ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THE CONTROLLED RADICAL POLYMERIZATION OF METHYL METHACRYLATE WITH IRON (III)\ TRIPHENYLPHOSPHINE COMPEXES

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DEMİR(III) \ TRİFENİLFOSFİN KOMPLEKSİ İLE KONTROLLÜ METİL METAKRİLAT POLİMERİZASYONU

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymers
M_w	: Weight average molecular weight of polymers
MWD	: Molecular weight distribution of polymers
PMMA	: Poly (methyl methacrylate)
Cat	: Catalyst
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
K_{eq},k_p	: Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively
k_{tc}, k_{td}	: Rate constant of termination by combination and rate constant of termination by disproportionation respectively
I, M	: Initiator and monomer respectively
Ph	: Phenyl
AIBN	: 2,2' azo-bis-isobutyrontrile
EDA	: Electron donor- acceptor
RAFT	: Reversible addition fragmentation chain transfer

THE CONTROLLED RADICAL POLYMERIZATION OF METHYL METHACRYLATE WITH IRON (III)\ TRIPHENYLPHOSPHINE COMPEXES

SUMMARY

Radical polymerization process important for the industrial production of commodity polymers, but they are not living polymerization, and the molecular weight and molecular weight distribution are very difficult to control because of the irreversible termination reactions between two propagating radicals. Traditionally, control of macromolecular architecture has been achieved by using living polymerization techniques such as anionic, cationic procedures. Specifically, controlled architecture possesses some characteristics, which are molecular weight control, end group control, ability to form block copolymers, and a living nature. In 1995, Matyjaszevski et al. reported a novel polymerizable method that is based on the transition metal catalyzed atom transfer radical polymerization (ATRP). In ATRP alkyl halide species ,RX, were used as an initiators and transition metal compounds at lower oxidation state with suitable ligands, M_t/L as catalyst. ATRP can be applied to polymerize both styrene and acrylic type monomers. These monomers were successfully polymerized by this method and they exhibit some characteristics of living polymerization.

The living\ controlled radical polymerization of MMA has been widely investigated using ATRP method, among them a large variety transition metal, compounds were used as catalyst: Cu(I), Ru(II), Ni (I), Rh(II) and Fe(II) – based system. PMMA with the well-controlled molecular weight distributions could be obtained with iron-based catalyst system.

Thought the above-mentioned conventional ATRP method is an efficient method to maintain living\ controlled radical polymerization. It has major two problems: the toxicity of the halide species RX and oxidation of the catalyst M_t/L, by the oxygen in air.

In the present work, we report that the controlled radical polymerization of MMA having low polydisperties can be prepared without

RX that have a toxicity or removal oxygen, if our initiation system is used. GPC (Gel Permeation Chromatography) studies of the obtained polymers show controlled polymers that are readily formed as a result of ATRP.

DEMİR(III) \ TRİFENİLFOSFİN KOMPLEKSİ İLE KONTROLLÜ METİL METAKRİLAT POLİMERİZASYONU

ÖZET

İktisadi önemi bulunan polimerler için radikal polimerizasyonu önemli bir prosestir. Bu polimerlerin molekül ağırlıklarını ve molekül ağırlığı dağılımını kontrol etmek büyüyen iki radikalin geri dönüşümlü sonlanma reaksiyonu yüzünden çok zordur ve bu polimerler yaşayan polimer değildir. Klasik olarak, makro moleküler mimarinin kontrolü yalnızca yaşayan anyonik ve katyonik polimerizasyon teknikleri ile başarılabilmektedir. Kontrollü mimari denilince, molekül ağırlık kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme ve yaşayan karakter akla gelmektedir. Matyjaszwski ve grubu 1995 yılında atom transfer radikal polimerizasyonunu (ATRP) gerçekleştirmişlerdir. ATRP, Cu(I) / ligand sistemi ile katalizlenen yaşayan serbest radikal polimerizasyon sistemidir. Başlatıcı olarak alkil halajenürleri ,RX, düşük oksidasyon basamaklardaki geçiş metalleri ve uygun ligantlar kataliz olarak kullanılır M_t\L. Sitiren ve akrilat türü monomerlerin polimerizasyonunda ATRP başvurulabilir. Bu monomerler başarılı bir şekilde bu methodla yaşayan karakterde polimerleştirilebilirler

Yaşayan kontrollü MMA polimerizasyonu ATRP methodu kullanılarak geniş araştırılmaktadır. Bu araştırmalarda bir çok Cu(I), Ru(II), Ni (I), Rh(II) ve Fe(II) – gibi geçiş element bazlı sistemler kullanılmaktadır. Kontrollü PMMA demir bazlı kataliz sistemleri ile elde edilebilir.

Yukarıda ki anlatılanlar baz alınarak düşünüldüğünde geleneksel ATRP kullanılarak kontrollü polimer elde etmek en etkili yoldur. Bu metod alkil halajenürlerin toksik olması RX, ve metal katalizin oksitlenmesi gibi problemler göstermektedir .

Bu çalışmada kontrollü ve düşük polidispersitesi olan MMA polimerizasyonunun toksik olan halajenürler olmaksızın ve oksijen uzaklaştırmadan elde edilebileceğini bizim tarafımızdan gösterildi. GPC(Jel Geçirgenlik Kromatografisi) cihazından alınan sonuçlar doğrultusunda elde edilen polimerlerin gerçekten de ATRP tekniği ile oluştukları belirlenmiştir.

1. INTRODUCTION

The development of new polymeric materials has recently become a vital facet for polymer science from both an academic and industrial viewpoint.

Almost half of the plastics are produced by free radical polymerization. There are so many initiation system for radical based polymerization. One of them is charge transfer initiation system that we interested in. The interaction between a suitable electron rich molecule with an electron deficient one leads to the formation a large number of charge transfer complexes. Hill at al[1]gave a list of some typical donor and acceptor monomers. The donor and acceptor monomers complexes often react with an organic halogen compound ,which initiate vinyl polymerization. Although the free radical polymerization is the most widely used commercial technique for preparing variety of vinyl polymers it has still some disadvantageous. One of the drawbacks of the conventional radical polymerization is the lack of control in both the molecular weight and the structure of the resulting polymers. Ability of getting polymers with controlled molecular weight and well-defined architecture is one of the main goals in modern synthetic polymer chemistry because the molecular weight and the molecular weight distribution of the polymer highly affect the final properties of the resulting materials. Generally, as the molecular weight increases the intermolecular forces also increase and this causes significant changes not only in mechanical and thermal properties, but also in process ability, electrical, optical and chemical properties.

There are number of methods that can be utilized to gain such control. These include living ionic polymerization, nitroxide-mediated polymerization of styrene, ruthenium (II)/aluminum based polymerization of methacrylates, cobalt (II)-mediated polymerization of acrylates, reversible addition fragmentation reaction(RAFT), iniferter method and of course atom transfer radical polymerization (ATRP) of a variety of monomers. However, since the synthetically demanding experimental requirements of ionic polymerization such as rigorous exclusion of water and oxygen

and the use of ultra pure reagents and solvents further reduce its general applicability ATRP seems to be the most versatile technique among all these methods.

The development of a living free radical procedure, which combines the desirable attributes of traditional free radical systems with desirable attributes of living polymerization, would be a significant development in not only polymer synthesis but also polymer science in general.

In this study, emphasis is placed on the synthesis of controlled poly methyl methacrylate with the new initiation system related with electron donor-acceptor EDA complexes.

2. THEORITICAL PART

2.1 FREE RADICAL POLYMERIZATION

Free radical polymerization is the most important commercial process for the preparation of the high molecular weight polymers. A wide variety of monomers can be polymerized or co-polymerized under relatively simple experimental conditions [2]. The polymers obtained via this method are used in the manufacture of numerous products such as fabrics, surface coatings, plastics, paints, packaging, and contact lenses [3]. Why free radical polymerization is of importance can be summarized as follows;

- ✓ Free radical polymerization can be carried out under relatively undemanding conditions.
- ✓ It exhibits a tolerance of trace impurities.
- ✓ High molecular weight polymers can be produced without removal of the stabilizers present in commercial polymers.
- ✓ Trace amount of oxygen does not disturb the polymerization.
- ✓ Free radical reactions can be conducted in aqueous media.
- ✓ Although a few types of monomers limit the ionic polymerization techniques, a variety of monomers can be polymerized via free radical polymerization route.

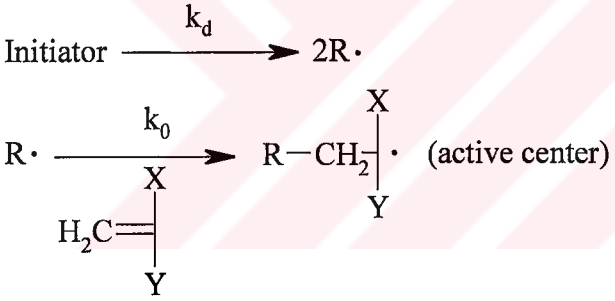
Free radical polymerization is initiated by radicals and propagated by macro radicals. These radicals exhibit an unpaired electron. Initiating radicals are rarely formed by

monomers themselves but rather thermally, electrochemically or photo chemically from the homolytic chain cleavage of the deliberately added initiators.

Free radical polymerization is a chain growth reaction and traditionally consists of three main steps: initiation, propagation and termination.

Initiation

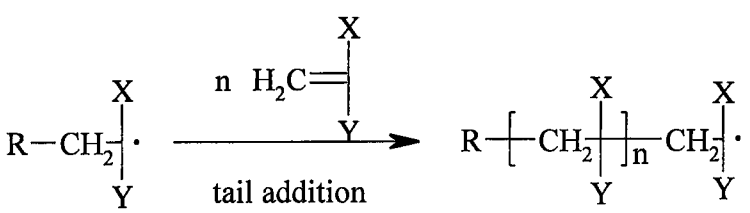
Initiation occurs from the reaction of an initiator-derived radical center with a monomer molecule. Firstly a couple of radical occurs by a homolytic cleavage of the initiator. If the radicals are formed in the presence of vinyl monomers, these radicals react with the double bond and generate a new radical. The first one is known as the dissociation and the second is the association step in the initiation of free radical polymerization. Since $k_d < k_o[M]$, the decomposition is the rate determining step in the initiation process [4].



(2.1)

Propagation

Propagation is the rapid addition of more monomer to the growing chain end, for example the rate constant of propagation is about 100-10000 [L/(mol*sec)]. These rates are very high compared to that of the other chemical reactions [5].



(2.2)

Termination

Termination is the disappearance of an active center by self-reaction of carbon-centered radicals, reaction of an active chain with an initiating radical or by chain transfers reactions.

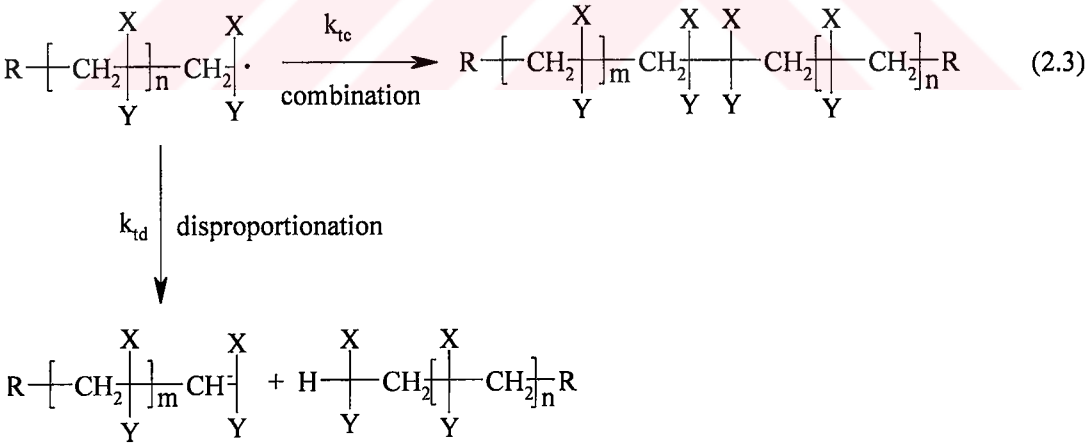
1) The Self Reaction of Carbon-Centered Radicals

a) Combination

Termination by combination occurs when two propagating radical chains of arbitrary degrees of polymerization meet at their free radical ends.

b) Disproportionation

Termination by disproportionation results in two terminated chains. Because of hydrogen transfer, one terminated chain will have an unsaturated carbon group while the other one is saturated.

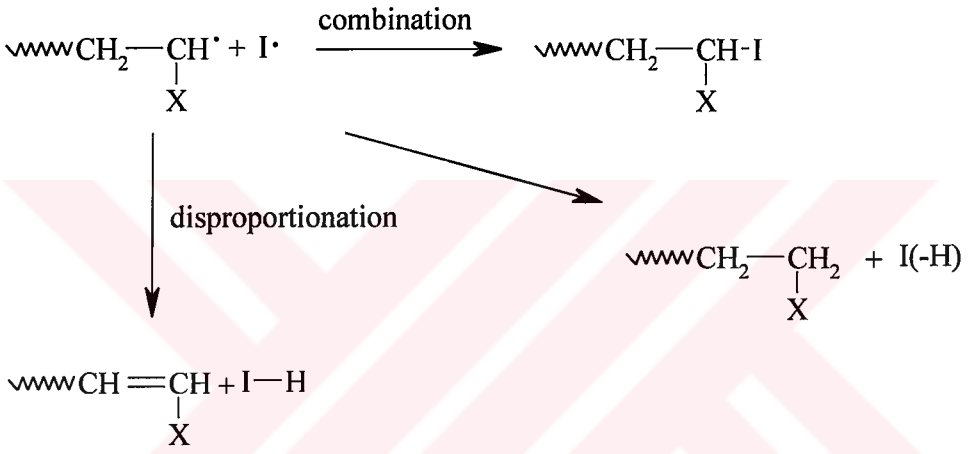


(2.3)

The rate of k_{tc} / k_{td} is dependent on the polymerization conditions and the type of monomers. For example, in normal conditions while styrene prefers termination by combination, methyl methacrylate chains are usually terminated by disproportionation.

2) Primary Radical Termination

Primary radical termination is the reaction of a propagating radical with a radical derived from the initiator. This type of termination gives products that may originate from either of three reaction; combination of the two radical species, hydrogen abstraction from the propagating radical by the initiator-derived radical or hydrogen abstraction from the initiator-derived radical by the propagating radical to give a polymer with saturated chain end. The schematic representation of primary radical termination is seen in (2.4).



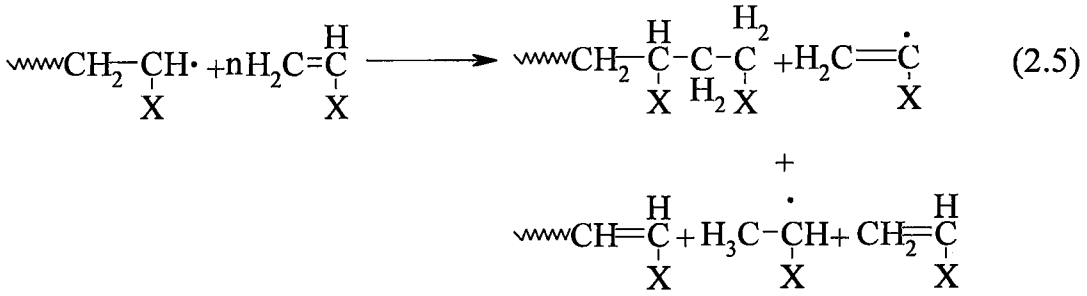
(2.4)

3) Chain Transfer Reactions

Chain transfer is the reaction of a propagating radical with a non-radical substrate to produce a dead polymer chain and a new radical capable of initiating a new polymer chain.

a) Transfer to Monomer

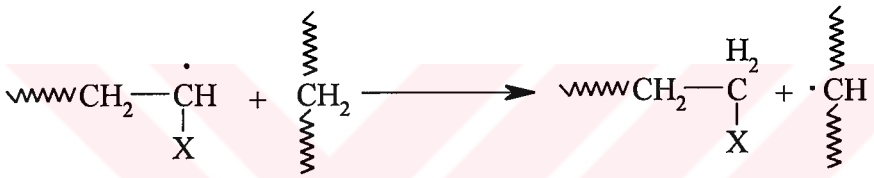
If the generated monomer radicals become stable via resonance structure they do not initiate polymerization of a new chain. An example is given in (2.5)



(2.5)

b) Transfer to Polymer Chain

The transfer of an active center exist on a growing chain radical to the another polymer chain results in branching but it does not influence the length of the chain.



(2.6)

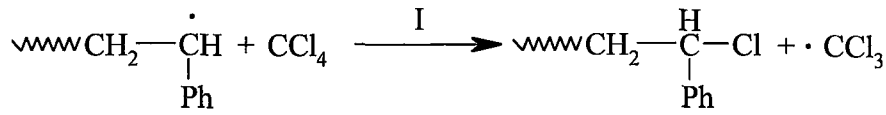
c) Transfer to Initiator

Transfer to initiator involves the termination of a propagating radical by reaction of a molecule of initiator. The resulting polymer possesses two initiator-derived end groups, and in the process, a new primary radical is formed, which may initiate a new chain.

(2.7)

d) Transfer to Solvent

The molecular weight of polymers obtained via a polymerization in a solvent is usually smaller than that of the polymers obtained in a solvent-free medium. This difference depends on the type of solvent used and the degree of the dilution.



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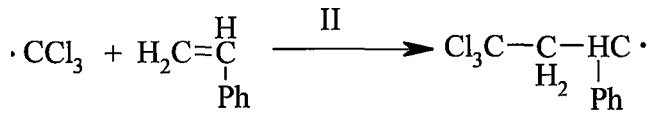
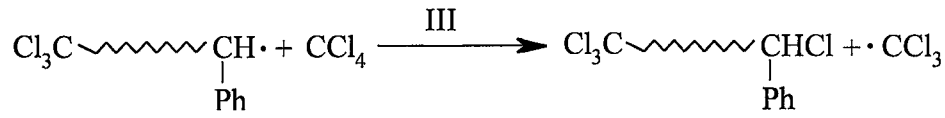
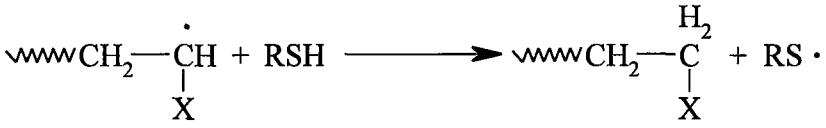




e) Transfer to Modifier



(2.9)

4) Termination by Impurities

The impurities or oxygen react with the formed radical centers and so terminate the polymerization.

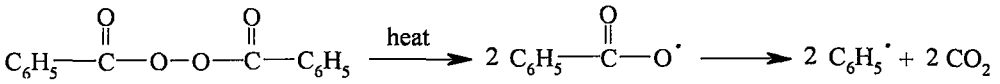
2.1.1 Free Radical Initiators

A good free radical initiator can be defined as a compound undergoing a homolytic chain cleavage when it is subjected to proper heat, radiation or chemical reaction and so resulting in formation of radicals whose activities are more than that of the monomer themselves. These radicals formed should be stable enough to be able to react with monomers and generate active centers.

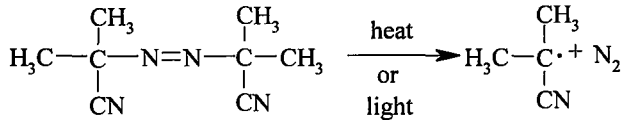
2.1.1.1 Initiators Giving Radicals via Homolytic Chain Cleavage of a Covalent Bond

Many organic compounds can produce free radicals for chain growth polymerization by absorbing thermal, photochemical, electrical or mechanical energy. Especially the thermal and photochemical chain breaking of an organic compound is the most widely used ones in the formation of free radicals. For example, organic peroxides

and azo-compounds like dibenzoyl peroxide and 2,2-azobisizobutironitrile (AIBN) generate radicals either by heat or light. Two examples to the formation of radicals via this method are given in (2.10) and (2.11), decomposition of dibenzoyl peroxide and AIBN respectively.



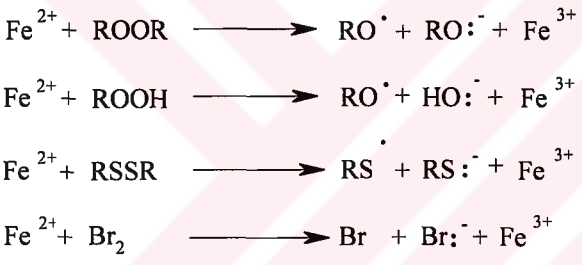
(2.10)



(2.11)

2.1.1.2 Initiators Giving Radicals by Electron Transfer

The most important one is the redox reactions.

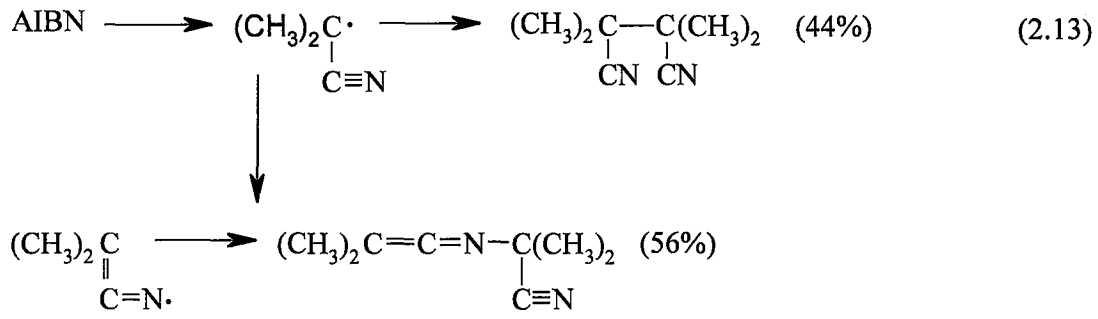


(2.12)

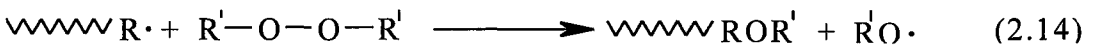
The pathway of the polymerization initiated by the electrochemically formed radicals usually undergoes over the anionic or cationic ions.

2.1.2 Initiator Efficiency

Although all of the initiator molecules are subjected to chain breaking in the polymerization medium, their efficiency to initiate the chain growth is rarely hundred percent. Some of the radicals formed cannot diffuse away due to the effect of solvent and hence react with each other. This is usually known as cage effect. An example to this kind of situation can be given as in the equation of (2.13).



Efficiency of the initiator is dependent on the type of solvent. Another reason reducing the effect of initiator is the reaction of some part of the initiator molecules with the active centers present in the polymerization medium.



As seen in (2.14) although one mole of initiator is used, as a result, the number of radicals is kept constant.

Because of the above reasons initiator efficiency is usually between 0,3 and 0,8 [6].

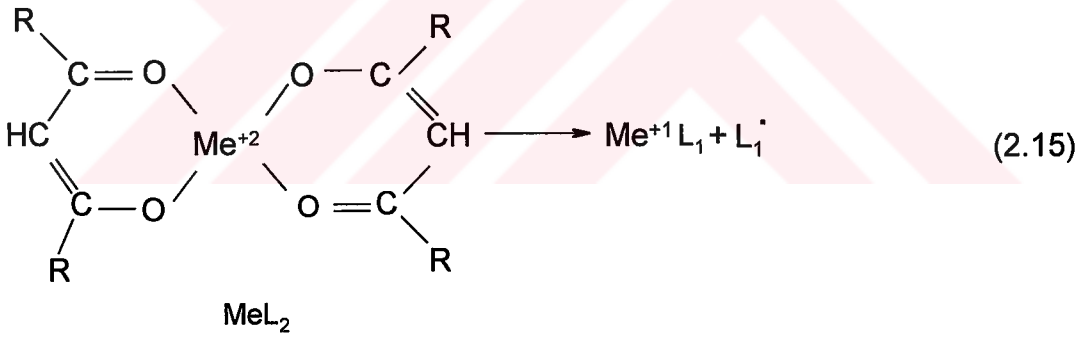
2.1.3 Complexes in initiation reactions of radical polymerization.

A primary condition for the successful initiation of radical polymerization of an unsaturated monomer is the presence of compounds reacting to give rise to radicals in the reaction system. The initiation step of the radical polymerization may be divided into the stage of radical formation and stage of radical information and the stage of the addition of a radical to monomer to monomer , the formation of a monomer radical. Since the rate constant for the addition of a radical to monomer is usually by several orders of magnitude higher than value of the rate constant for the formation of radicals (primary radicals) the decisive step of the initiation process is the production of primary radicals.

Initiating systems based on metal compounds are important for free radical polymerizations. The simplest systems are those based on salts ,complexes and metal chelates, the so-called one component initiating systems. In some cases efficient initiation by a metal compound requires addition of another component, the reaction of which with the metal component produces the initiating radicals. These two

component-initiating systems have found their main application in the synthesis of modified polymers.

One components systems: Metal complexes and metal chelates and their relation to the initiation of the free radical polymerization has been extensively studied. Charles and Pawlikowski [7] studied the thermal stability of acetylacetonates of metals at 191 °C in an inert atmosphere the most stable in the series of chelates were found to be acetylacetonates of Li^{+},Mg^{+2},Cu^{+2},Ni^{+2},Ca^{+2},and Cr^{+2}. The acetylacetonates of Mn^{+3} ,Fe^{+3}, and Co^{+3} were thermally less stable. These authors have also mentioned the possibility of applying some of these chelates to the initiation of the polymerization of styrene. Arnett and Mendelssohn [8] found a correlation between the thermo-oxidation stability of a chelate and its efficiency of styrene polymerization. The proposed mechanism for the thermal decomposition includes the reaction of the formation of acetyl acetone radical by hemolytic dissociation of the Me-O bond. The radical acetyl acetone (L_1•) is responsible for he initiation of the polymerization.(2.15)



(2.15)

Two-component and multi-component systems based on metal compounds : Initiation by metal compounds on the polymerization of unsaturated monomers[9,10] showed that halogen containing organic compounds significantly accelerated polymerization many substances have latter been found which increase the initiation efficiency of a metal component. The advantage of Two or multi-component systems in comparison with a one component system is easier regulation of the initiation process and the possibility of preparing an efficient initiating system by mixing individual components directly ''in situ'' in the reaction medium. It is therefore not necessary to use a metal complex prepared in advance ;this is advantages especially if the complex is readily decomposed in the presence of oxygen.

Detailed studies of multi-component initiating systems based on metal compounds and organic helogenides, both low molecular and high molecular have been reported [11].

Initiating systems based on complexes of organic compounds: In many multi-component initiating systems, formation of an adduct of a metal component with monomer or other component of the system is an inevitable condition for the formation of initiating radicals. The formation of adducts is, however, not confined only to the systems containing a metal component. Systems based on donor-acceptor complexes and on charge-transfer complexes in the ground or excited states constitute another important group of initiating systems for radical polymerization. Formation of a donor-acceptor complexes is conditioned by an interaction between donor D,i.e. a molecule with a low ionization potential, I_D, and an acceptor ,A,i.e. a molecule with high electron affinity, E_A [12] . The interaction is expressed: (2.16)

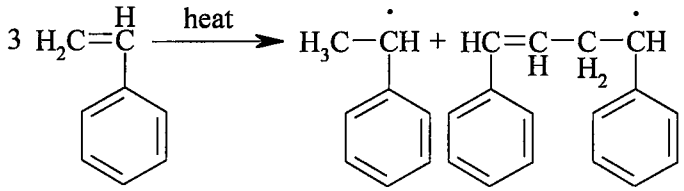
$$D + A \rightleftharpoons [D.....A] \rightleftharpoons [D^{\bullet+}, A^{\bullet-}] \qquad (2.16)$$

where the symbol [D....A] denotes of a donor acceptor complex in the ground state and the last symbol is the excited state of the donor-acceptor complex after electron transfer from donor to acceptor(EDA).[13]

2.1.4 Thermal Polymerization

Some of the monomers can initiate a polymerization without need of an initiator. In many cases, impurities exist in monomer, like peroxides and hydro-peroxides, formed due to the presence of oxygen, can initiate a polymerization by their thermal or photochemical degradations. The best examples to the thermally polymerizable monomers are styrene, methyl methacrylate and 2-vinyl tiyofen, 2-vinyl furan [14-15].

Although the exact mechanism is not known, the works done on this subject [16-17] shows that the thermal polymerization of styrene is initiated by two different mono-radicals in a termolecular reaction as seen in (2.17).



(2.17)

2.2 CONTROLLED OR LIVING RADICAL POLYMERIZATIONS

The control of macromolecular structure has recently become one of the most important subject for polymer science from both an academic and an industrial viewpoint, because ability to control macromolecular architecture can lead to development of the new polymeric materials with better mechanical and physical properties [18].

The classical techniques offering appreciable control over macromolecular structure, such as anionic and cationic polymerizations, cannot find a wide application area due to stringent requirements on reaction conditions and monomer purity. On the other hand, it is well known that free radical polymerization is the most important process to prepare high molecular weight polymers. A variety of monomers can be polymerized or co-polymerized under relatively simple conditions. Therefore, the development of a living free radical procedure, which combines the desirable attributes of traditional free radical systems with desirable attributes of living polymerizations, would be a significant development in polymer science in general.

In living process, number of growing chains is usually the same with the number of initiating molecules and it does not change during propagation until the total monomer consumption. Hence semi-logarithmic kinetic plots and molecular weights conversion dependences are linear, of course if the initiation is fast. Also low polydispersities can be achieved via the living process. However some polymerization systems provide well-defined polymers in which chain-breaking reactions cannot be avoided completely. These are called controlled or pseudo-living since they do not fulfill the criteria of living polymerization because of the presence

of either transfer or termination. Radical polymerization is one the pseudo-living polymerization techniques.

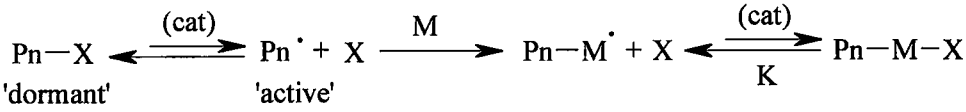
Three types of radical polymerization have been called living;

- Polymerizations where the normal termination process of radical-radical reaction is slow or absent because of the physical nature of the reaction medium or the immediate environment of the reactive chain end. Systems in this class include precipitation polymerization, certain template polymerizations and polymerizations in inclusion complexes.

- Systems with reversible termination where the bond formed by primary radical termination or chain transfer are stable. Narrow polydispersities are not available by these techniques.

- Systems with reversible termination where the bond formed by free radical termination or chain transfer is kinetically unstable under the reaction conditions. These polymerizations should be considered as true living polymerizations.

The latest developments in living free radical polymerizations of vinyl and cyclic monomers are base on the reversible protection of the growing chains in the form of inactive 'dormant' species exchanging reversibly with the active growing chain as seen in (2.18).



(2.18)

cat=Nu^-, Lewis acids, hv, heat
X=protective group
Pn=polymer chin
M=monomer
K=equlibrium constant

Controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weight sufficiently low. This necessitates a relatively high concentration of the initiator, or in other words, low $[M]_0 / [I]_0$ ratios. However when $[I]_0$ is high, since the termination is bi-molecular, contribution of termination becomes more significant when a large concentration of radicals [P.] is generated.

Therefore establishing an exchange between dormant and active species is necessary to solve this discrepancy. The concentration of dormant species can be equal to $[I]_0$, and the concentration of momentarily growing species to [P.]. The total number of growing chains will be equal to $[I]_0$, and radicals would be present at a very low stationary concentration, [P.], and therefore the contribution of termination should be very low. There are three possibilities to realize the concept of controlled radical polymerization.

1) Reversible Homolytic Cleavage of Covalent Species

$$P{-}R \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P\cdot + R\cdot \qquad (2.19)$$

An initiator with the structure of P-R is the adduct of the model of growing radical P., capable of propagation, and the scavenging or the dormant radical (R.), which ideally should react only with (P.) but not with the monomer itself.

This case probably the most postulated in controlled radical polymerization. As examples of (R.); Otsu and Yoshida [19] used dithiocarbamate radicals, Georges et al. [20-21] used nitroxyl radicals and Borsing et al. [22] used triaryl methyl species.

The problem with this method is that except nitroxyl radicals, the others may participate in side reactions leading to degenerative transfer

2) Reversible Homolytic Cleavage of Persistent Radicals

$$P\cdot + X \rightleftharpoons (P{-}X)\cdot \qquad (2.20)$$

The role of a scavenger radical may be also played by a neutral species. The persistent radical, (P-X)·, should only cleave homolytically to form (P.) and the species X, but it should not react with monomer. X should be inert compound capable of reacting only with (P.). X may be elementoorganic or organometalic species with an even number of electrons. Some success have been reported with group XIII and XV elements such as aluminum [23] and phosphorus [24] as well as with organometalic derivatives of Co [25], Cr [26], and other transition metals. In some cases not only radical but also ionic and coordinative polymerization may take

place. The pathway of the polymerization is dependent on the nature of metal or elements, ligands and medium effects.

3) Degenerative Transfer

$$Pn^{\cdot} + P1\text{-}R \xrightarrow{k_{tr}} P1^{\cdot} + Pn\text{—}R \qquad (2.21)$$

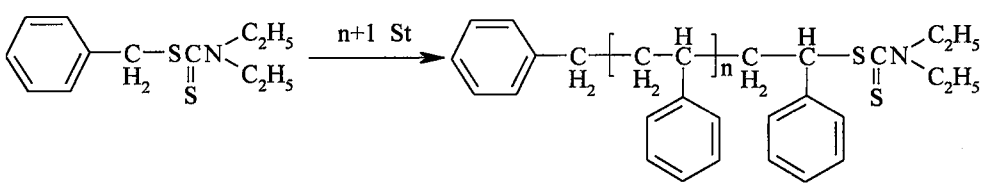
In this case growing radical (Pn.) reacts rapidly and selectively with a transfer agent (P1-R) to exchange the R group and form a dormant species (Pn-R) and a new radical (P1.), which is capable of chain growth. (P.) would be generated by a classical initiator such as AIBN, BPO and redox reactions. (P.) can react with monomer, for propagation, with (P-R), for degenerative transfer, and can also react one with another, for termination.

2.2.1 Initiation Systems

Four main types of initiator have been used for the reversible deactivation of growing radicals in controlled free radical polymerization.

a) Organosulfides

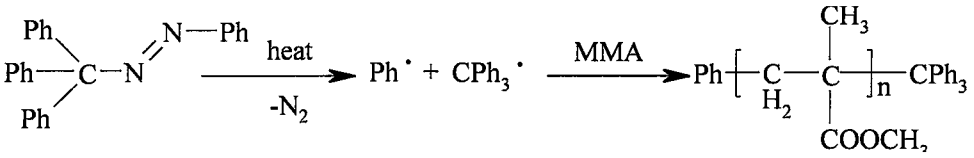
As discussed previously, the potential of organosulfides as initiators of living radical polymerization was first recognized by Otsu and Yoshida [19]. Living polymerization initiated by these species involves monomer insretion to C-S bond. BDC (Benzyl N,N-diethyl dithiocarbamate) and XDC (xylene bis (N-N diethyl dicarbamate), which are mono and di-functional photoiniferters, were used to initiate the living radical polymerizations of styrene and methyl methacrylate respectively [27]. As an example, living radical polymerization schematic of styrene with BDC is seen in (2.22).



(2.22)

b) Di and Triarylmethyl Derivatives

Otsu and Tezaki [28] reported on the use of triphenyl methyl azo-benzene as an initiator of living polymerization. The phenyl radical initiates polymerization and the triphenyl methyl radical reversibly terminates the chains.

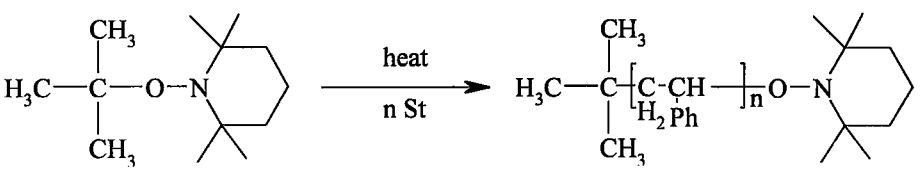


(2.23)

Living radical polymerization of methyl merthacrylate in the presence of triphenyl methyl azo-benzene is given in (2.23). The active end group of the initiator is reversibly decomposed over heating. The molecular weight of the polymer formed increases as the conversion increases and this is a one of the evidences of living radical polymerizations. Acar and Yagci [29] also used this initiator to prepare methacrylate block co-polymers.

c) Alkoxyamines

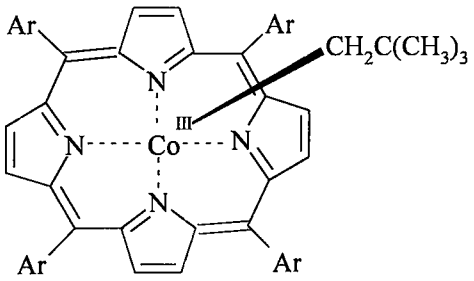
Rizzardo et al. [30] pioneered the use of alkoxyamines as initiators in living free radical polymerizations. The C-ON bond is relatively weak and undergoes homolysis on heating to yield a reactive carbon-centered radical and a stable nitroxide. The carbon-centered radical initiates the polymerization and the nitroxide radical is inert towards monomer but they react with the propagating radicals by primary radical termination to form new oligo- or polymeric alkoxyamine initiator. Controlled radical polymerization of styrene with an alkoxyamine type of initiator synthesized by the decomposition of azobis (isobutyronitrile) (AIBN) in the presence of 2,2,6,6-tetra methyl piperidine-N-oxyl (TEMPO) is given in (2.24) as an example.



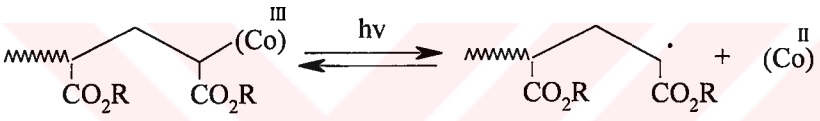
(2.24)

d) Organocobalt Compounds

Organocobalt compounds may function as initiators of quasi-living polymerization. Wayland et al. [26] have demonstrated that it is possible to synthesize high molecular weight poly (methyl acrylate) with very narrow polydispersities (1,1-1,3) using this reagents. A schematic representation of the pseudo-living radical polymerization of methyl acrylate with an organocobalt compound is seen in (2.

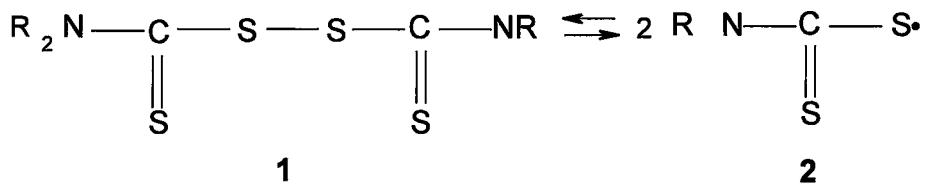


(2.25)



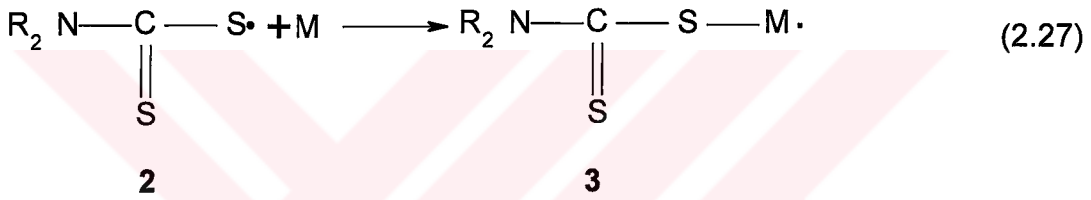
2.2.2 Iniferter Method

Iniferters are initiators that induce radical polymerization that proceeds via initiation propagation, primary radical termination, and transfer to initiator. Because bimolecular termination and other transfer reactions are negligible, these polymerizations are performed by the insertion of the monomer molecules into the iniferter bond, leading to polymers with two iniferter fragments at the chain ends The use of well-designed iniferters would give polymers or oligomers bearing. controlled end groups. If the end groups of the polymers obtained by a suitable iniferter serve further as a polymeric iniferter, these polymerizations proceed by a living radical polymerization mechanism in a homogenous system. In these cases, the iniferters (C-S bond) are considered a dormant species of the initiating and propagating radicals. Iniferters can be classified into several types: thermal or photoiniferters ;monomeric ,polymeric or gel iniferters ;monofunctional, difunctional, trifunctional or polyfunctional iniferters ;monomer or macro monomeriniferters.

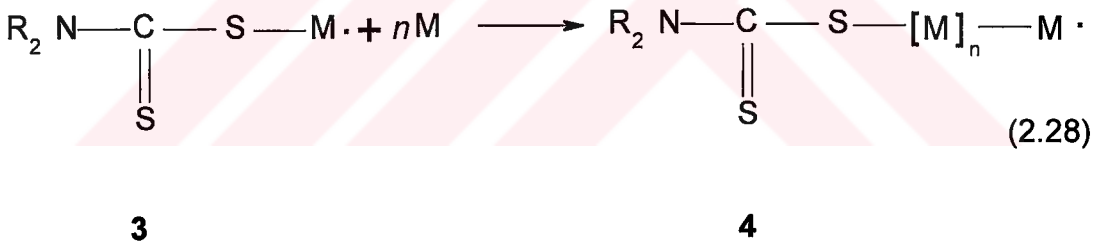


1 2 (2.26)

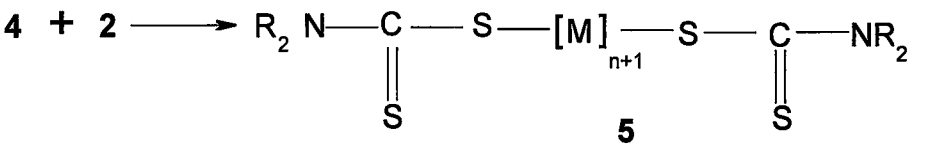
From the kinetic studies[31-32](2.26-1) was found to act not only as an initiator but also as a retarder, terminator, and transfer agent .Therefore, the polymerization of the monomer(M) with (2.26-1) proceeds via the dissociation of (2.26-1), initiation ,propagation, primary radical termination and chain transfer to (2.26-1), according to eqs (2.26-2.30)[32]respectively:



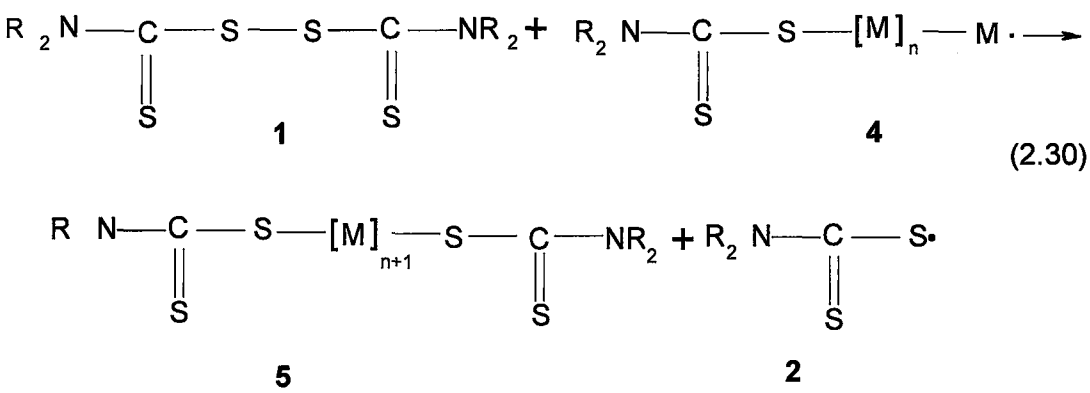
2 3 (2.27)



3 4 (2.28)



5 (2.29)



(2.30)

The ordinary bimolecular termination is neglected because primary radical (2.27-2) is less reactive for initiation and more reactive for primary radical termination. The chain transfer to (2.26-1) also occurs because the chain transfer constants are high values[33] 0,72 for St and 0,48 MMA at 60°C, yielding a relatively low molecular weight polymer ,(2.29-5), with two sulfide end groups.

When we consider polymer formation by radical polymerization, there are two extreme cases in regard to the activity of the initiators used :

Case 1 is radical polymerization with the usual strong initiators leading to high MW polymers without controlled end groups because bimolecular termination occurs by combination or disproportionation. However, the bulk polymerization of St benzoyl peroxide or AIBN gives a polymer with two initiator fragments, because the termination for St occurs only by combination .

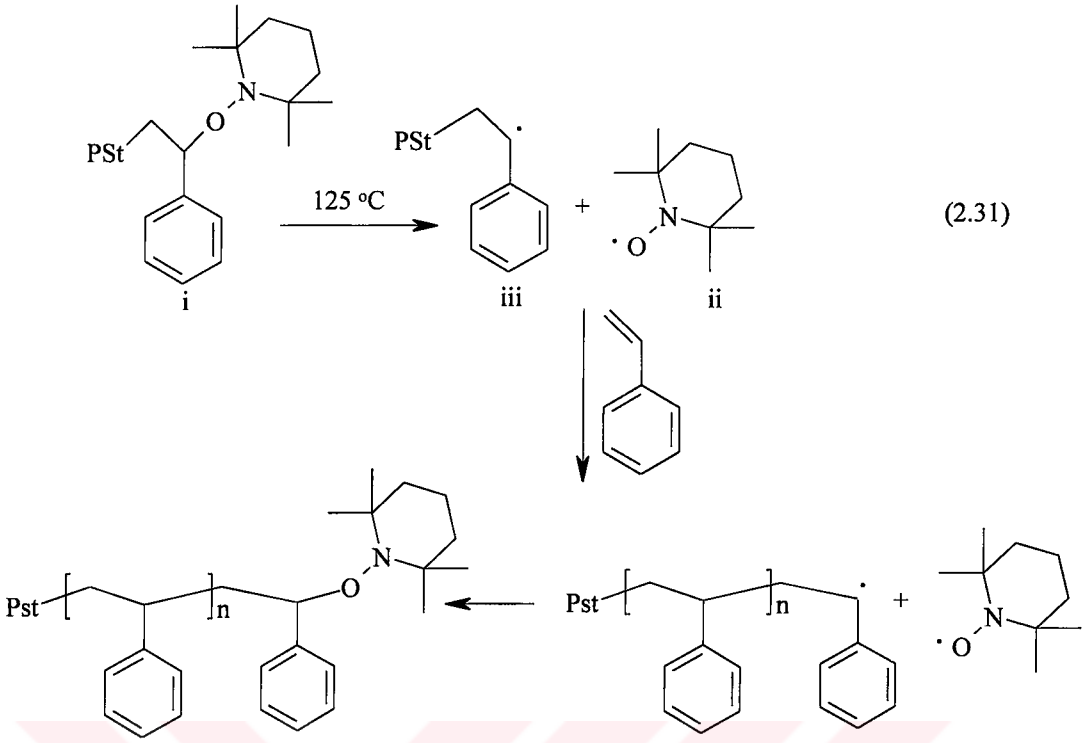
Case2 : Involves weak initiators such as (2.26-1) or chain transfer agents in which bimolecular termination is negligible and the polymers with controlled ends are formed by primary radical termination and chain transfer reaction . These polymerizations proceed by an insertion of monomer, (2.29-5) ,and the MWs of the polymers do not change or increase with the reaction time. These polymerization might provide a new route for preparing specialty polymers. As described in Case 2 if the initiators such as 1 induce such radical polymerization polymers with two initiators fragments at their ends such as, (2.29-5) are obtained as the result of monomer insertion . The use of well-designed initiators give various polymers with controlled end groups such as block polymers.

2.2.3 Stable Free Radical Polymerization (SFRP)

Early attempts to realize a living free radical procedure involved the concept of reversible termination of growing polymer chains by interferters, as discussed previously. Unfortunately, this strategy suffered from high polydispersities, because the stable radicals formed in iniferter case can further initiate chain polymerization and so reduce the control over the molecular weight and chain ends. Moad and Rizzardo [34] adopted a different approach and introduced the reversible end capping of the propagating chain ends by nitroxide free radicals, like 2,2,6,6-tetramethylpiperidinyl 1-oxy (TEMPO).

The use of TEMPO in living free radical polymerization was subsequently refined by Georges et al. who demonstrated that polystyrene with low polydispersity could be prepared using bulk polymerization conditions. These two seminal reports resulted in the true developments of living free radical procedures.

The origin of the unprecedented control in niroxide mediated living free radical polymerizations is believed to be the reversible termination of the growing polymeric radical to give a dormant, or inactive, species in which the nitroxide moiety is covalently bound to the polymer chain end. At lower temperatures, this trapping simply results in termination of the polymerization reaction, and infact nitroxides are good inhibitors for vinyl monomers. However, at elevated temperatures, typically 100 °C or greater, the C-ON bond of alkoxyamine t2ype of initiator, as seen in (2.30) as (i), is homolytically unstable and undergoes fragmentation to regenerate the stable free nitroxide radical (ii) and the polymeric radical (iii). The polymeric radical can then undergo chain extension with monomer to yield a similar polymeric radical in which the degree of polymerization has increased. The recombination of this finally formed polymeric radical with nitroxide then gives again dormant species, which essentially has the same structure as (i) and the cycle of homolysis / monomer addition can repeated as seen in (2.31).



(2.31)

Since the mediating nitroxide free radical does not initiate the polymerization of vinyl monomers, no additional propagating centers are created. An extremely favorable consequence of the presence of significant amounts of covalent, or inactive, chain ends is that the overall concentration of reactive chain ends is decreased substantially. This lowers the occurrence of unwanted side reactions such as termination, disproportionation, or combination, which enables the polymer chain to grow in a controlled process. However it should be pointed out that the occurrence of these side reactions is not eliminated, in the strictest sense, the polymerizations are not truly living. The possible side reactions also include the auto polymerization, e.g. of styrene, because at elevated temperatures for example higher than 100°C, styrene polymerizes by self initiation via formation of Diels-Alder adduct, which is further aromatized, generating radicals.

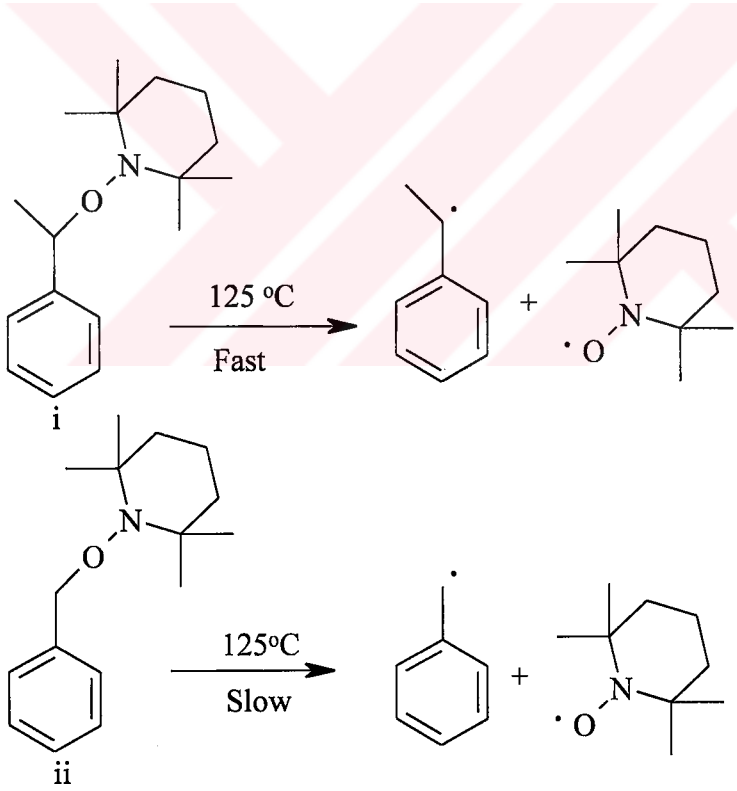
2.2.3.1 Mechanical Considerations

1) Structural effects of unimolecular Initiators

The alkoxyamine type of initiators, which on decomposition, gives an initiating8 benzylic radical and a nitroxide radical in the desired 1:1 stoichiometry. It has

recently been shown that the strength of the C-ON bond in alkoxyamine-based initiator is of crucial importance to the success of living free radical polymerization. If C-ON bond is too thermally stable then the homolysis is slow compared to the propagation, leading to uncontrolled polymerizations.

It was found that a variety of functional groups could be substituted on the aromatic ring, nitroxide unit or β-carbon without affecting the polymerization process deleteriously. However if the α-methyl group is removed to give parent benzyl-TEMPO derivative, as seen in (2.32) as (ii), a substantial loss of control over the polymerization is observed in the study of Malmstrom and Hawker [18]. The reasons for this dramatic change are shown in the same work as the difference in stability, or rate of formation, for the initiating benzylic radical.



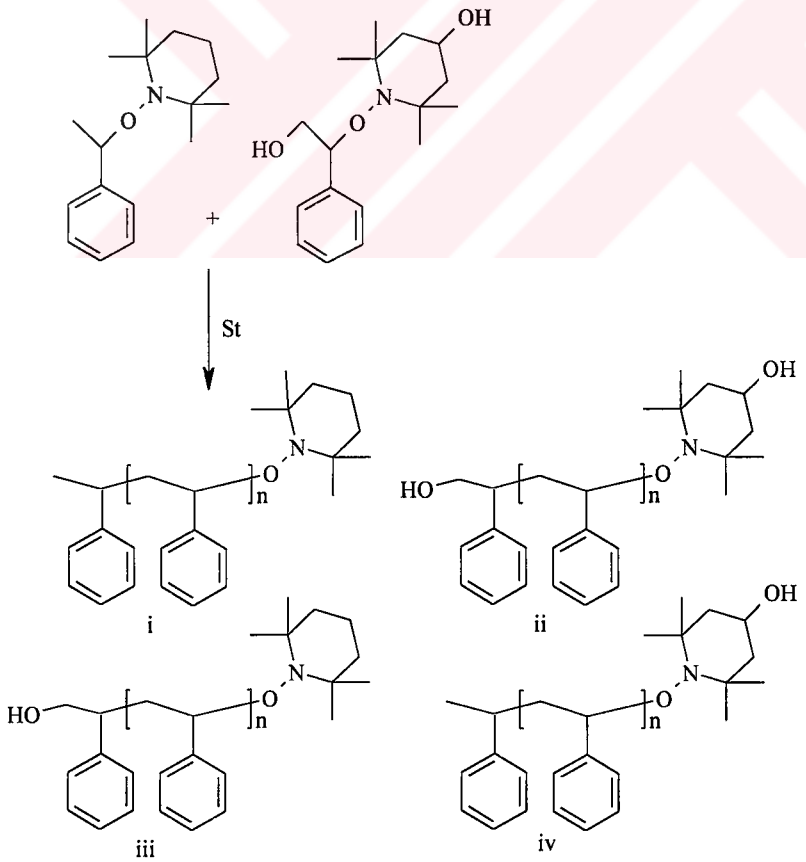
(2.32)

The steric or electronic nature of nitroxide can significantly increase the rate of polymerization [35]. For example Puts and Sogah [36] have shown that by replacement of two methyl groups with pheny groups to give 2,5-dimethyl-2,5-diphenylpyrolidine-1-oxyl, instead of TEMPO, a significant increase in the reaction

rates is observed, which allows the polymerization to be conducted at lower temperatures.

2) Mobility of Nitroxide Radical

The propagation step in nitroxide living free radical polymerization may either occur via an associative, or insertion type, mechanism or by dissociative mechanism, in which the nitroxide completely dissociates from the growing polymer chain end. To determine which of these are operating, Malmstrom and Hawker (1998) conducted series of experiments in the standard living polymerization conditions and in the presence of two similar initiators, which differ from each other in the presence of, or absence of hydroxy groups. Theoretically if an insertion type occurs only two products should be formed, seen in (2.33) as (i) and (ii). However, nitroxide is free to diffuse into polymerization medium and undergoes exchange with other propagating chain ends and so as a result, (iii) and (iv) types of products could also be obtained.



(2.33)

3) Role of Auto-polymerization

Since the stable free radical polymerizations are conducted at relatively high temperatures, auto-polymerization should not be ignored. To gain a better understanding of auto-polymerization a series of experiments, in which styrene was heated at 125°C in the absence of initiator, but in the presence of a nitroxy radical, TEMPO, was conducted by Malmstrom and Hawker [18]. At the end of the experiments polymers having low polydispersities and molecular weights that corresponded to the theoretically calculated ones were obtained. This shows that unexpectedly high degree of control occurred meaning that chains are being initiated by auto-polymerization, with growing radicals is high enough polymerization starts. This is evidenced by long induction period. As a result, according to Matyjaszevski it is not necessary to use radical initiators in SFRP of styrene.the role of nitroxide being to control the polymerization. The radicals are slowly formed during the polymerization. The radicals formed by self-initiation are initially trapped by the scavengers and then when the concentration of the scavengers is low enough and the concentration of the

The studies on the SFRP techniques generally show that;

a) Rate of the polymerization is dependent firstly on the monomer and then the alkoxyamine concentration.

b) Molecular weights increase linearly as the conversion and good control over the polymerization is obtained up to the molecular weights of 30000.

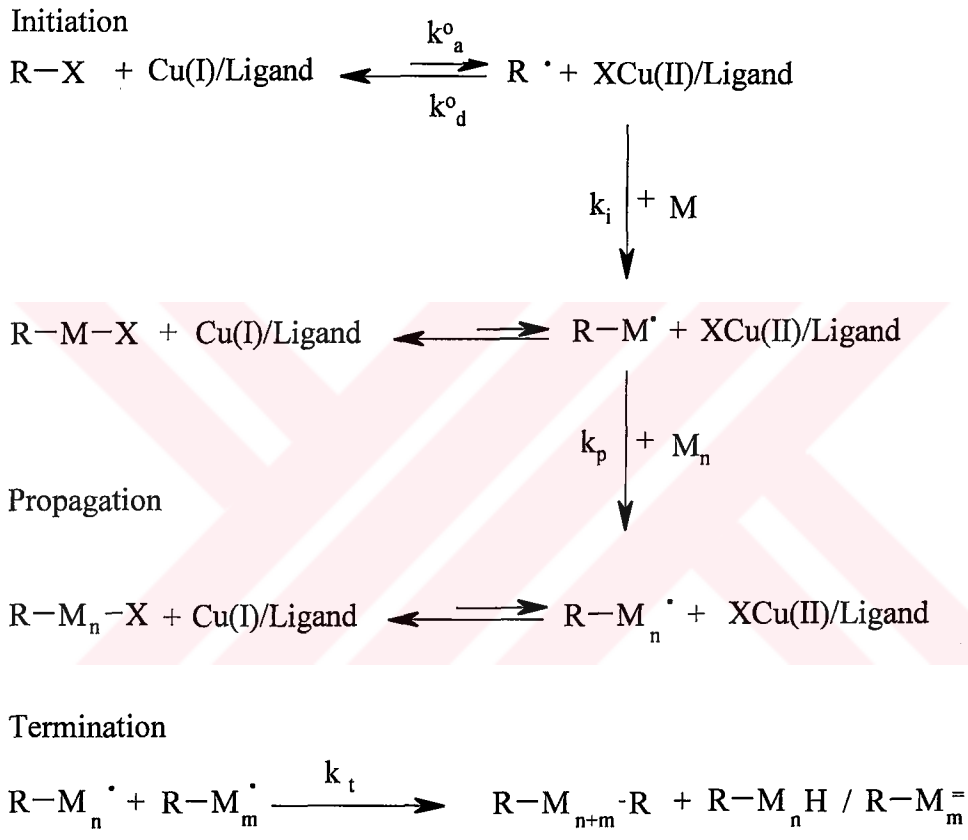
c) Polydispersities of smaller than 1,5 can be achieved.

d) The concentrations of TEMPO during the polymerization is about %0,1 –1 of that of TEMPO in the beginning.

2.2.4 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization is one of the most widely used living free radical polymerization techniques and seems to be the most versatile one. This technique can successfully be applied to the living radical polymerization of methyl methacrylate, acrylate and styrene monomers with well-controlled molecular weights and well-defined structures [37-40]. A typical ATRP system consists of alkyl halides,

as initiators, copper (I) halides complexed with some ligand(s), and of course monomer. Cu / Ligand complex behaves as a halogen atom transfer agent between the active and the dormant chains. By using an activated alkyl halide as an initiator, all of the chains can start growing at the same time. Furthermore, the equilibrium between the active and the dormant chains ensures a low concentration of propagating radicals and thus reduces the probability of termination. The schematic representation of the mechanism of ATRP is given in (2.34).



(2.34)

ATRP is a multi-component system, so concentrations and the structures of all these compounds affect the polymerization rate and the properties of the resulting polymer.

2.2.4.1 Initiators

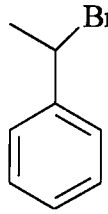
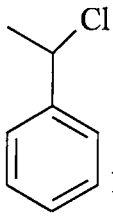
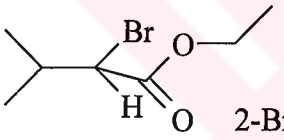
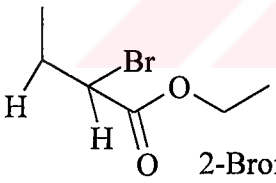
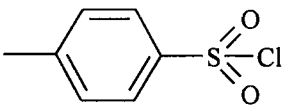
Organic halides, initiators, may either be a small molecule or a macromolecule. Hence, a variety of halogenated initiators and macro initiators activated by various types of aryl, sulfonyl and carbonyl groups can be used in ATRP systems.

A fast equilibrium between the active and the dormant chains is needed to observe low polydispersities in controlled or living radical polymerizations. In ATRP both

effective initiation and good control of the polymerization relay heavily on the position of the equilibrium in both the initiation and the propagation steps, and also on reactivities of the radicals generated in the initiation step. Thus, choosing a suitable organic halide and Cu(I) halide is necessary for the controlled polymerization.

The initiator usually, but not always, should have a structure homologous to the corresponding polymer end group. The most frequently used initiator types in ATRP systems are given in Table 2.1.

Table 2.1 Types of initiators used in ATRP sytems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethyl isobutyrate	Methylmethacrylate
 2-Bromo ethyl propionate	Methacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

2.2.4.2 Transition Metals Used in ATRP

Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting X-Mt $^{n+1}$ species (higher oxidation state of metal). The metal should participate in a one-electron process, which should result in oxidative addition / reductive elimination but not in atom transfers process. Additionally, the metal should have a high affinity for atom / group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β -hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control of the process. The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle Mt ^{n} / Mt $^{n+1}$ but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus the inner coordination sphere of Mt ^{n} must expand to accommodate a new X (halide) ligand. Expansion from tetra to penta-coordinated structure Cu (I) / 2 ligand $\rightarrow$ X-Cu (II) / 2 ligand or penta-coordinated structure X_2Fe (II) / $3PR_3 \rightarrow X_3Fe$ (III) / $3PR_3$ the most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, Ni(II), Ru(II) / Al $(OR)_3$ and Fe(II) / $3PR_3$.

2.2.4.3 Ligand

The role of ligands is three-fold. They affect the redox chemistry by their electronic effects. They control the selectivity by steric / electronic effects and they also make the catalytic system soluble. The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N",N" pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimetylamino) ethyl]amine (Me-TREN) and Alkylpyrdylmethanimines are also used.

Among all these ligands, amine ligands have been attracting the interest of the scientist in recent years. Since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper bipy complexes, the employment of the simple amines in ATRP may lead to faster polymerization rates [41]. The study of Xia and Matyjaszevski [41] also shows that when bipy or

TMEDA is used as ligand, a copper(I) to ligand ratio is usually selected as 1:2, while in the case of PMDETA is chosen as the ligand the ratio of 1:1 is sufficient to achieve maximum rates and control of polymerization. The low polydispersities can be ascribed to the less sterically hindered copper(II)-PMDETA complex, which facilitates the deactivation process

2.2.4.4 Monomers

In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. The polydispersities of the polymers obtained via ATRP techniques should be between 1,05 and 1,5.

2.2.4.5 Effects of Other Parameters

At higher temperatures ATRP usually gives better results, because K $°_{eq}$ and k_p, equilibrium and rate of propagation constants in ATRP respectively, increase as the temperature increases. The activation energy in the propagation step is much more higher than that in termination, either by disproportionation or combination, step resulting in higher kp / kt ratios leading to better control of polymerization at elevated temperatures. On the other hand, since the possibility of occurrence of the termination and the side reactions at high temperatures becomes more significant, it is necessary to make an optimization depending on the molecular weight and the functionality that the resulting polymer wanted to have.

When ATRP is conducted in a solvent, the rate of polymerization has been found to be slower with compared to solvent-free atom transfer radical polymerizations. 20As a result it can be said that using solvent in ATRP reduces the rate of the polymerization.

2.2.4.6 Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction usually negative first order with respect to the deactivator (CuX_2 / Ligand).

The rate equation of ATRP is obtained by the aid of some assumptions such that the contribution of termination on the rate of the polymerization is ignored, the initiating molecules are completely consumed in the initiation step and fast equilibrium, which is necessary for getting low polydispersities, is ensured. The rate of polymerization is formulated in discussed conditions and given in (2.35).

$$R_p = k_{app}[M] = k_p[P\cdot][M] = k_p K_{eq}[I]_O \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.35)$$

Control of the polymerization and thus the resulting polymer depends not only on the concentration of the growing radicals but also on the rate of propagation and deactivation steps in atom transfer radical polymerization. If the deactivation does not occurs, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in (2.36).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d[RX]_0}{k_p[XCu^{II}]}\right)\left(\frac{2}{p} - 1\right) \qquad (2.36)$$

p= poymerization yield
$[RX_0]$=concentration of the functional polymer chain
$[XCu^{II}]$=concentration of the deactivators
k_d=rate of deactivation
k_p=rate of propagation

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersites are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

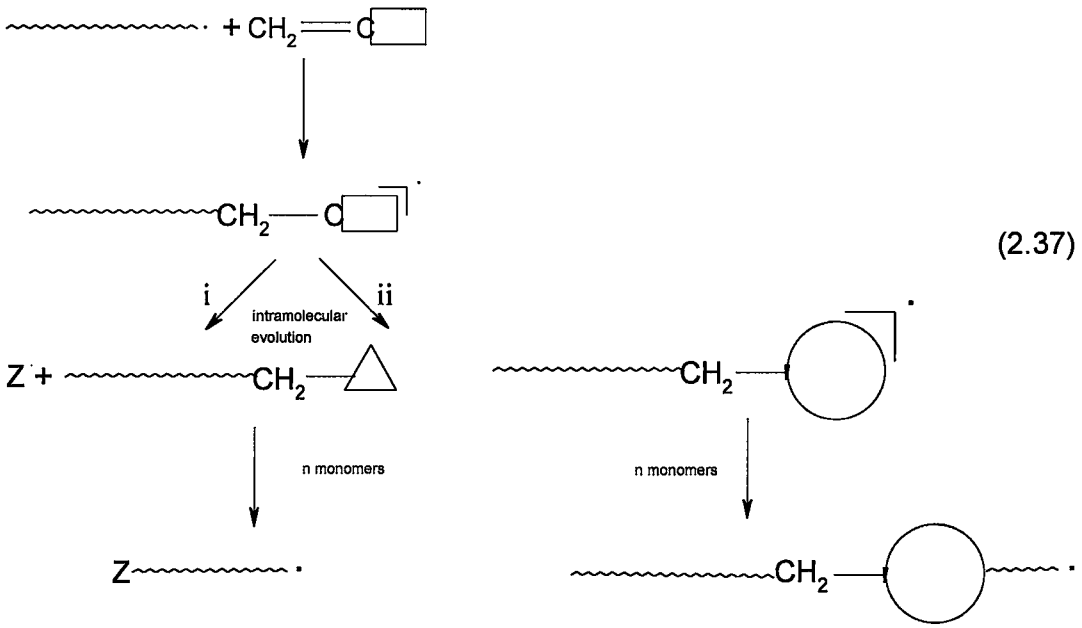
b) For the higher ratios of k_p / k_d, higher polydispersities (molecular weigh distributions) are usually obtained.

c) Resulting molecular weight distribution decreases as the concentration of the deactivators decreases.

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control over the molecular weights and the molecular weight distributions of the resulting polymers. Additionally, since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

2.2.5 Addition –Fragmentation Process

An addition-fragmentation process is said to occur in free radical polymerization whenever a growing polymer chain reacts with a compound bearing both an activated site of unsaturation and a weak bond located somewhere else in the molecule. The intermediate radical formed by the addition of propagating radical on the transfer agent undergoes fragmentation involving the weak bond generating another radical which can enter the polymerization cycle. Such a process occurs with the formation of a functional group on the backbone of the polymer(which carried also radical, Scheme (2.37-i) or at the end of the polymer chain (the radical resting another molecule Scheme (2.37-ii). The former case involves the use of an addition-fragmentation monomer and the latter the introduction of an addition-fragmentation chain transfer agent in the polymerization medium Scheme (2.37)



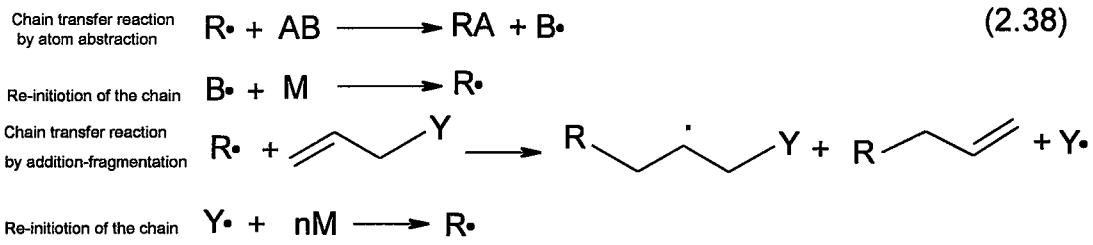
(2.37)

Many monomer and transfer agents based on these types of skeleton have already been developed . However the actual use of an addition-fragmentation chain transfer

agent or of an addition-fragmentation monomer in industrial applications is still limited at the present time ,because of various problems arising from their synthesis ,polymerizability and properties, although such compounds could inherently be useful in most industrial applications.

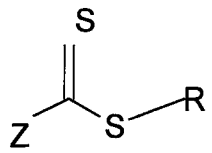
The control of molar mass in free radical polymerization is usually achieved by the addition of a chain transfer agent in the polymerization medium[42]. When a chain carrying radical is trapped by another specific compound XY to produce a radical Y• which is also reactive ,this radical Y• can re-initiate anew radical chain. In this case XY is called a chain transfer agent. Two kinds of chain transfer agents can be distinguished according to their mode of action:

1. *Atom or group transfer agents* operating by an abstraction pathway (scheme2.37) These additives are generally solvents such as CCl_4, mercaptans, substituted disulfides which react in the medium as atom donors to the growing macro radicals, thus terminating the polymer chain and generating, respectively a trichloromethyl a thiyl radical, able to re-initiate polymerization[43,44]
2. *Addition-fragmentation chain transfer agents* (scheme2.38) [43,44] The chain transfer agents which fallow the addition-fragmentation mechanism are particular interest in organic and polymer chemistry. Recently many studies have shown that ally, acrylyl and allenyl transfer to alkyl halides represent powerful synthetic tolls to prepare sophisticated molecules. Such a process was also identified as an effective means for controlling the molar mass of vinyl polymers ,avoiding the use of conventional chain transfer agents based on thioderivatives.



Thiocarbonylthio compounds of general structure (2.39-1) confer living characteristics to radical polymerization [45-46]. These reagents function by

establishing a dynamic equilibrium between propagating radicals ($P_n^{\bullet}$) and dormant chains (2.39-2) by a mechanism of reversible addition–fragmentation chain transfer (raft) as shown in scheme (2.39) 1.RAFT agents (2.39-1) function effectively only when the substituent on sulfur (R) is good homolytic leaving group when compared to the polymer chain P_n. With appropriate choice of the RAFT agent (2.39-1) a wide range of polymers of predetermined MW and narrow polydispersity can be prepared [45,46,47] The versatility and convenience of this process offer distinct advantages over other forms of living radical polymerization.[48-49]



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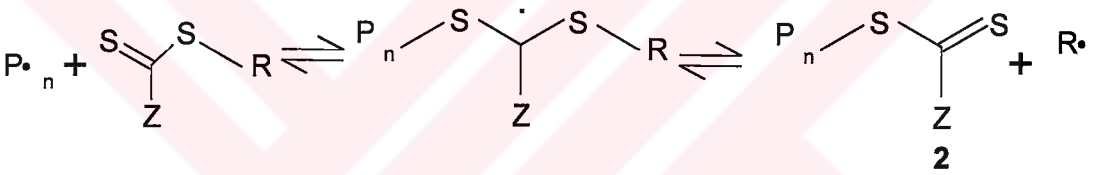
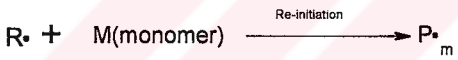
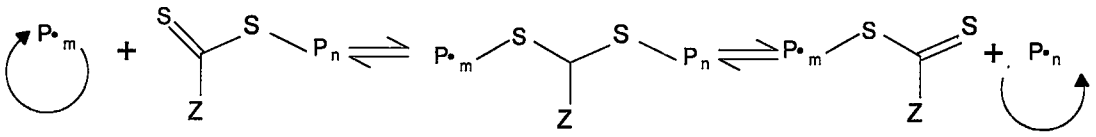




(2.39)

Equilibration



3. EXPERIMENTAL PART

3.1 CHEMICALS USED

a) Monomer

Methyl methacrylate (MMA, 99% Fluka) was passed through basic alumina column to remove inhibitors and then dried over CaH_2 and distilled under reduced pressure prior to use.

b) Solvents

Tetrahydrofuran (THF, 99.8%, J.T. Baker HPLC grade) was dried and distilled over lithium aluminium hydride. Diphenylether (DPE) (Aldrich) was used as received.

c) Ligand

Triphenylphosphine (Aldrich) was recrystallized from ethanol to eliminate triphenylphosphine oxide.

b) Other materials

$FeCl_3.6H_2O$ (Aldrich) was used as received

3.2 Synthesis of Poly (methyl methacrylate) under vacuum in solution.

The general procedure for atom transfer radical polymerization (ATRP) was as follows; to a schlenk tube equipped with magnetic stirring bar, degassed monomer , solvent ,ligand and catalyst were added in the order mentioned. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in thermostated oil bath at given temperature, 90°C for the ATRP studies in this work. After the polymerization, the reaction mixture was diluted with THF . Poly (methyl methacrylate), PMMA, sample was dissolved in THF and precipitated hexane, filtered and dried in vacuum oven at 50°C for overnight. The conversions were determined by gravimetrically. PMMA was prepared in 50 vol% diphenylether (DPE) solution at 90°C using $FeCl_3.6H_2O$ / PPh_3.

3.3 Synthesis of Poly (methyl methacrylate) under vacuum in bulk

The general procedure for atom transfer radical polymerization (ATRP) was as follows; to a schlenk tube equipped with magnetic stirring bar, degassed monomer, ligand, and catalyst were added in the order mentioned. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in thermostated oil bath at given temperature, 90°C for the ATRP studies in this work. After the polymerization, the reaction mixture was diluted with THF . Poly (methyl methacrylate), PMMA, sample was dissolved in THF and precipitated hexane, filtered and dried in vacuum oven at 50°C for overnight. The conversions were determined by gravimetrically. PMMA was prepared in bulk at 90°C using $FeCl_3.6H_2O$ / PPh_3.

3.4 Synthesis of Poly (methyl methacrylate) in the presence of air

All manipulations were performed in air. To a pyrex tube (approximately 27 mL in volume) equipment with the magnetic stirring bar monomer ligand , catalyst were added in order to mentioned. Tubes were closed with the rubber septum and placed in thermostated oil bath at given temperature, 90°C . After the polymerization, the reaction mixture was diluted with THF . Poly (methyl methacrylate), PMMA, sample was dissolved in THF and precipitated hexane, filtered and dried in vacuum oven at 50°C for overnight. The conversions were determined by gravimetrically.

3.5 Characterization

Gel permeation chromatographic (GPC) analysis were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was used as the eluent at a flow rate of 0,3 mL/min. Molecular weight of the polymers was calculated with the aid of polystyrene standards. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC 250 (250 MHz for proton and 62.90 MHz for carbon) in $CDCL_3$. UV-visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in dichloromethane.

4. RESULTS AND DISCUSSIONS

4.1 Synthesis of Poly (methyl methacrylate) under vacuum in bulk

The polymerization of MMA was carried out in bulk with the $FeCl_3 .6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0:[FeCl_3.6H_2O]_0:[PPh_3]_0$ = 60:0,5:1,5, the results are shown in Figure: 4.1.

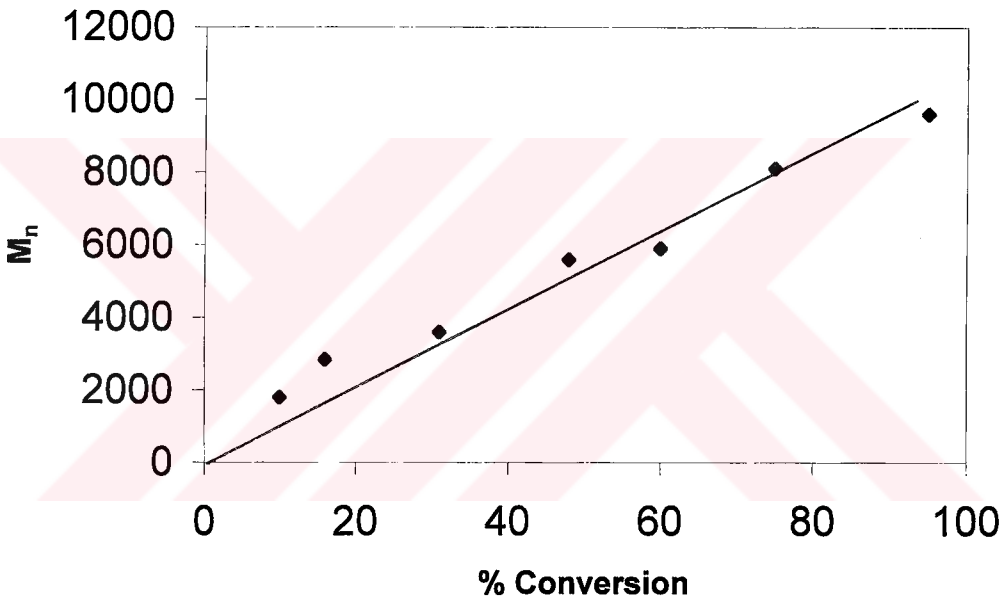


Figure: 4.1 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 90°C with $[MMA]_0:[FeCl_3 .6H_2O]_0:[PPh_3]_0$ = 60:0,5:1,5, $[MMA]_0$ = 9,35M

It shows that M_n(GPC) , the number-average molecular weight measured by GPC, increase linearly with conversion from 1800 to 9600, and the polydispersity index slightly close to 1,06 - 1,15 as the monomer conversion is increased from 10 to 95 respectively. It indicates that polymerization has proceeded like an conventional ATRP. However, the efficiencies of initiation *f* are generally low ($Mn_{theo.}/Mn_{GPC}$) 0.56. Also polymerization of MMA is slower when it get high conversion.

In a plot of $\ln([M]_0/[M])$ vs time as shown in Figure 4.2, a straight line is observed, indicated that the kinetics is first order in monomer. This means that the concentration of propagating radicals is constant during the polymerization.

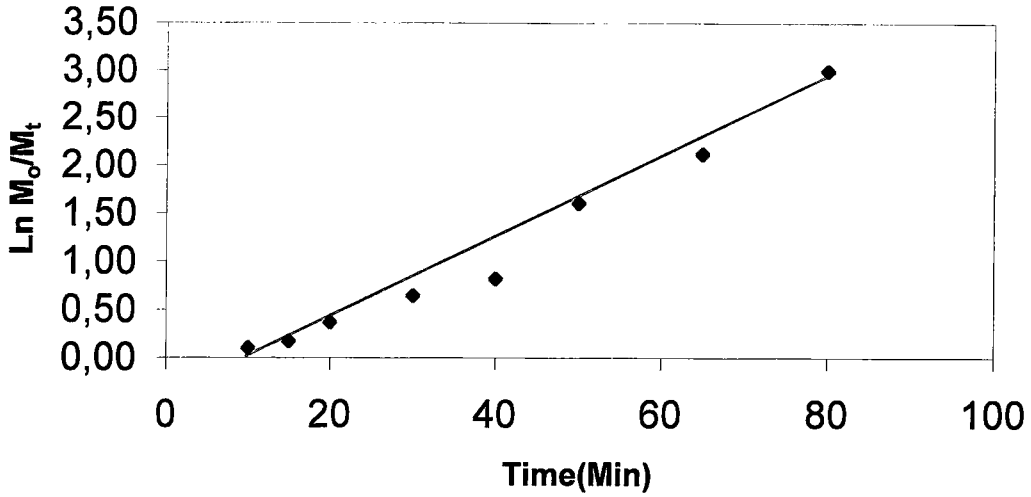


Figure 4.2: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 60:0,5:1,5 $[MMA]_0$ = 9,35M

To understand how concentration of radicals effect on the polymerization of MMA by decreasing the ratio of $[MMA]_0$/[$FeCl_3 .6H_2O]_0$.Firstly ; the polymerization of MMA was carried out in bulk with the $FeCl_3 .6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$:[$FeCl_3 .6H_2O$]$_0$:$[PPh_3]_0$ =120:0,5:1,5, the results are shown in Figure 4.3;

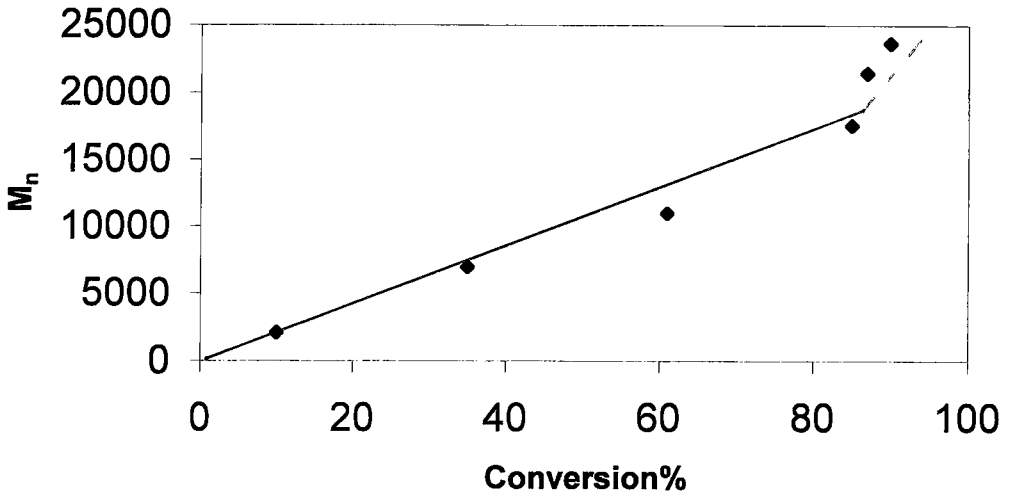


Figure: 4.3 Dependence of number average (Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 90°C with $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ =120:0,5:1,5 $[MMA]_0$= 9,35M

In a plot of $\ln([M]_0/[M])$ vs time as shown in Figure 4.4, a straight line is observed, indicated that the kinetics is first order in monomer. This means that the concentration of propagating radicals is constant of propagating radicals is constant during the polymerization. The polymerization of MMA was carried out in bulk with the $FeCl_3/PPh_3$ initiation system at 90°C. For $[MMA]_0$/[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 120:0,5:1,5, the results are shown in Figure 4.4. As it seen in figure 4.4 polymerization of MMA is getting slower when it reached high conversion.

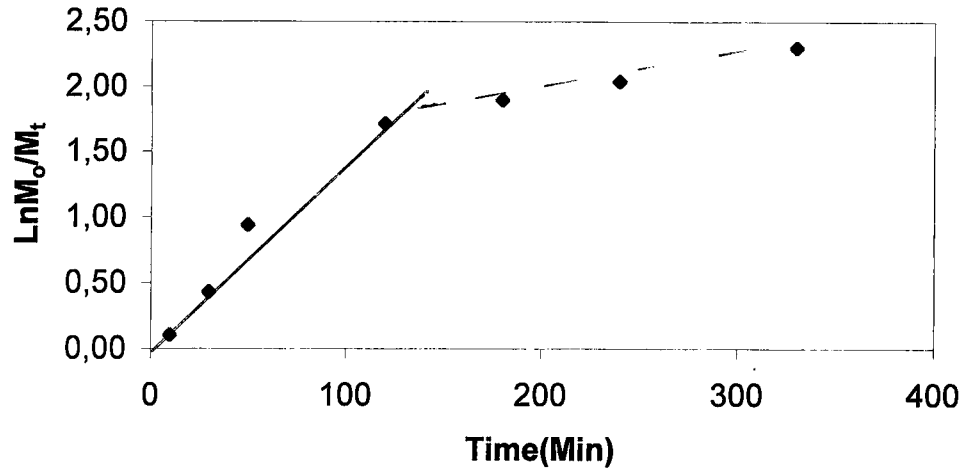


Figure 4.4: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with $[MMA]_0$: $[FeCl_3 .6H_2O]_0$: $[PPh_3]_0$ = 120:0,5:1,5, $[MMA]_0$= 9,35M

The polymerization of MMA by decreasing the ratio of $[MMA]_0/[FeCl_3.6H_2O]_0$.Secondly; the polymerization of MMA was carried out in bulk with the $FeCl_3.6H_2O/PPh_3$ initiation system at 90°C. For $[MMA]_0$: $FeCl_3.6H_2O]_0$:$[PPh_3]_0$ = 240:0,5:1,5,This results show us decreasing radicals inhibit the high conversion(78%). The results are shown in Figure 4.5;

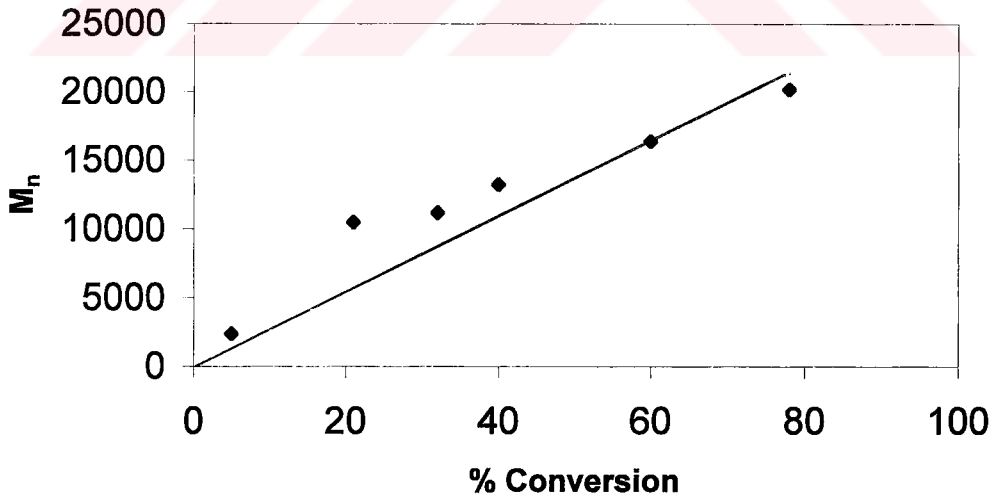


Figure: 4.5 Dependence of number average(Mn) molecular weight calculated from (GPC) on conversion in polymerization of MMA in bulk at 90°C with $[MMA]_0$: [$FeCl_3 .6H_2O$]$_0$:$[PPh_3]_0$ = 240:0,5:1,5, $[MMA]_0$= 9,35M

In a plot of ln([M]$_0$/[M]) vs time as shown in Figure 4.6, a straight line is observed, indicated that the kinetics is first order in monomer. This means that the concentration of propagating radicals is constant of propagating radicals is constant during the polymerization. The polymerization of MMA was carried out in bulk with the $FeCl_3 .6H_2O/PPh_3$ initiation system at 90°C.For $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 240:0,5:1,5, the results are shown in Figure 4.6. As it seen in figure 4.6 polymerization of MMA is getting slower when it reached high conversion.

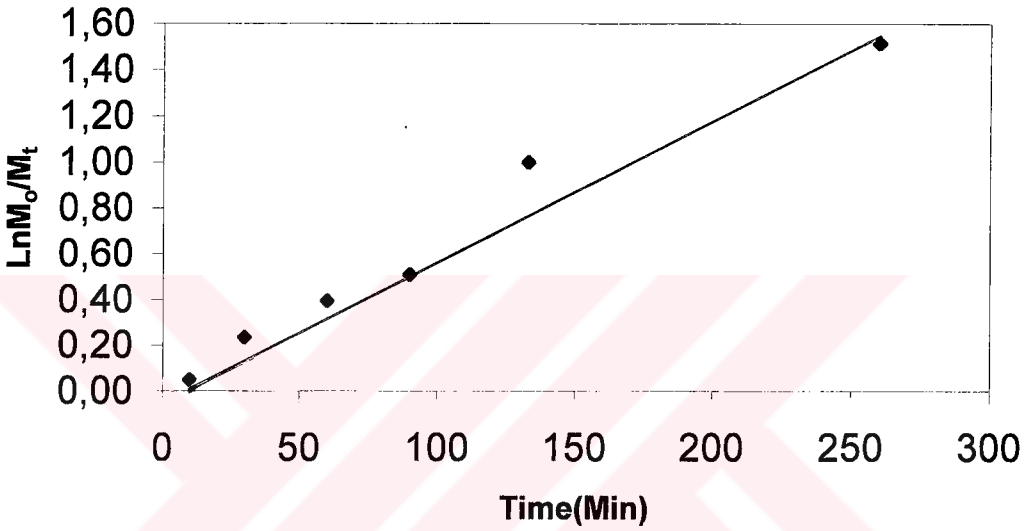


Figure 4.6: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with$[MMA]_0$:$[FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 120:0,5:1,5, $[MMA]_0$= 9,35M

4.2 Synthesis of Poly (methyl methacrylate) under vacuum in solution

The polymerization of MMA is getting slower when it reached high conversion in bulk polymerization. To overcome this problem I tried to polymerize PMMA in 50% vol. diphenyl ether (DPE) solution. The polymerization of PMMA was carried out in 50 vol % diphenylether (DPE) solution using $FeCl_3/PPh_3$ initiation system at 90°C. For $[MMA]_0$:[$FeCl_3$.$6H_2O$]$_0$:$[PPh_3]_0 \cong$ 120:0,5:1,5,the results are shown in Figure 4.7:

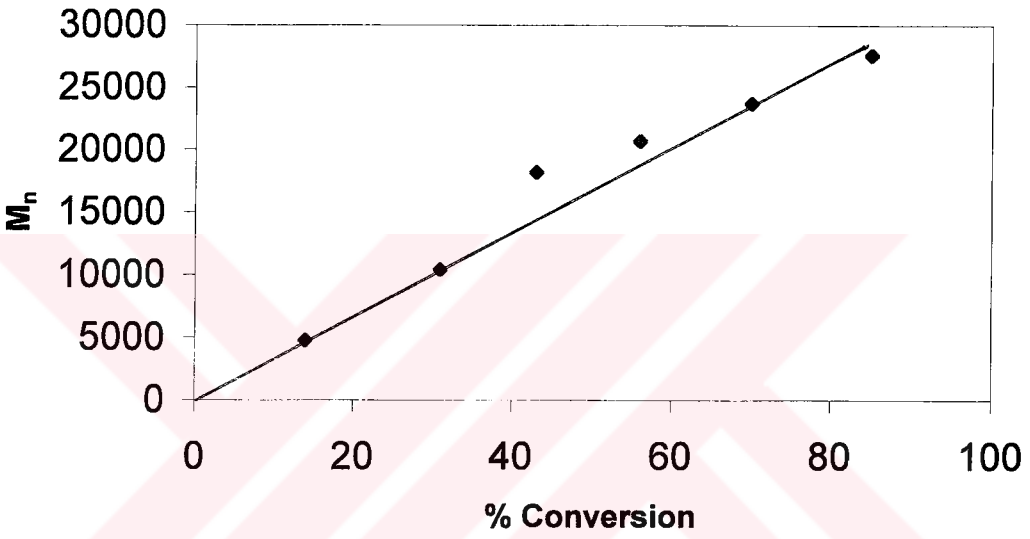


Figure: 4.7 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in 50 vol % diphenylether (DPE) solution using $FeCl_3$.$6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$:[$FeCl_3$.$6H_2O$]$_0$:$[PPh_3]_0$ = 120:0,5:1,5. $[MMA]_0$= 4,67 M

As a result we overcome this problem not reached high conversion by using DPE

In a plot of $\ln([M]_0/[M])$ vs time as shown in Figure 4.8, a straight line is observed, indicated that the kinetics is first order in monomer. This means that the concentration of propagating radicals is constant of propagating radicals is constant during the polymerization. The polymerization of MMA was carried out in50 vol % diphenylether (DPE) solution using $FeCl_3 .6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 120:0,5:1,5.

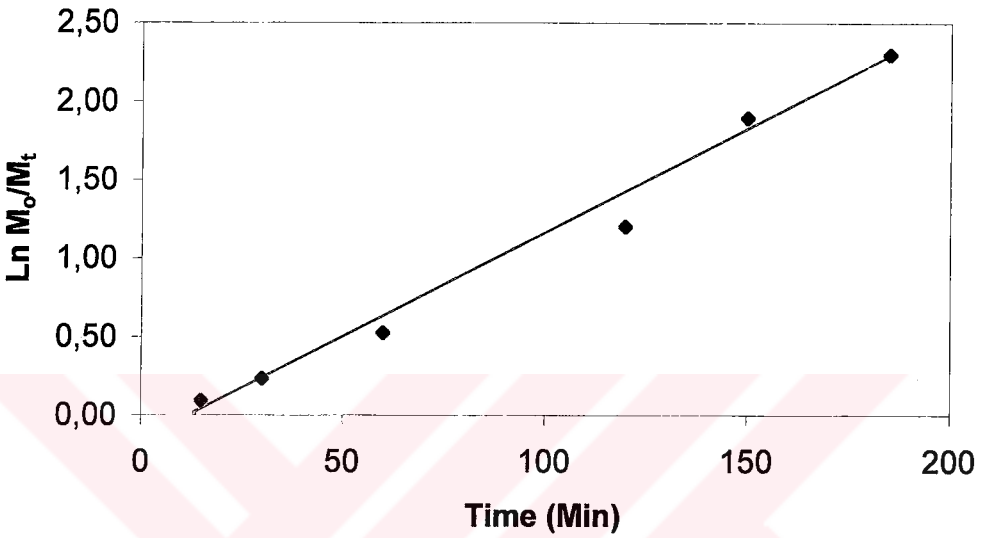


Figure 4.8: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in 50 vol % diphenylether (DPE) solution using $FeCl_3 .6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 120:0,5:1,5. $[MMA]_0$= 4,67 M

Figure 4.9 illustrated that conversion dependence of M_w/M_n for MMA polymerization.

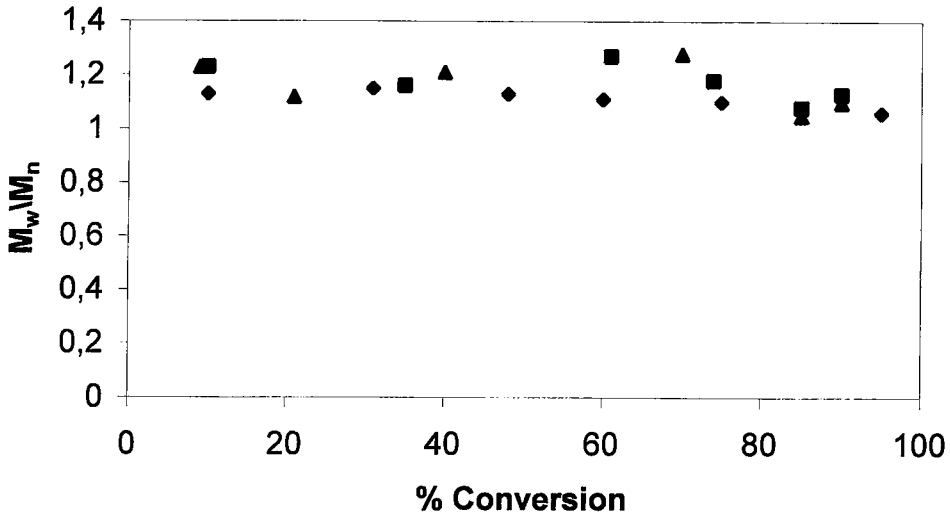


Figure 4.9 : ♦ represents polymerization of MMA in bulk at 90°C with $[MMA]_0$:[$FeCl_3$.$6H_2O$]$_0$:$[PPh_3]_0$ = 60:0,5:1,5, $[MMA]_0$ = 9,35M . ▲ represents polymerization of MMA in 50 vol % diphenylether (DPE) solution using $FeCl_3$.$6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$: [$FeCl_3$.$6H_2O$] $_0$:$[PPh_3]_0$ = 120:0,5:1,5. $[MMA]_0$ = 4,67 M. ■ represents polymerization of MMA in bulk at 90°C with $[MMA]_0$: [$FeCl_3$.$6H_2O$]$_0$: $[PPh_3]_0$ = 120:0,5:1,5, $[MMA]_0$= 9,35M

The polymerization of PMMA was carried out in 50 vol % diphenylether (DPE) solution using / $FeCl_3$.$6H_2O$ PPh_3 initiation system at 90°C. For $[MMA]_0$: $[FeCl_3 .6H_2O]_0$: $[PPh_3]_0$ = 240:0,5:1,5,the results are shown in Figure 4.10:

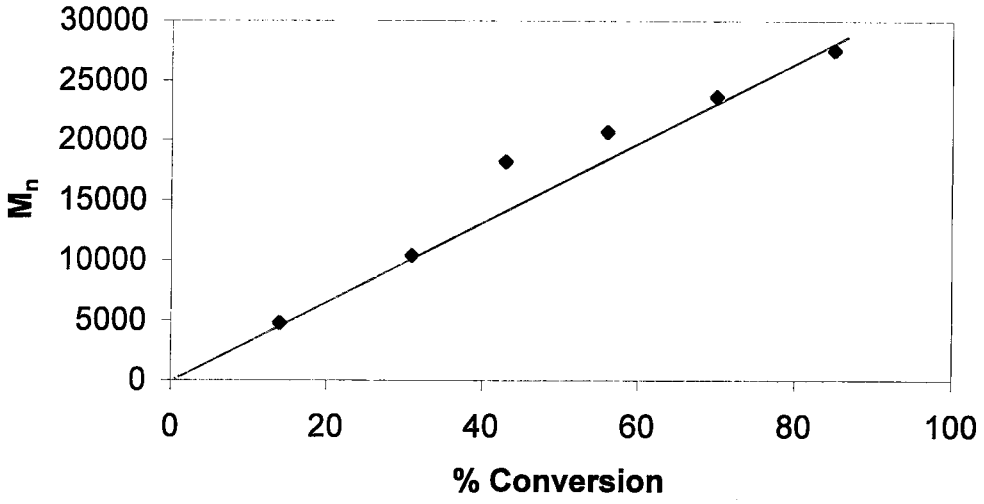


Figure: 4.10 Dependence of number average (Mn) molecular weight calculated from GPC on conversion in polymerization of MMA in 50 vol % diphenylether (DPE) solution using $FeCl_3$.$6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$: [$FeCl_3.6H_2O]_0$:$[PPh_3]_0$ = 240:0,5:1,5. $[MMA]_0$= 4,67 M

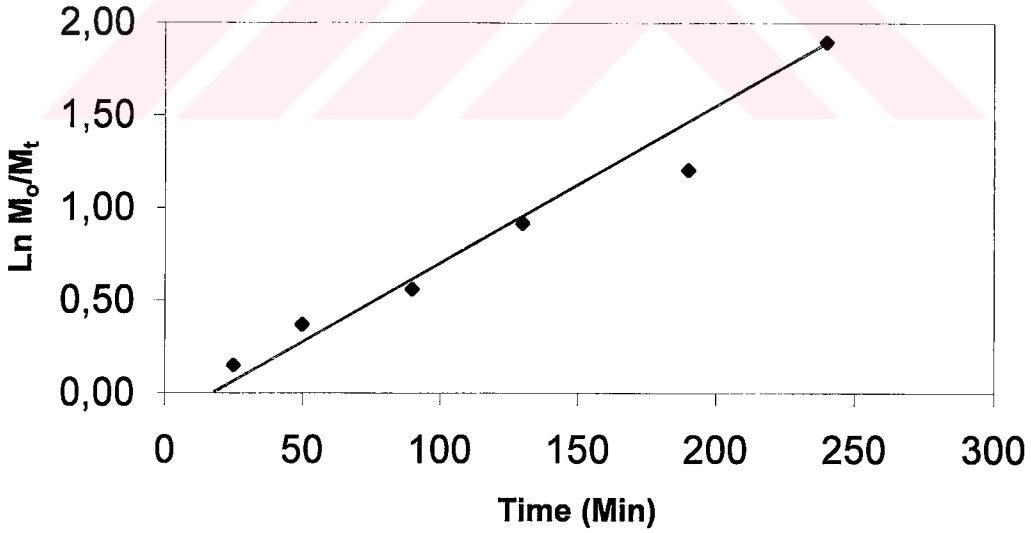


Figure 4.11 : Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in 50 vol % diphenylether (DPE) solution using $FeCl_3$.$6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$: $[FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 240:0,5:1,5. $[MMA]_0$= 4,67

4.3 Effect of the PPh_3 Ligand under vacuum

Table 4.1 illustrates the effect of triphenylphosphine on the MMA polymerization under vacuum.

Sample Name	$PPh_3/FeCl_3.6H_2O$	Time (min)	Conv. (%)	Mn_{theo}	Mn_{GPC}	M_W/M_n	Rp $mol.L^{-1}.sn^{-1}$
RUN1	0,50	15	9,5	600	1600	1,18	$9,9x10^{-4}$
RUN2	1,00	15	19,0	1150	2500	1,21	$1,9x10^{-3}$
RUN3	1,50	15	16,0	1000	2850	1,12	$1,65x10^{-3}$
RUN4	2,00	15	17,0	1000	1950	1,28	1,70x10-^{3}
RUN5	3,00	15	18,0	1100	2800	1,13	$1,90x10^{-3}$
RUN6	4,00	15	16,0	1000	1800	1,29	$1,63x10^{-3}$
RUN7	5,00	15	17,0	1000	2500	1,39	$1,74x10^{-3}$
RUN8	7,00	15	11,0	700	2200	1,45	$1,15x10^{-3}$

Table 4.1 the polymerization of MMA at 90°C with $FeCl_3$.$6H_2O$ /PPh_3 initiation system [M]o/$FeCl_3.6H_2O$ = 60 $[M]_0$= 9,35 M

As it seen Table 1 increasing the mole ratio of $PPh_3/FeCl_3.6H_2O$ is not effected on the monomer conversion except the minimum and maximum mole ratio of $PPh_3/FeCl_3.6H_2O$ (0,5;7.0). In this result conversion and rate of polymerization (Rp; $9,9x10^{-4}$, $1,15x10^{-3}$ $mol.L^{-1}.sn$) is slower than the other mole ratio.

The conversions were calculated gravimetrically by the following formula;

% Conversion = (W / M) * 100

Where W represents the weight of the formed polymer and M stands for the mass of the monomer initially taken.

The theoretical molecular weights were calculated by the formula of Mn_{theo} =($[M]_0$ /$[I]_0$ * conversion * $MW_{monomer}$),where $MW_{monomer}$ is the molecular weights of the monomer .

4.4 Synthesis of Poly (methyl methacrylate) in the presence of air in bulk

All manipulations were performed in air. To a Pyrex tube (approximately 27 mL in volume) equipment. The polymerization of MMA was carried out in bulk with the $FeCl_3 .6H_2O$ /PPh_3 initiation system at 90°C. For $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 60:0,5:1,5,the results are shown in Figure: 4.12

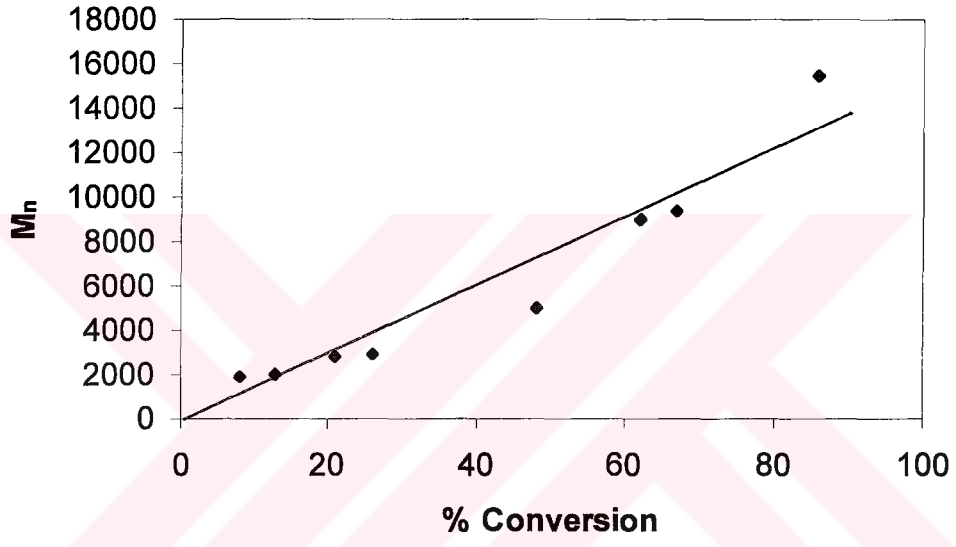


Figure: 4.12 Dependence of number average (Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in8 the presence of air in bulk at 90°C with $[MMA]_0$:[$FeCl_3 .6H_2O]_0$:$[PPh_3]_0$ = 60:0,5:1,5 $[MMA]_0$= 9,35M

It shows that $M_{n(GPC)}$, the number-average molecular weight measured by GPC, increase linearly with conversion from 1900 to 15500, as the monomer conversion is increased from 8 to 86 respectively. It indicates that polymerization has proceeded like an conventional atom transfer radical polymerization (ATRP).

In a plot of $\ln([M]_0/[M])$ vs time as shown in Figure 4.13, a straight line is observed, indicated that the kinetics is first order in monomer. This means that the concentration of propagating radicals is constant during the polymerization.

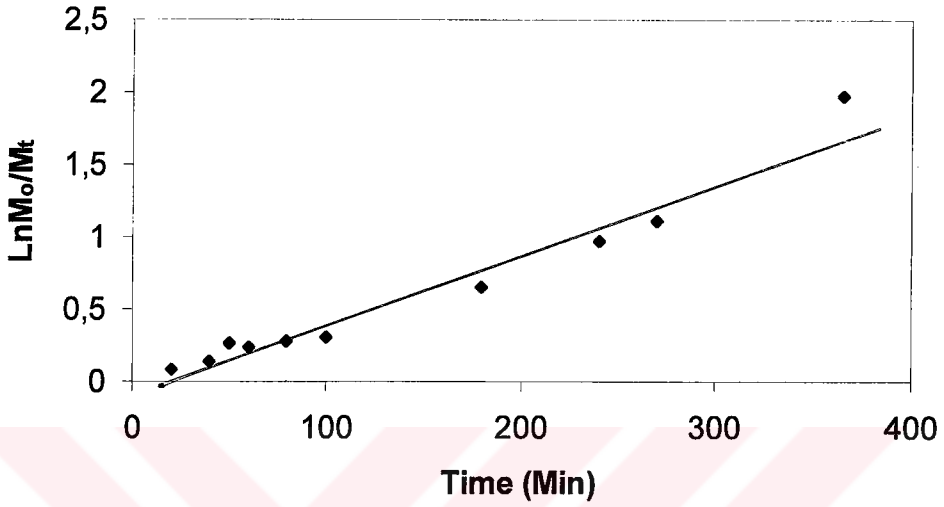


Figure 4.13: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in the presence of air in bulk at 90°C with $[MMA]_0$:$[FeCl_3]_0$:$[PPh_3]_0$ = 60:0,5:1,5, $[MMA]_0$= 9,35M

4.5 Effect of the PPh_3 Ligand in the presence of air

Table 4.2 illustrates the effect of triphenylphosphine on the MMA polymerization in the presence of air

Sample Name	$PPh_3/FeCl_3.6H_2O$	Time (min)	Conv. (%)	Mn_{theo}	Mn_{GPC}	M_W/M_n	Rp $mol.L^{-1}.sn^{-1}$
SAMPLE1	0,50	30	8,0	500	1900	1,17	$4.07x10^{-4}$
SAMPLE2	1,00	30	15,0	750	2900	1,14	$7.8x10^{-4}$
SAMPLE3	1,50	30	15,0	750	2750	1,06	$7,88x10^{-4}$
SAMPLE4	2,00	30	21,0	1000	2900	1,14	1,08x10-3
SAMPLE5	3,00	30	19,0	1000	3400	1,23	$9.86x10^{-4}$
SAMPLE6	4,00	30	25,0	1200	1200	1,12	$1,27x10^{-3}$
SAMPLE7	5,00	30	17,0	850	2250	1,08	$8,58x10^{-4}$
SAMPLE8	7,00	30	11,0	500	1700	1,24	$5,66x10^{-4}$

Table 4.2 illustrates the mole ratio of $PPh_3/FeCl_3.6H_2O$ between 1.5-4.0 increases the rate of the polymerization. The polymerization of MMA in the presence of air is slower reaction than the polymerization of MMA in vacuum. Rate of polymerization of MMA in vacuum at 90°C is rapid reaction than the rate of polymerization of MMA in the presence of air as it illustrated table 4.2.

Table 4.3 illustrates polymerization of MMA in different conditions:

Sample Name	$[M]_o$mol l^{-1}	$[M]o/FeCl_3.6H_2O$	$PPh_3/FeCl_3.6H_2O$	Time (min)	Conv. (%)	Mn_{theo}	Mn_{GPC}	M_W/M_n	Rp mol.L^{-1}.sn^{-1}
Ber1[a]	9,35	120,00	3,00	80	62	7500	12600	1,13	$1.20x10^{-3}$
Ber2[b]	9,35	120,00	3,00	80	74	8900	14800	1,18	$1.44x10^{-3}$
Ber3[c]	4,67	120,00	3,00	80	45	5400	9700	1,12	$8.76x10^{-4}$
Ber4[d]	9,35	-	-	60	<2	N/D	187000	1,06	-
Ber5	9,35	60,00	-	180	N/D	0	N/D	N/D	-
Ber6[e]	9,35	120,00	3,00	80	60	7200	13500	1,23	$1.17x10^{-3}$

Poly. Temp =90°C under Vacuum. a)(isolated from sun light) b)Bulk c)Polymerization is proceeded in solution(MMA:DPE=1.1) d)[M]o /PPh_3=35 e)$FeCl_2.4H_2O$

4.6 End Group Characterization

If the chain end is a chlorine atom, a recovered PMMA should be able to initiate the polymerization of a fresh feed of MMA in the presence of a ATRP catalyst (CuCl). Figure 4.14 The experience confirms this hypothesis as shown by chromatograms of an isolated PMMA(synthesis with $FeCl_3.H_2O/PPh_3$) of an final polymer obtained after 92 % conversion of an additional monomer. The polydispersity of the final polymer is actually lower than the one of the macro initiator. This experiment thus demonstrates the quantitative presence of a chlorine atom at the chain end of the macroinitiator.

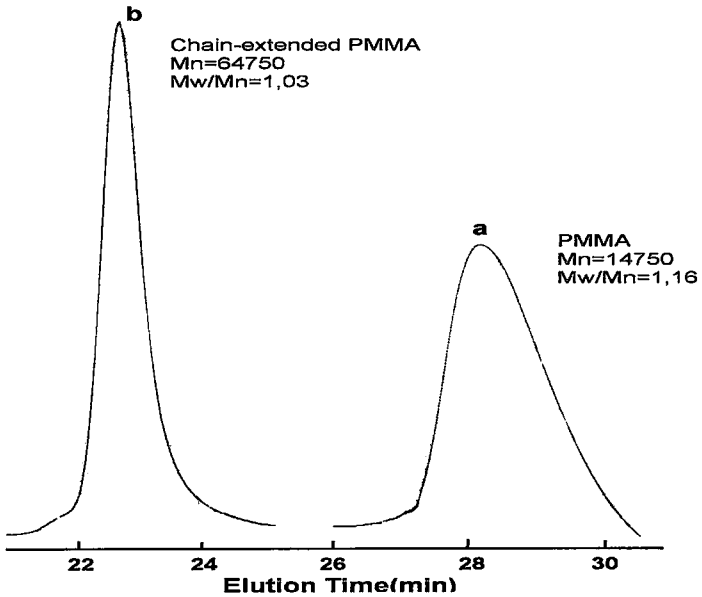


Figure 14. GPC chromatograms of the isolated PMMA(a)[Conditions: T= 90°C;$[MMA]_0$=4,67 mol.L^{-1} [$FeCl_3.H_2O$]= 0,16 mol.L^1 [PPh_3]=0,27 mol.L^1used as initiator and of the chain extended (b) (after precipitation in hexane). Conditions: T= 90°C; t =21h; solvent, DPE [macro initiator]$_0$=6,66 x 10^{-3} mol.L^{-1};$[MMA]_0$=4,67 mol.L^1;CuCl=9,3410^{-3} mol.L^{-1} ; $[PMDETA]_0$=9,34 x 10^{-3} mol.L^{-1}

5. CONCLUSIONS AND RECOMMENDATIONS

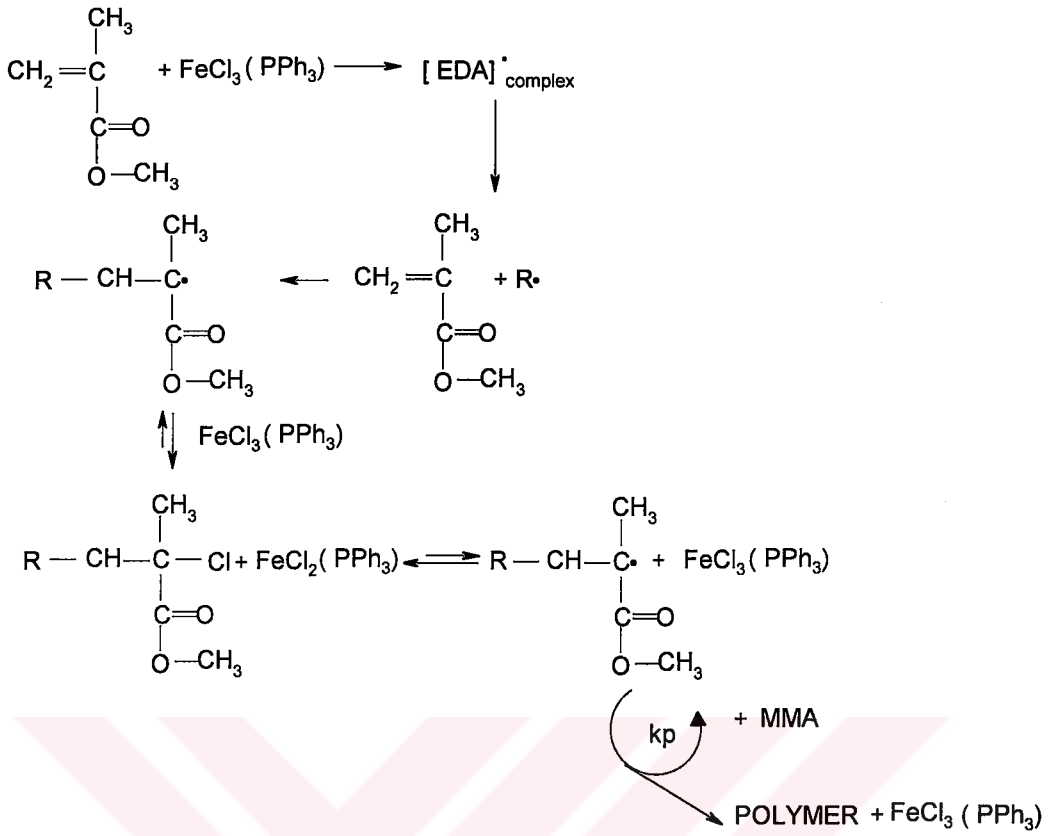
Controlled polymerization of MMA. MMA was polymerized in bulk and in different concentration (with DPE as a solvent - MMA:$FeCl_3.6H_2O$ = 60, 120, 240) at 90°C with the $FeCl_3.6H_2O$: PPh_3 initiation system under vacuum. The linear time dependence of ln $[M_o/M_t]$ (Figure 4-2,4,6,8,10) is consistent with a controlled polymerization that is firs order in monomer. That means propagating radicals is constant during the polymerization. Although the origin for the short induction period which is observed is not clear yet, it might be related to the formation of the actual initiating species as result of an interaction between $FeCl_3.6H_2O$: PPh_3.

The dependence of molecular weight on the MMA conversion are illustrated Figure: 4-1,3,5,7,9. The linear dependence observed for M_n is in agreement with a controlled process. However the linearity of M_n departs from straight line beyond high conversion. The dramatic increase of viscosity at high conversion is expected to change the rate of exchange between active and dormant species.

We also investigated the effect of PPh_3 on the MMA polymerization under vacuum in bulk and solution. We found that, there was no effect on the MMA polymerization under vacuum. (Table 4.1). Rate of polymerizations are closely some each other.(1,6-1,9x 10^{-3} mol $L^{-1}.sn^{-1}$)

Doing conventional ATRP carries out End group characterization. That is illustrated Figure 14. This confirms that, each our polymer chains consist of chlorine end.

So we suggest below scheme for this MMA polymerization mechanism in the inert environment.



Scheme 1: Polymerization of MMA with the $FeCl_3.H_2O$;PPh_3 initiation system. Under vacuum.

MMA was polymerized in bulk (MMA:$FeCl_3.6H_2O$ = 60) at 90°C with the $FeCl_3.6H_2O$: PPh_3 initiation system in the presence of air. The linear time dependence of ln $[M_0/M_t]$ (Figure 4-13) is consistent with a controlled polymerization that is firs order in monomer. That means propagating radicals concentration is constant during the polymerization.

The dependence of molecular weight on the MMA conversion is illustrated Figure: 4-12. The linear dependence observed for M_n is in agreement with a controlled process.

We investigated the effect of PPh_3 on the MMA polymerization in the presence of limited amount of air. We found that, increasing the concentration of PPh_3(Table 4.2).The rate of polymerization increase with the increasing PPh_3 concentration up to PPh_3/ $FeCl_3.6H_2O$ = 5 ($4{,}07x10^{-4}$-$1{,}27x\ 10^{-3}$ $mL^{-1}.sn^{-1}$). When the ratio of PPh_3/ $FeCl_3.6H_2O$ is higher than the 5 rate of polymerization dramatically decreases. ($8{,}58x10^{-4}$-$5{,}56x\ 10^{-4}$ $mL^{-1}.sn^{-1}$).

In this might be given :

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + PPh_3 \longrightarrow OPPh_3 + RO\cdot$$

$$RO\cdot + PPh_3 \longrightarrow R\bullet + OPPh_3$$

Oxygen is consumed by PPh_3.

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