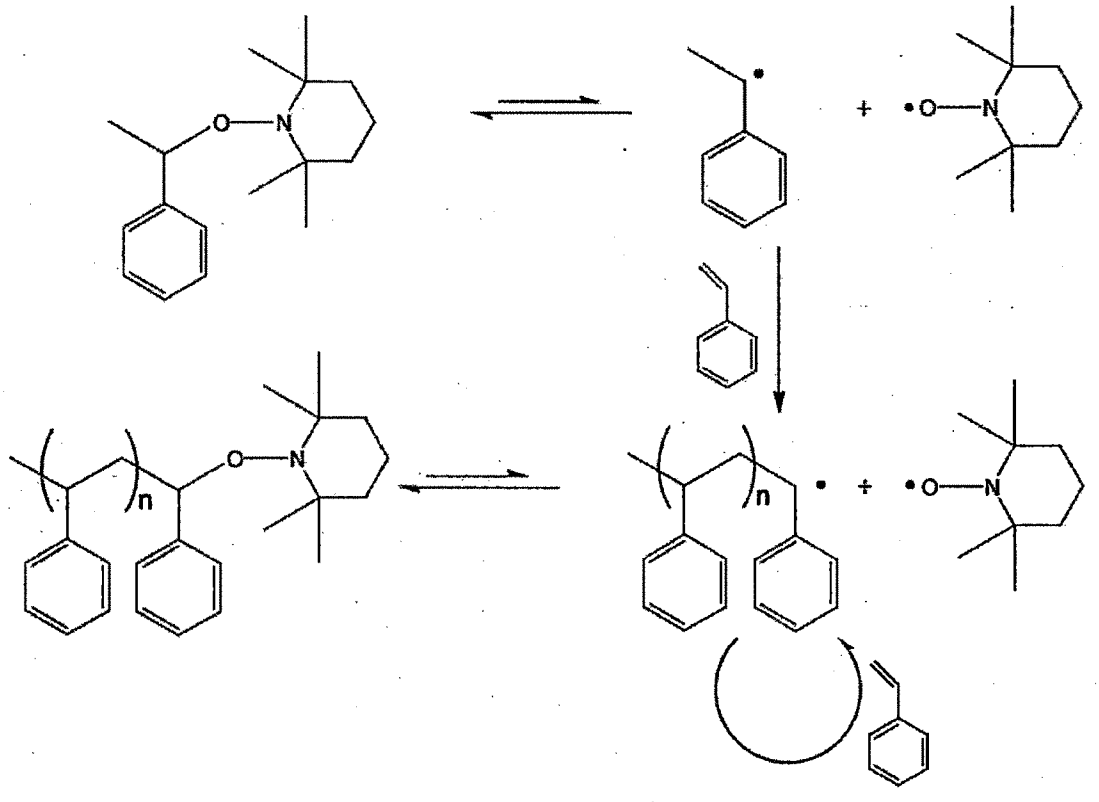
If initiation is rapid on the timescale of monomer consumption, then all chains are (approximately) the same size. To use once again the analogy of human populations, this is like a multitude of babies being born at the same time forever after they will be the same age. With living polymerization the situation is not exactly the same, because the stochastic nature of chemical kinetics means that some chains undergo more propagation events than others. However, the distribution of sizes is still relatively narrow. In fact, all going ideally the resulting molecular weight distribution is a Poisson distribution,[6] as shown in Figure 1.2. Both the distributions shown in Figure 1.2 have a number-average degree of polymerization of $\overline{DP}_n = 100$. This makes it clear just how much more *monodisperse* is the product polymer of LP. A further characteristic of living polymerization is that even after monomer supply is exhausted, chains remain active (unless a terminating agent is introduced).

Thus one can synthesize a block copolymer simply by introducing a second monomer after polymerization of the first monomer is complete. This exemplifies how LP also offers greater control over microstructure and architecture than does CFRP. Living polymerization is most commonly realized by *anionic polymerization.* However, it is synthetically demanding in that it is sensitive to trace quantities of impurities. Thus all reactants and solvents must be rigorously purified and polymerization must be carried out either under inert conditions or in high vacuum system in scrupulously-clean, sealed apparatus.[6] For this reason the process is very expensive to carry out commercially. Polar monomers undergo side reactions, leading to loss of control. Thus, anionic polymerization is applicable only to a small number of monomers. For the polymer chemist the eminently desirable goal is facile polymer synthesis by a process affording a high degree of control of the product polymer. While a narrow molecular weight distribution (MWD) is not always desirable in terms of product properties, in

general it is, and certainly it is always desirable to have control of microstructure and architecture. Thus, one needs to marry the best features of CFRP (synthetically easy, widely applicable) with the best of LP (narrow MWD, control of composition and topology). For a long time this goal seemed impossible as there was no way of using free radicals, which react easily and multitudinously, to mediate LP. But then in the 1980s living free-radical polymerization emerged.

1.1.2. The Paradigm of Living Free-Radical Polymerization

The key to living polymerization is elimination of termination, the process that leads to production of dead polymer chains of all sizes. It is impossible to prevent free radicals from reacting with each other, however, because propagation is first order in radical concentration, [R$^{\bullet}$], and termination is second order, it follows that one can promote propagation over termination by lowering the radical concentration. One way of accomplishing this is to include a reagent that can *reversibly deactivate* a radical. The reagent must *deactivate* the radical in order to protect it from termination, but the process must be *reversible* so that the radical can sporadically spring back to life and grow a bit more, before going back into hibernation. After many such deactivation/activation cycles, a radical will have grown to polymeric size, and it will be capable of further growth as long as monomer is present. Various reagents that more or less achieved the above paradigm were experimented with in the early 1980s.[3] However, it was not until the employment of alkoxyamines[3] by Rizzardo and co-workers in the mid-1980s that 'living free-radical polymerization' (LFRP) was born. Scheme 1.1 illustrates the principles involved by showing how a 2,2,6,6-tetramethylpiperidinyl-1-oxy, (TEMPO) adduct achieves LFRP of styrene.



Scheme 1.1. Use of 1-phenylethyl TEMPO to effect living free-radical polymerization of styrene.

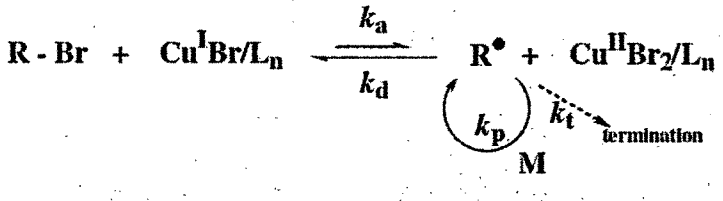
As is indicated, the activation/deactivation equilibria lie toward the deactivated ('*dormant*') species. This is because the reaction between TEMPO and a carbon-centred radical is fast – it is close to diffusion-controlled – whereas obviously the reverse reaction, involving bond scission, is much slower (even if the bond involved is labile). Thus the radical concentration is maintained low, and so termination is suppressed. At the same time the activation reaction is still fast enough that polymers of large chain lengths can be obtained on a comfortable timescale, viz. hours. The so-called '*nitroxide mediated polymerization*' (NMP) was the first form of LFRP to find widespread use. As is implicit in Scheme 1.1, the key to its successful use is that nitroxide radicals do not self-react, i.e., they are stable free radicals. On the other hand, propagating radicals do react with each other, even if they are only present in very low concentration. Thus the occurrence of conventional radical-radical termination is unavoidable in LFRP, which emphasizes that the process can never function as an ideal living polymerization. It has been established in (literally) thousands of experimental studies set that in a successful LFRP one obtains polymer with a MWD almost as narrow as the Poisson distribution of Figure 1.2.

Although Rizzardo did not discover NMP, C. J. Hawker *et al* has been its main champion,[7] and he developed an alkoxyamine as a 'universal initiator,[8] i.e., one that can be successfully employed for a large number of monomers over a wide variety of conditions. However, Hawker was never succeeded, because other forms of LFRP have emerged which are superior to NMP except for polymerization of styrenic monomers. Specifically, NMP paved the way for the development of so-called 'atom transfer radical polymerization' (ATRP) and 'reversible addition-fragmentation (chain) transfer' (RAFT) polymerization.

1.1.3 ATRP – Atom Transfer Radical Polymerization

Sawamoto *et al.*[9] were the first to recognize that the activation/deactivation equilibria of Scheme 1.1 can also be effected by transition metal complexes, using the Ru(II)/Ru(III) couple to demonstrate this. Their idea was almost instantaneously seized upon by Matyjaszewski, who without delay showed that Cu(I)/Cu(II) systems seem to

do an even better job.[10,11] The chemistry involved is shown in Scheme 1.2, active radicals (**R**$^{\bullet}$) are generated when a copper(I) complex (**$Cu^{I}Br/L_n$**) undergoes a one-electron oxidation to a copper(II) complex (**$Cu^{II}Br_2/L_n$**) with simultaneous extraction of a halogen atom (bromine) from an initiator (**R-Br**). The reverse of this process is extremely fast, meaning that the radical only has a small amount of time to react with monomer before it is converted back into an alkyl halide. But this cycle may occur over and over again, meaning that one has LFRP.



Scheme 1.2. General mechanism of copper-based atom transfer radical polymerization.

Because the process of Scheme 1.2 is just the application to polymerizing systems of the well-known organic chemistry process of 'atom transfer radical addition', it has become known as 'atom transfer radical polymerization' (ATRP). As just mentioned, (copper-based) ATRP is extremely versatile because there are many components that can be varied in striving for optimum results.[11] In ATRP the concentration of active species is kept very low by the presence of a catalytic transition metal complex, which reversibly deactivates growing polymer chains via a halogen atom transfer. As long as active radicals are present in a system, termination reactions i.e., radical coupling and disproportionation, cannot be suppressed fully. However, it has been shown that in a well controlled ATRP system only up to 5% of the polymer chains terminate, allowing a good level of molecular weight control of produced chains.[12]

In addition to offering control over molecular weight of produced polymer, ATRP also affords unprecedented command over other aspects of macromolecular design. Where ATRP is employed, functionality of a polymer can be predetermined by use of functionalized monomers[13] or monomer derivatives if the desired monomer itself cannot be polymerized using the method.[14] Initiators with various functionalities allow synthesis of chains with specific end-groups.[15,16] Through strategically placing certain

functionality on polymer chain-ends, it is possible to perform various chemical transformations of the polymer. Chains produced by the method of ATRP are normally capped by a halogen. This halogen can be displaced via a number of reactions, yielding polymer chains with new termini.[17] Block and gradient polymers can be synthesized by this method.[18] Even monomers that could not be homopolymerized via ATRP were incorporated into block copolymers where the first block was prepared by ATRP.[19] This new found capacity to tailor macromolecular design often serves as starting point for synthesis and is leading to many novel polymeric materials and thus promises an age of 'smart' polymers.

1.1.3.1. Initiator

The role of the initiator in ATRP is to form an initiating radical species via homolytic cleavage of its labile bond such as C-halogen by the metal catalysts. The number of the available initiators for ATRP is much larger than for other CRP methods. A variety of initiators, typically alkyl halides, have been used successfully in ATRP. Halogens (X) in the initiators (R-X) include chlorine, bromine, and iodine, where the reactivity of the CX bond increase in the order Cl < Br < I, with concomitant decrease in the stability of the C-X bond. Chlorides and bromides have thus been widely employed. Common initiators are shown in Figure 1.4.

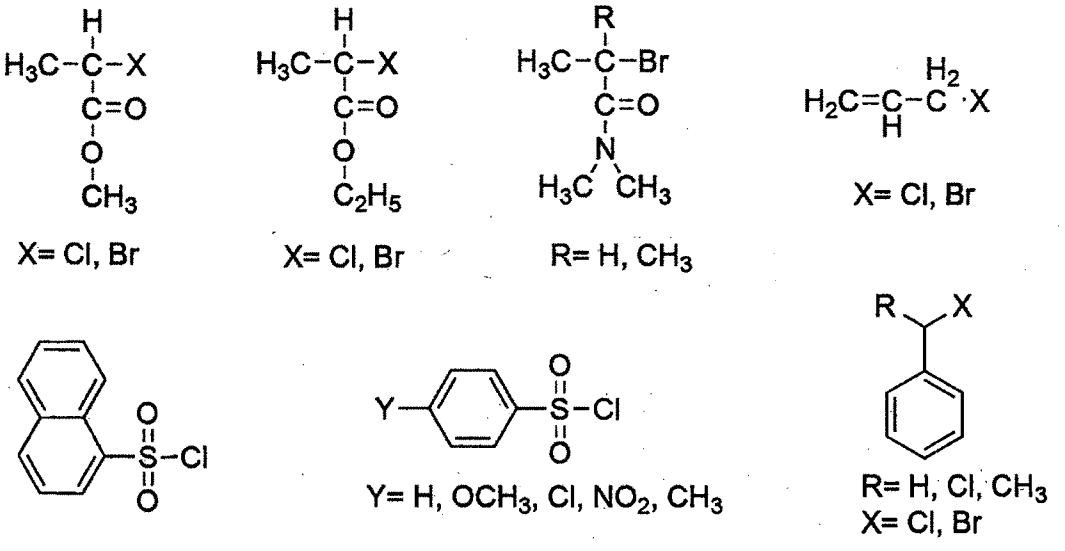


Figure 1.4. Typical initiators for (copper-based) ATRP.

The design of initiators has been a challenging task for the optimization of products. Many different types of halogenated compounds such as sulfonyl halides,[20] functionalized phenolic ester halides,[21] modified cholesterol,[22] and glucose[23] have been successfully used to initiate ATRP.

1.1.3.2. Monomer

Various monomers have been successfully polymerized via ATRP: styrene, acrylates, methacrylates, dienes, acrylonitriles, etc.[24-44] In particular, a wide range of styrene derivatives with different substituents on the aromatic ring and acrylates and ethacrylates with various side chains have been also polymerized in a well-controlled fashion. However, there are only a few reports on the attempted ATRP of acrylamides,[37,45] such as N,N-dimethylacrylamide. It was subsequently confirmed by Rademacher et al[44] that these systems were not "living". There are currently two major classes of monomers, which have not yet been successfully polymerized by ATRP.

Acidic monomers fail since they can protonate ligands and form the corresponding carboxylate salts. Halogenated alkenes, alkyl-substituted olefins, and vinyl ester are presently resistant to polymerization by ATRP. Nevertheless, the range of monomers polymerizable by ATRP is greater than that accessible by nitroxide-mediated polymerization, since it includes the entire family of methacrylates.

1.1.3.3. Ligand (L)

The main role of the ligand in ATRP is to control the solubility of a transition metal in the reaction mixtures. Furthermore ligands serve several purposes: they tune the atom transfer equilibrium constants and dynamics, adjust the selectivity of the catalysts, and ensure the stability of the complexes in different monomers, solvents, and at different temperatures. It is the solubility of the complex that will determine the actual concentration of the catalyst in the reaction mixture, therefore affecting the position of the equilibrium of Scheme 1.2.

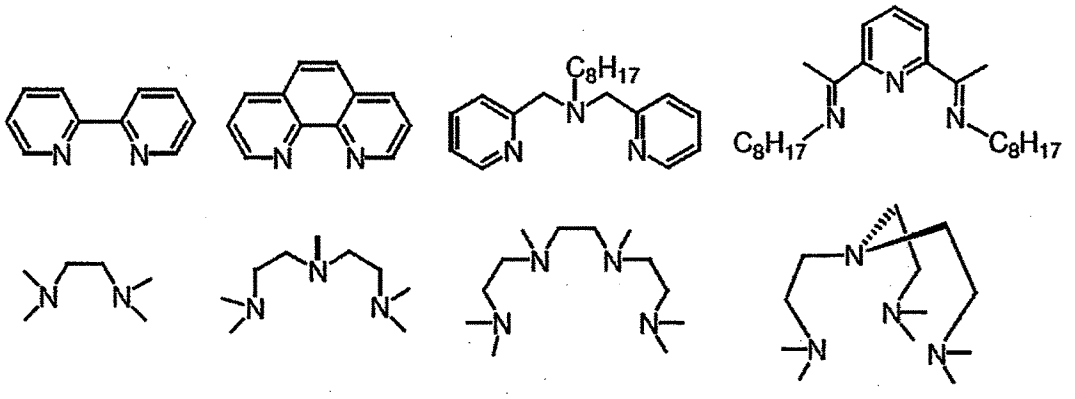


Figure 1.5. A selection of ligands that have been used for copper-based ATRP.[11]

This in turn influences the overall kinetics of the polymerization as well as the MWD of the produced polymer. Several different ligands that have been used for ATRP are described in the literature.[11] The common ligands used in copper-mediated ATRP are shown in Figure 1.5. Nitrogen ligands are usually used to complex copper and iron transition metals in ATRP.[46-50] Phosphorous ligands are employed for rhenium-, ruthenium-, iron-, rhodium-, nickel- and palladium-mediated ATRP.[51-54]

1.1.3.4. Solvent

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). 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.[12,29,38] Minimal chain transfer to solvent is one of the basic requirements for selecting a solvent. In fact several factors influence the solvent choice. In addition, interactions between solvent and the catalyst or other components in the ATRP system are also important. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphines in copper-based ATRP[55] and solvent-assisted side reactions, which are more pronounced in a polar solvent[56] should be minimized.

1.1.3.5. Additives in ATRP

The effects of different additives on ATRP have extensibly been studied.[55,57] Additives play an integral role for a successful ATRP, as a small amount of a zerovalent metal, such as copper or iron, was added to some ATRP systems, a significant rate enhancement was observed.[58] In contrast, when a small amount of Cu(II) halide was added to a copper-based ATRP, the polymerization was slower but could be better controlled.[59] The reason could be Cu(0) reduces "excess" Cu(II), which is generated primarily during the early stages of the polymerization through irreversible radical termination to form in situ Cu(I) by a single electron transfer (SET) process. This process reduces the concentration of Cu(II) and simultaneously increases the concentration of Cu (I). Haddleton and coworkers found that various phenols accelerated the polymerization rate of methyl methacrylate, at no expense to molecular weight control or to the resulting polydispersities.[60] Further, additives such as carboxylic acids[61] enhanced the polymerization rate, but the polydispersities also increased with an increase in the acid-to-copper ratio.

1.1.4. 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.[54,56,62,63] 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,[64] which are important for the subsequent synthesis of block copolymers. To avoid end group loss, it is suggested that the conversion not exceed 95%.[12]

1.1.5. Kinetics and Molecular Weights

While the idea behind LFRP may seem "obvious" as presented above, a conundrum soon emerges: if the process is started by a reaction that generates radicals and stable species (nitroxide radical, Cu(II) complex, etc.) in equal number, and if cross-reaction of these products occurs essentially equally quickly as self-reaction of radicals (both processes are essentially diffusion controlled), why is it that that the former reaction is so heavily favoured over the latter? In other words, how is it that LFRP works? In a series of brilliant articles, Fischer developed the answer.[65-67]

In summary, it is the extreme selectivity of LFRP – that radical-radical reaction is suppressed almost to the point of non-occurrence while cross-reaction between radicals and stable species occurs almost exclusively. This is due to concentration effect rather than a reactivity effect. In the early stages of LFRP, conventional radical-radical terminations does occur, and this process is indispensable in that it depletes the radical concentration while the stable species, not being able to self-react, and their concentration keeps on rising. Thus, an extreme imbalance in concentration develops, and as long as this happens relatively quickly on the timescale of polymerization, LFRP will subsequently take place. Because the situation just described relies on production of a stable species, it has been named the 'persistent radical effect'.[65-67]

For ideal living polymerization, $\overline{DP}_n = x\left(\frac{[M]_0}{[\text{Initiator}]_0}\right)$ and $\text{PDI} = 1 + 1/\overline{DP}_n$.

Here M denotes monomer, x is the fractional conversion of monomer into polymer and *PDI* stands for polydispersity index. For example, $PDI = 2$ for the exponential distribution of Figure 1.2, $PDI = 1.01$ for the Poisson distribution of Figure 1.2, and $PDI = 1$ when all polymer molecules are exactly of the same size. Fischer was able to show that to reasonable approximation the two just given expressions hold also for LFRP.[66,67] (graphed in Figure 1.6)

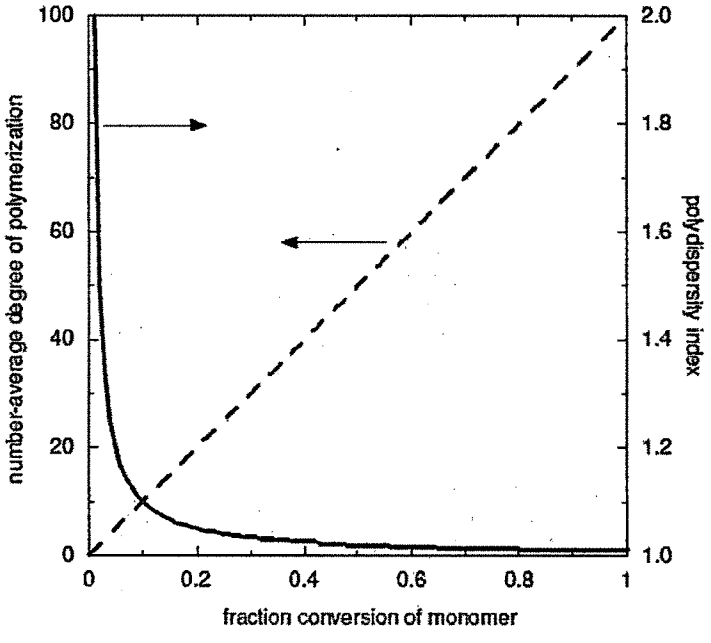


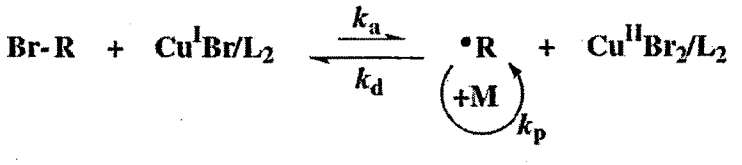
Figure 1.6. Evolution of the number-average degree of polymerization ($\overline{DP}_n$, broken line) and polydispersity index (PDI, solid line) with fraction conversion of monomer (x) for ideal living polymerization in which $[M]_0/[I]_0 = 100$.

The displayed behaviours are considered the hallmark of 'successful' LFRP. There is a linear increase of average polymer size ($\overline{DP}_n$) as the reaction proceeds, with the final value simply being equal to the starting ratio of monomer to initiator. *PDI* is low and decreases slightly during the polymerization. In practice it is not possible to achieve *PDI* as low as in Figure 1.6, but PDI = 1.1–1.2 is routinely obtained with LFRP. Fischer also derived[65-67] that in LFRP there is an unusual dependence of monomer consumption with time: $\ln([M]_0/[M]) \sim t^{2/3}$.

One of the fascinating aspects of Fischer's recent review[67] is the history he gives of the persistent radical effect. He shows that this concept is present in organic and inorganic chemistry right from 1930s. Researchers were only intuitively aware of the unusual preference for the unsymmetrical coupling reaction. Now that physical chemists have given the concept a sound theoretical backing and polymer chemists have demonstrated just how potent an idea it is, one wonders if it might find wider use in organic and inorganic chemistry.

1.1.6. Mechanism of ATRP

As a multicomponent system, a typical ATRP system consists of a monomer, an ATRP initiator and a transition metal species in a complex with a ligand (L). As with any other free-radical polymerization, ATRP starts with generation of free radicals. Free radicals (R) are generated when a halogen atom (Br) is abstracted from the initiator e.g., R-Br, by the transition metal e.g., Cu^IBr/L_2 complex. Upon the halogen atom transfer, Cu^IBr/L_2 complex is converted into a corresponding $Cu^{II}Br_2/L_2$ complex,



Scheme 1.3. Reaction scheme for copper-mediated ATRP.

Active radical chains initiate and grow by reacting with monomer (M) with the rate constant of propagation k_p. This process would result in a polymerization which is

not different from a conventional free-radical process if it not for a deactivation reaction, in which the halogen atom is abstracted from the deactivator i.e., $Cu^{II}Br_2/L_2$ complex, by the growing radical species. Now the growing radicals are capped by the halogen atom and are in their dormant or unreactive state, therefore unable to propagate further unless the halogen cap comes off again. As a result of deactivation, Cu^{II} gets reduced back into Cu^{I}.

1.1.6.1. Metal-Ligand Catalyst

The transition metal species utilised in the ATRP process is often termed a catalyst. It is the most important component of ATRP as its properties determine the position of the equilibrium that governs concentration of active and dormant radical species. A catalyst must satisfy a number of requirements in order to keep the polymerization process under control:

(1) The metal centre must have two oxidation states, interchange between which should be achieved by a single electron transfer via abstraction and addition of a halogen atom.

(2) As transition metals are often insoluble in organic solvents, addition of a suitable ligand to the ATRP mixture improves the solubility of the metal catalyst by forming a complex with the latter.[12] Solubility of the complex will determine the actual concentration of the catalyst in the reaction mixture, therefore affecting the position of the equilibrium, the overall kinetics of the polymerization and the molecular weight distribution of produced polymer chains.

(3) When the complex abstracts the halogen atom from the initiator, the coordination sphere of the complex must expand, and thus the metal centre should have a coordination site available for the addition to occur. It was found that for copper-mediated ATRP four coordination sites must be filled by ligands, leaving one site available for the abstraction of the halogen atom. In the case of bidentate ligands, the kinetically optimal ratio of the ligand species to the $Cu^{I}Br$ was found to be 2:1.[12]

(4) Ligands should form a strong complex with the metal centre, as high lability of the complex will result in displacement of the ligands by solvent or monomer molecules.

That might result in formation of a new strong complex, in which all coordination sites of the metal will be filled, therefore preventing transfer of the halogen counter ion and resulting in uncontrolled polymerization.

As the transition metal undergoes a one-electron oxidation, it abstracts the halogen atom from the initiator by cleaving the carbon-halogen bond, which results in formation of a carbon-centred radical. Polymer chains start growing by the addition of newly-formed radicals to monomer. The key to a controlled polymerization is suppression of termination reactions. In ATRP this is achieved by keeping the concentration of reacting radicals at a low level. This is done by creating and maintaining an equilibrium at which formation of dormant species is favoured, i.e., K_{eq} ($= k_a/k_d$) is low. It is evident that if the value of K_{eq} is very low, polymerization would occur at a very slow rate. A high value of K_{eq} will result in faster polymerization rates, however, due to the increase in concentration of actively growing chains the extent of termination reactions would also increase, resulting in a formation of dead-polymer chains throughout the process. Much desired control of molecular weight and molecular weight distribution of produced chains would be lost. It is thus clear that a successful ATRP involves a balancing act between the need for a practicable rate (high K_{eq}) and controlled character (low K_{eq}). Activation and deactivation reactions identified in Scheme 1.3 occur with the rate constants k_a and k_d respectively.

The rate constants depend on the structure of monomer, on the halogen and the transition metal complex. As indicated in the scheme by the arrows, the equilibrium must lie heavily toward the reactant side to assure that the majority of polymer chains are capped and in a dormant state. The position of the equilibrium is also determined by relative concentrations of activating Cu^{I} and deactivating Cu^{II} species. These concentrations will depend on the initial amount and the stability of ligands that form the complexes with the metals. Higher solubility of the catalytic species results in higher concentration of the latter in the reaction mixture. It is evident that higher relative concentration of deactivating species Cu^{II} will ensure production of polymer chains with reduced polydispersity.

1.1.7. Emulsion polymerization

Free-radical polymerization can either be performed in a homogeneous or heterogeneous system. In a homogeneous system, such as bulk or solution polymerization, monomer, solvent and polymer all are miscible, i.e. all are present in the same phase. In a heterogeneous system, such as emulsion polymerization, monomer is emulsified in water with a micelle-forming surfactant. A water-soluble initiator creates radicals in the aqueous phase, which after addition of a few monomer units become surface-active, and subsequently enter the monomer-swollen micelles, and later the monomer swollen polymer particles. Subsequently, polymerization continues in the particles. After the polymerization, an aqueous dispersion of submicron particles (typically between 50 nm and 500 nm) is obtained. Emulsion polymerization has a lot of advantages compared to homogeneous polymerizations. The polymerization rate is much higher than that of a homogeneous polymerization, due to a reduced rate of termination. This also leads to higher molecular weights compared to homogeneous polymerization. Moreover, emulsion polymerization has a high rate of heat transfer to the continuous aqueous phase, so that reaction heat can be removed easily. Even at a high solid content, the viscosity of the final latex is relatively low, which makes processing of the polymer easier. Finally, a water-based system is much more environmentally friendly than a solvent-based system. The first true emulsion polymerization was reported in 1910,[68] but emulsion polymerization first gained industrial importance during World War II when a crash research program in the United States resulted in the production of styrene-co-butadiene synthetic rubber. A qualitative description of emulsion polymerization was first given by Harkins,[69] after which this description was quantified in 1948 by Smith and Ewart.[70] However, current thinking is not entirely in accord with the Smith-Ewart model, although it is still widely referenced in the technical literature because some aspects of the model provide valuable insights into operating procedures. An excellent, up-to-date quantitative overview of emulsion polymerization was provided in 1995 by Gilbert.[71]

1.1.7.1. The ATRP Process and Emulsion Polymerization

As was stated in the general introduction, it is a challenge to apply controlled radical polymerization in dispersed aqueous media. In the next section, a qualitative overview of emulsion polymerization is given, without completely repeating the classical descriptions of emulsion polymerization that are available in many textbooks.[71,72] Further on, the implementation of ATRP process in emulsion polymerization will be discussed.

1.1.7.2. Emulsion Polymerization: A Qualitative Description

Traditionally, emulsion polymerizations are considered to be a three-stage process[73] depicted in Figure 1.7. A traditional emulsion as used in emulsion polymerization comprises a heterogeneous mixture of water, monomer(s), surfactant and a water-soluble free-radical initiator. The reaction starts in Interval I. The monomer is emulsified by fast agitation. A small amount of monomer is dissolved in the aqueous phase, but most of the monomer is present in the form of monomer droplets ($\overline{D_n}$ > 1 μm), stabilized by surfactant. The remainder of the surfactant is dissolved in the aqueous phase at a concentration above the critical micelle concentration (CMC), so that a large number of micelles ($\overline{D_n}$ ~ 5 nm) is present. These micelles are also swollen with monomer. Hydrophilic radicals, generated from the dissociation of the water-soluble initiator, are formed in the aqueous phase. These radicals react with the monomer that is dissolved in the water phase to form oligomeric radicals. Provided that no termination takes place, monomer units are added to these oligomeric radicals until a critical chain length, z is reached (2-5 monomer units for common monomers like styrene and methyl methacrylate in polymerizations using a persulfate initiator[74]), at which the oligomeric radical becomes surface-active and enters the monomer swollen micelles, thereby initiating particles. This process is called particle nucleation. Entry of these oligomeric radicals into the monomer droplets can be neglected, if the total surface area of the droplets is several orders of magnitude smaller than that of the micelles.

The radicals that have entered the micelles to form particles continue to grow, thereby consuming monomer which is replenished by diffusion from the monomer droplets, through the aqueous phase, into the growing particle. Throughout Interval I, particle nucleation continues until all micelles have either been nucleated to form particles, or have been dissolved to stabilize the growing particle surface area. This increases the number of polymerization loci, and thus also the polymerization rate.

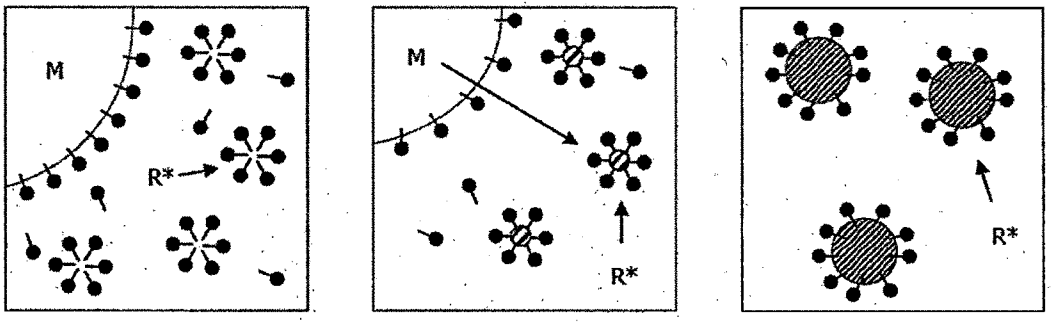


Figure 1.7. Classical three-stage concept for the emulsion polymerization process[73]. Interval I is characterized by the presence of large monomer droplets, and small monomer swollen micelles. Radicals generated in the aqueous phase initiate the particles and continue polymerization, fed by monomer diffusing from the droplets to the particles. At the start of Interval II the particle formation stage is over and there are no more micelles present. Polymerization continues in the particles, fed by monomer diffusing from the droplets. Interval III starts when all monomer droplets have been depleted. The polymerization continues until all monomer that still remains in the particles has been consumed. During Interval III, the rate of the polymerization continuously decreases, provided that no gel effect[75,76] takes place.

Once the micelles have been depleted, Interval II starts. This point typically corresponds with a monomer conversion of 5-15%, depending on the recipe. Interval II is characterized by a constant number of particles in which polymerization takes place, and the presence of monomer droplets. As long as the monomer droplets are present, equilibrium swelling of the particles with monomer is maintained, as the monomer droplets are able to supply the particles with fresh monomer at roughly the same rate at which it is consumed by polymerization. The constant number of particles together with the relatively constant monomer concentration inside them causes the polymerization rate to be constant as well during this interval. Interval III starts when the monomer droplets are depleted, after which the remaining monomer in the particles is

polymerized. This point corresponds to a monomer conversion of 50-80%, depending on the recipe. Interval III is characterized by a continuously decreasing polymerization rate, as the monomer concentration in the particles also gradually decreases. However, this is not the case if the gel effect occurs.[75,76] A distinguishing feature of conventional emulsion polymerization is compartmentalization of the propagating radicals, which profoundly affects both the reaction kinetics, and the molecular weight. When polymerizations are conducted in dispersed aqueous systems in which the particle size is relatively large, such as suspension and dispersion polymerizations ($\overline{D_n}$ = 20-1000 μm), the kinetics and molecular weight are very similar to bulk reactions.

Essentially, the particles act as micro bulk reactors. However, when the particle size is lower than approximately 100 nm, depending on the monomer(s), the particle volume becomes sufficiently small to change the kinetics. For these particles, the zero-one assumption is used, meaning that any polymer particle contains either none or one single growing radical, giving an average number of radicals per particle ($\bar{n}$) of 0.5. If a radical enters a particle that already contains a growing chain, instantaneous termination will take place due to the extremely high, local radical concentration, reducing the radical concentration again to zero. This system results in an on-off mechanism for any given polymer particle. Propagating radicals are thus isolated from each other, or compartmentalized, to such a degree that termination reactions between two growing chains become less likely. The overall effect of compartmentalization is an increase in reaction rate and a much higher average molecular weight as compared to bulk polymerization, because of the impact of reducing the effective termination rate.[77]

During polymerization, small radicals can leave the particles, thereby lowering the number of radicals per particle and therefore also the reaction rate. The probability of exit of a small radical from the latex particle depends on its partitioning between the particles and the aqueous phase. Radicals formed by chain transfer to monomer can often leave the particle, but the probability of exit rapidly decreases as monomer units are added to the monomeric radicals by propagation. It will be obvious that the large number of variables, conditions, concentrations and types of ingredients indicate that

emulsion polymerization is a remarkably complex system based on a mechanism of interrelated kinetic and thermodynamic events.

1.1.8. ATRP in Emulsion

It will be clear from the previous sections that from the outlook of controlled radical polymerization, an advantageous effect is to be expected from a compartmentalized system, such as an emulsion polymerization. The quality of all controlled radical processes is influenced by the contribution of bimolecular radical termination. In bulk and solution polymerizations, this problem is dealt with by keeping the initiator concentration very low, but this also implies low rates of polymerization. Emulsion polymerization, however, provides an ideal alternative to overcome this problem, as it implies high reaction rates with little termination, due to the compartmentalization of the radicals. One of the key factors for successful implementation of controlled radical polymerization in emulsion systems is to get the deactivator in the locus of polymerization, and to keep it there. Another important factor is the undisturbed occurrence of the nucleation stage, i.e. Interval I, when particles are generated. During Interval I, a relatively high radical flux is desired in order to create a large number of particles, as the existing particles compete for surfactant with the formation of new ones. This feature evidently conflicts with the prerequisite for controlled radical polymerization, which asks for a low radical concentration. A low radical flux during the nucleation stage, i.e. Interval I, however, is known to yield broad particle size distributions.[78] Furthermore, chain growth in the water phase should not be hampered extensively, as this will prevent the initiator derived oligomeric radicals to grow to the critical chain length that is required for entry of the micelles, and thus for starting the polymerization.

In spite of the advantages that are expected for ATRP-emulsion systems, the use of the ATRP process in dispersed media has not yet enjoyed the same successes as it did in solution and bulk polymerizations.

1.1.8.1. General Consideration

Among all ATRP systems, those mediated with copper complexes have been most extensively studied in the heterogeneous aqueous media. The following discussions are therefore focused on copper-based ATRP. Analogous to the polymerizations carried out in the organic system, the atom transfer equilibrium was approached in both directions in the aqueous dispersed media. Starting with an alkyl halide and a copper (I) complex, the system is named *direct ATRP*; while beginning with a conventional radical initiator and a copper (II) complex, the polymerization is called *reverse ATRP*.

A relatively extensive body of work on ATRP emulsion polymerization exists in the literature. The presence of water can have a significant effect on the ATRP process itself but these effects are relatively minor in aqueous dispersed systems due to the main locus of polymerization being the organic phase.[79] The implementation of ATRP in an ab initio emulsion system using direct ATRP initially led to significant problems with poor colloidal stability,[80-84] mainly due to complications associated with the nucleation step. It was however soon realized that reverse ATRP is a more suitable approach. Reverse ATRP ab initio emulsion systems have been demonstrated to proceed with both good control/livingness and colloidal stability. However, the initiator efficiencies tend to be very low ($M_n > M_{n,th}$).[84-89] Seeded emulsion ATRP can in general be carried out in a fairly straightforward manner with good colloidal stability and control/livingness under appropriate conditions.[90-96] In order to obtain satisfactory control/livingness in emulsion ATRP, it is crucial that the metal complexes are present in appropriate concentrations at the polymerization loci, i.e. the polymer particles, and it is difficult to adjust both the amount and rate of transfer of reagents from monomer droplets to micelles/particles throughout the polymerization. This requires sufficiently rapid transport from the droplets to the particles through the aqueous phase (kinetic factors), as well as favorable partition coefficients (thermodynamic factors).

These fundamental requirements are the same for NMP and RAFT. The choice of emulsifier is pivotal nonionic and cationic emulsifiers have thus far given the most

satisfactory results, whereas anionic emulsifiers are incompatible with ATRP.[80,81,87,93] Copper is by far the most commonly employed metal in ATRP,[97] and all successful reports of emulsion ATRP deal with Cu-based systems.

1.1.8.2. Emulsifiers

ATRP appears to be compatible with both nonionic and cationic emulsifiers but incompatible with anionic emulsifiers. *Ab initio* emulsion ATRP of n-butylacrylate (*n*BA)[81] and n-butylmethacrylated (*n*BMA)[87] with the anionic emulsifier sodium dodecyl sulfate (SDS) resulted in essentially no control/ livingness, speculated to be caused by interaction between $CuBr_2$ and SO_4^{2-} of SDS in the aqueous phase.[80,81,93] The use of the cationic emulsifiers dodecyltrimethylammonium bromide (DTAB) and tetradecyltrimethylammonium bromide (TTAB) in *ab initio* ATRP of 2-ethylhexyl methacrylate (EHMA) resulted in either poor colloidal stability (DTAB) or broad MWDs (TTAB).[83] DTAB has also been employed in *ab initio* ATRP of *n*BMA with good control/livingness but poor colloidal stability.[81]

Nonionic emulsifiers do not interact with Cu(II) in a detrimental manner and have thus far been the emulsifiers of choice in most studies. A wide range of nonionic emulsifiers have been employed with various degrees of success: Brij 97,[82,83,85,86] Brij 98,[80,81,84,85,89,93,95,98,99] Brij 35,[87] Tween 20,[84,98] Tween 80,[83,90,91,94] Antarox CO-880,[82] Igepal CO-720,[84] Igepal CO-850,[84] Igepal CO-890,[93] HV25,[84] Makton 30,[84] Triton X-405,[84] NP 10,[84] OP-10,[87,100] PEG,[80] and PVA-*co*-PVAc.[93]

1.1.8.3. Direct ATRP

In direct ATRP, the polymerization mixture initially contains the initiator (an alkyl halide) and the Cu complex in its lower oxidation state (e.g., CuBr/ligand).[97] The general trend in direct ATRP in ab initio emulsion systems is that good control/livingness is obtained but that colloidal stability is relatively poor, often with d ~1 μm and broad particle size distributions.[80,82,83,98] These polymerizations are likely to proceed in a manner akin to a suspension/miniemulsion polymerization,[80,81,84] because the initiator (e.g., EBiB) will be primarily located in the monomer droplets and very

significant monomer droplet nucleation is thus highly probable. Droplet nucleation results in large particles and concomitant micellar nucleation (giving smaller particles) thus results in broad particle size distributions. Gaynor et al.[80] reported ab initio Cu-based emulsion ATRP of nBA, nBMA, styrene, and methyl methacrylate (MMA) using nonionic emulsifiers and various ligands. Ligands rendering excessively water-soluble Cu complexes (e.g., bpy) yielded uncontrolled polymerizations, whereas good control/livingness was obtained with sufficiently hydrophobic ligands (e.g., dNbpy).[80,81,100,101] Loss of control, as well as an accompanying increase in polymerization rate (M s^{-1}) (*R*p), is caused by the Cu(II) concentration in the particles being too low due to partitioning to the aqueous phase.[81,102] The colloidal stability was in general poor, as evidenced by extensive coagulation, the exception being the combination Brij 98/*n*BMA, which gave a stable emulsion.[80]

The particles were large, generally greater than 1 μm. Jousset et al.[84] investigated direct ATRP of MMA in ab initio emulsion using the ligand 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy1) and a variety of nonionic emulsifiers at 60 °C. Brij 97 led to significant coagulation at low conversion, with as much as 40 wt % coagulum based on the initial amount of monomer at the end of the polymerization. The use of Brij 98 resulted in less coagulation (19 wt % coagulum) than for Brij 97, and when increasing the Brij 98 concentration to 25 wt % relative to monomer, coagulation at low conversion was avoided. Emulsifiers of various hydrophilic-lipophilic balance (HLB) values were investigated for alkylphenolethoxylates (NP10, Igepal CO-720, Igepal CO-850, HV25, Makon 30, and Triton X-405). The extent of coagulation decreased with increasing HLB value but went through a minimum at a certain HLB value. In this particular direct ATRP system, the emulsifier HV25 (HLB) 16.6) gave the best results both in terms of colloidal stability and MW control, with no coagulation for 18 wt % emulsifier relative to monomer (d ~ 800 nm).

Zhu and Eslami[83] studied Cu-based ab initio emulsion ATRP of EHMA with the ligand dNbpy2. In general, good control/livingness was achieved, but the colloidal stability was poor, and large particles were obtained (300-1000 nm). The best results

were obtained with Brij 98 and Tween 80. Increasing the temperature from 50 to 70 °C had a detrimental effect on colloidal stability. In the case of nonionic emulsifiers, an increase in temperature leads to more extensive coagulation because the concentration of emulsifier in the aqueous phase is reduced as a result of emulsifier dehydration, which causes the emulsifier to partition more toward the organic phase.[83,84,85] Therefore, a large amount of emulsifier is needed at high temperature. All of the above studies employed hydrophobic initiators (e.g., EBiB). However, Matyjaszewski et al.[81] also carried out ab initio emulsion ATRP using either EBiB or the watersoluble 2-hydroxyethyl 2-bromoisobutyrate (OH-EBiB) as initiator, reporting satisfactory control/livingness in both cases but severe coagulation in the case of the water-soluble initiator. Copolymerizations of MMA/nBA and MMA/*n*BMA as well as block copolymer synthesis employing macroinitiators using direct ATRP in ab initio emulsion have also been reported to proceed with good control/livingness.[98] Direct ATRP in ab initio emulsion has also been applied to the synthesis of hyperbranched polyacrylates.[99]

1.1.8.4. Reverse ATRP

In reverse ATRP, the polymerization mixture initially contains a radical initiator and the Cu complex in its higher oxidation state.[97] The advantage of using reverse ATRP is that the nucleation process is anticipated to proceed similarly to in a conventional nonliving emulsion polymerization in the aqueous phase, and as such monomer droplet nucleation would be avoided. Monomer droplet nucleation is believed to be the main reason for the poor colloidal stability and broad particle size distributions obtained in direct ATRP in ab initio emulsion systems. Radicals would be generated on initiator decomposition in the aqueous phase followed by monomer addition until the propagating radicals attain surface activity,[71] and these oligoradicals would subsequently enter monomer-swollen micelles, leading to nucleation.

The entering radicals would be deactivated by reaction with $CuBr_2$/ligand located in the micelles, generating dormant species. Reverse ATRP in ab initio emulsion has yielded much better results than direct ATRP with regard to colloidal stability and particle size distributions (more narrow).[84-89] Matyjaszewski and co-

workers[85,89] carried out reverse ATRP of nBMA in ab initio emulsion using water-soluble initiators and Brij 98. The use of KPS required the addition of a buffer to prevent potassium persulfate (KPS) decomposition (which changes the pH, reducing the initiation efficiency and Rp).[89] The buffer is however believed to have compromised the colloidal stability. Such problems were avoided with the azoinitiators 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) and 2,2 ′ ,-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, (VA-044) resulting in good colloidal stability, small particles with a relatively narrow particle size distribution (d_n = 85 nm; d_w/d_n =1.36), as well as good control/livingness (M_w/M_n =1.28 at 84% conversion).[89] The CMC of Brij 98 is 6×10^{-6} M,[103] i.e. consistent with micellar nucleation. However, the initiator efficiencies were as low as 30%,[85] mainly due to termination of oligomeric radicals in the aqueous phase, with a possible minor contribution from deactivation of oligomeric radicals in the aqueous phase by $CuBr_2$.[85,89] Due to the low water solubility of CuBr, subsequent activation in the aqueous phase would be slow, leading to highly delayed growth of dormant water-soluble species in the aqueous phase ($CuBr_2$ is much more watersoluble than CuBr). In addition,□β-hydrogen abstraction from oligomeric radicals in the aqueous phase by $CuBr_2$ may also occur.[85,104] In the case of the water-soluble azoinitiator V-50, the amount of emulsifier did not greatly affect the MWs or Rp, but the particle size decreased with increasing emulsifier content (13 wt % Brij 98 vs monomer: d_n ~ 190 nm).[85] At 90 °C, 90% of the initiator V-50 has decomposed in 30 min, and thus radical generation occurs mainly via the ATRP activation throughout most of the polymerization (as is normal in reverse ATRP).

An induction period is observed, during which initiator decomposition occurs, generating radicals that consume $CuBr_2$ until its concentration is sufficiently low for polymerization to occur. Sufficient hydrophobicity of the ligand is an important criterion also in reverse ATRP to prevent excessive partitioning of the Cu complexes to the aqueous phase. Peng et al.[87] investigated reverse ATRP of *n*BMA in ab initio emulsion using the nonionic emulsifier Brij 35 and CuCl with ligands of different hydrophobicity. Control/livingness was not obtained for the ligands bpy and bis(N,N′-

dimethylaminoethyl) ether, (bde) whereas good control/livingness resulted using the more hydrophobic dNbpy1. Jousset et al.[84] carried out reverse ATRP of MMA in ab initio emulsion at 80 °C using the nonionic emulsifier HV25 and the water-soluble azoinitiator VA-044, employing $CuBr_2$ or $CuCl_2$. The polymerizations proceeded with good control/livingness with no coagulation when using 10 wt % HV25 (vs MMA) and d_n = 43-48 nm, but low initiator efficiencies were obtained, as previously observed for *n*BMA.[85] The cmc of HV25 was determined as 2.5×10^{-4} M, i.e. consistent with micellar nucleation.

1.2. Organotellurium-Mediated Living Radical Polymerization (TERP)

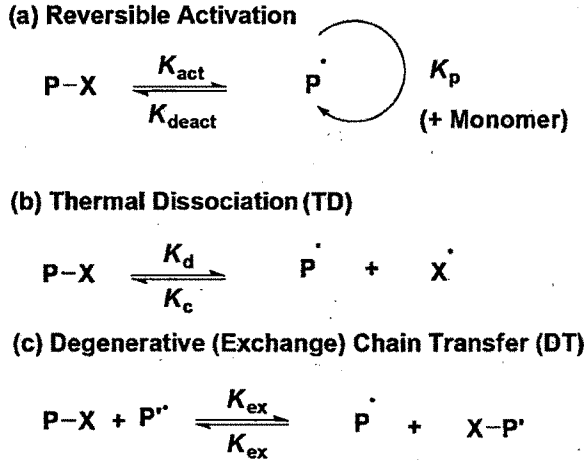
More recently, a highly versatile method for the synthesis of block copolymers based on organo*te*llurium-mediated Living Radical Polymerization (TERP).[105] has been reported. The basic concept of TERP is reversible activation-deactivation processes (Scheme 1.4). The dormant species P-X is activated by thermal, photochemical, and/or chemical stimuli to produce the propagating radical P$^{\cdot}$. In the presence of monomer M, P$^{\cdot}$ will undergo propagation until it is deactivated back to P-X. A number of activation-deactivation cycles allow all the chains to have an almost equal chance of growing, yielding low polydispersity polymers. Thus, sufficiently large k_{act} and k_{deact} are a requisite to obtain low-polydispersity polymers in a reasonable period of time; k_{act} and k_{deact} are the generalized (pseudo-first-order) rate constants of activation and deactivation, respectively (Scheme 1.4).

TERP is extremely general and can polymerize different families of monomers, such as styrenes,[105,106] acrylates, and methacrylates, using the same initiators in a highly controlled manner suggesting sufficiently large k_{act} values for these monomers. Furthermore, the versatility of TERP allows the synthesis of various AB-, BA- ABA-, and ABC-block copolymers starting from a single monofunctional initiator, regardless of the order of monomer addition. It can also provide copolymers with well-defined structures and is tolerant of various functional groups. TERP is thus a powerful synthetic tool to access novel functional materials. TERP possibly includes Thermal Dissociation (TD) and degenerative (exchange) chain transfer (DT) as the activation

mechanisms. If both processes coexist, k_{act} will take the form in which k_d and k_{ex} are the rate constants for TD and DT, respectively (Scheme 1). When the polymerization proceeds solely by DT mechanism, the rates of activation and deactivation naturally equal to that of exchange reaction (eq 1).

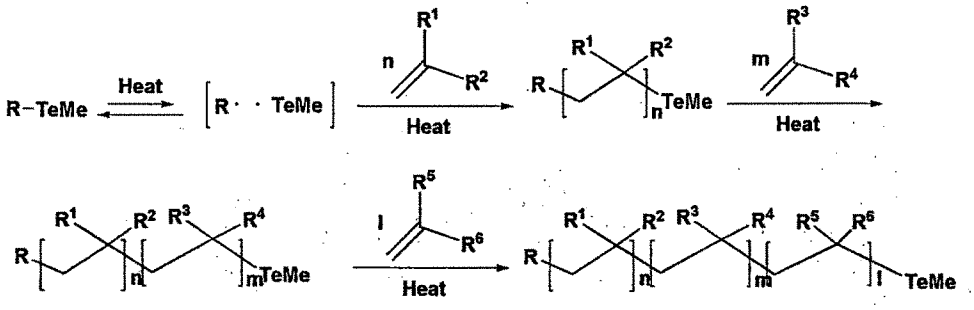
$$K_{act} = K_d + K_{ex}[\dot{P}] \tag{1}$$

Thus, by determining k_{act} as a function of the polymerization rate R_p (hence [P˙]), we can obtain k_d and k_{ex}.

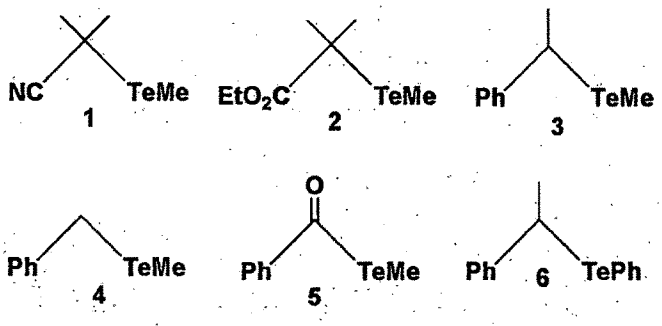


Scheme 1.4. Reversible Activation Processes in Living Radical Polymerization.

Mechanistically, TERP is based on the reversible activation-deactivation processes (scheme 1.5). The dormant species R-TeMe (also called organotellurium mediators), is activated by thermal, photochemical, and/or chemical stimuli to produce the propagating radical R˙. In the presence monomer, R˙ will undergo propagation until it is deactivated back to R-TeMe. If a living chain experiences the activation-deactivation cycles frequently enough over a period of polymerization, all living chains will have a nearly equal chance to grow, yielding low-polydispersity polymers



Scheme 1.5. Schematic representation of theTERP mechanism.



Structures of organotellurium mediators.

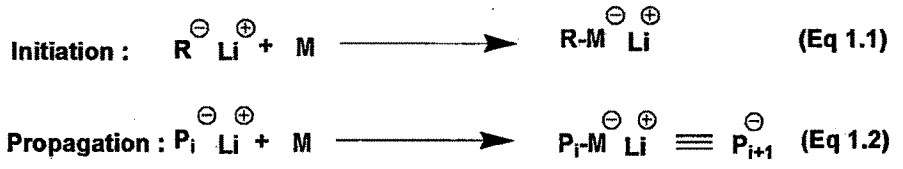
1.3. Living Anionic Polymerization

Since the initial discovery by Szwarc[5] that anionic polymerization under certain conditions can be living, that is termination-free; the technique has been developed to allow controlled synthesis of polymers with a variety of structures. Thus living anionic polymerization is the mechanism of choice for the synthesis of homo- and copolymers with well controlled molecular weight, molecular weight distribution, functionality, topology, composition, and microstructure. Due to the reactivity of the growing chain ends the polymerization reaction must be conducted under dry and oxygen-free condition.

A high vacuum technique has traditionally been the method of choice to achieve such conditions. The most important feature of alkyllithium-initiated living anionic

polymerization is the ability to proceed in the absence of chain transfer and termination during the whole course of polymerization reaction (Eqs 1.1, 1.2).[4,107]

Accordingly, the molecular weight of the resulting polymer can be readily controlled by the stoichiometry of the reaction and degree of conversion.



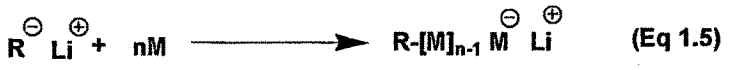
Based on the ratio of the amount of monomer to the moles of initiator, the desired number average molecular weight (M_n) at complete monomer conversion can be calculated (Eq 1.3) M_o is the formula weight of the repeating unit, $[M]_o$ is the initial concentration of monomer and [I] is the concentration of initiator.

$$M_n = M_o [M]_o / [I] \qquad \text{(Eq 1.3)}$$

Generally, using the living anionic polymerization method, a narrow molecular weight distribution ($M_w/M_n \leq 1.1$), the so-called Poisson distribution, can be achieved when the initiation rate (R_i) is comparable to or faster than propagation rate (R_p).[108] In other words, all chains should start at almost the same time and grow for the same period of time to obtain polymers with narrow molecular weight distributions. Theoretically, for living polymerization systems, polydispersity can be expressed in terms of degree of polymerization as shown in Eq 1.4.[109] The use of initiators with less reactivity,[110] a mixture of initiators,[111] or addition of initiator in a continuous process during polymerization[23] can result in broader molecular weight distributions.

$$X_w/X_n = 1 + [X_n/(X_n + 1)^2] \equiv 1 + (1/Xn) \qquad \text{(Eq 1.4)}$$

Another advantage of living anionic polymerization is the unique ability for all chains to retain their active chain ends even after complete monomer consumption (Eq 1.5).[107] Therefore, versatile post-polymerization reactions of the anionic chain ends provide



(Eq 1.5)

useful methodologies to produce block copolymers by sequential monomer addition,[112] diverse in-chain and chain-end functional polymers by nucleophilic substitution or addition reactions with electrophiles,[113] and branched polymers by linking reactions with multi-functional linking agents.[114] Consequently, the living nature of anionic polymerization provides methods to achieve well-defined structure, microstructure and architecture, which affect the ultimate properties of the resulting polymers.

1.4. History and Commercial Use of Polyacrylates

Polyacrylate is a chemical class of acrylate polymers derived from the polymerization of acrylic acid esters and salts. Each acrylate monomer contains a vinyl group: a pair of double-bonded carbon atoms attached to the carbon of a carboxyl group. Due to the high reactivity of carbon double bonds, acrylates polymerize readily and are used in a variety of plastics, adhesives and chemical binder applications. Polyacrylate emulsions are useful in pigment suspensions, most notably in latex and acrylic paint applications.

In 1873 methyl, ethyl and allyl acrylate were prepared but only allyl acrylate was observed to polymerize. However, Kahlbaum[115] reported the polymerization of methyl acrylate in 1880. Fitting[116] found that methacrylic acid and some of its derivatives polymerize readily. Ethyl methacrylate[117] was prepared in 1891. In 1901 in Tuebingen, Germany, Dr. Otto Rohm published his doctoral thesis in which he described the chemical structure of the liquid condensation products obtained from the action of sodium alkoxides on methyl and ethyl acrylate, and characterized in some detail the solid polymeric material formed simultaneously. As a result of this work, a patent was issued describing rubber substitutes made by vulcanizing polyacrylates with sulfur[118]. A polyacrylate rubber is actually being manufactured as an out-growth of work by the Eastern Regional Research Laboratory of the U.S. Department of Agriculture[119].

In 1927, Rohm and Haas in Darmstadt began limited production of polymethyl acrylate under the trade names Acryloid, as a suggested ingredient for surface finishes and lacquers, and Plexigum, for use as a safety glass interlayer.

Methyl methacrylate soon became the most important member of the acrylic family. Research[120] on cast sheets from methyl methacrylate was carried out by Röhm & Heas, A.-G. in Germany, and by Imperial Chemical Industries Ltd. in England. R. Hill of Imperial Chemical Industries (ICI) discovered that methacrylate ester polymers, especially MMA polymers, were rigid, optically clear plastics suited to replace glass in such applications as aircraft windows.

The elastomeric acrylic ester polymers and higher alkyl methacrylate polymers are becoming increasingly important in a wide variety of applications.[121,122] They are used in textile sizing, in special adhesives and lacquers and as oil additives Acrylic glass can be used for high-strength applications, light redirection through laser surface cutting and for medical technologies such as eye lens replacement and bone cement implants. Polymethylacrylates is another class of acrylate polymer that is used specifically in the production of superabsorbent polymer. Sodium polyacrylates and polymethylacrylates can be found in products such as diapers, fire-retardant gels and wound bandages.[119]

Acrylics are sometimes referred to as "plastic glass" which have not only captured the novelty trade for costume jewelry, pocketbooks, hairbrushes, umbrella handles, trays and ornaments, but also have found more practical purposes in many industrial and commercial products for every day use, such as outdoor signs, patio-roofs, watch crystals, airplane windows, automobile tail light, sky light, sun glass lenses, dentures, and acrylic-water-latex paints.[123,124] Acrylic glass can be used for high-strength applications, light redirection through laser surface cutting and for medical technologies[121,122,125] such as eye lens replacement and bone cement implants.

The industrial applications of solutions or emulsion of acrylic ester polymer as coating or impregnants are many and varied.[123] The inherent stability, durabilty and pigment binding characteristics of acrylic polymers have been important factors in

selection of such systems in various coating applications such as in leather and textile finishing. Acrylic ester emulsion polymers are used in the paper industry as pigment binders, saturants, fibers and wet-end additions for high strength paper The properties of polyacrylate emulsion allow acrylic paint to dry faster than oil-based paints yet still retain a high level of miscibility when wet. Aside from its popular adhesive iterations, polyacrylate is also well known for its break-resistant glass sheeting.[126]

1.5. This Thesis

1.5.1 Aim and rationale

Radical polymerization is of enormous industrial importance; approximately 50% of all commercial polymers are produced by radical polymerization. This process is tolerant to impurities, compatible with water, relatively easy to implement in an industrial plant, and very versatile with respect to compatibility with functional monomers. The major drawback is that radical polymerization proceeds with very limited control; it is not possible to prepare block copolymers, polymers of narrow molecular weight distributions (MWDs), and more complex architectures due to the high reactivity of the propagating radicals and their propensity to undergo bimolecular termination, transfer, and other side reactions. Living anionic polymerization offers high levels of control in terms of well-defined polymers and precise molecular architectures, but the process is much less flexible than radical polymerization, as it is very intolerant to functionality and impurities. Thus, it has been a long-standing goal in the field of polymer chemistry to develop a process that combines the robustness of radical polymerization with the control and precision offered by living anionic polymerization. CLRP today offers levels of control almost as good as those of living anionic polymerization, while maintaining the robustness of a free radical process in terms of tolerance and flexibility.

Compared to living anionic polymerization, the use of radical polymerization methods appears more attractive from the point of view of ease of practice and the number of monomers capable of being polymerized. Atom transfer radical polymerization (ATRP) has rapidly become one of the versatile methods in polymer synthesis. Copper catalyzed ATRP has been successively used in controlling polymerization of many styrenes, acrylates, methacrylates and several other relatively reactive monomers such as acrylamides, vinyl pyridines, and acrylonitrile.

The objective of this research was to investigate and prepare well-defined polymers using the advantages of "Living"/Controlled Radical Polymerization

techniques (L/CRP) in various known controlled polymerization systems. Research was initially focused on the synthesis and characterization of various acrylic monomers particularly by ATRP, but the scope evolved as the knowledge gained in ATRP and was used to exploit opportunities in the similar fields of L/CRP like TERP and living anionic polymerization.

With the knowledge gained in the synthesis of block copolymers using ATRP and TERP it was felt to extend this argument to using other living techniques for similar purposes i.e anionic polymerization. Therefore, some attempts were used to remove the stringent conditions traditionally used for anionic polymerization. Thus apart from polymerizing some monomers at very low temperatures like -78 or -98 °C, the same was also polymerized at room temperature. This thesis contains some of the results obtained in this direction to synthesize thermoplastic elastomer (TPE).

A greater part of the work described in this thesis, therefore, aims to investigate the application of ATRP and TERP in the synthesis of homo- and block copolymers of various vinylic monomers including methacrylates, styrene, isoprene, and vinyl pyridines, with controlled molecular weight, narrow molecular weight distribution. Furthermore, the composition of the final polymer was explored for their self-assembly behavior in various solvents polar and non-polar solvents. The polymerizations were carried out in bulk, in solution as well as in aqueous medium. Another important aspect of these studies was to optimize the polymerization process which is of high importance in order to control the block copolymer architecture.

The results thus obtained from the studies will hopefully aid in creating a better understanding of the aspects that need to be considered when using block copolymers for various applications.

1.5.2. Outline

Chapter 2 of this thesis describes the experimental techniques used. A brief discussion about the facilities such as Size Exclusion Chromatography (SEC), reversed-phase temperature gradient interaction chromatography (RP-TGIC), Energy-dispersive

X-ray spectroscopy (EDX), Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM). Experimental setup for the three different techniques used for the polymerizations are explained in this chapter.

Chapter 3 describes that ATRP can be used to synthesize BAB and CBABC tri- and pentablock copolymers of styrene, n-butyl methacrylate and methyl methacrylate with controlled molecular weights and narrow molecular weight distributions. The structures of the block copolymers, living nature, thermal and morphological properties of the synthesized polymers have been studied. The block copolymers are synthesized for the first time via solution atom transfer radical polymerization with good control on the molecular weight and the molecular weight distribution resulting in the unique core-shell type flower-like micellar structures in nonpolar solvent.

In chapter 4 a novel approach is used to synthesize nanosized polymethylmethacrylate polymer beads with narrow particle size distribution by emulsion ATRP, using mixed ligand system at room temperature. The synthesis, the reaction details, the description of the experimental set-up, the raw materials used and the conditions for the synthesis have been discussed at length. A great deal of work has been undertaken to optimize the conditions for the synthesis of desired block copolymers.

Chapter 5 deals with a novel and simple method of preparation of oligomer like diblock copolymers of styrene and 2-vinyl pyridine via organotellurium-mediated living radical polymerization (TERP). The work concerns design and well defined synthesis of low-molecular weight polystyrene-*b*-poly (2-vinylpyridine) (PS-*b*-P2VP) and (P2VP-*b*-PS) an amphiphilic olgimer like diblock copolymer via TERP by sequentially adding the monomers. The block copolymer synthesized was used as a template for the synthesis of nanoporous TiO_2 membranes. The morphology (shape and size) of the synthesized block copolymers and the nanoporous TiO_2 membranes were also studied using SEM and TEM.

Chapter 6 describes the synthesis and characterization of linear and radial block copolymers of styrene and isoprene through a novel coupling agent by living anionic

polymerization. The synthesis of linear di-, tri-, and star-block copolymers (polystyrene-*b*-polyisoprene (SI), polystyrene-*b*-polyisoprene-L-polyisoprene-*b*-polystyrene (TB), and (polystyrene-*b*-polyisoprene)$_3$-L' (SB), respectively). A novel mechanism is also proposed for the synthesized block copolymers. The molecular weights of the polymers were determined by size-exclusion chromatography multiangle laser light scattering (SEC-MALLS) after separating them by Reversed Phase Temperature Gradient Interaction Chromatography (RP-TGIC) technique.

Concluding thoughts are presented in Chapter 7.

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