İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ARYLDIAZONIUM SALT INITIATED REVERSE ATOM TRANSFER POLYMERIZATION OF METHYLMETHACRYLATE

M.Sc. Thesis by

Recep UÇAN

Department : **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

MAY 2002

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ARYLDIAZONIUM SALT INITIATED REVERSE ATOM TRANSFER POLYMERIZATION OF METHYLMETHACRYLATE

M.Sc. Thesis by

Recep UÇAN
515991035

Date of submission: 18 May 2002

Date of defance examination: 27 May 2002

Supervisor (Chairman) : Prof. Dr. Gürkan HIZAL

Members of the Examining Committee : Prof. Dr. Ümit TUNCA

Prof. Dr. Çakıl ERK

MAY 2002

İSTANBUL TEKNİK ÜNİVERSİTESİ★ FEN BİLİMLERİ ENSTİTÜSÜ

DİAZONYUM TUZU İLE BAŞLATILMIŞ METİL METAKRİLATIN TERSİNİR ATOM TRANSFER RADİKAL POLİMERİZASYONU

YÜKSEK LİSANS TEZİ

Recep UÇAN

515991034

Tezin Enstitüye Verildiği Tarih : 18 Mayıs 2002

Tezin Savunulduğu Tarih : 27 Mayıs 2002

Tez Danışmanı : Prof. Dr. Gürkan HIZAL

Diğer Jüri Üyeleri : Prof. Dr. Ümit TUNCA

Prof. Dr. Çakıl ERK

MAYIS 2002

ACKNOWLEDGEMENT

This master study has been carried out at Istanbul Technical University, Chemistry Department of the Science & Letter Faculty.

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Gürkan HIZAL and co-supervisor Prof. Dr. Ümit TUNCA for offering invaluable help in all possible ways, continuous encouragement and helpful critisms throughout this research.

I would like to thank to my colleagues Şebnem İNCEOĞLU, Tuba ERDOĞAN, Dolunay ŞAKAR, Murat PEHLİVAN, Berkant BEDRİ, Mine BARLAN for their friendly and helpful attitude during my laboratory works.

Finally, I would like to dedicate this thesis to my parents Miyase and Mehmet UÇAN and my brother Bülent UÇAN for their patience, understanding and morale support during all stages involved in the preparation of this thesis.

May 2002 Recep UÇAN

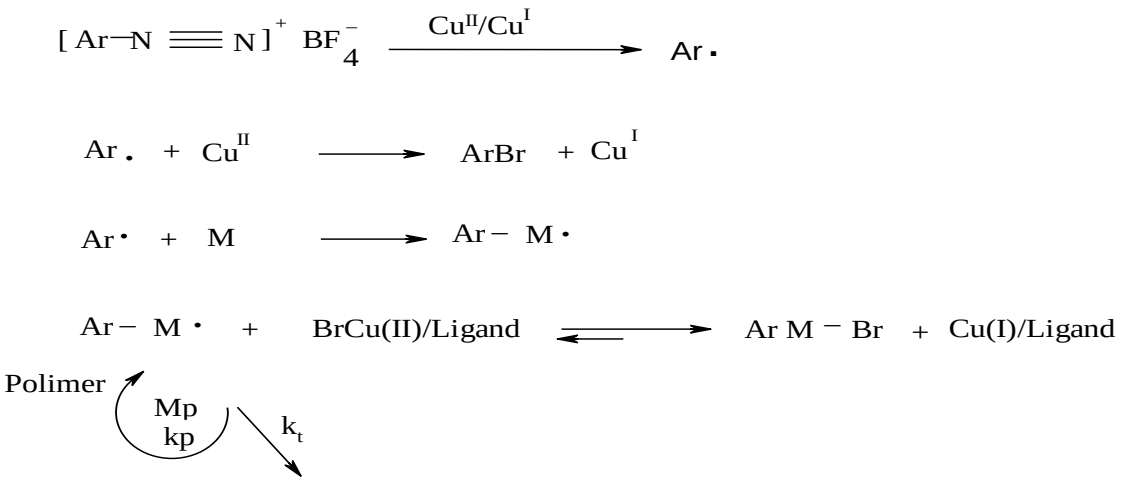
DİAZONYUM TUZU İLE BAŞLATILMIŞ METİL METAKRİLATIN TERSİNİR ATOM TRANSFER RADİKAL POLİMERİZASYONU

ÖZET

Polimer biliminde kompleks ve kontrollü mimariye sahip makromoleküllerin sentezi üzerine yapılan çalışmalar gittikçe önem kazanmaktadır. Klasik olarak, makromoleküler mimarinin kontrolü yalnızca yaşayan anyonik ve katyonik polimerizasyon teknikleri ile

başarılabilmektedir. Kontrollü mimari denilince, molekül ağırlığı kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme yeteneği ve yaşayan karakter akla gelmektedir. Son yıllarda, iyi tanımlanmış düşük molekül ağırlığı dağılımına sahip polimerlerin sentezinde kontrollü/'yaşayan' polimerizasyon yöntemleri kullanılmaktadır. Bu yöntemlerden M_t^n/Amin ligand ile katalizlenen atom transfer radikal polimerizasyonu (ATRP) başlıca stiren ve akrilat vb. monomerlerinin polimerizasyonunda başarıyla kullanılmaktadır.

Bu çalışmada, p-kloroaril diazonyum tetrafloroborat tuzu, metilmetakrilat (MMA) monomerinin tersinir atom transfer radikal polimerizasyonunda başlatıcı olarak kullanılmıştır. Diazonyum tuzunun katalizlenmesi ve/veya ısısal bozunması sonucu oluşan radikallerin metal tuzu/amin kataliz varlığında, farklı sıcaklıklarda MMA'nın kontrollu polimerizasyonunu başlattığı gözlenmiştir. Genellikle tersinir ATRP yüksek sıcaklıklarda(60-100^oC) gerçekleşmesine rağmen, bu çalışmada aryl diazonyum tuzu/Cu^{II} X_2/Ligand sisteminin, metilmetakrilatın oda sıcaklığında da kontrollü polimerizasyonunu başlattığı bulunmuştur.



ARYLDIAZONIUM SALT INITIATED REVERSE ATOM TRANSFER POLYMERIZATION OF METHYLMETHACRYLATE

SUMMARY

The ability to synthesize macromolecules with complex and controlled architectures is becoming an increasingly important aspect of polymer science. Traditionally, control of macromolecular architecture has been achieved 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, Matyjaszewski et al. developed an alternative living free radical polymerization process using a copper (I) - catalyzed atom transfer process (ATRP). ATRP can be applied to polymerize both styrenic and acrylic type monomers.

In this study, reverse Atom Transfer Radical Polymerization of MMA monomers initiated with p-choloroaryl diazonium tetraflouroborate salts was used. The radicals formed from catalyst of diazonium salt or thermal decompositon of diazonium salt have initiated the well-uncontrolled polymerization of MMA in the presence at metal salt/amine –catalyst system of different temperatures. Although reversible ATRP occurs at high temperatures (60-100^{o} c), in this study, ıt has ben found that Diazonium salt / $Cu^{II}X_2$ / Ligand system has initiated the well-controlled polymerization of Mma at room temperature.

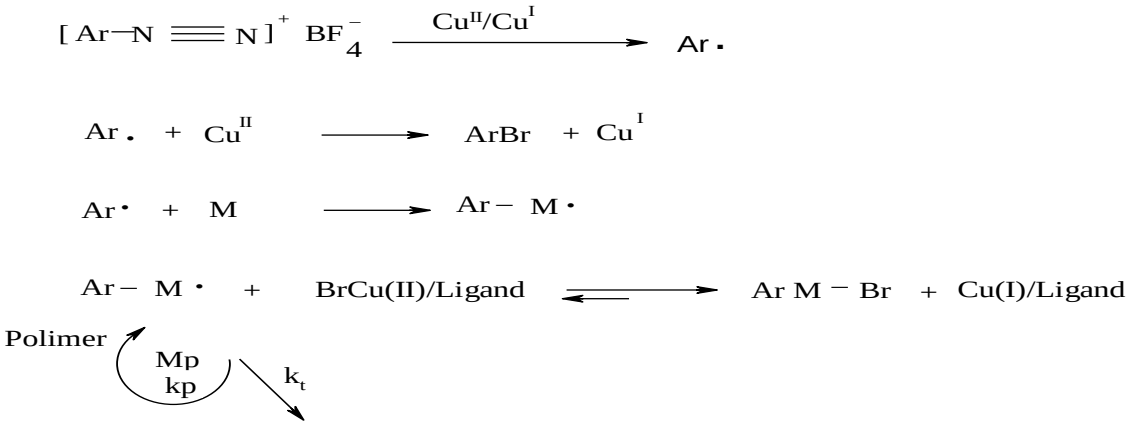


TABLE OF CONTENTS

ACKNOWLEDGEMENT	**III**
LIST OF TABLES	**VI**
LIST OF FIGURES	**VII**
LIST OF SYMBOLS	**IX**
SUMMARY	**X**
ÖZET	**XII**

1. INTRODUCTION **1**

2. THEORITICAL PART 4

2.1 FREE RADICAL POLYMERIZATION 4

2.1.1 Free Radical Initiators 9

2.1.1.1 Initiators Giving Radicals via Homolytic Chain Cleavage of a Covalent Bond 9

2.1.1.2 Initiators Giving Radicals by Electron Transfer 10

2.1.2 Initiator Efficiency 10

2.1.3 Complexes in initiation reactions of radical polymerization. 11

2.1.4 Thermal Polymerization 13

2.2 CONTROLLED OR LIVING RADICAL POLYMERIZATIONS 14

2.2.1 Initiation Systems 17

2.2.2 Iniferter Method 19

2.2.3 Stable Free Radical Polymerization (SFRP) 22

2.2.3.1 Mechanical Considerations 23

2.2.4 Atom Transfer Radical Polymerization (ATRP) 26

2.2.4.1 Initiators 27

2.2.4.2 Transition Metals Used in ATRP 28

2.2.4.3 Ligand 30

2.2.4.4 Monomers 30

2.2.4.5 Effects of Other Parameters 30

2.2.4.6 Kinetics of ATRP 31

2.2.5 Addition –Fragmentation Process 32

2.2.6 Reverse Atom Transfer Radical Polymerization. 35

2.3. DİAZO CHEMİSTRY 40

2.3. DİAZO CHEMİSTRY 40

2.3.1 Photochemistry of aromatic diazonium salts 40

2.3.2 Sandmeyer reaction 41

2.3.3 Replacement of the Diazonio Gruop by Alkenes and Alkynes: The Meerwein Reaction 43

3. EXPERIMENTAL PART 46

3.1 Chemicals Used 46

3.2 Typical Synthesis of Poly (methyl methacrylate) under vacuum in bulk. 47

3.3 Synthesis of Poly (methyl methacrylate) under vacuum in bulk at room temperature. 47

3.4 Typical Synthesis of Poly (methyl methacrylate) under vacuum in solution.4**Hata! Yer işareti tanımlanmamış.**

3.5 Characterization 48

4. RESULTS AND DISCUSSIONS 49

4.1 The synthesis of poly(MMA) using diazonium salt/CuBr2/PMDETA system 49

4.2 The synthesis of poly(MMA) using diazonium salt/CuCl2/PMDETA system 53

4.3 The synthesis of poly(MMA) using diazonium salt/CuBr/CuBr2/PMDETA system 57

4.4 End Group Characterization 59

4.5 Synthesis of Poly (methyl methacrylate) under vacuum in various solution at 90°C 60

5. CONCLUSIONS AND RECOMMENDATIONS 61

63

REFERENCES

AUTOBIOGRAPHY **67**

LIST OF TABLES

Table 2.1. Types of initiators used in ATRP sytems……...… **29**

Table 4.1. Polymerization of MMA in bulk at 90°C with *p*-chlorobenzene diazo niumtetrafluoroborate / $CuBr_2$ / PMDETA…… **50**
Table 4.2. Polymerization of MMA in bulk at room temperature with p-chloro benzenediazoniumtetrafluoroborate / CuCl2 / PMDETA……. **52**
Table 4.3. Polymerization of MMA in bulk at 90°C with with *p*-chlorobenzenediazo niumtetrafluoroborate /CuBr/$CuBr_2$ / PMDETA **54**
Table 4.4. Polymerization of MMA in bulk at 60°C with *p*-chlorobenzenediazo niumtetrafluoroborate / $CuCl_2$ / PMDETA……. **56**
Table 4.5. Polymerization of MMA in bulk at 60°C with p-chlorobenzenediazoni umtetrafluoroborate / CuBr2 / PMDETA…… **58**
Table 4.6. Polymerization of MMA in bulk at room temperature with p-chloro benzenediazonium tetrafluoroborate / CuBr2 / PMDETA…… **59**
Table 4.7. Illustrates the effect of various solvents on the MMA polymerization under vacuum……. **61**

LIST OF FIGURES

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 *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA…..... **49**

Figure 4.2: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with *p*-chlorobenzene diazo niumtetrafluoroborate / $CuBr_2$ / PMDETA…… **50**

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 room temperature with p-chloro benzenediazonium tetra fluoroborate / CuCl2 / PMDETA…… **51**

Figure 4.4: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at room temperature with p-chloro benzenediazoniumtetrafluoroborate / CuCl2 / PMDETA……... **52**

Figure: 4.5: 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 p-chlorobenzenediazoniumtetrafluoroborate /CuBr/CuBr2 / PMDETA……... **53**

Figure 4.6: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with with p-chlorobenzene diazoniumtetrafluoroborate /CuBr/CuBr2 / PMDETA……... **54**

Figure: 4.7: Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 60°C with *p*-chlorobenzenediazoniumtetrafluoroborate / $CuCl_2$ / PMDETA…….. **55**

Figure 4.8: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 60°C with *p*-chlorobenzene diazo niumtetrafluoroborate / $CuCl_2$ / PMDETA…… **55**

Figure: 4.9: Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 60°C with p-chlorobenzenediazoniumtetrafluoroborate / CuBr2 / PMDETA……. **56**

Figure 4.10: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 60°C with p-chlorobenzene diazo niumtetrafluoroborate / CuBr2 / PMDETA……
……..…….. **57**

Figure: 4.11: Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at room temperature with p-chloro benzene diazonium tetrafluoroborate / CuBr2 / PMDETA……..……..… **58**

Figure 4.12: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at room temperature with p-chloro benzenediazoniumtetrafluoroborate / CuBr2 / PMDETA…….. **59**

Figure 4.13: illustrated that conversion dependence of M_w/M_n for MMA polymerization…….. **60**

Figure 4.14: End Group Characterization…….. **61**

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_k, 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

I, M : Initiator and monomer respectively

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.

Atom transfer radical polymerization (ATRP) is among the most promising approaches to controlled radical polymerization. Copper-mediated ATRP has been successfully used to prepare polymers with predetermined molecular weights, low polydispersities, and precise end functionalities as well as a variety of (co)polymers with controlled topologies and compositions. ATRP can be realized using two different initiating systems: either an alkyl halide and transition-metal compound in its lower oxidation state (e.g., CuBr complexed by two molecules of 4,4’-di(alkyl)-2,2’-bipyridine or one molecule of N,N,N’,N’’,N’’-pentamethyldiethylenetriamine) or a conventional radical initiator such as azobis(isobutyronitrile) (AIBN) with the transition-metal compound in its higher oxidation state (e.g., $CuBr_2$ complexed by an appropriate ligand). The latter approach has been named reserve ATRP and

was successfully used for copper-based heterogeneous and homogeneous systems in solution and in emulsion as well as for iron complexes. [2]

In reverse ATRP, it is important to use metal halides (e.g., cupric dibromide), since salts with anions that cannot be efficiently transferred by a radical mechanism, such as cupric ditriflate or cupric diacetate, cannot reversibly deactivate the growing radicals.

In this work, the initiator efficiency of p-chloro aryldiazonium tetrafluoroborate investigated by reserve atom transfer radical polymerization technique using radically polymerizable monomers such as methylmethacrylate or styrene

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 [3]. 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 [4]. 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.

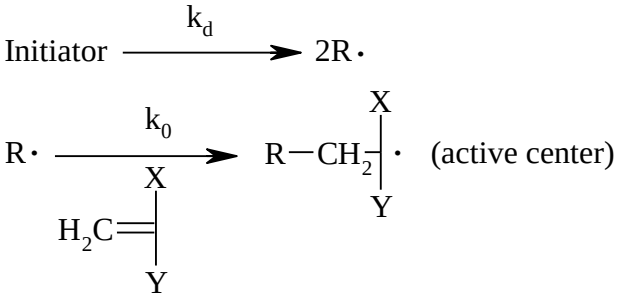
Free radical polymerization is initiated by radicals and propagated by macro radicals. These radicals exhibit an unpaired electron. Initiating radicals are rarely formed by

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

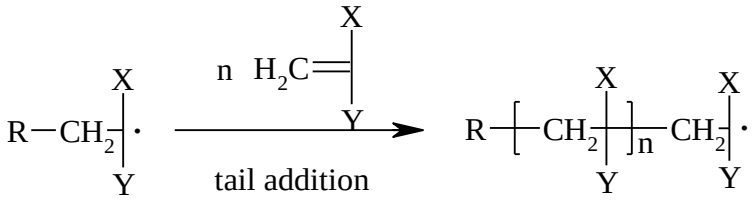
Initiation occurs from the reaction of an initiator-derived radical center with a monomer molecule. Firstly a couple of radical occurs by a homolytic cleavage of the initiator. If the radicals are formed in the presence of vinyl monomers, these radicals react with the double bond and generate a new radical. The first one is known as the dissociation and the second is the association step in the initiation of free radical polymerization. Since kd < ko[M], the decomposition is the rate determining step in the initiation process [5].



(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 [6].



(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.

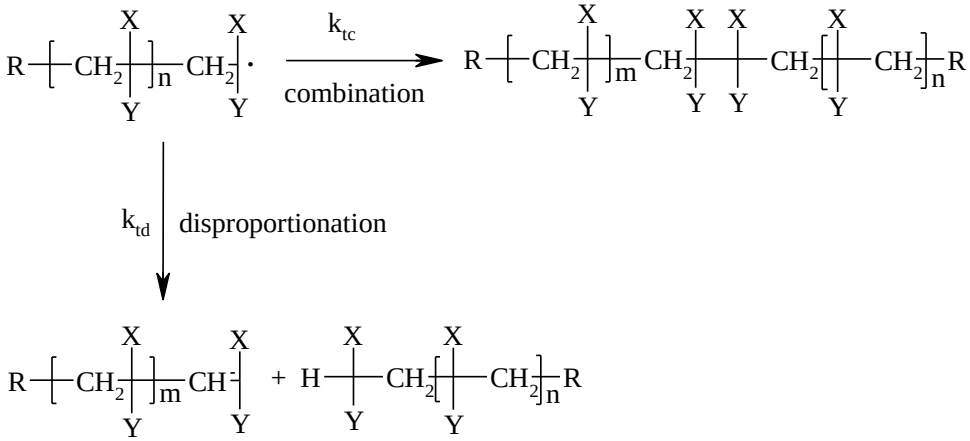
1) The Self Reaction of Carbon-Centered Radicals

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.

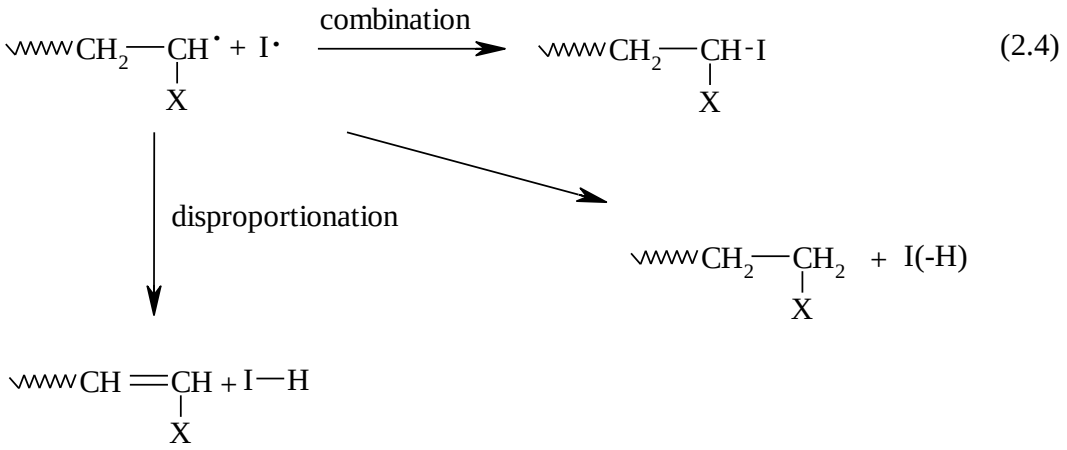


(2.3)

The rate of ktc / ktd 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).



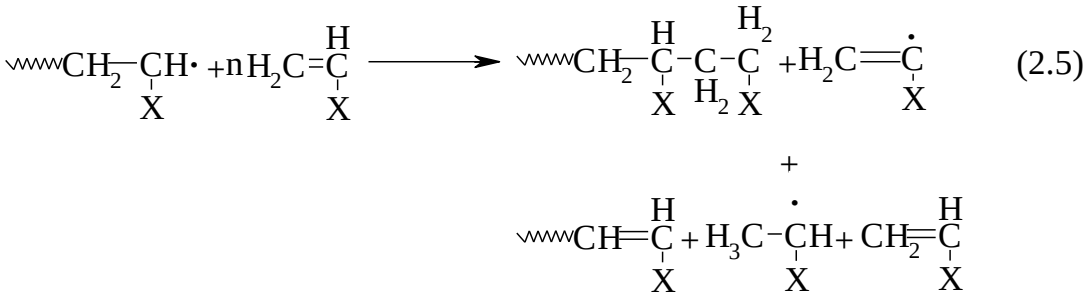
(2.4)

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

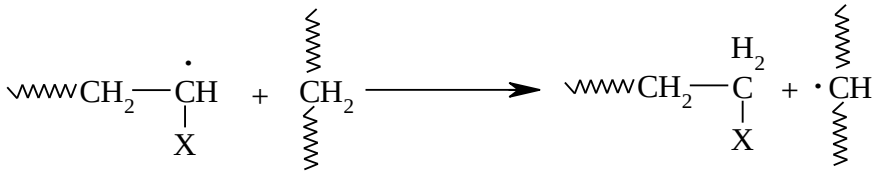
If the generated monomer radicals become stable via resonance structure they do not initiate polymerization of a new chain. An example is given in (2.5)



(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

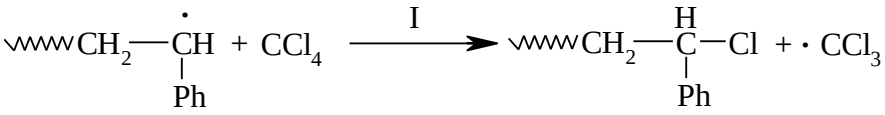
Transfer to initiator involves the termination of a propagating radical by reaction of a molecule of initiator. The resulting polymer possesses two initiator-derived end groups, and in the process, a new primary radical is formed, which may initiate a new chain.



(2.7)

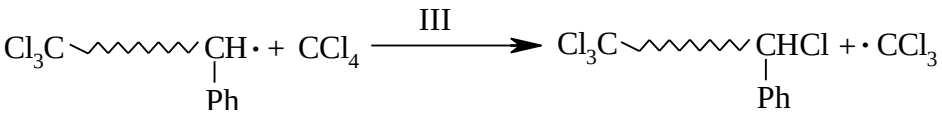
d) Transfer to Solvent

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.

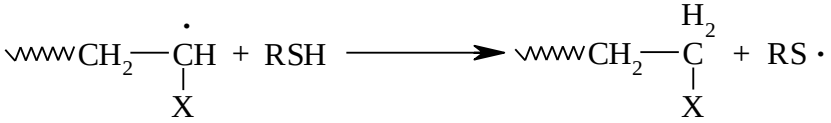


(2.8)





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.

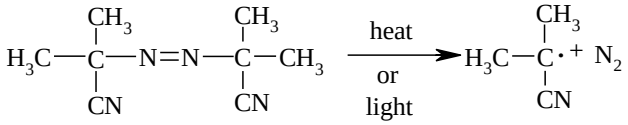
2.1.1.1 Initiators Giving Radicals via Homolytic Chain Cleavage of a Covalent Bond

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.



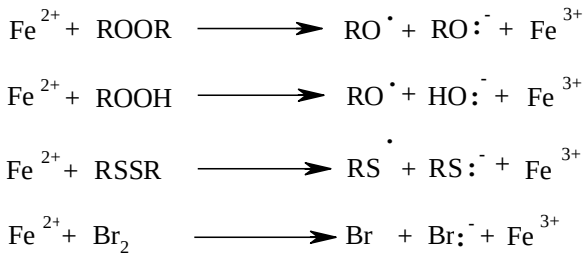
(2.10)



(2.11)

2.1.1.2 Initiators Giving Radicals by Electron Transfer

The most important one is the redox reactions.

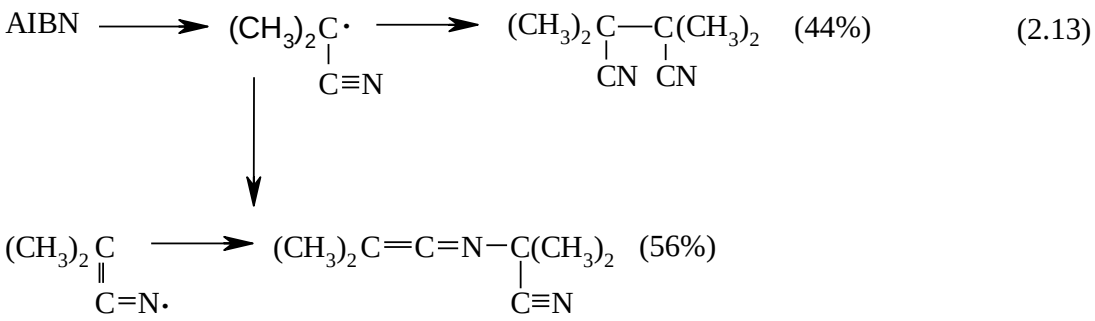


(2.12)

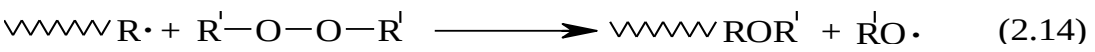
The pathway of the polymerization initiated by the electrochemically formed radicals usually undergoes over the anionic or cationic ions.

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 [7].

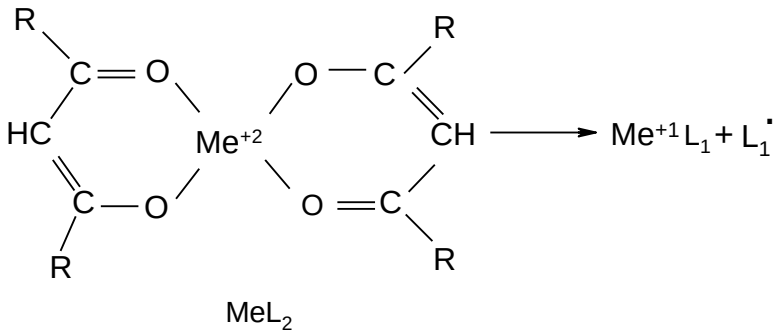
2.1.3 Complexes in initiation reactions of radical polymerization.

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 [8] 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 [9] 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 ($L_1\bullet$) 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[10-11] 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 [12].

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 [13] . The interaction is expressed: (2.16)

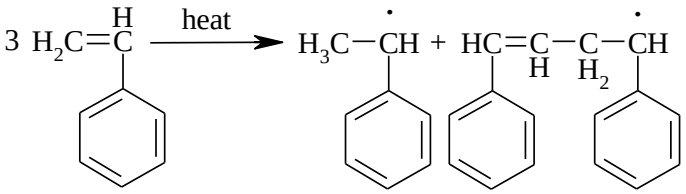
$$D + A \rightleftharpoons [D \cdots\cdots A] \rightleftharpoons [D^{\bullet +}, A^{\bullet -}] \qquad (2.16)$$

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).[14]

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 [15-16].

Although the exact mechanism is not known, the works done on this subject [17-18] 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 [19].

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.

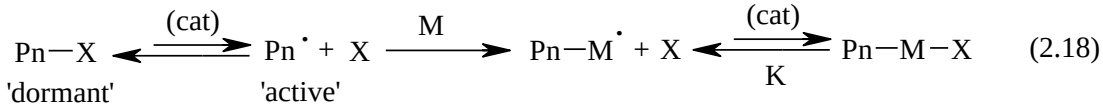
Three types of radical polymerization have been called living;

- 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 [20] used dithiocarbamate radicals, Georges et al. [21-22] used nitroxyl radicals and Borsing et al. [23] 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, $(P\text{-}X)^{\cdot}$, 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 [24] and phosphorus [25] as well as with organometalic derivatives of Co [26], Cr [27], 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

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

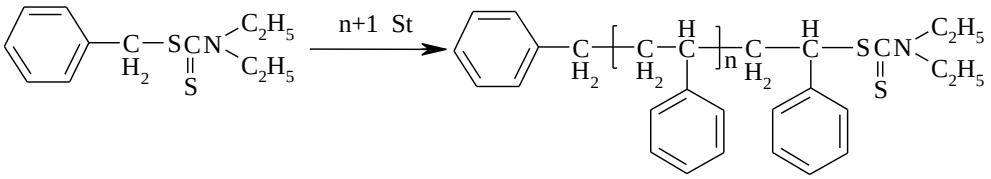
In this case growing radical (Pn**.**) reacts rapidly and selectively with a transfer agent (P1-R) to exchange the R group and form a dormant species (Pn-R) and a new radical (P1**.**), which is capable of chain growth. (P**.**) would be generated by a classical initiator such as AIBN, BPO and redox 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.

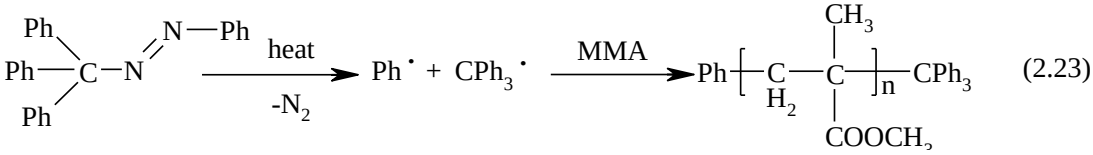
a) Organosulfides

As discussed previously, the potential of organosulfides as initiators of living radical polymerization was first recognized by Otsu and Yoshida [20]. 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 [28]. As an example, living radical polymerization schematic of styrene with BDC is seen in (2.22).



b) Di and Triarylmethyl Derivatives

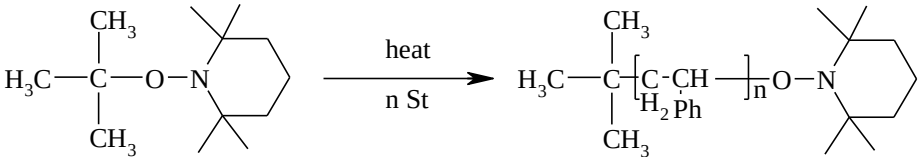
Otsu and Tezaki [29] reported on the use of triphenyl methyl azo-benzene as an initiator of living polymerization. The phenyl radical initiates polymerization and the triphenyl methyl radical reversibly terminates the chains.



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 [30] also used this initiator to prepare methacrylate block co-polymers.

c) Alkoxyamines

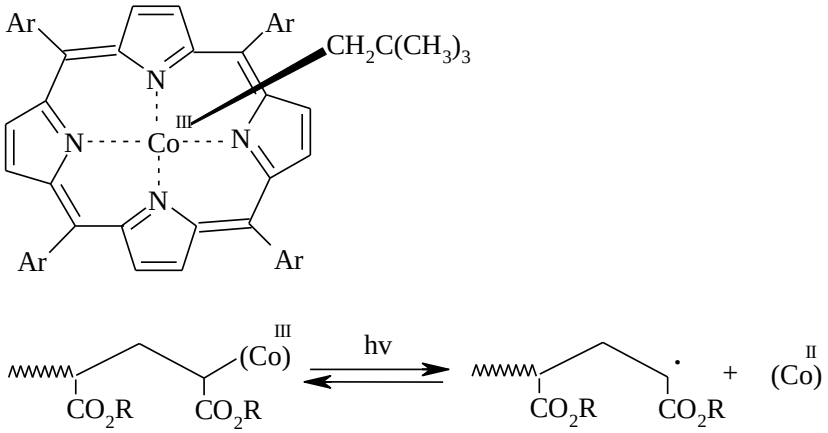
Rizzardo et al. [31] pioneered the use of alkoxyamines as initiators in living free radical polymerizations. The C-ON bond is relatively weak and undergoes homolysis on heating to yield a reactive carbon-centered radical and a stable nitroxide. The carbon-centered radical initiates the polymerization 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. [27] 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 (2.25).

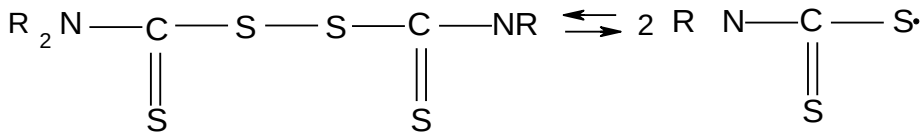


(2.25)

2.2.2 Iniferter Method

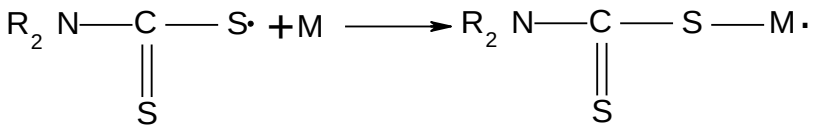
Iniferters are initiators that induce radical polymerization that proceeds via initiation propagation, primary radical termination, and transfer to initiator. Because bimolecular termination and other transfer reactions are negligible, these polymerizations are performed by the insertion of the monomer 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.

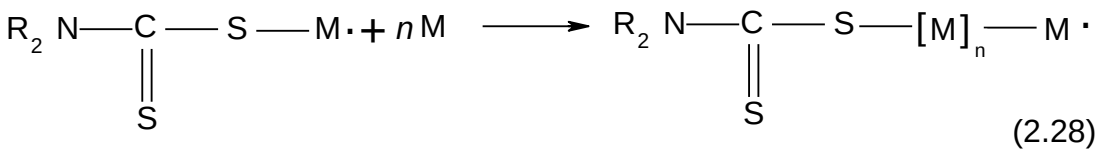


1 **2** (2.26)

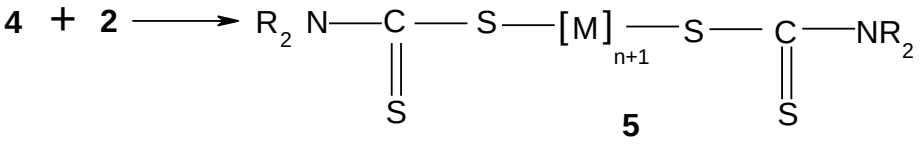
From the kinetic studies[32-33](2.26-1) was found to act not only as an initiator but also as a retarder, terminator, and transfer agent .Therefore, the polymerization of the monomer(M) with (2.26-1) proceeds via the dissociation of (2.26-1), initiation ,propagation, primary radical termination and chain transfer to (2.26-1), according to eqs (2.26-2.30)[33]respectively:



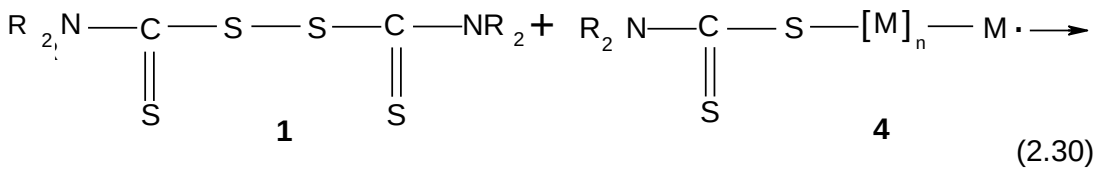
2 **3** (2.27)



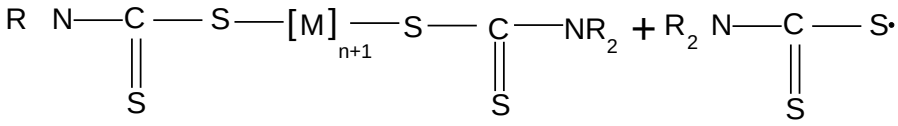
3 **4** (2.28)



(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[34] 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. This polymerization might provide a new route for preparing specialty polymers.

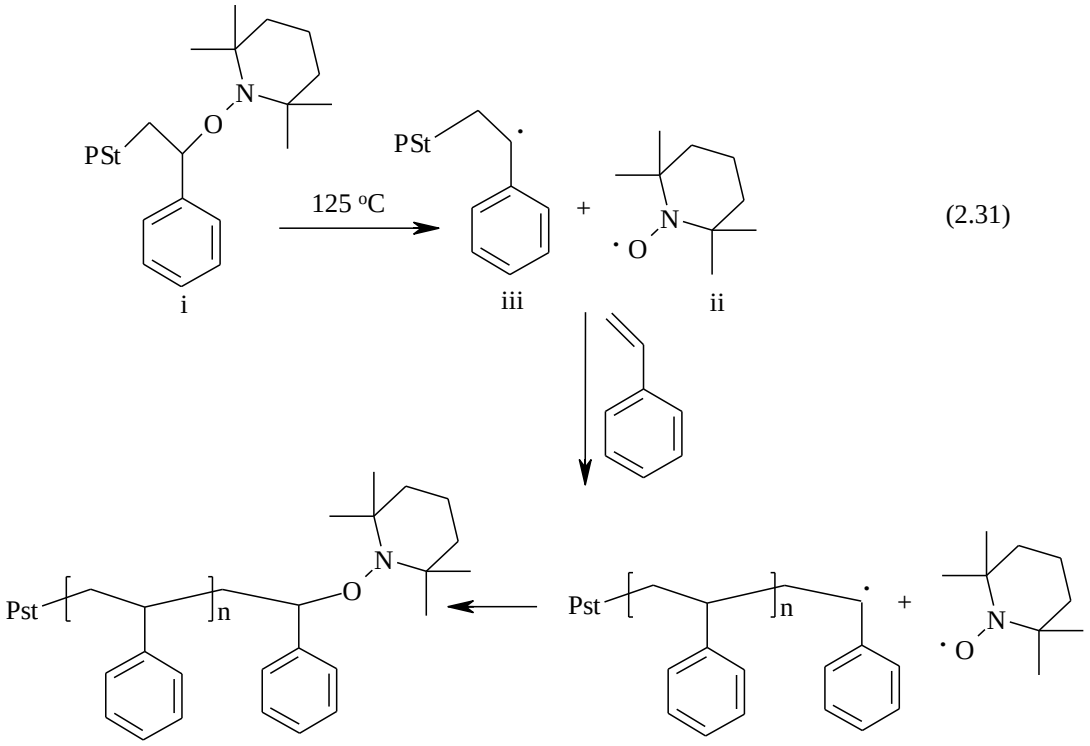
As described in Case 2 if the initiators such as 1 induce such radical polymerization polymers with two initiators fragments at their ends such as, (2.29-5) are obtained as the result of monomer insertion. The uses of well-designed initiators give various polymers with controlled end groups such as block 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 [35] 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.

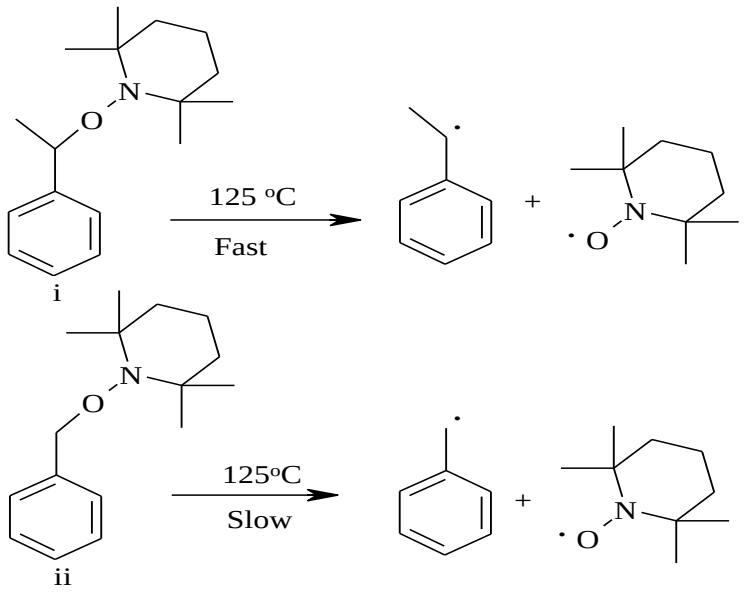
2.2.3.1 Mechanical Considerations

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 [19]. 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.

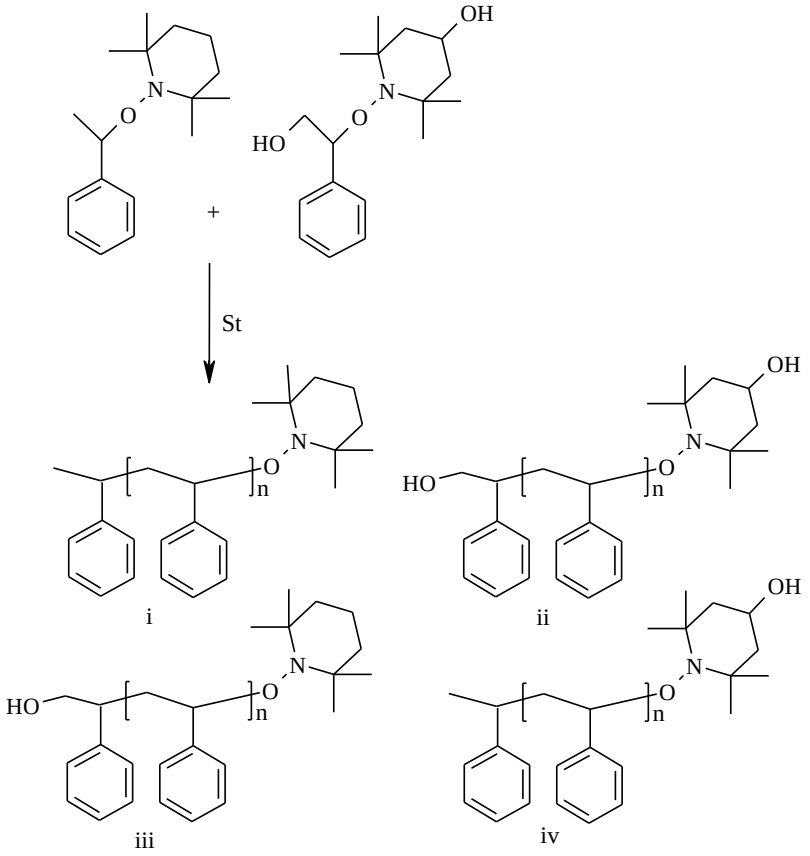


(2.32)

The steric or electronic nature of nitroxide can significantly increase the rate of polymerization [36]. For example Puts and Sogah [37] 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 [19]. 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.

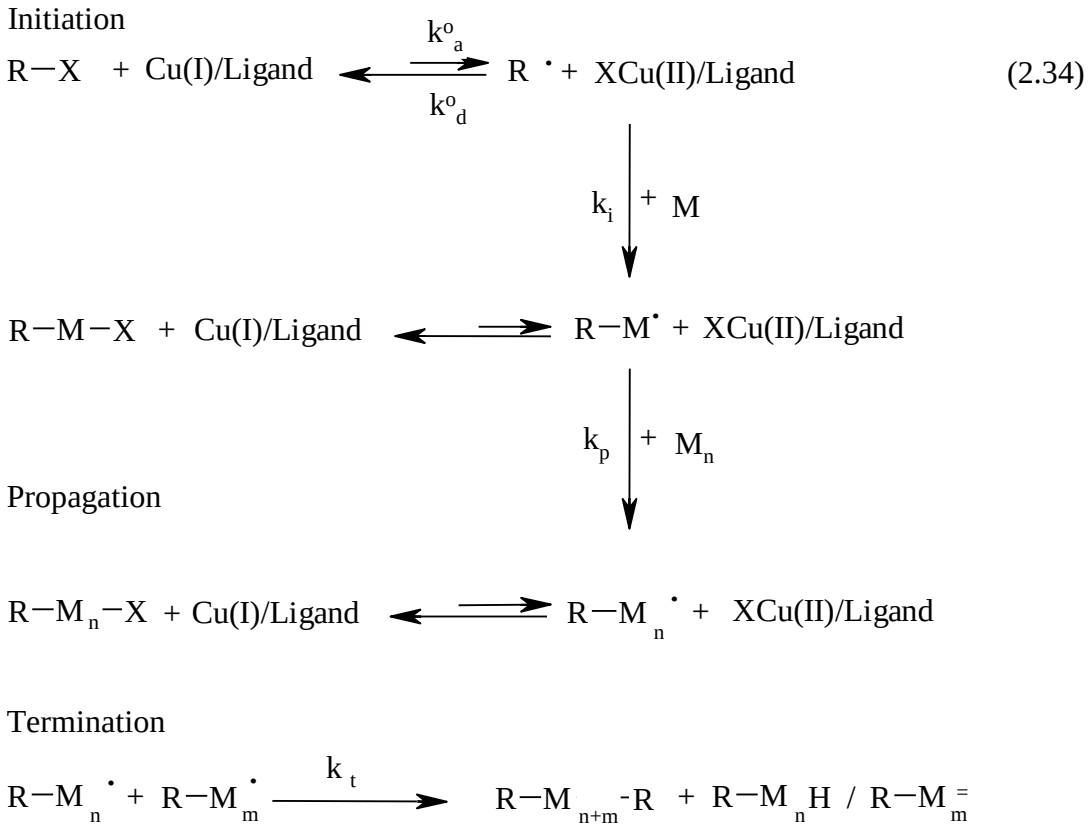
c) Polydispersities of smaller than 1, 5 can be achieved.

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 [38-41].

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.

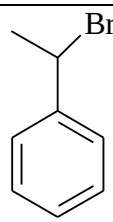
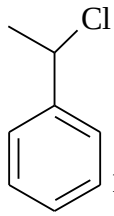
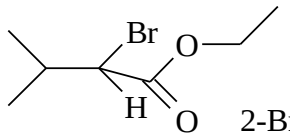
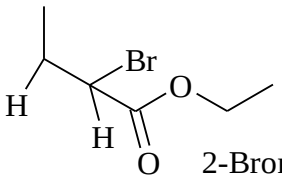
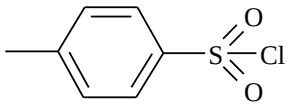
A fast equilibrium between the active and the dormant chains is needed to observe low polydispersities in controlled or living radical polymerizations. In ATRP both effective initiation and good control of the polymerization relay heavily on the position of the equilibrium in both the initiation and 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.

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) / $3PR_3$.

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

2.2.4.3 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 [42] 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 $K\,^{\circ}_{eq}$ 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 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).

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

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.

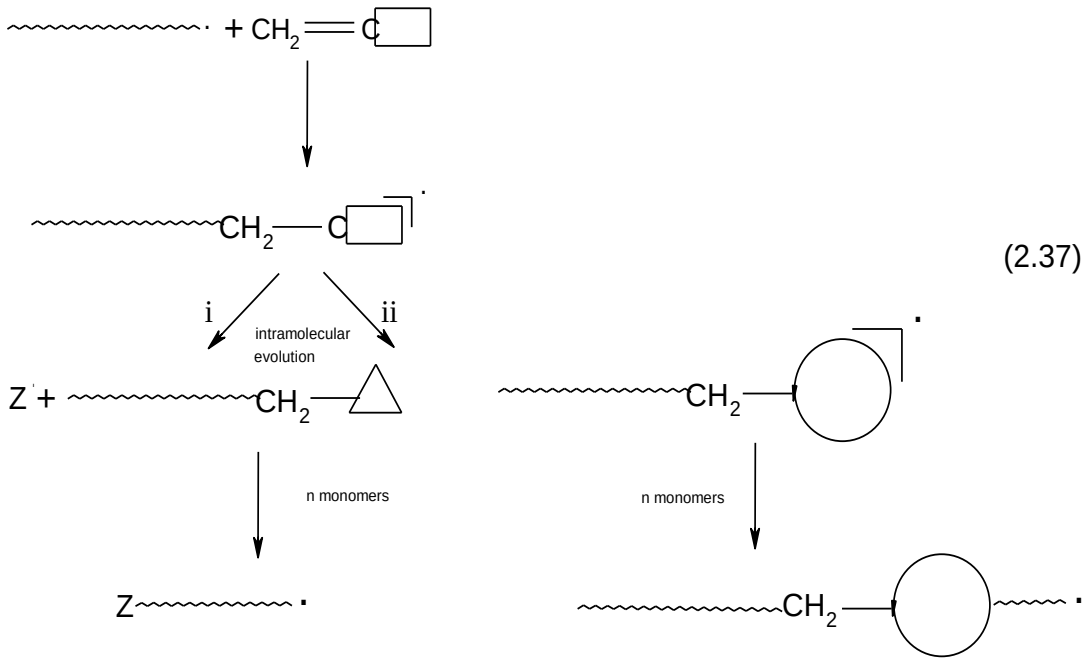
c) Resulting molecular weight distribution decreases as the concentration of the deactivators decreases.

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)



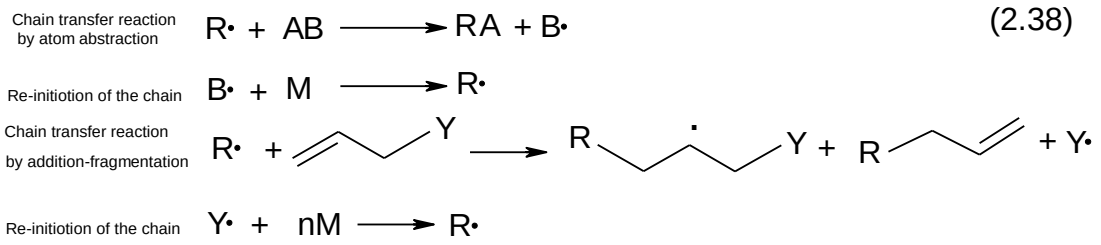
(2.37)

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.

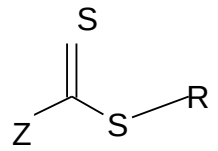
The control of molar mass in free radical polymerization is usually achieved by the addition of a chain transfer agent in the polymerization medium[43]. When a chain carrying radical is trapped by another specific compound XY to produce a radical Y• which is also reactive, this radical Y• can re-initiate 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[44-45]

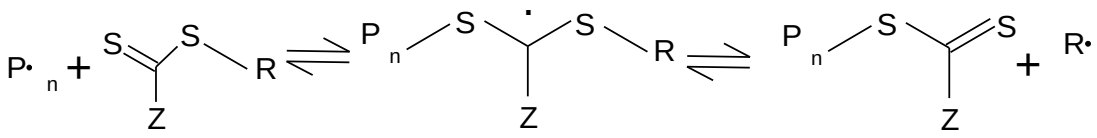
2. *Addition-fragmentation chain transfer agents* (scheme2.38) [44-45]. The chain transfer agents which fallow the addition-fragmentation mechanism are particular interest in organic and polymer chemistry. Recently many studies have shown that ally, acrylyl and allenyl transfer to alkyl halides represent 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 [46-47]. 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 [46-47-48] The versatility and convenience of this process offer distinct advantages over other forms of living radical polymerization.[49-50]



1

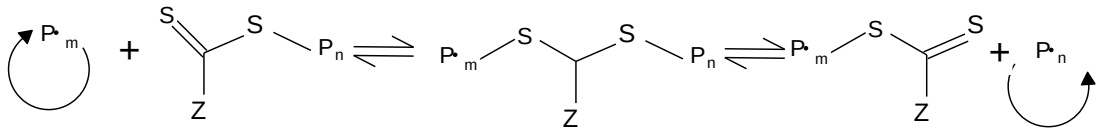


2



(2.39)

Equilibration



2.2.6 Reverse Atom Transfer Radical Polymerization.

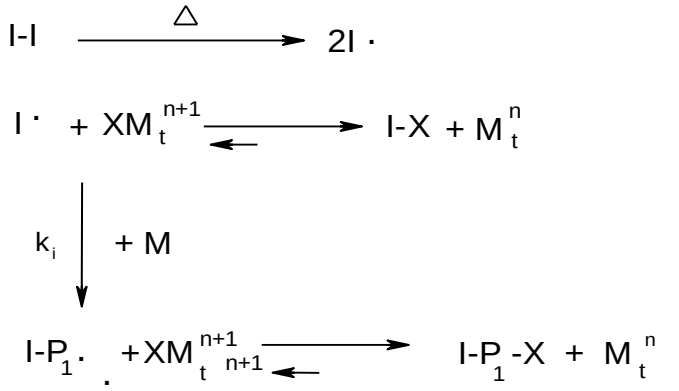
Atom transfer radical polymerization (ATRP) is among the most promising approaches to controlled radical polymerization. Copper-mediated ATRP has been successfully used to prepare polymers with predetermined molecular weights, low polydispersities, and precise end functionalities as well as a variety of (co)polymers with controlled topologies and compositions. ATRP can be realized using two different initiating systems: either an alkyl halide and transition-metal compound in its lower oxidation state (e.g., CuBr complexed by two molecules of 4,4’-di(alkyl)-2,2’-bipyridine or one molecule of N,N,N’,N’’,N’’-pentamethyldiethylenetriamine) or a conventional radical initiator such as azobis(isobutyronitrile) (AIBN) with the

transition-metal compound in its higher oxidation state (e.g., $CuBr_2$ complexed by an appropriate ligand). The latter approach has been named reserve ATRP and was successfully used for copper-based heterogeneous and homogeneous systems in solution and in emulsion as well as for iron complexes. [2]

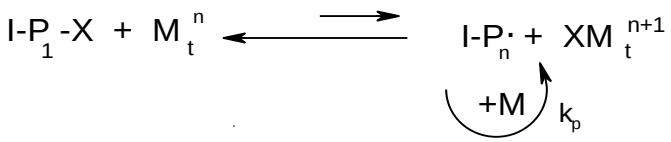
Reverse ATRP differs from normal ATRP in its initiation process, where a conventional radical initiator, such as AIBN, is used.[51] As shown in Scheme 2.1, in the initiation step, once generated, the initiating radicals or the propagating radicals, I^* or $I\text{-}P_1{}^*$, can abstract the halogen atom X from the oxidized transition-metal species, XM_t^{n+1}, to from the reduced transition-metal species, M_t^n, and the dormant species, I-X or $I\text{-}P_1\text{-}X$. In the subsequent steps, the transition-metal species, M_t^n, promotes exactly the same ATRP process as normal ATRP where $R\text{-}X/M_t^n/L_x$ are used as the initiation system. Instead of first activation of a dormant species, R-X, with M_t^n, as in the case of normal ATRP, reverse ATRP originates from the deactivation between radicals, I^* or $I\text{-}P_1{}^*$, andXM_t^{n+1}.[52]

Scheme 2.1. Mechanism of Reverse ATRP

Initiation:



Propagation:



It is known that cuprous salts act as very efficient accelerators in the decomposition of peroxides.[3-53] The resulting radical anions decompose to radicals and anions

(e.g., carboxylate) which can initiate polymerization and coordinate to the salt in the higher oxidation state, respectively.

Scheme 2.2 presents the reactions involved in the ATRP process initiated by BPO/CuBr/2dNbpy (dNbpy ligand was omitted to simplify the Scheme 2.2).

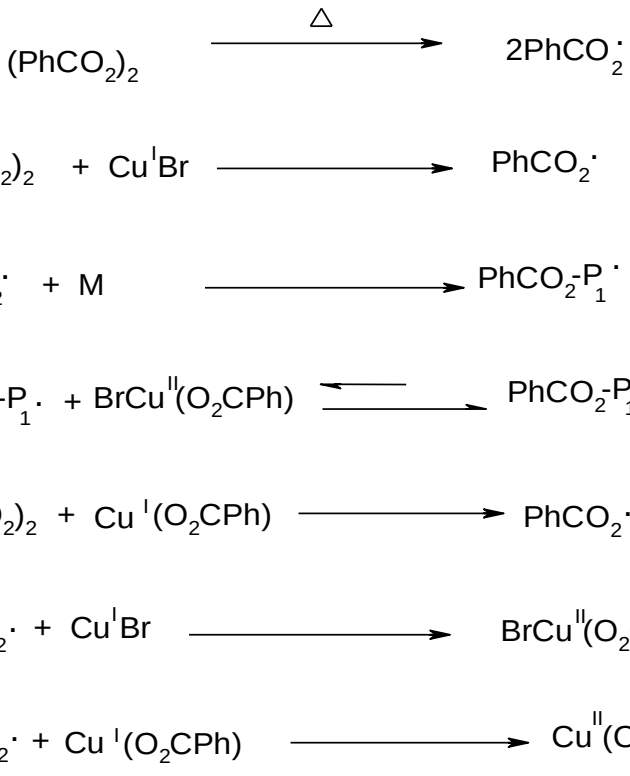
The benzoyloxy primary radicals are generated from the BPO initiator either by the thermal decomposition or by the induced decomposition through the OSET process. The significantly faster OSET process makes it the dominant pathway to generate the benzoyloxy primary radicals. In addition to the formation of oligomers with benzoate tail groups (some phenyl tail groups from decarboxylation can also be formed) and bromine headgroups, the initiation process generates $Cu(O_2CPh)$, which can participate in the induced decomposition of the BPO initiator and result in the formation $Cu(O_2CPh)_2$. Since $Cu(O_2CPh)_2$/2dNbpy does not reversibly deactivate the growing radicals, the benzoyloxy radicals generated cannot from oligomers with bromine headgroups. As a result, initiator efficiency is reduced. The benzoyloxy radicals may also oxidize CuBr and $Cu(O_2CPh)$ to the corresponding Cu(II) speces, resulting in the decrease of initiator efficiency and the consumption of active catalyst. Propagation proceeds similarly to conventional ATRP, with the produced $Cu(O_2CPh)$/2dNbpy and the remaining CuBr/2dNbpy acting as the catalyst to generate radicals and reversibly form $CuBr_2$/2Nbpy and $BrCu(O_2CPh)$/2dNbpy as deactivators. Radicals propagate by adding monomer, are reversibly deactivated, and can also terminate. In the absence of the ligand, only bromine-terminated oligomers are obtained as they cannot be activated for propagation. When a sufficient excess of BPO over CuBr is used, the copper species are completely and irreversibly converted to $Cu(O_2CPh)_2$, which can no longer participate in the ATRP process.

In contrast.$CuBr_2$/2dNbpy does not accelerate the decomposition of BPO (Scheme 2.3). However, it deactivates the growing radicals and generates in situ, in addition to bromine-terminated oligomers, CuBr/2dNvpy which then induces the decomposition of BPO by OSET. After deactivation of the growing radicals by $BrCu(O_2CPh)$/2dNbpy, the newly formed $Cu(O_2CPh)$/2dNbpy also participates in the induced decomposition of BPO. As a result, the intermediate Cu(I) species, both CuBr and $Cu(O_2CPh)$, are reoxidized to Cu(II) species byBPO. In other words, for the BPO/$CuBr_2$/2dNbpy system, there are almost no Cu(I) species for activation, and only $CuBr_2$, $BrCu(O_2CPh)$, and $Cu(O_2CPh)_2$ are present. Thus, ATRP cannot occur.

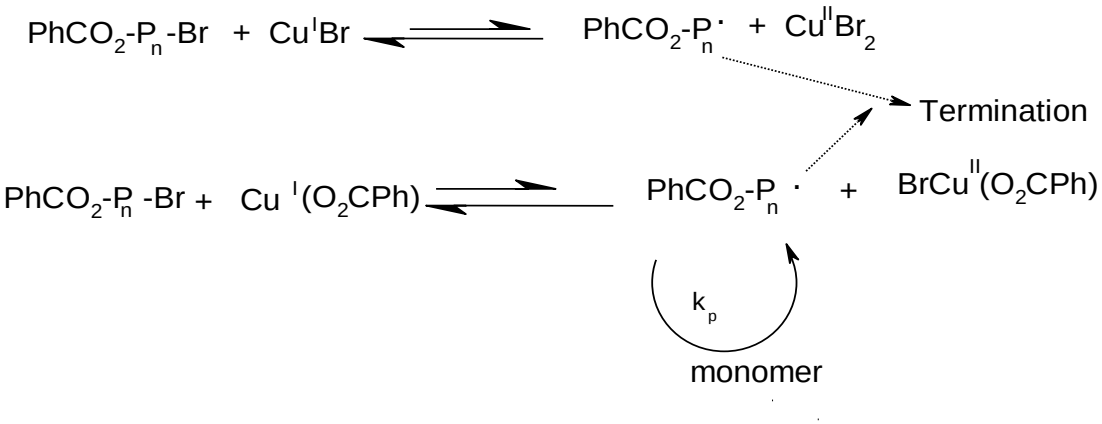
From Scheme 2.3, it can be seen that 1 equiv of $CuBr_2$/2dNbpy can react with 2 equiv of BPO and generate 2 equiv of bromine-terminated oligomers.

Scheme 2.2 Mechanism of reverse ATRP Initiated by BPO/CuBr

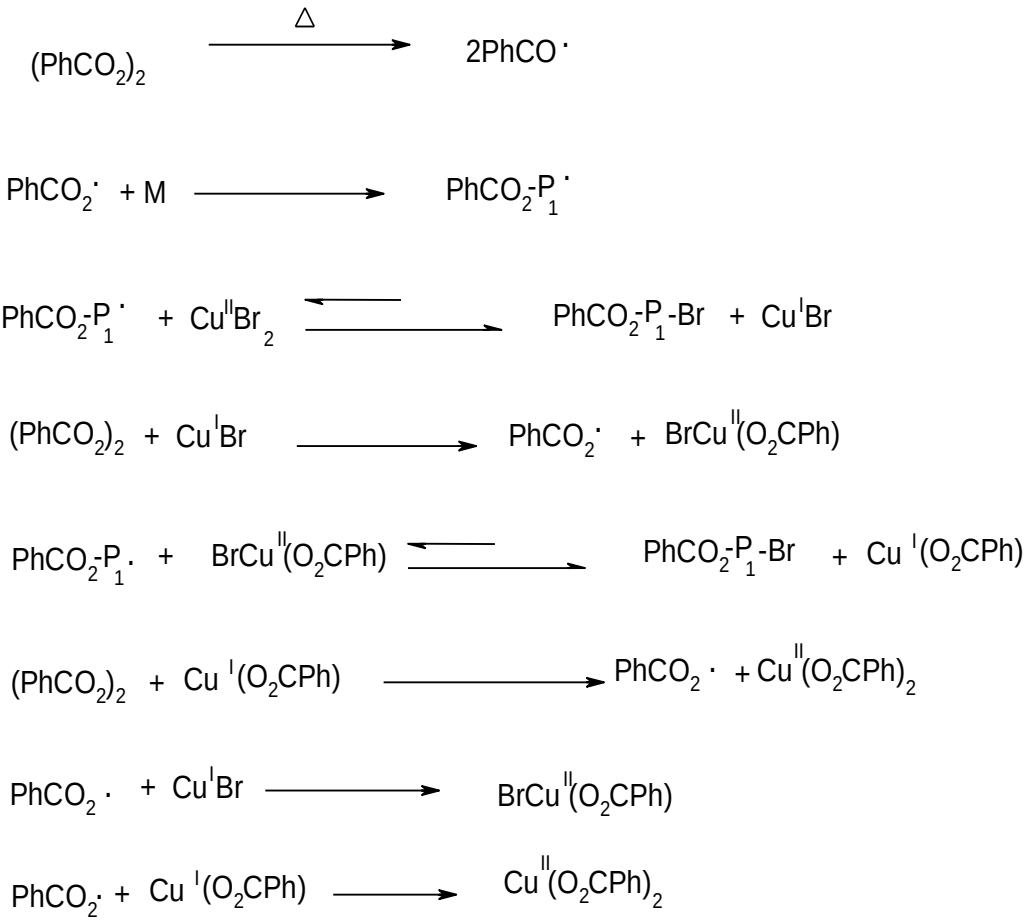
Initiation :



Propagation :



Scheme 2.3. Mechanism of Initiation Using BPO/$CuBr_2$



In summary, we would like to emphasize the differences in the homogeneous reverse ATRP initiated by azo compounds and peroxides. In the former process, reverse ATRP occurs efficiently in the presence of CuBr/2dNbpy, which can scavenge initiating/growing radicals and from CuBr/2dNbpy and RBr species. In addition, initiating/growing radicals do not interact with CuBr/2dNbpyspecies. In contrast, $CuBr_2$/2dNbpy is an inefficient component of reverse ATRP initiated by BPO. This is due to electron transfer from Cu(I) to BPO and coordination of benzoate anions to copper. Such an induced decomposition reoxidizes Cu(I) back to Cu(II) species and disables the catalytic reaction. However, the polymerization initiated by BPO can be controlled in the presence of a sufficient amount of CuBr. After the induced decomposition of BPO, the growing radicals are deactivated by Cu(II) species to produce bromine-terminated oligomers and Cu(I) species. Both

$Cu(O_2CPh)$ and CuBr complex by the ligand can then successfully catalyze ATRP.[2]

2.3. Diazo Chemistry

Aromatic diazonium compounds became industrially very important after Griess (1866a) discovered in 1861/62 the azo coupling reaction, by which the first azo dye was made by C.A. Martius in 1865. This is still the most important industrial reaction of diazo compounds. Hantzsch and Traumann (1888) discovered that a heteroaromatic amine, namely 2-aminothiazole, can also be diazotized. Heteroaromatic diozonium compounds were, however, only used for azo dyes much later, to a small extent in the 1930's, but intensively since the 1950's.

Aromatic diazonium salts are almost as important for reactions in which the diazonio group is lost as molecular nitrogen and in which aryl cations and radicals are the reagents proper.

2.3.1 Photochemistry of aromatic diazonium salts

At the end of the last century, Andressen[54] established that aqueous solutions of diazo compounds decompose under the influence of light. The mechanism of the photochemical decomposition is not completely understood; it appears that it is largely determined by the environment and by the chemical species present. The effect of substituents on the light sensitivity of diazo compounds has been studied by many investigators [55-56].

Aryldiazonium salt photoinitiators

These salts are photosensitive and undergo photolysis togive aryl halides [57-58]. When aryldiazonium salts are photolysed, an aryl halide, nitrogen gas, and the Lewis acid BF_3 are generated. For example,

$$[\ Ar\text{-}N \equiv N\ ]^{+}\ BF_4^{-} \xrightarrow{h\nu} Ar\text{-}F + N_2 + BF_3 \qquad (2.40)$$

If the photolysis is carried out in the presence of a polymerisable monomer, the Lewis acid which is produced initiates cationic polymerization.

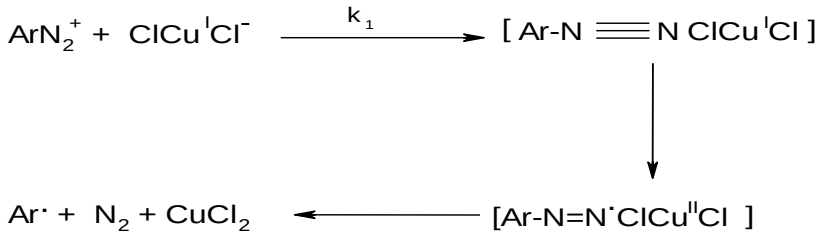
Aryldiazonium salts are effective photoinitiators for the ring opening polymerization of epoxides which find interest in U.V. curing. Many mechanistic pathways are proposed to explain the Lewis acid catalysed polymerization of epoxides [59].

The efficiency of aryldiazonium salts as photoinitiators depends upon the structure of both the cationic and anionic portions of these salts [60]. Dreyfuss and Dreyfuss predicted [61] the order of stability of anionic portions as $PF_6^- > BF_4^- > SbCl_6^-$ which refers to the efficiency of initiation. They also showed good evidence of the absence of termination and transfer processes. Since it is possible to modify the structure of the arly portion of aryldiazonium salts, a great number of these compounds can be synthesized having variation in their spectral absorption characteristics

2.3.2 Sandmeyer reaction

The rate of formation of **(**X = Cl) catalysed by cuprous chloride is first order in diazonium ion and in catalyst but inversely proportional to $[Cl^-]$ [62]. The latter observation is explained by the conversion of $Cu^1Cl^-_2$ (the active form of the catalyst) to $Cu^1Cl^3{}_4^-$. The rate-determining step is probably the initial coordination step; electron-withdrawing groups in Ar aid reaction. Zollinger [63] has pointed out

the similarity of this sequence to electron transfer by an inner sphere mechanism, in which one of the ligands acts as a bridge between reductant and oxidant, proposed by Taube [64]. The electron-transfer sequence is also similar to the proposed mechanism of radical formation outlined**;** the same sequence has also been proposed for other catalytic reagents, e.g. $FeCl_2$ [65]. The relative reactivities shown in the Sandmeyer reaction (-CN>-I>-Br>-Cl) follow the same sequence followed in electron transfer by the inner sphere mechanism.

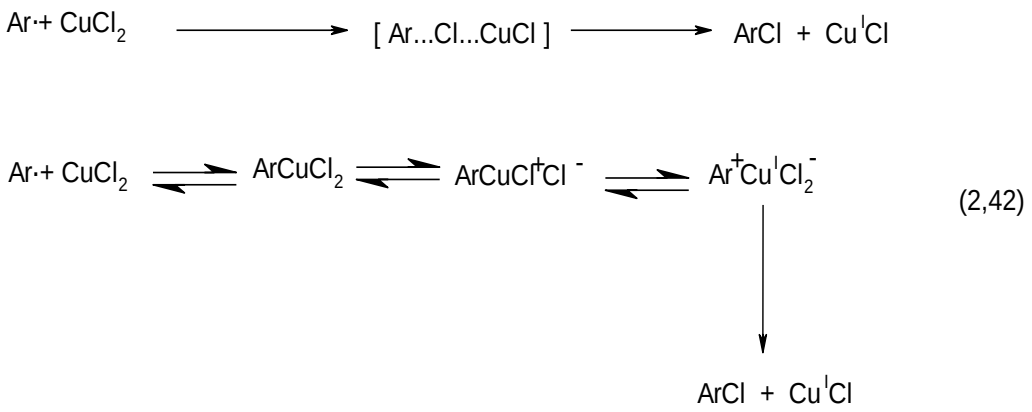


(2.41)

Extensive work by Kochi's group [66-67] shows that aryl radical reaction with $Cu^{11}Cl$ can occur; an alternative oxidative substitution process involving electron transfer to Cu^{11} may also occur and this is most likely when the initial radical can from a relatively stable carbonium ion species. These ligand transfer reactions are extremely fast, with rate constants close to the diffusion-controlled limit (second-order rate constants are $3{\cdot}6 \times 10^8$, $1{\cdot}1 \times 10^9$ and $4{\cdot}3 \times 10^9$ $1mol^{-1}$ sec^{-1} at 25 ^0C for transfer of thiocyanate, chloride and bromide respectively) [68]. Of course the steps outlined in these equations can take place in rapid succession without dissociation of the complex, in which case it would be difficult to trap free aryl radicals in solution.

Apparent catalysis by cupric ion or by metallic copper is less effective than that by cuprous ion and it seems likely that initial electron transfer occurs to form Cu^1 as the active catalytic species [69].

The corresponding Sandmeyer-type reaction to form iodoarenes proceeds in the absence of a catalyst at room temperature. This has been attributed to the low oxidation potential of I^-, which allows it to reduce the aryldiazonium ion, leading to aryl radical species.



(2,42)

2.3.3 Replacement of the Diazonio Gruop by Alkenes and Alkynes: The Meerwein Reaction

The diazonio gruop of arenediazonium salts can be replaced by alkenes and alkynes or, seen from the other reaction partner, alkenes and alkynes cen be arylated with arenediazonium salts. The reactions are catalyzed by copper salts and, as found more recently, also by salts of palladium and other metals.

Some observations are important for improvement of the yield and for the elucidation of the mechanism of the Meerwein reaction. Catalysts are necessary for the process. Cupric chloride is used in almost all cases. The best arylation yields are obtained with low $CuCl_2$ concentrations (Dickerman et al., 1969) [70]. One effect of $CuCl_2$ was detected by Meerwein et al. (1939) [70] in their work in water-acetone systems. They found that in solutions of arenediazonium chloride and sodium acetate in aqueous acetone, but in the absence of an alkene, the amount of chloroacetone formed was only ane-third of that obtained in the presence of $CuCl_2$. They concluded that chloroacetone is formed according to Scheme 10-50. The formation of

chloroacetone with $CuCl_2$ in the absence of a diazonium salt was investigated by Kochi (1955a, 1955b) [70]. Some Cu^{11} ion is reduced by acetone to Cu^{1} ion, which provides the electron for the transfer to the diazonium ion (see below).

$$ArN_2^+ + Cl^- + CH_3COOCH_3 \xrightarrow{CUCl_2} ArH + N_2 + ClCH_2COCH_3 \quad (2,43)$$

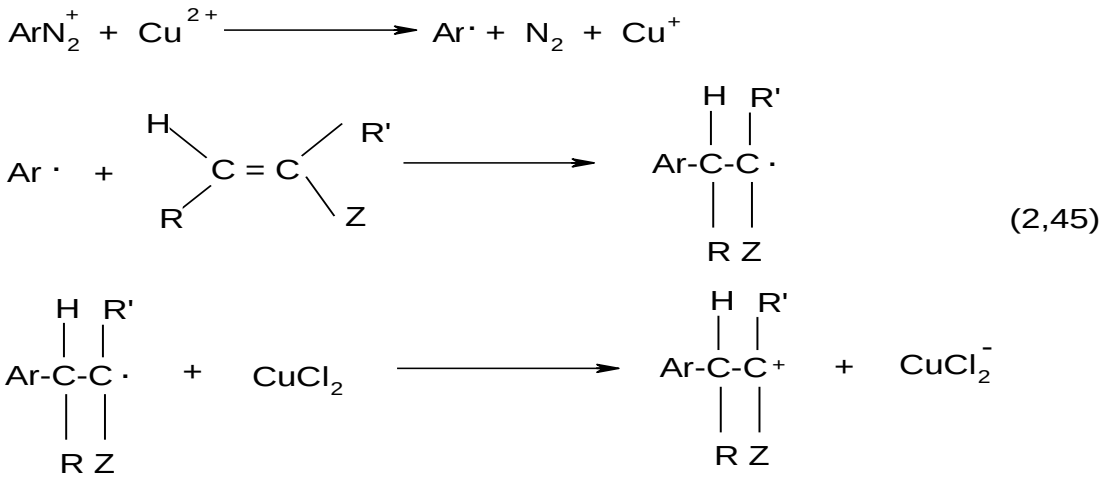
$$2Cu^{2+} + Cl^- + CH_3COCH_3 \longrightarrow 2Cu^+ + ClCH_2COCH_3 + H^+$$

Kochi (1955a, 1955b) [70] showed that the chlorination of acetone by $CuCl_2$ provides the cuprous ion as the initiator which, by electron transfer to the arenediazonium ion, starts the chain reaction by forming an aryl radical. This radical adds to the double bond of the alkene (Z= electron-withdraving group, R,R'=alkyl or H) giving the arylethane radical. As realized by Galli (1988,p.780) [70], this addition is relatively fast, and therefore Meerwein reactions do not in general suffer from competition of ligand transfer steps to the aryl radical. For substitution, the electron of the arylethane radical is transferred to $Cu^{11}Cl_2$ and the aryl ethene is formed by removal of a proton from the carbocation **(**Citterio, 1981) [70]. For the addition product a $CuCl_2$ ion pair provides the arylethane radical with a chlorine atom and Cu^{11} is reduced to Cu^{1}. It is unlikely that carbocation is also converted to the addition product by a simple chloride ion addition. For such a pathway to the addition product, one would expect to observe also the addition of nucleophiles other than Cl^-, in particular H_2O, which could even be dominant. However, the corresponding 2-arylethanol derivatives have not been found in the presence of chloride ions.

$$Ar^{\cdot} + CuCl_2 \longrightarrow ArCl + CuCl$$

$$Ar^{\cdot} + CH_3COCH_3 \longrightarrow Ar\,H + CH_3COCH_2^{\cdot} \quad (2,44)$$

$$CH_3COCH_2^{\cdot} + CuCl_2 \longrightarrow CH_3COCH_2Cl + CuCl$$



(2,45)

The chain process of the Meerwein reaction can be visualized as shown in (2,45). There are at least two likely termination reactions for the chain process, namely the addition of a chlorine atom from $CuCl_2$ to the aryl radical or reaction of the aryl radical with a hydrogen atom of acetone, followed by the formation of chloroacetone.[70]

Polymerization of some acrylic monomers can be redox initiated by mixtures (1 : 1) of transition metal derivatives (acetates, metallocenes) and arenediazonium salts (DS) [71].

Behavior of the polymerization of MMA initiated by mixtures of transition metal acetates with *p*-chlorobenzenediazonium tetrafluoroborate. The fastest polymerization was observed with the initiating system based on $Ce(OAc)_3$-DS, 90% conversion after 6h. With $Rh(OAc)_2$-DS, an induction period was found during the first 2-3 hours. Molecular weights increased monotonously with $Rh(OAc)_2$-DS.It seemed that the number of chains was constant for Ce-, Co-, and Cr- based initiating systems but it increased with $Rh(OAc)_2$-DS.

Despite slow initiation, $Rh(OAc)_2$-DS yielded polymers with the lowest polydispersities (M_w/M_n=1.2-1.45). There other systems provided polymers with higher polydispersities, although the molecular weights increased with conversion

and polydispersities were lower than in a typical radical or anionic polymerization at these temperatures.

In addition to metal acetates, various metallocenes have been reacted with diazonium salts in order to initiate the polymerization of acrylic monomers, acrylates, and methacrylates. Among various metallocenes based on Zr (IV), Ru(II), Cr(II) and Ni(II), dicyclopentadienylchromium, Cp_2Cr, appeared to have the best control of the polymerization of both methyl acrylate and MMA (e.g. PMMA, $M_{n,theor}$ =20,000, M_w/M_n =1,24).[72]

3. EXPERIMENTAL PART

3.1 Chemicals Used

a) Monomer

Methyl methacrylate (MMA, 99% Acros) 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.

c) Ligand

PMDETA (N, N, N', N', N''- Pentamethyldiethylenetriamine, 99% Acros) was dried and over sodiumhydroxide.

d) Other materials

$CuCl_2$, CuCl, CuBr, $CuBr_2$, Diphenylether, Cyclohexanone, Acetone, N,N'-Dimethylformamide. p-chlorobenzenediazonium tetrafluoroborate was kindly supplied from Prof. Yagci.

3.2 Typical 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, added initiator under nitrogen, again tube was degassed and placed in thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with THF. Poly (methyl methacrylate), PMMA, and then passed through a column of neutral alumina to remove metal salts. The excess of THF was evaporated under reduced pressure, sample was dissolved in THF and precipitated methanol, added HCl (4 drops) , filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined by gravimetrically.

3.3 Synthesis of Poly (methyl methacrylate) under vacuum in bulk at room temperature.

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, added initiator under nitrogen, again tube was degassed and placed in magnetic stirring. After the polymerization, the reaction mixture was diluted with THF. Poly (methyl methacrylate), PMMA, and then passed through a column of neutral alumina to remove metal salts. The excess of THF was evaporated under reduced pressure, sample was dissolved in THF and precipitated methanol, added HCl (4 drops), filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined by gravimetrically.

3.4 Typical 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, added initiator under nitrogen, again tube was degassed and placed in thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with THF.

Poly (methyl methacrylate), PMMA, and then passed through a column of neutral alumina to remove metal salts.

The excess of THF was evaporated under reduced pressure, sample was dissolved in THF and precipitated methanol, added HCl (4 drops), filtered and dried in vacuum oven at 25°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 poly(methyl methacrylate) standards.

4.RESULTS AND DISCUSSION

4.1 The synthesis of poly(MMA) using diazonium salt/$CuBr_2$/PMDETA system

The polymerization of MMA was carried out in bulk using *p*-chlorobenzenediazonium tetrafluoroborate (**1)** as an initiator/ $CuBr_2$/ PMDETA system, $[MMA]_0 / [I]_0 = 100$ and diazonium salt / $CuBr_2$/ PMDETA = 1:1:1 in mole ratio, at room temperature (20^oC), 60 and 90^oC. M_n vs. conversion % (Fig.4.1 - 4.3 - 4.5) and $\ln([M]_0/[M])$ vs. time (Figure 4.2 – 4.6 – 4.10) plots are established to monitor whether the polymerization proceeds in a controlled manner. Figure 4.1 shows a typical behavior of the polymerization of MMA initiated with **1**/$CuBr_2$/PMDETA system at 90^oC.

The number average molecular weight, measured by GPC, up to 42500 increased linearly with conversion (to 85%), and the polydispersities were in the range of 1.13 and 1.25. However, the efficiencies of initiator, *f* ($M_{n,,theo}/M_{n,,GPC}$), are generally low such as 0.17-0.20, the polymerization is closely controlled. In a plot of $\ln([M]_0/[M])$ vs. time as shown in Figure 4.2, a straight line is observed indicating that the kinetics is first-order with respect to monomer concentration for the polymerization carried out at 90^oC.

This also reveals that the concentration of propagating radicals is constant throughout the polymerization. For the polymerization at room temperature, a deviation from linearity is observed (Fig. 4.5). The control of the polymerization is getting lost after

ca. 60% conversion while the polydispersities, 1.44-1.57, support this fact, which are rather higher than those obtained with conversions (<60%). Obviously, the polymerization rates decreased in the order of 90^{o}C> 60^{o}C> room temperature.

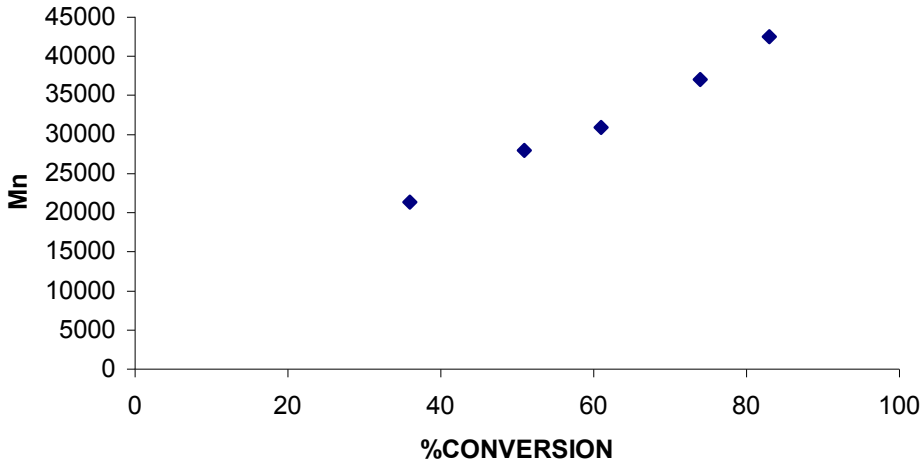


Figure: 4.1 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 90°C with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

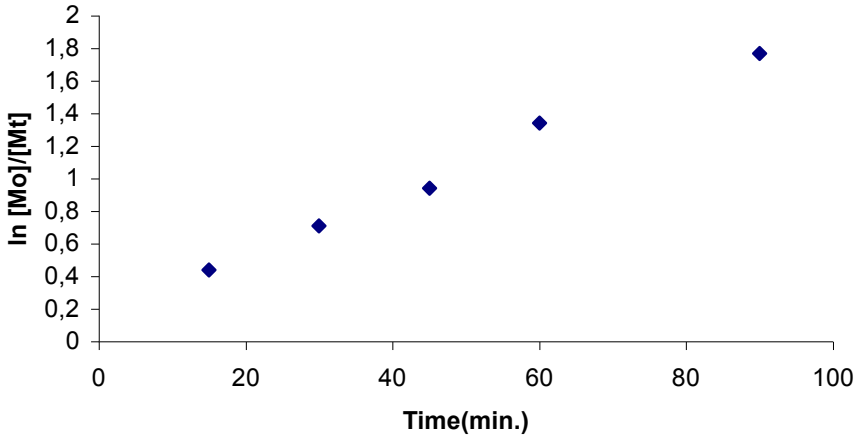


Figure 4.2: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

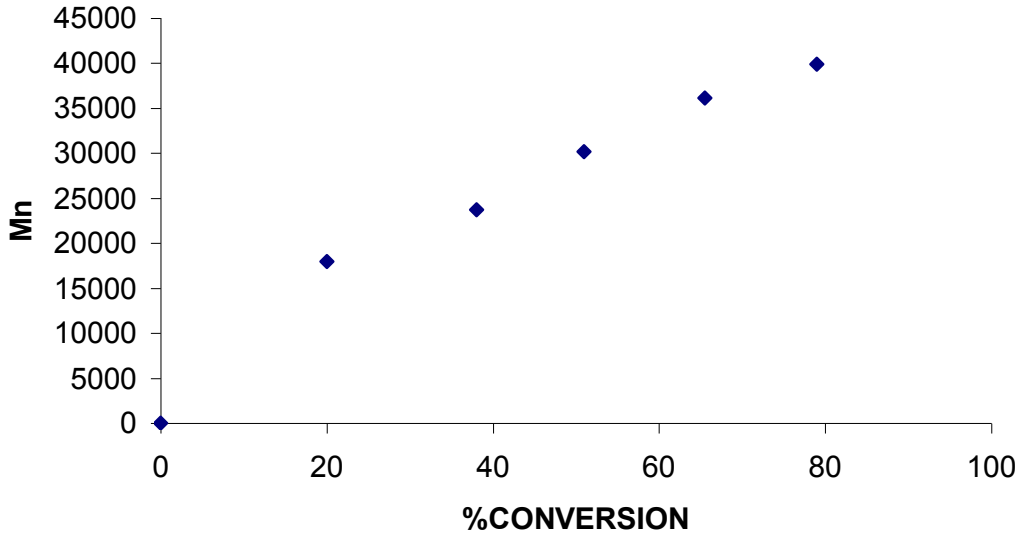


Figure: 4.3 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 60°C with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

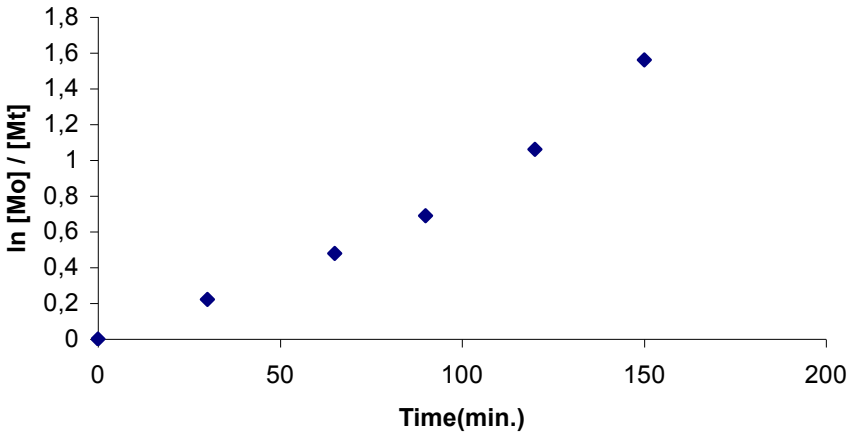


Figure 4.4: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 60°C with $[MMA]_0 / [I]_0$ =100, *p*-

chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

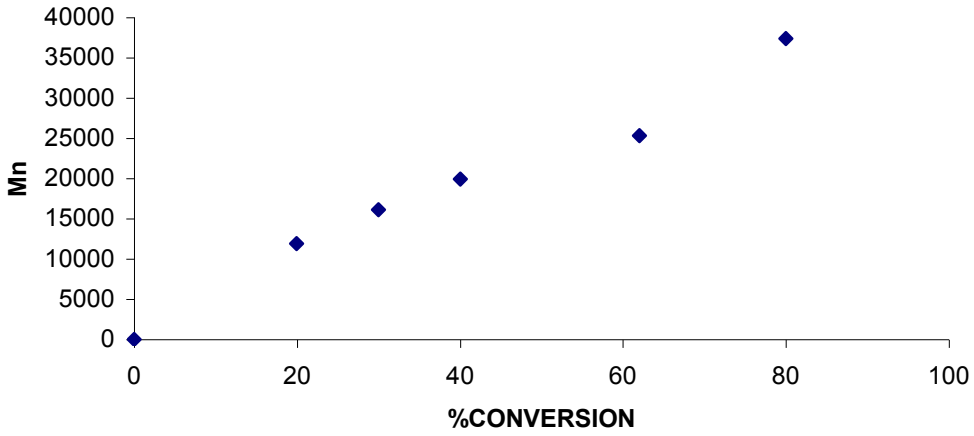


Figure: 4.5 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at room temperature with $[MMA]_0$ / $[I]_0$ =100, *p*-chloro benzene diazonium tetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

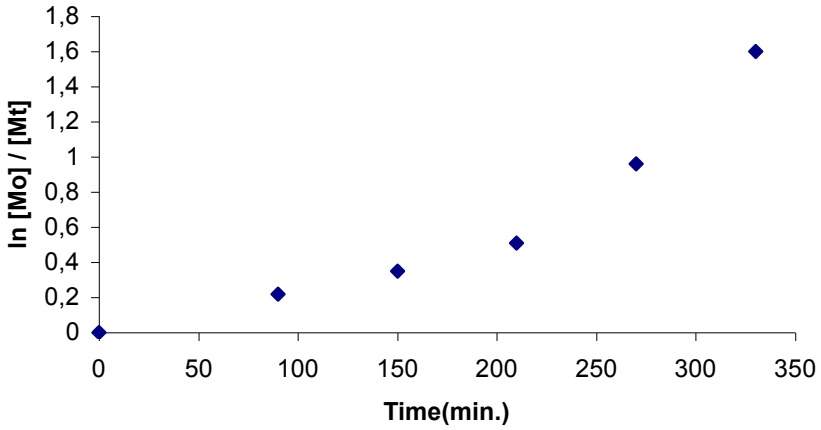


Figure 4.6: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at room temperature with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

Samp. N.	[M]o/[I]o	Mn sec	Mn theo.	Con %	PDI	Time(min)	Temp.	Ini. Eff.
I	100	21300	3600	36	1,13	15	90	0,17
II	100	28000	5150	51	1,13	30	90	0,18
III	100	31000	6100	61	1,18	45	90	0,20
IV	100	37000	7500	74	1,25	60	90	0,20
V	100	42500	8300	83	1,16	90	90	0,20

Table 4.1 Polymerization of MMA in bulk at 90°C with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

Samp. N.	[M]o/[I]o	Mn gpc	Mn theo.	Con%	PDI	Time(min.)	Temp.	Ini. Eff.
Ⅰa	100	18000	2050	20	1,07	30	60	0,11
Ⅱa	100	23700	3850	38	1,09	65	60	0,16
Ⅲa	100	30150	5000	50	1,27	90	60	0,16
Ⅳa	100	36100	6700	65,5	1,11	120	60	0,18
Ⅴa	100	39900	7900	79	1,17	150	60	0,19

Table 4.2 Polymerization of MMA in bulk at 60°C with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

Samp. N.	[M]o/[I]o	Mn gpc	Mn theo.	Con%	PDI	Time(min.)	Temp.	Ini Eff.
Ⅰb	100	11900	2000	20	1,18	90	Room T.	0,16
Ⅱb	100	16100	3050	30	1,24	150	Room T.	0,19
Ⅲb	100	19900	4050	40	1,11	210	Room	0,20

							T.	
Ⅳb	100	25500	6600	62	1,44	270	Room T.	0,26
Ⅴb	100	37300	8100	80	1,57	330	Room T.	0,21

Table 4.3 Polymerization of MMA in bulk at room temperature with $[MMA]_0 / [I]_0$ =100, *p*-chloro benzene diazonium tetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0 = 9,36M$

4.2 The synthesis of poly(MMA) using diazonium salt/$CuCl_2$/PMDETA system

The bulk polymerization of MMA was initiated at 60°C and at room temperature by mixtures of **1**/$CuCl_2$/PMDETA in the mole ratios given previously. For the polymerization at 60°C, M_n values increased linearly with conversion up to 80% indicating that polymerization proceeded in a controlled manner (Fig. 4.7). The polydispersity index throughout the reaction is at around 1.10-1.25. A straight line obtained from a plot of $\ln([M]_0/[M])$ vs. time with a slight deviation around 65% conversion (Fig. 4.8) reveals that the kinetics is first-order with respect to monomer concentration. *f* values are still low in the range of 0.10-0.21. The polymerization rate is slower than that of the system using $CuBr_2$. In the case of room temperature polymerization (Fig.4.9 – 4.10), it is observed that there is a linear dependence between M_n and conversion %, however, in $\ln([M]_0/[M])$ vs. time graph, an induction period is monitored up to 150 minutes.

The induction period observed for PMDETA/$CuCl_2$ complex initiated polymerization is probably a result of the differences between reduction potential of PMDETA/$CuBr_2$ and PMDETA/$CuCl_2$ complexes. Polydispersities in the range of 1.18-1.3 9 are lower than those of the system using $CuBr_2$ at room temperature.

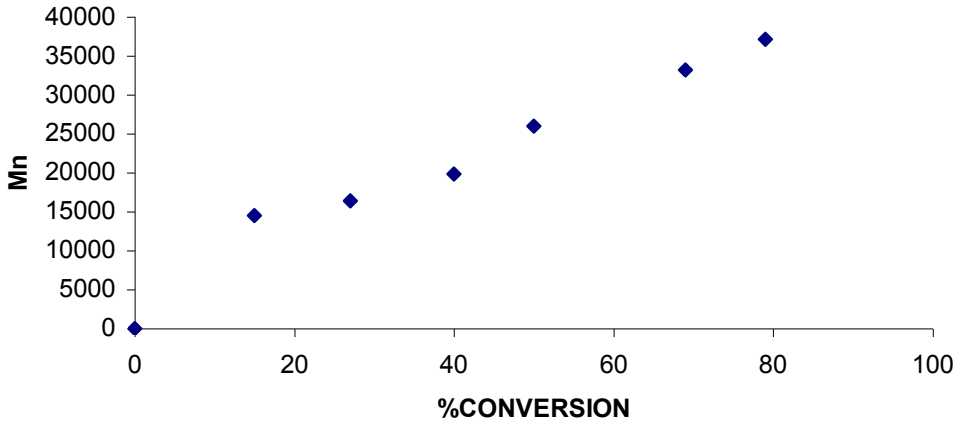


Figure: 4.7 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 60°C with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuCl_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

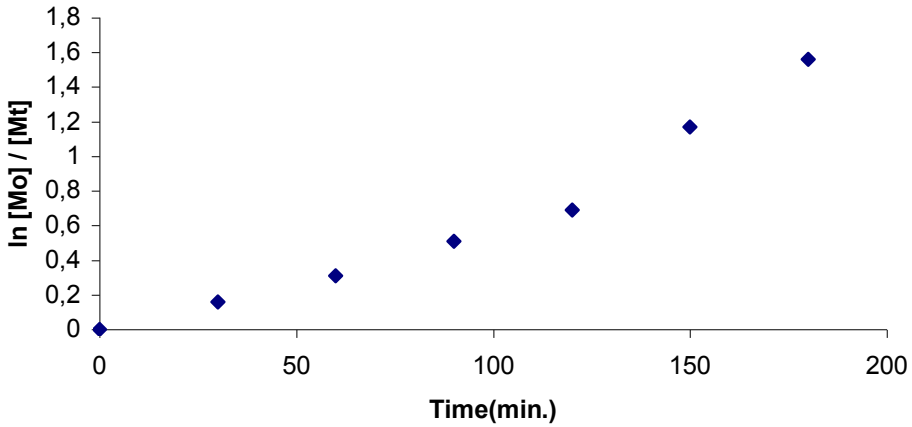


Figure 4.8: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 60°C with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuCl_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

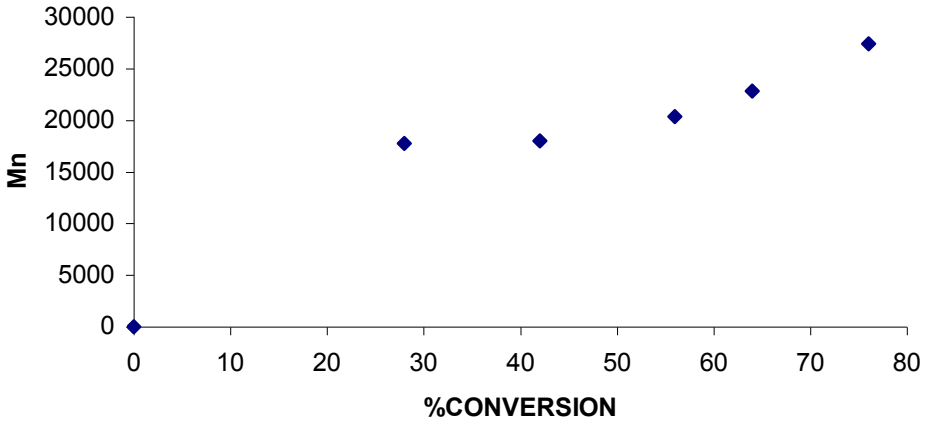


Figure: 4.9 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at room temperature with $[MMA]_0$ / $[I]_0$ =100, *p*-chloro benzene diazonium tetrafluoroborate / $CuCl_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

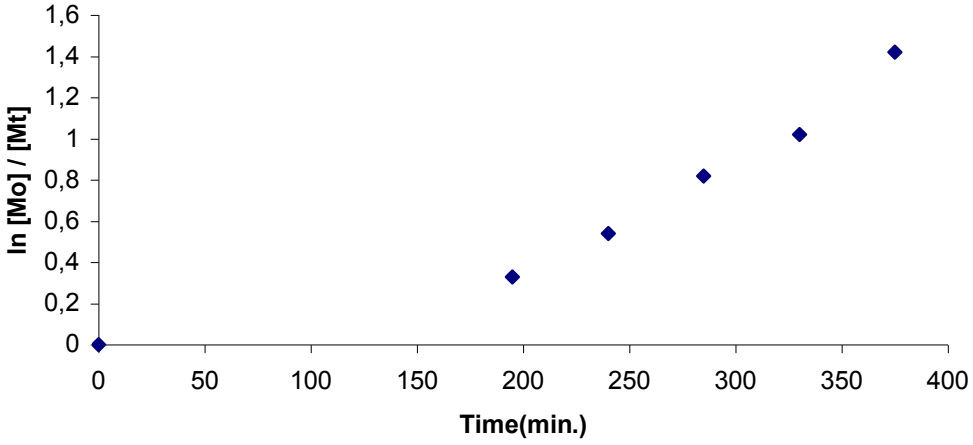


Figure 4.10: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at room temperature with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuCl_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M.

Samp. N.	[M]o/[I]o	Mn gpc	Mn the.	Con%	PDI	Time(min.)	Temp.	Ini. Eff.
VIa	100	14500	1500	15	1,13	30	60	0,10
VIIa	100	16400	2700	27	1,13	60	60	0,16
VIIIa	100	19900	4050	40	1,16	90	60	0,20
IXa	100	26000	5000	50	1,12	120	60	0,19
Xa	100	33200	6900	69	1,10	150	60	0,21
XIa	100	37100	7900	79	1,25	180	60	0,21

Table 4.4 Polymerization of MMA in bulk at 60°C with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuCl_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M

Samp. N.	[M]o/[I]o	Mn gpc	Mn theo.	Con%	PDI	Time(min.)	Temp.	Ini. Eff.
VIb	100	17750	2800	28	1,35	195	Room T.	0,16
VIIb	100	18000	4200	42	1,18	240	Room T.	0,23
VIIIb	100	20300	5600	56	1,28	285	Room T.	0,27
IXb	100	22800	6400	64	1,26	330	Room	0,28

							T.	
							Room	
Xb	100	27400	7600	76	1,39	375	T.	0,27

Table 4.5 Polymerization of MMA in bulk at room temperature with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuCl_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M.

4.3 The synthesis of poly(MMA) using diazonium salt/CuBr/$CuBr_2$/PMDETA system

The bulk polymerization of MMA was accomplished with **1**/CuBr/$CuBr_2$/PMDETA system at 90°C taking $[MMA]_0$ / $[I]_0$ = 100 and **1**/CuBr/$CuBr_2$/ PMDETA = 1:0.2:0.4:1 in mole ratio. The plots of M_n vs. conversion and ln($[M]_0$/[M]) vs. time both demonstrated a controlled polymerization behavior (Fig.s 4.11 and 4.12). The addition of extra CuBr as an activator to the polymerization system increased the rate than that of the system using $CuBr_2$ only, since it also takes place in the decomposition step of aryldiazonium salt (**1**) in order to produce aryl radicals via an electron transfer to **1**.

Samp. N.	[M]o/[I]o	Mn gpc	Mn theo.	Con%	PDI	Time (min)	Temp.	Ini. Eff.
VI	100	16000	3000	30,56	1,11	15	90	0,19

Ⅶ	100	23200	5300	53	1,06	30	90	0,22
Ⅷ	100	33900	7100	70	1,18	45	90	0,21
Ⅸ	100	35600	7500	75,5	1,22	60	90	0,21
Ⅹ	100	38900	8200	82	1,20	75	90	0,21

Table 4.6Polymerization of MMA in bulk at 90°C with with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate /CuBr/$CuBr_2$ / PMDETA =1 : 0.2 :0.4 :1 $[MMA]_0 = 9{,}36M$

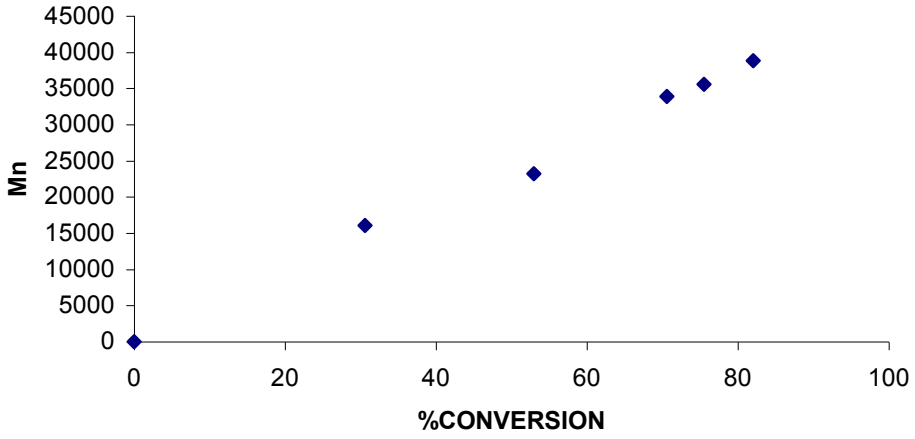


Figure: 4.11 Dependence of number average(Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in polymerization of MMA in bulk at 90°C with $[MMA]_0 / [I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate /CuBr/$CuBr_2$ / PMDETA =1 : 0.2 :0.4 :1 $[MMA]_0 = 9{,}36M$

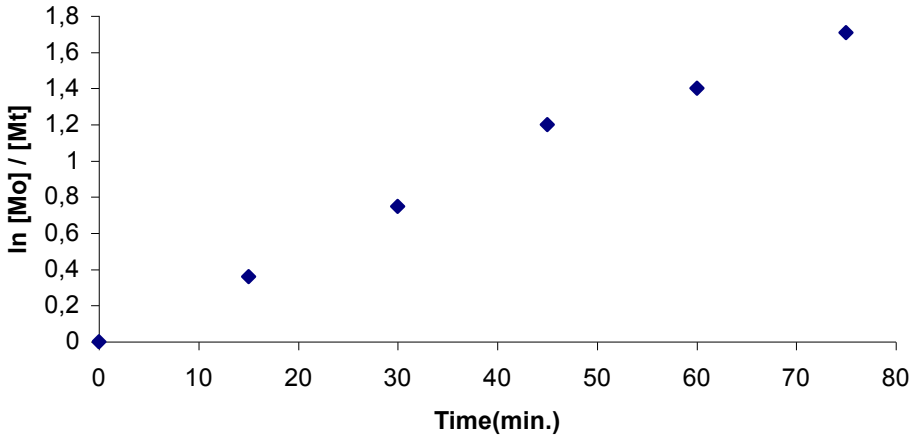


Figure 4.12: Comparison of the semi-logarithmic kinetic plots of PMMA's obtained with polymerization of MMA in bulk at 90°C with with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate /CuBr/$CuBr_2$ / PMDETA =1 : 0.2 :0.4 :1 $[MMA]_0$ = 9,36M

Figure 4.13 illustrated that conversion dependence of M_w/M_n for MMA polymerization.

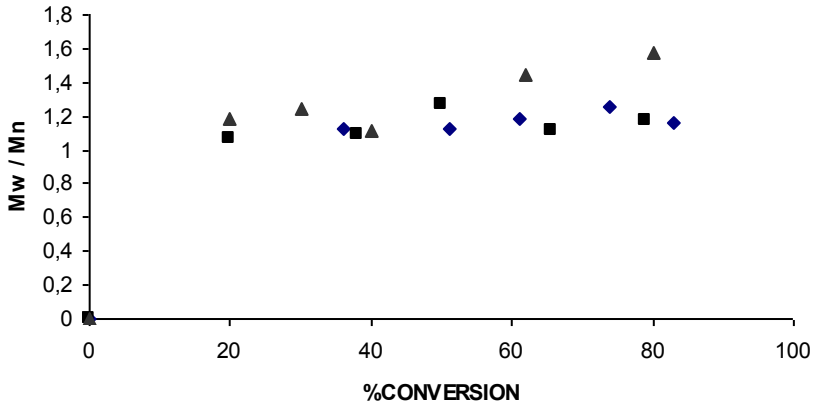


Figure 4.13 : ♦ represents polymerization of MMA in bulk at 90°C with $[MMA]_0$ / $[I]_0$ =100, *p*-chloro benzene diazonium tetrafluoroborate / CBr_2 / PMDETA =1 : 1

: 1 $[MMA]_0$ = 9,36M. ■ represents polymerization of MMA in bulk at 60°C with $[MMA]_0$ / $[I]_0$ =100, *p*-chloro benzene diazonium tetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M. . ▲ represents polymerization of MMA in bulk at room temperature with $[MMA]_0$ / $[I]_0$ =100, *p*-chloro benzene diazonium tetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M.

4.4End Group Characterization

If the chain end is a bromine 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 of an final polymer obtained after 28 % conversion of an additional monomer. This experiment thus demonstrates the quantitative presence of a bromine atom at the chain end of the macroinitiator.

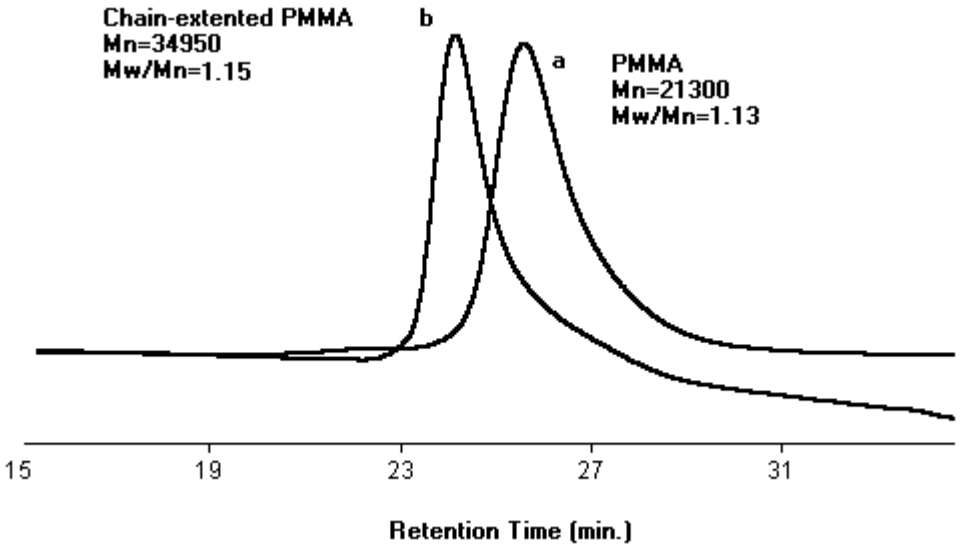


Figure 14. GPC chromatograms of the isolated PMMA(a)[Conditions: *T*= 90°C; with $[MMA]_0$ / $[I]_0$ =100, *p*-chlorobenzenediazoniumtetrafluoroborate / $CuBr_2$ / PMDETA =1 : 1 : 1 $[MMA]_0$ = 9,36M used as initiator and of the chain extended

(b) (after precipitation in methanol). Conditions: *T*= 90°C; *t* =50 min.; solvent, DPE ;$[MMA]_0$=4.67 ; $[MMA]_0$ / $[I]_0$ =400 ; macro initiator / CuCl / PMDETA = 1 : 1 : 1

4.5Synthesis of Poly (methyl methacrylate) under vacuum in various solution at 90°C

Table 4.7 illustrates the effect of various solvents on the MMA polymerization under vacuum.

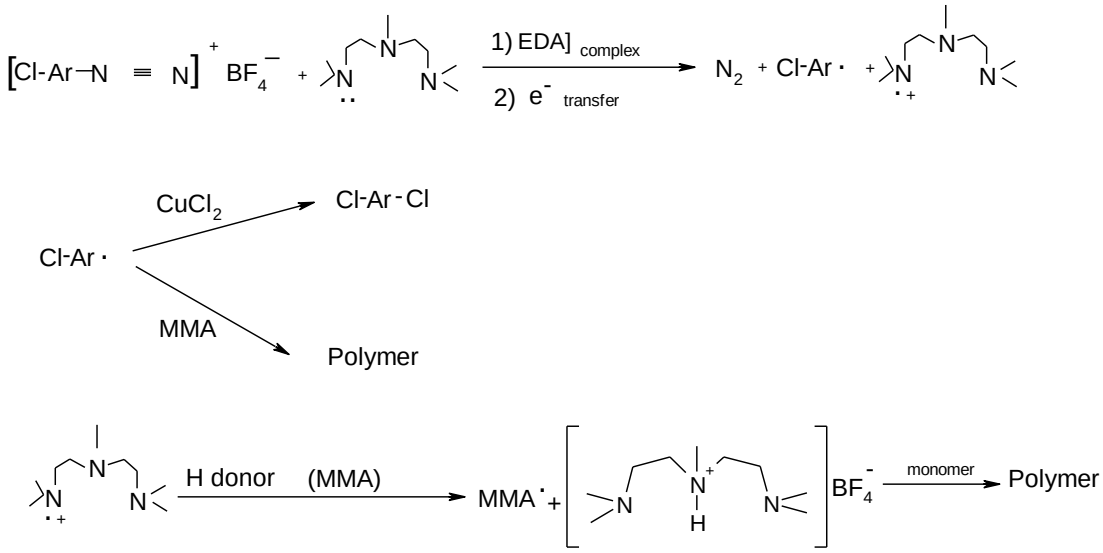
Samp. N.	Mo / Io	Solvent	Mn theo.	Con%	PDI	Time	Temp.	Mn gpc	Mon/Solv. (v/v)
A	100	DPE	5306	53	1,36	240	90	34500	50%
B	100	Acetone	4004	40	1,27	240	90	15170	10%
C	100	DMF	1087	11	1,11	380	90	4200	10%
D	100	Siklohek.	-	-	-	240	90	-	50%

Polymerization can not be controlled and two different phase (solid and liquid) were formed in solution system.. A key observation is that control is completely lost when the polymerization is carried out in various solvents.

5. CONCLUSION

Well-defined PMMA with a narrow polydispersity and a halogen atom as end group can be obtained using a new initiation system: **1**/Cu(I) and/or Cu(II)/PMDETA at various temperatures. A plausible mechanism of the polymerization is proposed to be similar to the reverse ATRP. The obtained PMMA functionalized by an halide atom may then be used to achieve the chain-extended polymer by addition of MMA in a classical ATRP process.

We suggest below scheme for this MMA polymerization mechanism in bulk for using $CuBr_2$, $CuCl_2$ and at room temperature.



In the initiation step, tertiary amine (PMDETA) transfers a pair of nonbonding electrons to a diazonium salt (**1**) in order to give a diazoammonium ion ($Ar\text{-}N_2N^+R_3$), which rapidly decomposes into a diazenyl radical ($Ar\text{-}N_2^{\cdot}$) and a PMDETA radical cation.

Similar reactions of diazonium salts with tertiary amines were reported by Levit et al.[8] A diazenyl radical decomposes into an aryl radical that can react with monomers to produce propagating chains. They may also directly abstract the halogen atom, Br, from the $CuBr_2$, which results in a reduction of $CuBr_2$ to CuBr and alkyl halide. The following propagation proceeds like conventional ATRP process.

On the other hand, a tertiary amine radical cation may probably abstract a hydrogen radical from any hydrogen donor source, e.g. MMA and/or PMDETA, which may then initiate the free radical polymerization of MMA. The halogen atom transfer from $CuBr_2$ to an active center may afford a process proceeding in a controlled manner. To clarify the role of PMDETA

REFERENCES

[1] **D.G.T Hill G.G.H O'Donnel**, (1982), Prog. Polym. Sci. A.D. JENKINS and V.T. STANNETT8, **215**

[2] **Xia, J., Matyjaszevski, K.,** (1999), Macromolecules,**32,**5199

[3] **Moad, G., Solomon, D.H.,** (1995), The Chemistry of Free Radical Polymerization, Pergamon Press, Oxford,

[4] **Solomon, J.C.,** (1996), Polymeric Materials Encyclopedia, CRN Press, Massachusetts, **V4**

[5] **Matyjaszevski, K.,** (1995), Macromol. Eng., (Ed, Mishara, M.K.), Plenum Press, New York.

[6] **Baysal, B.,** (1981), Polimer Kimyasi, ODTU Basim Isbirligi, Ankara,

[7] **Akar, A.,** (1999), Polimer Kimyasina Giris, ITU, Istanbul,

[8] **R.G. Charles, M.A Pawlowski.,** (1958), J.phys. Chem. 62 440.

[9] **E.M. Arnett, M.A Pawlowski.** (1958), J.phys. Chem 62 440.

[10] **E.G Kasting, H. Naarmann, H. Reis,** (1965), Anyew Chem. 77 313.

[11] **K. Uehara, M. Tanaka N. Murata,** (1967), J.Chem. Soc. (Japan) Ind. Chem. Sect 70 1564.

[12] **J. Nemcek, J. Barton,** (1969), Eur. Poly. J. Suppl. 265.

[13] **R.S Mulliken,** (1952), J. Amer. Chem. Soc.74 811.

[14] **E.M. Kosowe,** (1965), Progr. Phys. Org . Chem. 3 81.

[15] **Sato, T., Abe, M., Otsu, T.,** (1997), Macromol. Chem., **178**, 1267.

[16] **Sticler, M., Meyerhoff, G.,** (1978), Macromol. Chem., **179**, 2729.

[17] **Mayo, F.,** (1953), J. Am. Chem. Soc., **75**, 6136.

[18] **Burnet, G.M., Loan, L.D.,** (1955), Trans. Faraday Soc., **51**, 214.

[19] **Malmstrom, E.E., Hawker, J.C.,** (1998), Macromol. Chem. Phys., **199**, 923.

[20] **Otsu, T., Yoshida, M.,** (1982), Macrolom. Chem. Rapid Commun., **3**, 127.

[21] **Georges, M.K., Veregin, R.P.N., Kazmaier, P.M., Hamer, G.K.,** (1993), Macromolecules, **26**, 2987.

[22] **Georges, M.K., Veregin, R.P.N., Kazmaier, P.M., Hamer, G.K.,** (1993), Macromolecules, **26**, 5316.

[23] **Borsig, E., Lazar, M., Capla, M., Fldrian, S.,** (1969), Angew. Macromol. Chem., **9**, 89.

[24] **Mardare, D., Matyjaszewski, K.,** (1994), Am. Chem. Soc. Polym. Preprints, **27**, 645.

[25] **Greszia, D., Mardare, D., Matyjaszewski, K.,** (1994), Am. Chem. Soc. Polym. Preprints, **35** (1), 466.

[26] **Harwood, J.H., Arvanitopoulos, L.D., Gravel, M.P.,** (1994), Am. Chem. Soc. Polym. Preprints, **35** (2), 549.

[27] **Wayland, B.B., Pszmik, G., Mukerjee, S.L., Fryd, M.,** (1994), J. Am. Chem. Soc., **116**, 7943.

[28] **Otsu, T., Kuriyama, A.,** (1985), Polym. J., **17**, 97.

[29] **Otsu, T., Tazki, T.,** (1986), Polym. Bull., **16**, 277.

[30] **Acar, M.H., Yağcı, Y.,** (1991), Macromol. Rep., A28 (Suppl. 2), **177.**

[31] **Rizzardo, E.,** (1987), Chem. Aust., **54**, 32.

[32] **Otsu, T., Nayatani, K.,** (1958), Macromol. Chem. 27,149.

[33] **Otsu, T.,** (1961), Memoirs Of Faculty Engineering Osaka City University,3,205.

[34] **Otsu, T., Yoshida, M.,** (1982), Macromol. Chem. Rapid Comn.,31,27.

[35] **Moad, G., Rizzardo, E., Solomon, D.H.,** (1982), Macromolecules, **15**, 909.

[36] **Benoit, D., Grimaldi, S., Finet, J.P., Tordo, P., Fontanikle, M., Gnanov, Y.,** (1997), Am. Chem. Soc. Polym. Preprints, **38**, 729.

[37] **Puts, R.D., Sogah, D.Y.,** (1996), Macromolecules, **29**, 3323.

[38] **Matyjaszewski, K.,** (1997), Am. Chem. Soc. Polym. Preprints, **38** (1), 736.

[39] **Gaynor, S.G., Matyjaszewski, K.,** (1997), Am. Chem. Soc. Polym. Preprints, **38** (1), 758.

[40] **Arehart, S.V., Greszta, D., Matyjaszewski, K.,** (1997), Am. Chem. Soc. Polym. Preprints, **38** (1), 705.

[41] **Greszta, D., Matyjaszewski, K.,** (1997), Am. Chem. Soc. Polym. Preprints, **38** (1), 709.

[42] **Xia, J., Matyjaszewski, K.,** (1997), Macromolecules, **30**, 7697.

[43] **G. Odian,** (1991), Principle of Polymerization,3rd edition, Wiley, New York.

[44] **J.K. Kochi,** (1973), Ed. Free Radicals, Vols. I-II John Wiley, New York.

[45] **B. Giese,** (1976-1982), Ed. Free Radicals In Biology. I-V Academic Press, New York.

[46] **LE. T. P. Moad, G.Rizzardo, E. Thang, S.,** (1998), H.PCT Int. Application WO 9801478 A1 Chem. Abstr., 128 115390.

[47] **Chiefari, J. Mayadunne, R.T. Moad, G.Rizzardo, E. S.H.PCT,** (1999), Int. Application WO 9931144 A1 990624; A1 Chem. Abstr., 131,45250.

[48] **Chong, Y.K.; Le,T.P.; Moad, G.; Rizzardo, E Thang, S. H.** (1999), Macromolecules, 32, 2071-2074.

[49] **Matyjaszewski, K. Acs,** (1998), Symp. Ser., 685, 2-30.

[50] **Rizzardo, E. Moad, G.,** (1996), In The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications; Salamone J.C. , Ed CRC Press. Boca Raton, FL, Vol. 5, p 3834.

[51] **Wang, J. S., Matyjaszewski, K.,** (1995), Macromolecules, 28, 7572.

[52] **Xia, J., Matyjaszewski, K.**, (1997), Macromolecules, 30, 7692.

[53] **Barton, J., Borsig, E.** (1988), Complexes in Free-Radical Polymerization; Elsevier: New York.

[54] **M. Andressen,** (1895), Chem. Zentr., 66, 550.

[55] **M. S. Dinaburg,** (1964), Photosensitive Diazo Compounds, Focal Press, New York.

[56] **H. Zollinger,** (1961), Azo and Diazo Chemistry, Interscienc, London.

[57] **A. Reo,** (1949), Org. Reactions, 5, 193, 228.

[58] **J. Calvert, J. N. Pitts,** (1966), Photochemistry , John Willey and Sons Inc., New York.

[59] **N. M. Bikales,** (1967), Encyc. of Poly. Sci. and Tech., Vol. 6, 224, John Willey and Sons, New York.

[60] **S. I. Schessinger,** (1974), Photogr. Sci. and Eng, 18(4), 387.

[61] **P., Dreyfuss, M. P. Dreyfuss,** (1967), Adv. Polymer Sci., Vol. 4, pp. 528-590.

[62] **W. A. Cordrey, D. S. Davies,** (1952), Quart. Revs, 6, 358.

[63] **H. Zollinger,** (1973), Accounts Chem. Res.,6, 335.

[64] **H. Taube, J.** (1968), Chem. Ed., 45, 452.

[65] **J. P. Synder, R. J. Boyd, M. A. Whitehead,** (1972), Tetrahedron Letters, 4347.

[66] **J. K. Kochi,** (1957), J. Amer. Chem. Soc., 79, 2942.

[67] **C. L. Jenkins, J. K. Kochi,** (1972), J. Amer. Chem. Soc., 94, 856.

[68] **J. K. Kochi, R. V. Subramanian,** (1965), J. Amer. Chem. Soc., 87, 1508.

[69] **T. Cohen, R. J. Lewarchiik, J. Z. Tarino,** (1974), J. Amer. Chem. Soc., 96, 7753.

[70] **H. Zollinger,** (1994), Diazo Chemistry.

[71] **A. Citterio, F. Minisci, A. Albinati, S. Brockner,** (1980), Tetra Hedron Lett, 21, 2909.

[72] **K. Matyjaszewski, S. Gaynor, D. Greszta, D. Mardare, T. Shigamoto,** (1995), Lournal of Physical Organic Chemistry, 8, 306-315.

AUTOBIOGRAPHY

He was born in 1976 in Istanbul. In 1993, He graduated from Istanbul Vefa High School and attempted to the Chemical Department of Karadeniz University in 1993.

After graduating from KaradenizUniversity in 1998, he was accepted as a master student to Istanbul Technical University, Polymer Science and Technology Department of the Institute of Science and Technology in which he is about to graduate at the moment.