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IANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

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SYNTHESIS AND CHARACTERIZATION OF TELECHELIC POLYMERS BY
THE COMBINATION OF REVERSE ATOM TRANSFER RADICAL
POLYMERIZATION AND ATOM TRANSFER RADICAL COUPLING PROCESSES

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Date of submission : 19 December 2005

Date of defence examination: 31 January 2006

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JANUARY 2006

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**KARŞIT ATOM TRANSFER RADİKAL POLİMERİZASYONU VE ATOM TRANSFER
RADİKAL BİRLEŞMESİ YÖNTEMLERİNİN KOMBİNASYONU İLE TELEKELİK
POLİMERLERİNİN SENTEZLENMESİ VE KARAKTERİZASYONU**

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Tezin Enstitüye Verildiği Tarih : 19 Aralık 2005

Tezin Savunulduğu Tarih : 31 Ocak 2006

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OCAK 2006

ACKNOWLEDGEMENTS

I am deeply indebted to my thesis supervisor, Prof. Yusuf YAĞCI, for his kind guidance, valuable comments, suggestions, support, offering invaluable help in all possible ways and helpful criticism throughout this research.

I also owe a debt of gratitude to Dr. Ioan CIANGA for his kind guidance during the experiments. He assisted me in many ways.

I wish to express my special thanks to my Laboratory colleagues for all their help. Assist. Prof. Dr. Ali Ekrem MÜFTÜOĞLU, Atilla TAŞDELEN, Ayfer FIRAT, Barış KIŞKAN Burçin GACAL, Demet GÖEN ÇOLAK, Hakan DURMAZ, Laika BORAZAN, Dr. Luminita CIANGA, Nihan YÖNET, Seda YURTERİ, Yasemin DURMAZ with all of you, it has really been a great pleasure.

I would also like to thank my friend Murat GÜLÇÜR for his help and support during my master education.

Special thanks to Gökhan TEMEL. I could not succeed in all these things without his support.

Finally, I would like to thank to my parents and my sister for their patience, understanding and moral support during all stages involved in the preparation of this thesis.

December 2005

Binnur AYDOĞAN

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LIST of ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
RATRP	: Reverse Atom Transfer Radical Polymerization
ATRC	: Atom Transfer Radical Coupling
ROP	: Ring-Opening Polymerization
PS	: Polystyrene
¹H-NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
GPC	: Gel Permeation Chromatography
AIBN	: α,α' -Azobisisobutyronitrile
MWD	: Molecular Weight Distribution
CRP	: Controlled Radical Polymerization
RP	: Radical Polymerization
PDI	: Polydispersity Index
Bipy	: 2,2'-Bipyridine
dTBipy, dHBipy	
dNBipy	: Substituted Bipyridines
PMDETA	: <i>N,N,N',N'',N'''</i> -Pentamethyldiethylenetriamine
Me₆-TREN	: Tris[2-(dimethylamino)ethyl]amine
THF	: Tetrahydrofuran
RAFT	: Reversible Addition-Fragmentation Chain Transfer Polymerization
NMP	: Nitroxide Mediated Polymerization
SFRP	: Stable Free Radical Polymerization
PBA	: Poly(butyl acrylate)
PMA	: Poly(methyl acrylate)
PtBA	: Poly(<i>tert</i> -butylacrylate)
PPh₃	: Triphenylphosphine
M₀	: Initial molar concentration of the monomer
I₀	: Initial molar concentration of the initiator
M_{n,th}	: Theoretical molecular weight
M₁	: Molecular weights of the initiator
St	: Styrene
LRP	: Living Radical Polymerization

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LIST of SYMBOLS

λ	: Wavelength
$R\cdot$: Radical
I	: Initiator
M	: Monomer
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution
P_n^*	: Propagating species
M_t^n	: Transition metal
$P_n^=$: Polymer having a double bond at the chain end due to termination by disproportionation
P_{n+m}	: Polymer terminated by chain combination
X	: Halide group
k_a	: Rate constant of activation
k_{da}	: Rate constant of deactivation
k_p	: Rate constant of propagation
k_t	: Rate constant of termination

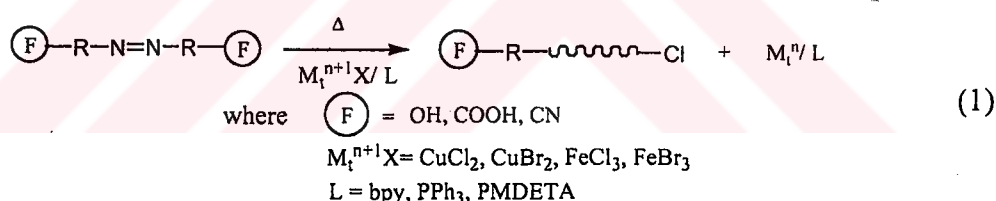
SYNTHESIS AND CHARACTERIZATION OF α,ω -TELECHELIC POLYMERS BY THE COMBINATION OF REVERSE ATOM TRANSFER RADICAL POLYMERIZATION AND ATOM TRANSFER RADICAL COUPLING PROCESSES

SUMMARY

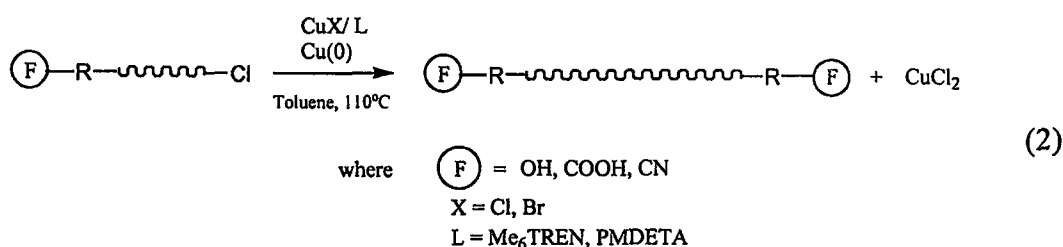
Conventional free radical polymerization (FRP) with azo containing initiators is not well controlled because of facile coupling and disproportionation reactions between the propagating species during the polymerization. FRP can be converted to controlled polymerization by using iron based catalyst system via so-called reversible atom transfer radical polymerization (RATRP).

Telechelic polymers, defined as macromolecules that contain two reactive end groups, are available via many polymerization techniques including controlled radical polymerization [1].

In this work, an alternate route is proposed for obtaining directly α,ω -telechelics by combination of RATRP and Atom Transfer Radical Coupling (ATRC) processes. By using RATRP and different types of functional azo initiators, polymers with functional group at one end and the halide group on the other end have been synthesized and characterized.



As it was shown previously [2], monofunctional telechelics have readily been converted to bifunctional telechelics by applying ATRC process. The bifunctional telechelics were characterized and the number of functionalities was determined .



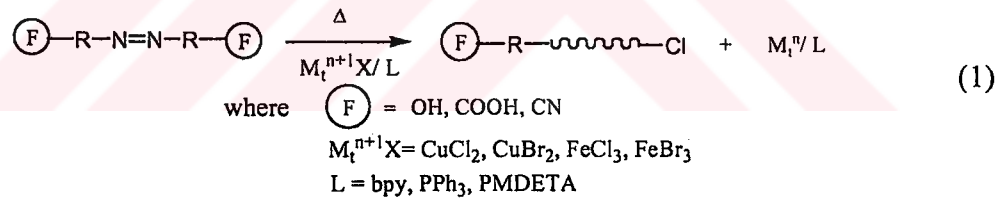
KARŞIT ATOM TRANSFER RADİKAL POLİMERİZASYONU VE ATOM TRANSFER RADİKAL BİRLEŞMESİ YÖNTEMLERİNİN KOMBİNASYONU İLE α,ω -TELEKELİK POLİMERLERİNİN SENTEZLENMESİ VE KARAKTERİZASYONU

ÖZET

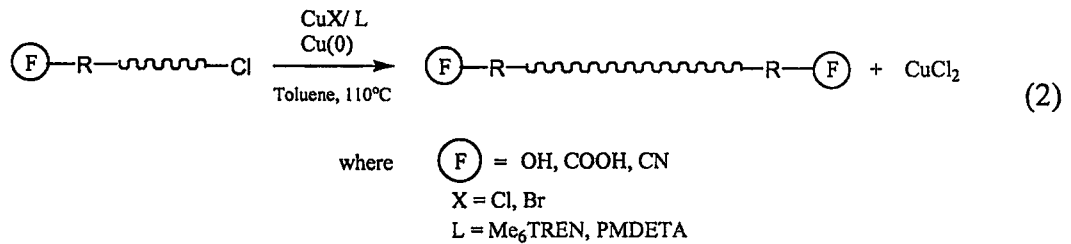
Polimerizasyon süresince büyüyen zincirler arasındaki basit birleşme ve orantısız sonlanma reaksiyonlarından dolayı azot içeren serbest radikal başlatıcıları ile gerçekleştirilen serbest radikal polimerizasyonu (FRP) iyi kontrol edilememektedir. FRP, karşıt atom transfer radikal polimerizasyonu (RATRP) vasıtasıyla metal kataliz sistemleri kullanılarak kontrol edilebilir.

İki adet etkili uç grubu içeren makromoleküller olarak tanımlanan telekelik polimerler (çift fonksiyonlu) kontrollü radikal polimerizasyonu da dahil olmak üzere pek çok polimerizasyon tekniğinde kullanılmaktadır [1].

Bu çalışmada, RATRP ve atom transfer radikal birleşmesi (ATRC) tekniklerinin kombinasyonu ile α,ω -telekelik (çift fonksiyonlu) polimerlerinin sentezi için alternatif bir yol sunulmaktadır. RATRP ve çeşitli yapıdaki fonksiyonel azo başlatıcıları kullanılarak, bir ucunda fonksiyonel grup ve diğer ucunda halojen grubu bulunan polimerler sentezlenmiş ve karakterize edilmiştir.



Daha önce de gösterildiği gibi [2] ATRC prosesi kullanılarak tek fonksiyonlu telekelik polimerler çift fonksiyonlu telekelik polimerlere kolaylıkla dönüştürülmüştür. Bu çalışmada da çift fonksiyonlu polimerler sentezlenerek fonksiyonel grup sayıları saptanmıştır.



1. INTRODUCTION

Telechelic polymers are important building blocks for the construction of various polymer materials [3,4]. Telechelic polymers having a variety of functional groups are prepared by a wide range of polymerization methods, namely anionic [5], cationic [6], ring opening [7], group transfer [8,9], free radical [10], metathesis [11-18], step growth [3] polymerization and chain scission [3] processes. Among them living ionic polymerization methods are usually preferred since they allow the preparation of well-defined telechelics with better control of functionality, molecular weight and polydispersity. On the other hand ionic techniques have serious limitations because of the requirement of high purity monomer and solvents, and monomer selectivity. Telechelics can also be prepared under classical free radical polymerization conditions by using a large amount of functional initiator or performing the polymerization in the presence of a functional transfer agent. Free radical copolymerization of olefinic monomers with suitable heterocyclic monomers also yields telechelics. However, nonfunctionalized end group formation is unavoidable due to the mutual side reactions of the free radical process. Therefore, the overall structure of telechelics was not controlled or well-defined. Controlled radical polymerization has recently become an established method to obtain various polymer architectures such as block, graft, star and gradient/ statistical copolymers, hyperbranched polymers and inorganic/ hybrids [19,20]. Atom transfer radical polymerization (ATRP) [20-23], nitroxide mediated polymerization (or stable radical mediated polymerization (NMP) [24,25], reversible addition fragmentation transfer (RAFT) [26,27] processes and reverse atom transfer radical polymerization (RATRP) [28] are well known techniques in this field.

ATRP provides monofunctional polymers by using functionalized halogenated initiators. The second functional group could be incorporated by transformation of the halogen end group. Such transformation may be realized by means of standard organic procedures like nucleophilic substitutions or radical additions of allylic

compounds. However, these reactions often do not proceed quantitatively and some side reactions such as elimination may also occur concomitantly.

The α - ω difunctionality can be introduced by combined ATRP and ATRC processes. In this concept, in the first stage monofunctional polymers were obtained by using functional initiators in ATRP. Subsequent radical coupling of the polymers thus obtained yields α,ω functional telechelic polymers. This work focuses on the synthesis of telechelic polymers with a new but conceptually similar procedure. Alkyl halide used as initiator in ATRP is formed by homolytic cleavage of a functional azo-initiator in RATRP. Then the propagating species are formed by abstraction of halogen from a higher oxidation state transition metal compound and process goes on as a classical ATRP initiation step. Subsequently, we applied this method to the synthesis of α,ω -telechelic polymers by combination with ATRC.



2. THEORETICAL PART

2.1 Telechelic Polymers

Telechelic polymers are defined as macromolecules that contain two reactive end groups. A pioneering work on the synthesis of functional polymers and their conversion to the final products with specific properties by reacting with functional groups may be dated back to 1947 [29]. However, the concept was not fully recognized until 1960 [30]. Significant contributions to the development of this class of polymeric materials are still found in the current literature. In the last decade there has been a rapid growth in the development and understanding of new controlled radical polymerizations [31]. Precise control of functionality, molecular weight and uniformity (molecular weight distribution) can now be made not only by ionic polymerization routes but also by newly developed living radical polymerization techniques. The range of monomers and functional groups used in the preparation of telechelic polymers has been expanded in recent years as a result of such developments.

A polymer can be considered to be telechelic if it contains end groups that react selectively to give a bond with another molecule. Depending on the functionality, which must be distinguished from the functionality of the end group itself, telechelics can be classified as mono-, di-, tri-, and multi-functional telechelics (polytelechelics) [4]. The functionality is defined as

$$f = \frac{\text{number of functional groups}}{\text{number of polymer chains}} \quad (2.1)$$

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Moreover, star and hyper-branched or dendric polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. Various macromolecular architectures obtained by the reactions of telechelics are represented in Figure 2.1.

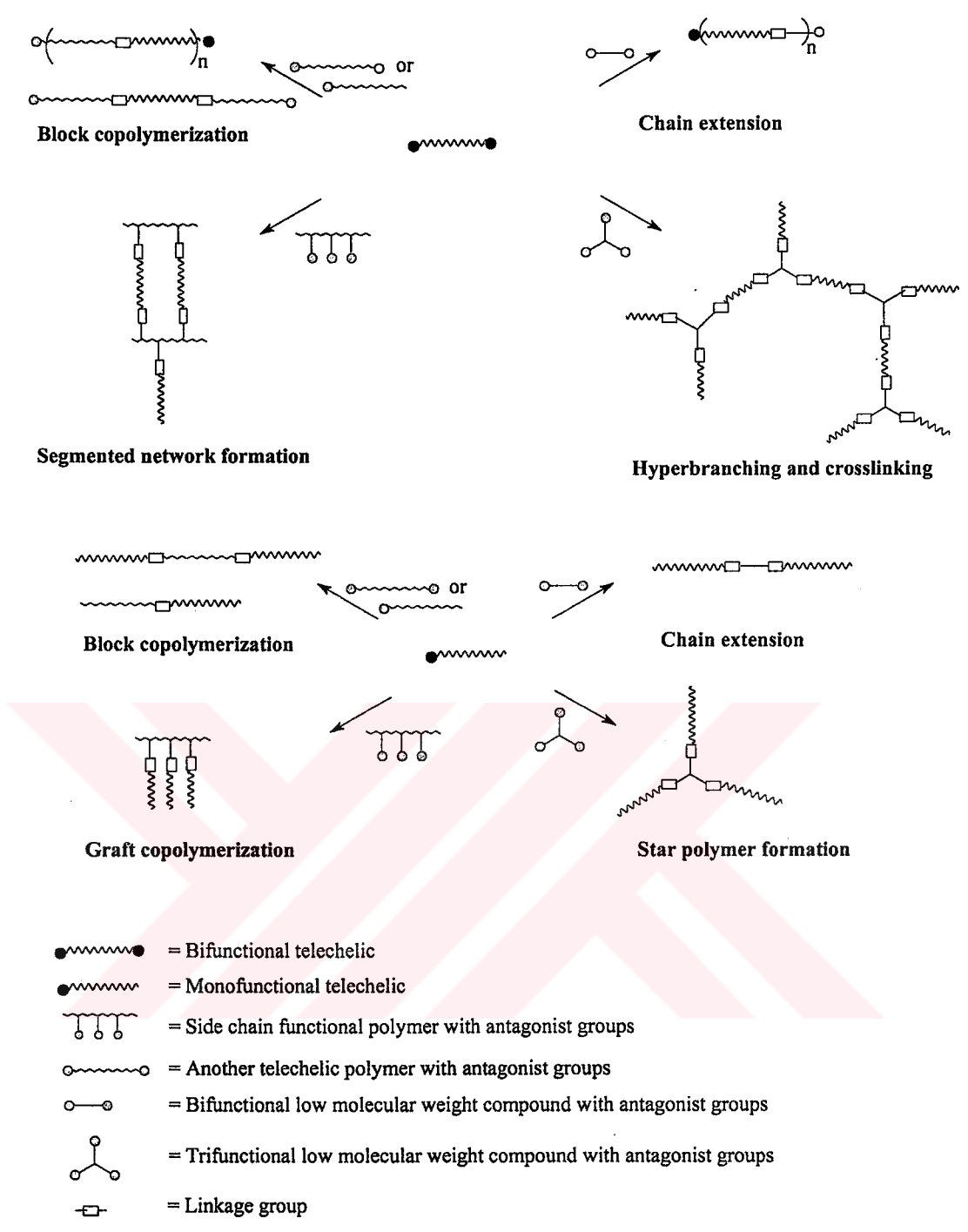


Figure 2.1 : Various architectures obtained by the reactions of telechelics

The functionality of the end group itself is important. When such groups are bifunctional (eg, vinyl groups) participate in polymerization reactions, yielding graft copolymers or networks, such telechelic polymers are called macromolecular monomers, macromonomers, or macromers.

Industrial interest in telechelics was stimulated by the development of thermoplastic elastomers (TPE), which consist of ABA block and multiblock copolymers. Liquid telechelic polymers are the basis for reaction injection moulding (RIM). Liquid telechelics that can be used for network formation offer processing advantages and may result in materials with improved properties [32].

The general techniques for the preparation of telechelics can be summarized as follows [1];

- Radical Polymerization
- Transfer Techniques
- Anionic Polymerization
- Carbocationic Techniques
- Ring–Opening Polymerization
- Metathesis Polymerization
- Chain Scission
- Step-Growth Polymerization
- Controlled / “Living” Radical Polymerization (CRP)
 - Nitroxide Mediated Living Radical Polymerization (NMP)
 - Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)
 - Atom Transfer Radical Polymerization (ATRP)
 - Reverse Atom Transfer Radical Polymerization (RATRP)
- Atom Transfer Radical Coupling

In this work only CRP and ATRC techniques will receive detailed consideration.

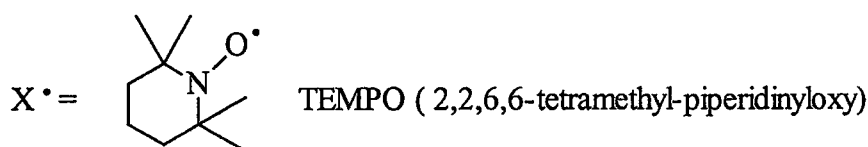
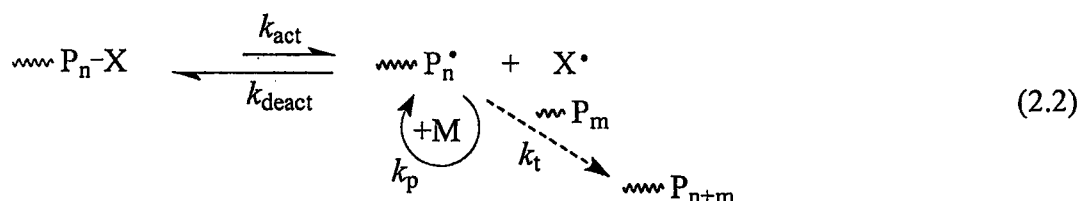
2.2 Controlled / “Living” Radical Polymerization (CRP)

Accurate control of polymerization process is an important aspect for the preparation of well-defined telechelics and end-functionalized macromolecules. Such control of chain ends was traditionally accomplished using living ionic polymerization techniques. But it is well known that the ionic processes suffer from rigorous synthetic requirements and in some cases they are sensitive to the functional groups to be incorporated. As described above in detail, free radical polymerization is a flexible and less sensitive to the polymerization conditions and functional groups.

However, conventional free radical processes yield polydisperse polymers without molecular weight and chain end control. Competing coupling and disproportionation steps and the inefficiency of the initiation steps lead to functionalities less than or greater than theoretically expected. For example, number of initiator fragments incorporated to per polymer chains by using conventional radical polymerization varied from 1.4 to 2.3. Recent developments in controlled/living radical polymerization provided possibility to synthesize well-defined telechelic polymers with controlled functionality also with radical routes [33]. All the four standard methods for controlled/living radical polymerization, namely, Atom Transfer Radical Polymerization (ATRP) [23,34], Stable Free Radical Mediated Polymerization (SFRP), also called as Nitroxide Mediated Polymerization (NMP) [35], Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) [36] and Reverse Atom Transfer Radical Polymerization (RATRP) [2] were used for the preparation of telechelic polymers.

2.2.1 Stable Free Radical Polymerization

Nitroxide mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations (SFRP). In this type of process, the propagating species ($P_n\cdot$) reacts with a stable radical ($X\cdot$) as seen in reaction (2.2). The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). The resulting dormant species (P_n-X) can then reversibly cleave to regenerate the free radicals once again. Once $P_n\cdot$ forms it can then react with a monomer, M, and propagate further.

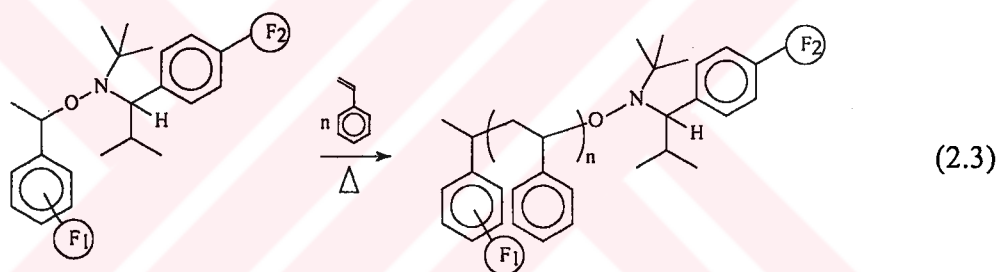


Unfortunately, TEMPO can only be used for the polymerization of styrene-based monomers at relatively high temperatures ($>120^\circ\text{C}$). With most other monomers, the

bond formed is too stable and TEMPO acts as an inhibitor in the polymerization, preventing chain growth.

Numerous advances have been made in both the synthesis of unimolecular initiators (alkoxyamines) that can be used not only for the polymerization of St-based monomers, but other monomers as well [37-41]. Most recently, the use of more reactive alkoxyamines and less reactive nitroxides has expanded the range of polymerizable monomers to acrylates, dienes, and acrylamides [42-44]. Several nitroxides that have been employed as mediators in Stable free-radical polymerizations are given in Table 2.1.

It is also possible to prepare telechelic polymers by NMP procedure since it tolerates a wide variety of functional groups [46]. For the synthesis of telechelics by NMP there are two general methods, i.e., functional groups can be placed at the initiating chain end, F₁, or the nitroxide mediated chain end, F₂.



It was reported that high degree of functionalization i.e., greater than 95 % is possible even at molecular weights up to 50 000-75 000 by NMP method [66].

A wide variety of functional groups including polynuclear aromatic pyrene group can also be introduced by taking advantage of monoaddition of maleic anhydrides and maleimide derivatives to alkoxy amine end followed by elimination of mediating nitroxide radical [67]. The thermal stability of the telechelics was increased as the alkoxyamine group was removed.

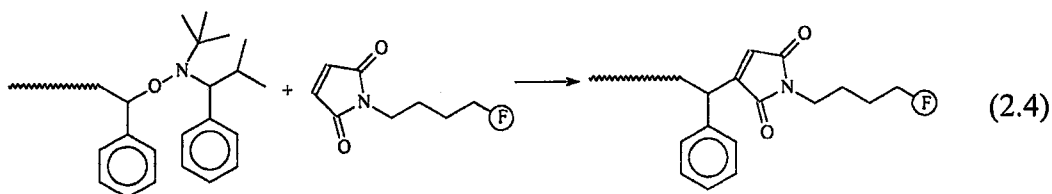
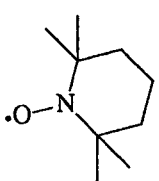
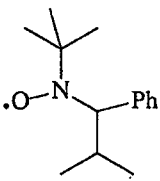
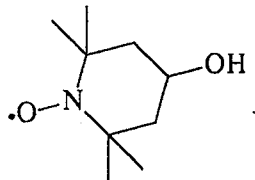
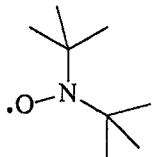
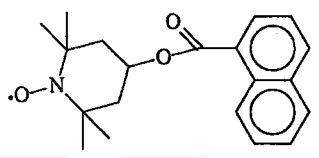
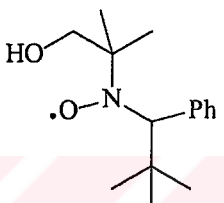
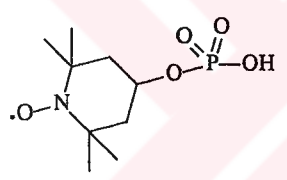
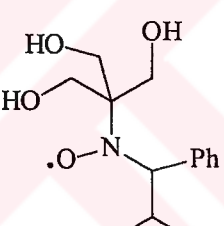
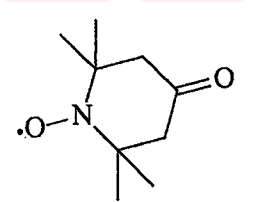
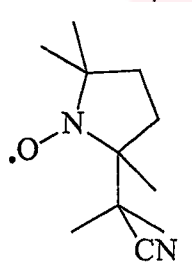
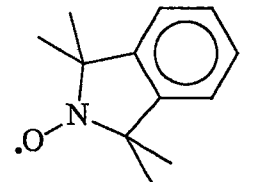
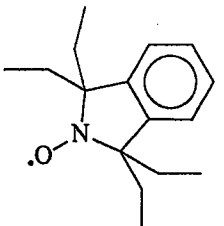
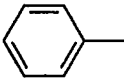
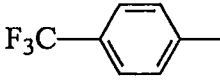
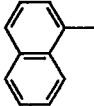
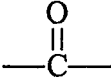


Table 2.1: Structures of Several Nitroxides Employed in SFRP

Structure	Reference	Structure	Reference
	[45]		[42]
	[46]		[51]
	[47]		[52]
	[48]		[53]
	[49]		[54]
	[50]		[55]

Telechelics with a variety of functional groups can essentially be prepared by using functional nitroxides (Table 2.2)

Table 2.2: Functional Groups Attached to Polymers by Nitroxide Mediated Living Free Radical Procedures

Functional group	Reference
OH	46, 48, 53, 56-61
	42, 62
	61
	47, 62
	47, 49, 53, 55, 63
CN	41, 42
PO(OR) ₂	42, 44, 64, 65
P(O) ₂ OH	48
NH ₂	46
COOH	46

2.2.2 Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)

In terms of polymerizable monomers, RAFT is at present the most versatile technique for conducting CRP, that is, it can be applied to a larger range of monomers than SFRP and ATRP. In contrast to NMP and ATRP, this system relies on chain transfer for the exchange between active and dormant chains. The chain end of a dormant chain carries a thiocarbonylthio moiety, which is chain-transfer-active. Upon chain transfer, the thiocarbonylthio moiety is transferred to the previously active chain, which now becomes dormant, and the previously dormant chain carries the radical activity and is able to propagate.

There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: (1) dithioesters (Z = aryl or alkyl), (2) trithiocarbonates (Z = substituted sulfur), (3) dithiocarbonates (xanthates) (Z = substituted oxygen), and (4)

dithiocarbamates ($Z =$ substituted nitrogen). Representative examples of thiocarbonylthio RAFT agents are shown in Figure 2.2.

To some extent the choice of RAFT agent determines the degree of control obtained. The general structure of a RAFT agent is depicted in Figure 2.2, where the Z group is the activating group, and R is the homolytically leaving group. To a large extent, the Z group determines the rate of addition, and the R group determines the rate of fragmentation. The choice of Z and R groups is dependent on the nature of the monomer to be polymerized.

RAFT polymerization is performed by adding a chosen quantity of an appropriate RAFT agent (Figure 2.2) to a conventional free radical polymerization mixture and yields polymers of predetermined chain length and narrow polydispersity. Polydispersity indices of less than 1.1 can be usually achieved under optimal conditions. The RAFT process offers the same versatility and convenience as conventional free-radical polymerization being applicable to the same range of monomers (e.g., (meth)acrylates, styrenes, acrylamides, vinyls), solvents, functional groups (e.g., OH, CO₂H, NR₂, NCO) and reaction conditions (e.g., bulk, solution, suspension and emulsion). The RAFT process yields thiocarbonylthio-terminated polymers (or 1,1-disubstituted alkene-terminated oligomers if macromonomers are used as RAFT agents) that can be chain extended to yield a variety of copolymers (e.g., AB, ABA blocks, gradient).

The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below (2.5a-e). As for conventional free-radical polymerization, initiation by decomposition of an initiator leads to formation of propagating chains. In the early stages, addition of a propagating radical ($P_n\cdot$) to the RAFT agent [$S=C(Z)SR$] followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical ($R\cdot$). The radical $R\cdot$ reinitiates polymerization by reaction with monomer to form a new propagating radical ($P_m\cdot$). In the presence of monomer, the equilibrium between the active propagating species ($P_n\cdot$ and $P_m\cdot$) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow. This feature of the RAFT process leads to the production of narrow polydispersity polymers. When the polymerization is complete, the great majority of the chains contain the thiocarbonylthio moiety as the end group (2.5e) which has been identified by ¹H-

NMR and UV-vis spectroscopy [68]. Additional evidence for the proposed mechanism was provided by the identification of the intermediate thioketal radical ((A) and/or (B), 2.5b,d) by ESR spectroscopy [69, 70].

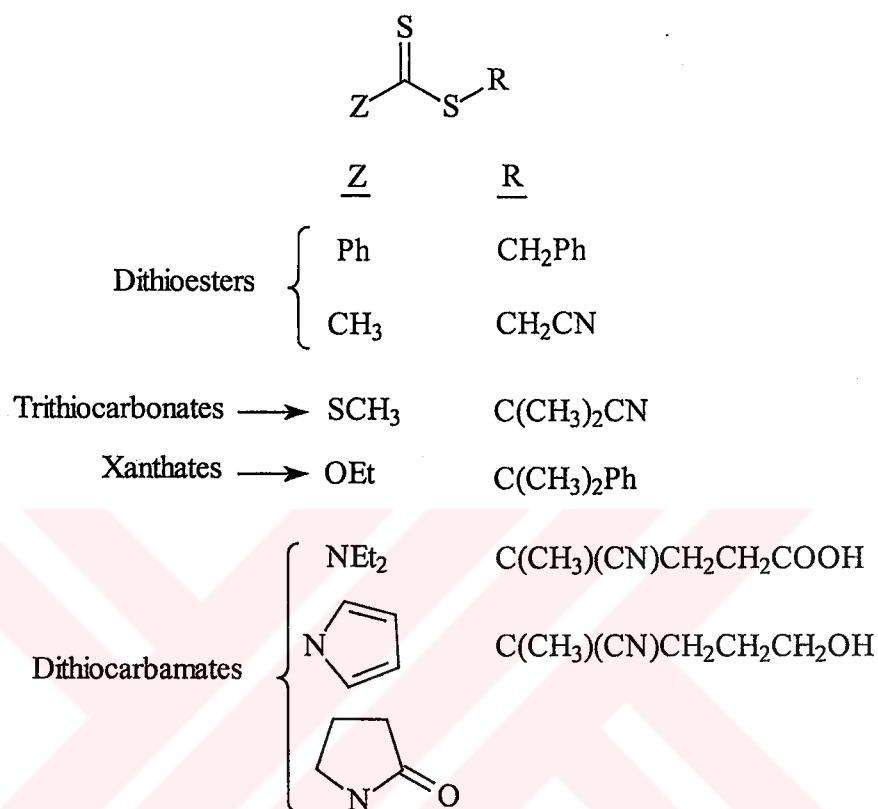


Figure 2.2: Examples of the different classes of thiocarbonylthio RAFT agents

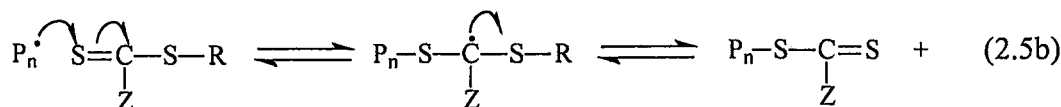
Telechelics can be prepared by RAFT process by selecting suitable RAFT agents [70].

Among the controlled radical polymerization methods discussed here, ATRP is the most applied route for the preparation of telechelics since besides the initiator functionalization, the terminal halogen produced in ATRP can easily be converted to many useful functionalities, e.g., by nucleophilic substitution [71]. Displacement of nitroxides and dithioesters is more difficult in respective NMP and RAFT processes.

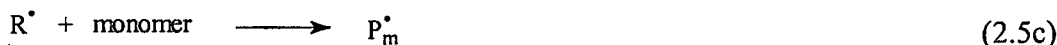
Initiation and propagation



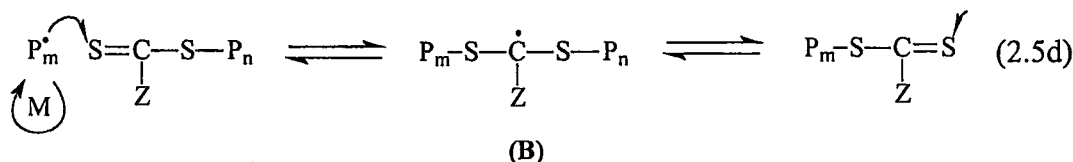
Addition to RAFT agent



Reinitiation



Chain equilibration by reversible addition fragmentation

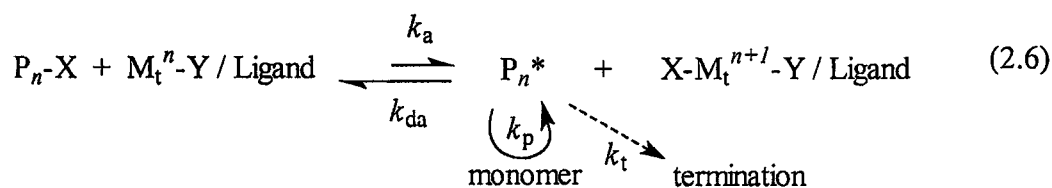


Overall



2.2.3 Atom Transfer Radical Polymerization (ATRP)

The name atom transfer radical polymerization comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [21]. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [72, 73].

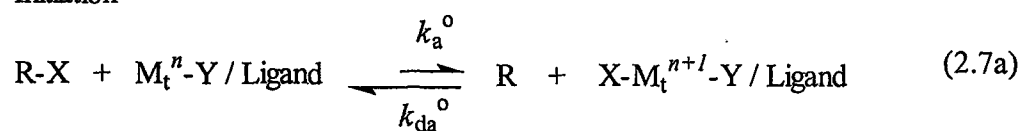


A general mechanism for ATRP is represented by (2.6). The radicals, i.e., the propagating species P_n^\bullet , are generated through a reversible redox process catalyzed by a transition metal complex (activator, $\text{M}_t^n\text{-Y / ligand}$, where Y may be another

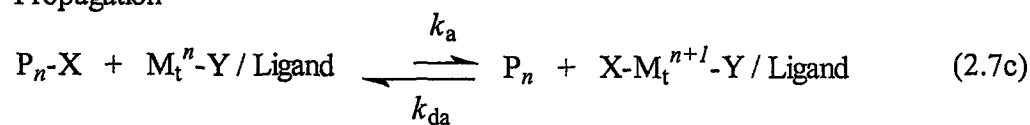
ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, P_n-X . Radicals react reversibly with the oxidized metal complexes, $X-M_t^{n+1}$ / ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a , and deactivation k_{da} , respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p . Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below [70]. (2.7a-e)

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [75]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

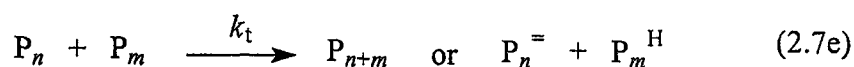
Initiation



Propagation



Termination



As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used.

2.2.3.1 Monomers

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

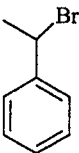
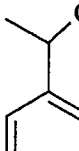
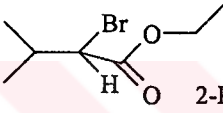
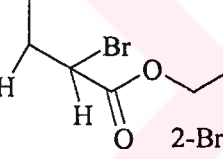
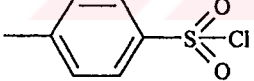
2.2.3.2 Initiators

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 rely 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 2.3.

Table 2.3: Types of initiators used in ATRP systems

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

2.2.3.3 Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

1. The metal center must have at least two readily accessible oxidation states separated by one electron.
2. The metal center should have reasonable affinity toward a halogen.

3. The coordination sphere around the metal should be expandable on oxidation

to selectively accommodate a (pseudo) halogen.

4. The ligand should complex the metal relatively strongly.

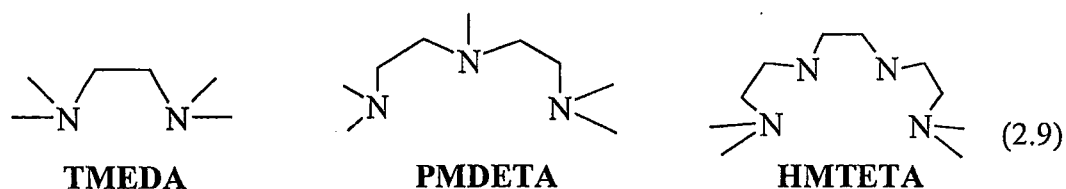
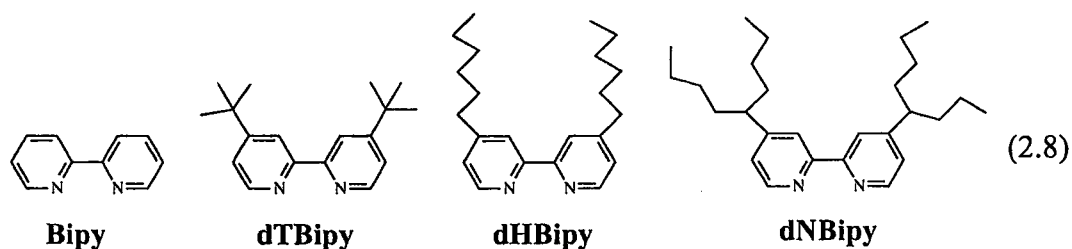
5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [76].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [77], Ni [78], Ru [79], etc have been used to some extent. Recent work from Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [80].

2.2.3.4 Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me₆-TREN). Examples of ligands used in copper-mediated ATRP are illustrated below [21,81].



2.2.3.5 Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [82] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, [83] should be minimized.

2.2.3.6 Temperature

At higher temperatures ATRP usually gives better results, because K_{eq} and k_p , equilibrium and rate of propagation constants in ATRP respectively, increase as the temperature increases. The activation energy in the propagation step is much more higher than that in termination, either by disproportionation or combination, step resulting in higher k_p / k_t 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.

2.2.3.7 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 is 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 (2.10).

$$R_p = k_{app} [M] = k_p [P\cdot] [M] = k_p K_{eq} [I]_0 \frac{[\text{Cu(I)}]}{[\text{Cu(II)X}]} [M] \quad (2.10)$$

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 ($k_p \gg k_d$), 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 (2.11).

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

p = polymerization yield (2.11)

$[RX]_0$ = concentration of 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;

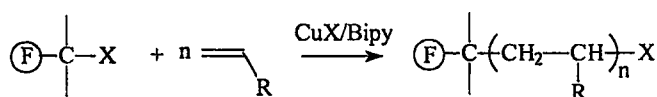
- For the smaller polymer chains, higher polydispersities are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.
- For the higher ratios of k_p / k_d , higher polydispersities (molecular weight distributions) are usually obtained.
- 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.

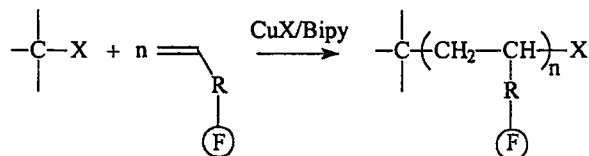
2.2.3.8 Polymer Functionalization by ATRP

Polymer functionalization by ATRP can be achieved by using functional initiators and monomers and the chemical transformation of the halogen end groups. These routes are summarized in Figure 2.3.

Through Initiator Functionality



Through Monomer Functionality



Through Chemical Reaction of Halide End Groups

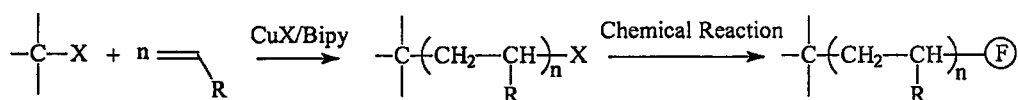
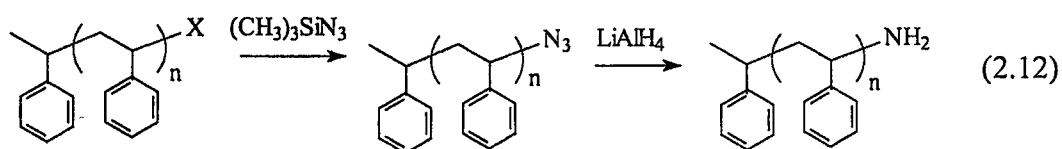


Figure 2.3: Polymer functionalization by ATRP

Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers [71]. For this purpose initiators should be equipped not only with the desired functional groups and also with a radical stabilizing group on the α -carbon atom such as aryl, carbonyl, nitrile, multiple halogens to ensue successful ATRP. Notably, direct bonding of halogen to aryl or carbonyl group does not facilitate radical generation. In this connection, it should also be pointed out that any functionalities in the initiator should not interfere with ATRP, i.e., should be inert to catalyst. The telechelic polymers prepared by using functional initiator approach in ATRP are presented in Table 4, along with the functional groups. Carboxylic acid functionalization by ATRP is rather difficult since the acid functionality poison the catalyst. However, ATRP of MMA by using 2-bromoisobutyric acid was reported to proceed. Various protected initiators were also reported for carboxylic acid functionalization [84, 85]. Hydrolysis of the protecting groups yields polymers with the desired carboxylic acid functionalities.


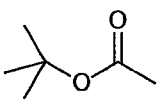

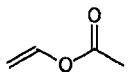
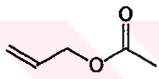


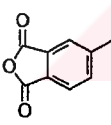
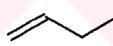
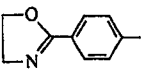
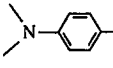
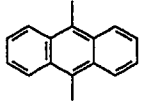

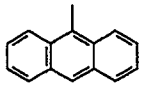

Some other functionalities including biofunctionalities [113-115] were introduced to polymers by ATRP. Substituted aromatic and alifatic sulphonyl chlorides were shown to be efficient initiators for ATRP and also used as initiators for the incorporation of functionalities to polystyrenes and polyacrylates [116]. In these applications heterogeneous $\text{CuCl}(\text{bpy})_3$ systems was utilised.

Obviously, ATRP leads to the formation of monofunctional telechelics since the other chain always contains halogen due to the fast deactivation process. Therefore, α - ω - telechelics can only be prepared by transformation of the halide end group by means of nucleophilic substitution, free radical chemistry or electrophilic addition of catalyzed by Lewis acids [117]. Typical example of such displacement is represented in equation 2.12 which illustrates the reactions used to replace the halogens with azides and consequently leading to amino-functional telechelics [118-120].



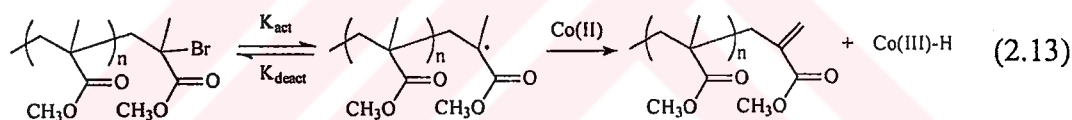
Other examples of halogen atom displacement to produce alcohol are C_{60} , epoxy, maleic anhydride, triphenylphosphine and ketone functionalized polymers [121-123]. The halide displacement is particularly important to prepare bifunctional

Table 2.4: Monofunctional Telechelic Polymers Prepared by Using Functional Initiators in ATRP

Functional Group	Polymer	Reference	Functional Group	Polymer	Reference
 $X = H, CH_3, Br, CN, NH_2, CHO, NO_2, OCH_3$	PSt, PMA	86-90	CN	PSt, PMA	91, 92
	PSt, PMA	88		PSt, PMA, PtBA	93
	PSt	102	OH	PSt, PMA, PBA PMMA	90, 94-101
	PSt, PMA	103		PSt, PMA	88
	PSt	88	COOH	PMMA	104
	PSt	88		PMA	106-108
	PSt	105		PSt	2
	PSt	109		PMMA	111
	PMMA	110		PSt, PMMA	112

hydroxy telechelics which find application in the preparation of segmented polyester and polyurethanes [124]. In such applications the first hydroxyl group can be incorporated by using hydroxy-functional initiator derivatives [125]. The second hydroxyl group functionalization can then be achieved by direct displacement of halogen group with an amino alcohol or utilizing allyl alcohol.

Incorporation of polymerizable end groups to polymers by ATRP is limited to certain groups. As it was shown in Table 2.4, among the olefinic groups only ally and vinyl acetate groups were successfully incorporated. Obviously, the other polymerizable groups such as epoxides and oxazolines are not reactive towards radicals. In order to produce polymers with a more reactive unsaturated end groups such as methacrylates, a combined ATRP and catalytic chain transfer (CCT) processes were proposed [126]. In this methodology, the catalytic chain transfer agents was added to the ATRP of MMA near to the end of polymerization leading to the formation of ω -unsaturated PMMA macromonomer with low polydispersity and controlled molecular weight.



Here, the CTC agent acts as a chain transfer terminator but does not initiate new chain in the classical manner. This process was equally applicable to the well-defined diblock macromonomers.

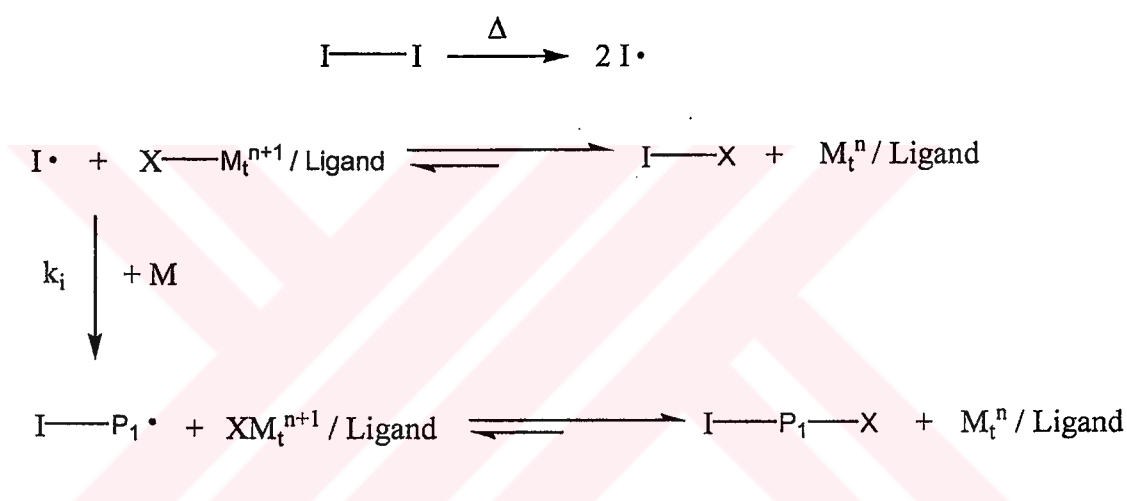
Similarly, Haddleton and co-workers [127] reported the use of methyl 2-bromomethylacrylate as means of installing methacrylate end groups on poly(methyl methacrylate). Also in this case, the functional group containing halide compound is added at the conclusion of the polymerization.

More recently, a convenient, one-pot synthesis of telechelic polymers with unsaturated end-groups was developed [18]. Addition of excess ethyl 2-bromomethacrylate to ATRP of acrylate monomers after 80-90 % conversion resulted in the formation of mono and bifunctional polymers. The average degree of end-functionality was almost quantitative.

2.2.4 Reverse Atom Transfer Radical Polymerization (RATRP)

The catalyst system of ATRP is generally toxic and expensive and the catalyst such as CuCl is unstable under air and moisture. To overcome these shortcomings, a so-called reverse ATRP have been developed. Reverse ATRP has been explored [28, 128-130] since 1995, and in this new process, a higher oxidation state transition-metal species M_t^{n+1}/L_x and a conventional radical initiator were used instead of a lower oxidation state M_t^n/L_x (easily oxidized by oxygen) and halide species RX (usually toxic), respectively. The reverse ATRP initiating systems, ie 2,2'-azo-bisisobutyronitrile (AIBN)/CuCl₂ (or CuBr₂)/bipy, [29, 128, 130] AIBN/FeCl₃/PPh₃ [129] have been reported in the literature.

Initiation



Propagation

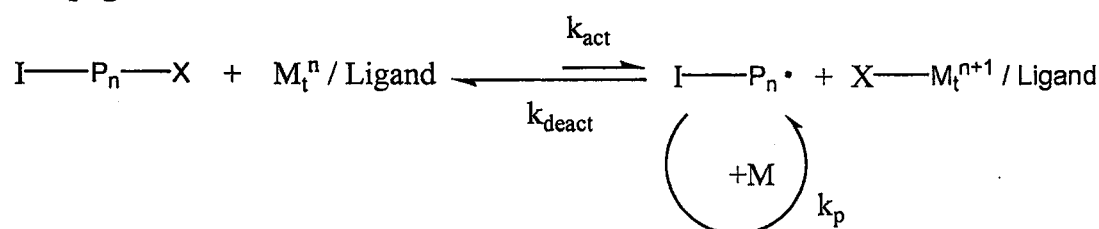


Figure 2.4: Mechanism of Reverse ATRP

Reverse ATRP differs from ATRP in its initiation process, where a conventional radical initiator, such as AIBN (2,2'-Azobisisobutyronitrile), is used. As shown in Figure 2.4, in the initiation step, once generated, the initiating radicals or the propagating radicals, I· Or I-P_n·, can abstract the halogen atom X from the oxidized transition-metal species, XM_t^{n+1} , to form the reduced transition-metal species, M_t^n ,

and the dormant species, I-X or I-P₁-X. In the subsequent steps, the transition-metal species, M_tⁿ, promotes exactly the same ATRP process as normal ATRP where R-X/M_tⁿ/L_x are used as the initiation system. Instead of first activation of a dormant species, R-X, with M_tⁿ, as in the case of normal ATRP, reverse ATRP originates from the deactivation reaction between radicals, I[•] or I-P[•], and XM_tⁿ⁺¹ [128].

2.2.4.1 Monomers

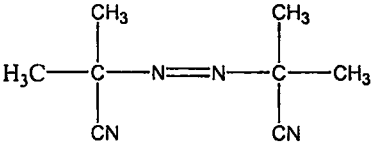
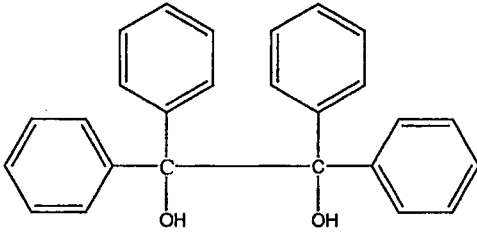
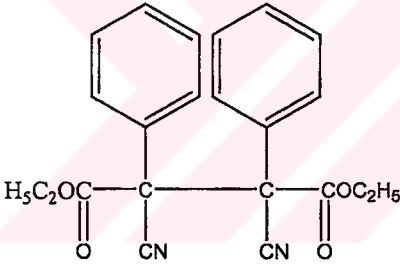
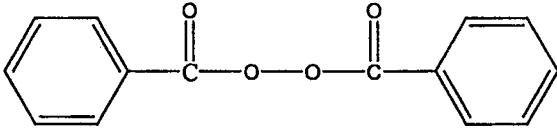
Various monomers have been successfully polymerized using RATRP: styrene [28, 82, 128, 131, 132, 135], (meth)acrylates [128, 130, 133, 136, 137], some monocyclic olefins like methyl 1-cyclobutenecarboxylate [134] and acrylonitrile [138] which contain substituents that can stabilize the propagating radicals.

The most commonly used monomers in RATRP are Styrene, MA and MMA.

2.2.4.2 Initiators

In the past, only two kinds of initiators, such as azo- and peroxide compounds, were employed as the initiator in the reverse ATRP system. It is well known that the decomposition of conventional initiators is irreversible, which makes the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature, and it is also difficult to realize living radical polymerization for some high reactivity monomers. For example, the AIBN/CuCl₂/bipy initiation system was successfully used for the living/controlled radical polymerization of St via a reverse ATRP process, but it was uncontrolled for (meth)acrylate monomers [28, 128]. The development of new type initiators for reverse ATRP, using carbon-carbon bond initiator instead of azo or peroxide ones, is of interest. At the same time this new type initiator (an iniferter) could provide the initiation step of reverse ATRP, in which the iniferter reversibly decomposes to primary radicals, unlike other conventional initiators (AIBN or BPO) having an irreversible decomposition step, resulting in suitable amounts of primary radicals being generated.

Table 2.5: Initiators used in RATRP.

Initiator	Reference
 <p>2,2'-Azobisobutyronitrile (AIBN)</p>	[82, 128, 130, 131, 134, 137]
 <p>1,1,2,2-Tetraphenyl-1,2-ethandiol (TPED)</p>	[132, 133]
 <p>Diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS)</p>	[135, 136]
 <p>Benzoyl peroxide</p>	[138-140]

2.3 Atom Transfer Radical Coupling (ATRC)

There is an interest in preparing telechelic polymers with the same functional end group on each chain end. A new approach for the preparation of telechelic polymers that avoids hetero-telechelicity problem is atom transfer radical coupling (ATRC). ATRC is a recent method used for coupling reactions of halide telechelic polystyrene prepared via ATRP [2, 141-143]. The method was initially investigated

by Fukuda et al. [141]. The technical term 'atom transfer radical coupling' was introduced by Yagci who was the first to realize the synthetic potential of ATRC for the preparation of α,ω -telechelic functional polystyrene [2]. Boutevin reported the successful ATRC of a poly(α -fluoroacrylate) [144]; moreover, the successful ATRC of a styrene-terminated poly(methyl acrylate) was reported by Matyjaszewski et al. [145]. ATRC is based on the application of Cu(0) to an ATRP system, leading to the reduction of any Cu(II) in the reaction medium to form Cu(I). The increase of Cu(I) in the reaction medium dramatically shifts the equilibrium between active and dormant species to the side of the active radical species (Figure 2.5). A significant increase in radical concentration leads to the reaction between radical chain ends. In the case of PS, the preferential reaction is the radical coupling reaction, the rate of which is estimated to increase by about three orders of magnitude if compared to the reaction conditions of ATRP [141]. Up to now, ATRC has been used for the preparation of α,ω -telechelic functional polymers by coupling of an α -functional polystyrene prepared by ATRP; in these cases dimerization occurs. Furthermore, the application of ATRC to PS prepared with bifunctional ATRP initiators leads to a significant increase in molecular weight and a multimodal molecular weight distribution due to the formation of a mixture of dimers, trimers etc. [1]. Although from the mechanistic point of view, Cu(I) species are a prerequisite for the reactivation of the dormant species, some authors [142, 144] use halide telechelic polymers and Cu(0) in the presence of a ligand without addition of a Cu(I) species. In these cases, *in situ* formation of oxidized Cu species must be assumed.

The principle of ATRC is to force the recombination of macroradicals formed from the activation reaction by drastically decreasing the deactivator concentration in the system. Macroradicals can recombine or disproportionate, but the recombination dominates in free radical polymerization of styrene and may approach 95%.

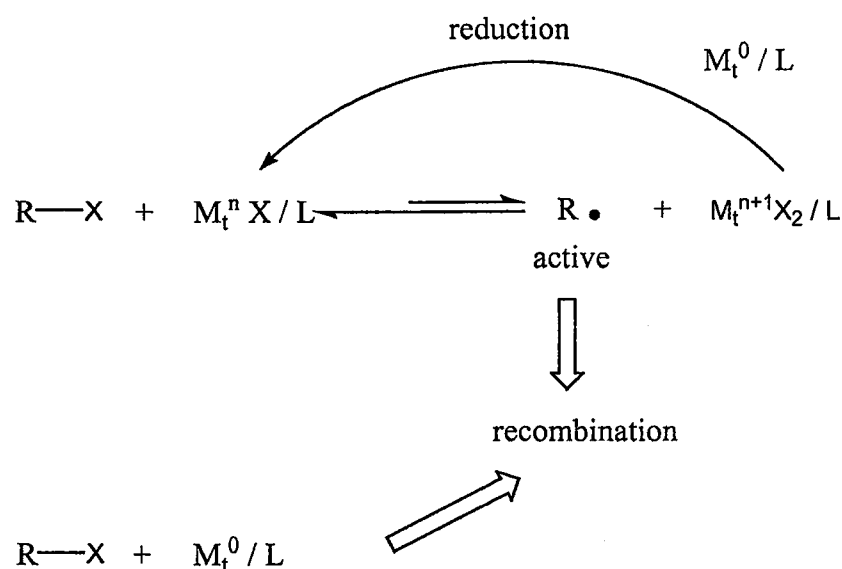


Figure 2.5: Principle of the atom transfer radical coupling (ATRC) (L=ligand, M = Cu, X = Cl, Br) [146]

When the halide-terminated polymer is reacted with copper(I) halide/ ligand, the ATRP equilibrium is established, as presented in Figure 2.6. In contrast with polymerization process, in ATRC the monomer is absent, and therefore the only possible reactions are the activation- deactivation cycles and eventually termination. By addition of a sufficient amount of zerovalent metal, the deactivation - formed reversibly in activation step and irreversibly in termination - is reduced in lower oxidation state (activator). In this way, the ATRP equilibrium can be affected by suppressing the deactivation, resulting in higher concentrations of macroradicals in the system and thus favoring the bimolecular termination.

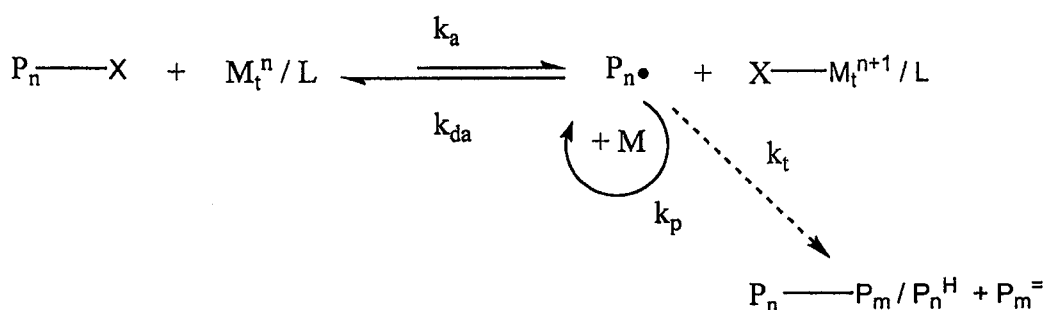


Figure 2.6: Equilibrium between active and dormant species in ATRP

3. EXPERIMENTAL PART

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St) (Aldrich)

It was first washed with 5% aq. NaOH solution in order to remove inhibitors, and then washed with water. It was dried with calcium chloride (CaCl_2) several hours and distilled over calcium hydride (CaH_2) at reduced pressure.

3.1.2 Solvents

Methanol (Technical)

Methanol was used for the precipitation of polymers without further purification.

Tetrahydrofuran (THF) (J.T.Baker)

Predried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately before use.

Toluene (Merck)

Refluxed over CaH_2 for 24 hours, then distilled over sodium wire and benzophenone prior to use.

3.1.3 Other Chemicals and Reagents

2, 2'-Azobisisobutyronitrile (AIBN) (Aldrich)

It was used as initiator and recrystallized from ethanol.

2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (AMHP) (Wako)

It was used as initiator without further purification.

1,1'-Azobis(cyclohexane-1-carbonitrile) (ACCN) (Wako)

It was used as initiator without further purification.

4,4'-Azobis(4-cyanopentanoic acid) (ACPA) (Wako)

It was used as initiator without further purification.

2,2-Bipyridine (bpy) (Aldrich)

It was used as a ligand without further purification.

N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA) (Aldrich)

It was used as a ligand without further purification.

Tris[2-(dimethylamino)ethyl]amine (Me₆TREN)

It was used as a ligand and prepared according to Matyjaszewski et al [147] from commercially available tris-(2-aminoethyl)amine (TREN).

Triphenylphosphine (PPh₃) (Fluka)

It was used as a ligand without further purification.

Copper (I) Bromide (CuBr) (Aldrich)

It was used as received.

Copper (II) Bromide (CuBr₂) (Aldrich)

It was used as received.

Copper (I) Chloride (CuCl) (Aldrich)

It was used as received.

Copper (II) Chloride (CuCl₂) (Aldrich)

It was used as received.

Iron (III) Chloride (FeCl₃) (Acros)

It was used as received.

Iron (III) Bromide (FeBr₃) (Acros)

It was used as received.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.2 Infrared Spectrophotometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.3 Gel Permeation Chromatography (G.P.C)

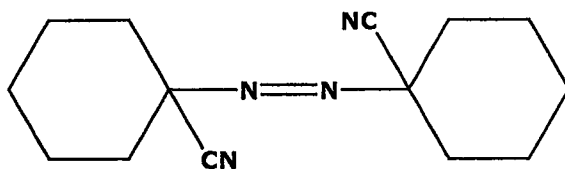
Gel permeation chromatography (GPC) analyses were performed with a set up consisting of a Waters 410 Differential Refractometer, a Waters 515 HPLC Pump and an apparatus equipped with three Waters ultrastyrigel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular weights were calculated on the basis of a calibration curve recorded with monodisperse polystyrene standards.

3.3 Preparation Methods

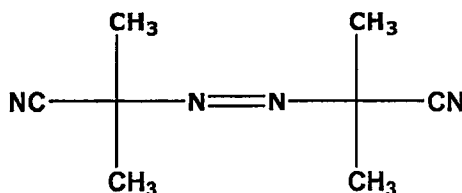
3.3.1 General Procedure for Reverse Atom Transfer Radical Polymerization

(RATRP) Reactions

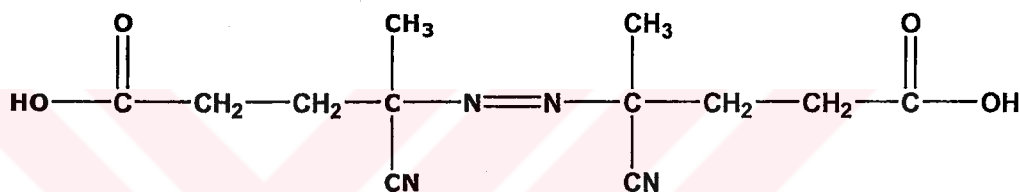
A round bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst (CuBr_2 , CuCl_2 , FeCl_3 or FeBr_3), ligand (bpy, PPh_3 or PMDETA), initiator (AIBN, AMHP, ACCN or ACPA, Scheme 3.1) and styrene were introduced under inert atmosphere. The flask was placed in an oil bath warmed at 110°C or 130°C according to the chosen metal/ ligand system and kept under stirring at that temperature for a given time, after which the reaction was stopped and the mixture was diluted with THF and finally poured into ten-fold methanol. The solid was collected after filtration and dried in an oven at 40°C and at reduced pressure overnight. The polymers were purified by passing through a silicagel column using THF as eluent and reprecipitated in methanol.



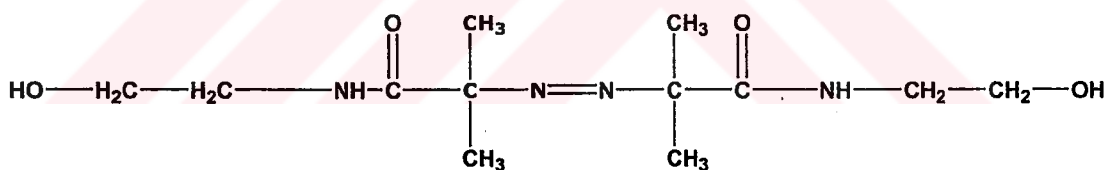
1,1'-Azobis(cyclohexane-1-carbonitrile) (ACCN)



2, 2'-Azobisisobutyronitrile (AIBN)



4,4'-Azobis(4-cyanopentanoic acid) (ACPA)



2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (AMHP)

Figure 3.1: Initiators used in RATRP.

3.3.2 General Procedure for Atom Transfer Radical Coupling (ATRC)

A round bottom flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Monotelechelic PS obtained by RATRP, catalyst (CuBr or CuCl), ligand (Me₆TREN or PMDETA), Cu⁰ and toluene (solvent) were introduced in the flask under nitrogen. The flask was placed in an oil bath warmed at 110°C and stirred at that temperature. After a given time, the system was opened, the solution was

concentrated by passing a flow of nitrogen and the polymer precipitated in methanol. The solid was collected after filtration and drying at 40°C in vacuum overnight. Further purification was achieved by passing the polymer through a silica gel column using THF as solvent and reprecipitation in methanol.



4. RESULTS and DISCUSSION

Monofunctional polymers were obtained by RATRP of styrene using initiators **ACPA** (for acid functionality), **AIBN** (for cyano functionality), **ACCN** (for cyano functionality) and **AMHP** (for hydroxyamide functionality) in the presence of many metal halide/ ligand complexes such as CuCl_2/bpy , CuBr_2/bpy , $\text{CuCl}_2/\text{PMDETA}$, $\text{CuBr}_2/\text{PMDETA}$, $\text{FeCl}_3/\text{PPh}_3$ and $\text{FeBr}_3/\text{PPh}_3$.

The polymerizations were performed in bulk, at 110°C and 130°C. The theoretical molecular weights ($M_{n,\text{th}}$) were calculated by using the following Equation (4.1).

$$M_{n,\text{th}} = \frac{[M_0]}{2[I_0]} (M_w)(\text{conversion}) \quad (4.1)$$

M_0 and I_0 are the initial molar concentrations of monomer and initiator, M_w is the molecular weight of the monomer.

Polymerizations by $\text{FeX}_3/\text{PPh}_3$ initiating system exhibited low molecular weight values and high polydispersities (Table 4.1). The initiator efficiencies I_{eff} (calculated from $I_{\text{eff}} = M_{n,\text{th}}/M_{n,\text{GPC}}$) for the polymerizations to obtain **M1**, **M2** and **M3** products were found to be 0,95; 1,00 and 0,87, respectively. These results confirmed that calculated molecular weights and molecular weights determined by GPC were feasible. On the other hand, **M4**, **M5**, **M6** and **M7** did not indicate the same characteristics.

As shown in Table 4.2, the lowest polydispersities and the highest molecular weights were obtained when CuX_2/bpy initiating system was used. It was observed that the conversions were close to those obtained by $\text{FeX}_3/\text{PPh}_3$ initiating system. Both the initiating system and the temperature could be the reasons of these results. The polymerization become much better controlled when the time was increased.

Table 4.1: Conditions^a and results of RA TRP of styrene using initiators with different functional groups in the presence of FeX₃/ PPh₃ complex.

Polymer	Initiator	Functional Group	Metal Halide	Time (min.)	Conv. %	M _{n,th} ^b	M _{n,GPC}	M _w /M _n	I _{eff} ^c
M1	ACPA	COOH	FeCl ₃	70	18	2000	2100	2,20	0,95
M2	ACPA	COOH	FeCl ₃	90	24	2500	2500	1,76	1,00
M3	AIBN	CN	FeCl ₃	90	27	2700	3100	1,62	0,87
M4	ACPA	COOH	FeCl ₃	60	11	1100	2300	1,74	0,49
M5	ACCN	CN	FeCl ₃	90	10	1000	2500	1,65	0,39
M6	AMHP	CONHCH ₂ CH ₂ OH	FeCl ₃	90	14	1400	2200	1,47	0,64
M7	ACCN	CN	FeBr ₃	90	48	3100	4900	1,83	0,63

^a Temperature: 130 °C; [St]₀ = 8,75 mol L⁻¹; [M]₀: [I]₀: [FeX₃]₀: [PPh₃]₀ = 200 : 1 : 4 : 12

^b M_{n(th)} = 104 x ([St]₀/2 [I]₀) x Conv.

^c I_{eff} = M_{n,th}/ M_{n,GPC}

Table 4.2: Conditions^a of styrene using functional groups in bpy complex.

Polymer	Initiator	Functional Group	Metal Halide	Time (min.)	Conv. %	$M_{n,th}$ ^b	$M_{n,GPC}$	M_w/M_n	I_{eff} ^c
M8	ACCN ^d	CN	CuBr ₂	300	2	680	2400	1.24	0,28
M9	ACCN ^d	CN	CuBr ₂	1200	59	17300	25900	1,21	0,67
M10	ACPA ^f	COOH	CuBr ₂	90	3	340	8900	1,65	0,04
M11	ACPA ^f	COOH	CuBr ₂	120	14	1400	11400	1,55	0,12
M12	ACPA ^e	COOH	CuCl ₂	90	13	1300	22700	1,64	0,06
M13	ACPA ^f	COOH	CuCl ₂	90	15	1500	13100	1,69	0,11

and results of RA TRP initiators with different the presence of CuX₂/

^a Temperature: 110°C; [St]₀ = 8,75 mol L⁻¹

^b $M_{n,th} = 104 \times ([St]_0 / 2 [I]_0) \times Conv.$

^c $I_{eff} = M_{n,th} / M_{n,GPC}$

^d [M]₀: [I]₀: [CuX₂]₀: [L]₀ = 564: 1: 2: 6

^e [M]₀: [I]₀: [CuX₂]₀: [L]₀ = 192: 1: 2: 4

^f [M]₀: [I]₀: [CuX₂]₀: [L]₀ = 200: 1: 2: 6

Table 4.3: Conditions^a and results of RA-TRP of styrene using initiators with different functional groups in the presence of CuX₂/ PMDETA complex.

Polymer	Initiator	Functional Group	Metal Halide	Time (min.)	Conv. %	M _{n,th} ^b	M _{n,GPC}	M _w /M _n	I _{eff} ^c
M14	AMHP	CONHCH ₂ CH ₂ OH	CuBr ₂	30	82	2100	12400	2,26	0,17
M15	AMHP ^d	CONHCH ₂ CH ₂ OH	CuBr ₂	5	46	1200	7500	2,04	0,16
M16	ACPA	COOH	CuBr ₂	30	38	990	8600	1,33	0,11
M17	ACCN	CN	CuBr ₂	30	99	2500	11500	1,65	0,22
M18	AIBN	CN	CuBr ₂	30	59	1500	6000	2,37	0,25
M19	AIBN	CN	CuCl ₂	35	50	1300	4600	1,54	0,28
M20	ACCN	CN	CuCl ₂	30	11	280	2600	1,45	0,11
M21	AIBN	CN	CuBr ₂	20	98	2500	7300	2,32	0,35

^a Temperature: 110°C; [St]₀ = 8,75 mol L⁻¹; [M]₀: [I]₀: [CuX₂]₀: [L]₀ = 50: 1: 2: 2

^b M_{n,th} = 104 x ([St]₀/2 [I]₀) x Conv.

^c I_{eff} = M_{n,th}/ M_{n,GPC}

^d T= 130°C

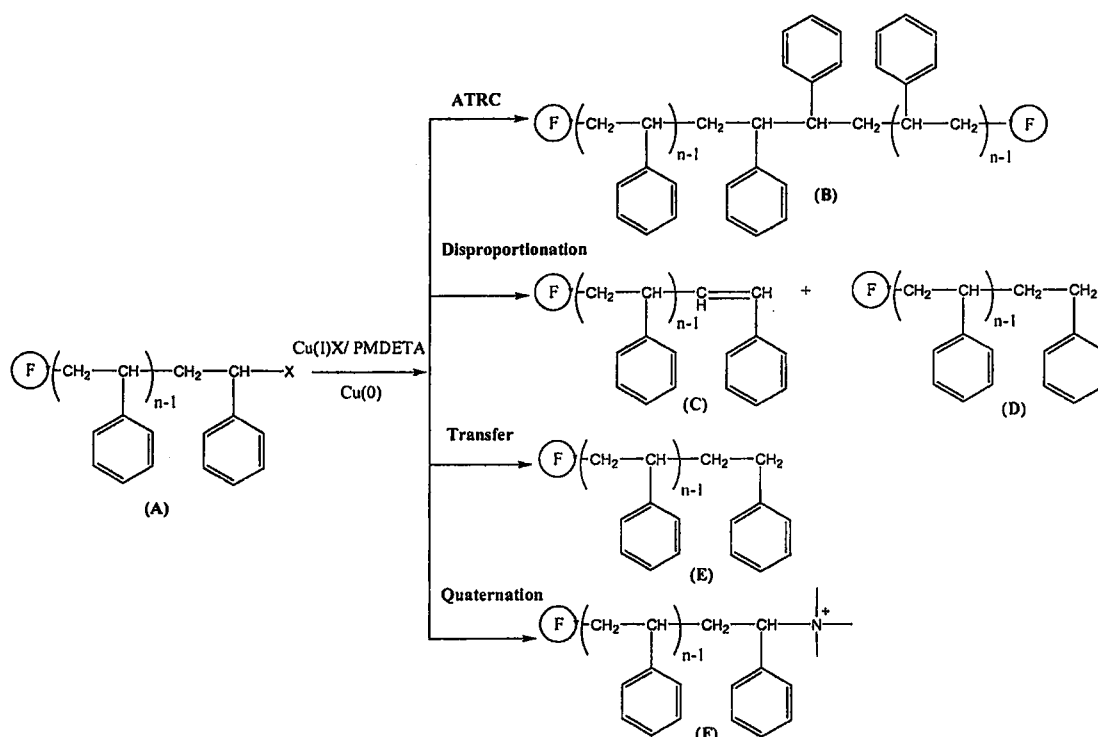
The initiator efficiencies for the polymerizations obtained by CuX_2 / PMDETA initiating system were close to those obtained by CuX_2 / bpy initiating system (Table 4.3). Although shorter reaction times were used for generation of **M14**, **M15**, **M16**, **M17**, **M18**, **M19**, **M20** and **M21** monofunctional polymers, conversions were the highest ones obtained in this work. Besides, $[\text{M}]_0: [\text{I}]_0$ ratio was decreased in order to decrease the molecular weights of monofunctional polymers and this led to increased conversions.

Despite the fact that some polydispersities of monofunctional polymers prepared by reverse ATRP were not compatible with preceding works [28, 29, 82, 128-132, 135], previously it wasn't observed any molecular weights as low as those obtained in this work.

The resulting polymers with preferred molecular weights were used for generation of α,ω -telechelic polymers by ATRC process. In order to identify end groups of both monofunctional and bifunctional telechelic polymers easily, low molecular weight monofunctional polymers were used in ATRC.

Before achieving atom transfer radical coupling (ATRC) reactions of α -functional ω -bromopolystyrenes (F-PS-X) we considered the possible reactions which could occur when F-PS-X reacts at high temperature in the presence of metal halide/ligand system. Scheme 4.1 illustrates several potential products which could be obtained from F-PS-X.

Product B, resulting from ATRC of F-PS-X, is the anticipated targeted product. Products C and D result from disproportionation reaction of F-PS-X. This reaction is a minor one, because termination in styrene polymerization occurs predominantly by recombination [148]. The third potential reaction, leading to compound E, is a transfer reaction which could occur if PMDETA acts as a transfer agent [149]. In addition, it should be considered the reaction of tertiary amines and halogen end groups leading to quaternary ammonium (Product F) [150].



Scheme 4.1: Possible reactions of α -functional ω -halopolystyrene using $\text{Cu(I)X/PMDETA/Cu(0)}$ system at 110°C .

Conditions and results of ATRC of monofunctional polymers prepared by reverse ATRP are presented in Table 4.4 and Table 4.5.

Telechelic polymers **B1**, **B2**, **B3**, **B4**, **B5**, **B6**, **B7**, **B8** and **B9** (Table 4.4) were prepared by monotelechelic polymers presented in Table 4.1. It was observed that coupling efficiencies of these telechelic polymers were limited with 50 % which may result from the participation of residual Fe species, coming from precursor, in the subsequent redox reaction.

Monotelechelic polymers **M14**, **M16**, **M17**, **M18** and **M20** were used as precursors for telechelic polymers (Table 4.5). An increase in molecular weights was observed, indicating that coupling reaction occurred. Initiator efficiencies increased up to 97 %. A decrease in polydispersities of resulting polymers were observed, suggesting a complete coupling of chains. It is also interesting to note the effect of the concentration of the monotelechelic polymer on the coupling efficiency. Lower concentration (Table 4.5, **B12**, **B13**, **B15**) resulted in lower efficiency, as a consequence of lower radical concentration in the system.

Telechelic polymers with the highest coupling efficiencies were chosen in order to make a better characterization. ^1H NMR spectras of telechelic polymers **B10**, **B14** and **B16** are compared with ^1H NMR spectras of their precursors **M14**, **M20** and **M16** in Figure 4.1, Figure 4.3 and Figure 4.5, respectively.

It is quite possible that some dead chains (without bromine end groups) are also formed as it was shown in Scheme 4.1, but their contribution to the final polymers should be low, as no discrepancy was observed in the ^1H NMR spectra between the integrals of the final protons.

In order to characterize both monofunctional and bifunctional polymers easily, ^1H NMR spectras and GPC traces of monotelechelic **M14**, **M20** and **M16** were compared with ^1H NMR spectras and GPC traces of telechelic polymers **B10**, **B14** and **B16**, respectively.



Table 4.4: Conditions^a and results of ATRC of monofunctional polymers (synthesized in the presence of FeX₃/ PPh₃).

Monofunctional Polymer	Functional Group	Ligand	Metal Halide	Time (h.)	Bifunctional Polymer	M _n (GPC ⁰)	M _n (GPC)	PDI	q ^b
M3	CN	Me ₆ TREN	CuCl	1	B1	3100	3600	1,65	0,28
M3	CN	PMDETA	CuCl	1	B2	3100	3900	1,67	0,41
M6	CONHCH ₂ CH ₂ OH	Me ₆ TREN	CuCl	48	B3	2200	2800	1,62	0,43
M6	CONHCH ₂ CH ₂ OH	PMDETA	CuCl	72	B4	2200	3000	1,72	0,53
M7	CN	PMDETA	CuBr	72	B5	3100	3400	1,77	0,18
M5	CN	PMDETA	CuCl	72	B6	2200	2500	1,63	0,24
M4	COOH	PMDETA	CuCl	72	B7	2300	2800	1,73	0,36
M7	CN	PMDETA	CuCl	72	B8	3100	3300	1,64	0,12
M3	CN	PMDETA	CuCl	72	B9	3100	3300	1,64	0,12

^a Temperature: 110°C; solvent = toluene; [MFP] : [CuX] : [Ligand] : [Cu⁰] = 1 : 1 : 2 : 5
concentration of monofunctional polymer = [MFP] = 15x10⁻³ mol L⁻¹

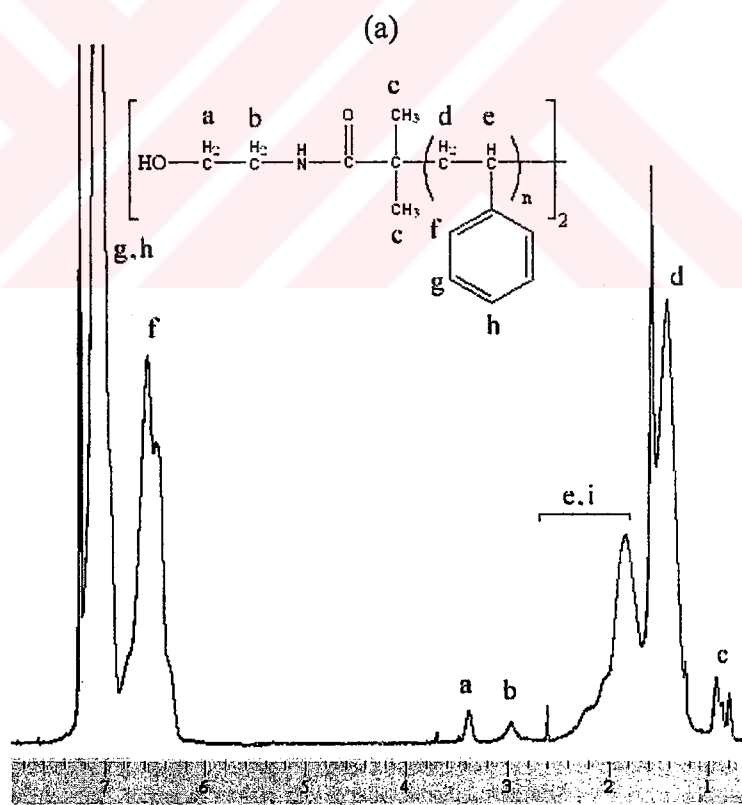
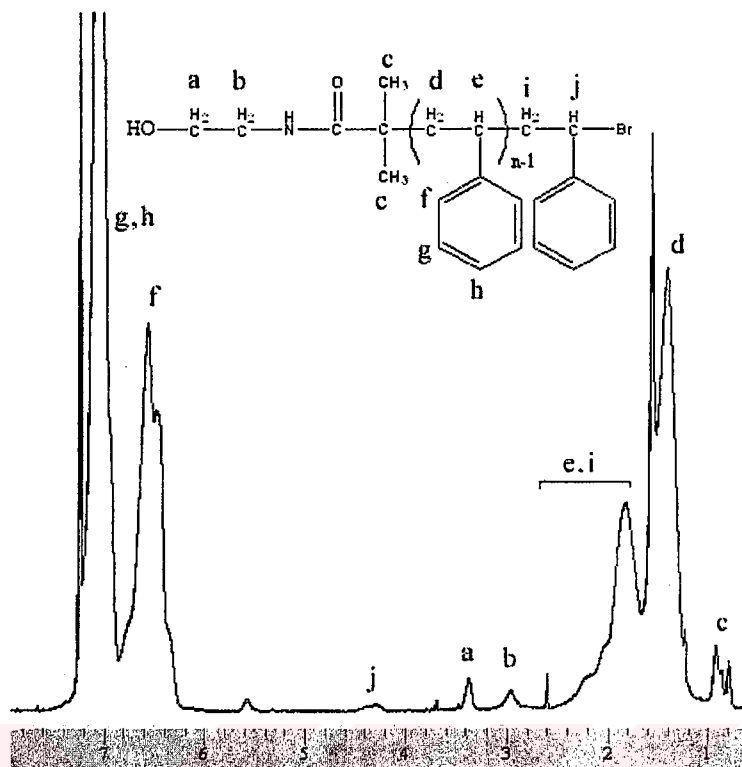
^b The extent of coupling = $q = 2[1 - (M_{n, GPC(0)} / M_{n, GPC})]$

Table 4. 5: Conditions^a and results of ATRC of monofunctional polymers (synthesized in the presence of CuX₂/PMDETA).

Monofunctional Polymer	Functional Group	Polymer Concentration (mmol L ⁻¹)	Metal Halide	Time (h.)	Bifunctional Polymer	M _{n,GPC(0)}	M _{n,GPC}	PDI	q ^b
M14	CONHCH ₂ CH ₂ OH	15	CuBr	72	B10	12400	24000	1,75	0,97
M16	COOH	15	CuBr	28	B11	8600	12900	1,23	0,67
M17	CN	5	CuBr	28	B12	11500	13000	1,95	0,23
M18	CN	10	CuBr	27	B13	6000	6600	2,16	0,18
M20	CN	15	CuCl	24	B14	2600	4100	1,48	0,76
M17	CN	5	CuCl	46	B15	11500	11600	1,79	0,02
M16	COOH	10	CuCl	46	B16	8600	12800	1,26	0,66

^a Temperature: 110°C; solvent = toluene; [MFP] : [CuX] : [Ligand] : [Cu⁰] = 1 : 1 : 2 : 5

^b The extent of coupling = $q = 2[1 - (M_{n,GPC(0)} / M_{n,GPC})]$



(b)

Figure 4.1: ^1H NMR spectra (CDCl₃) of monotelechelic PS M14 and telechelic PS B10.

Figure 4.1(a) shows the ^1H NMR spectra of monobrominated PS **M14**. It reveals the signal at 4,3 ppm due to the methane protons in α -position to the bromine atom. Two CH_2 groups of initiator a and b absorb at 3,4 and 3,0 ppm. CH_3 groups of initiator absorb at 0,9 ppm. The signal at 5,5 ppm might belong to both OH and NH protons.

^1H NMR of the obtained telechelic PS **B10** is presented in Figure 4.1(b). ^1H NMR shows essentially complete disappearance of the signal j located at 4,3 ppm corresponding to the CH at α -position to the bromine atom, confirming the efficient coupling reaction of the Br-terminated chains. Protons $-\text{CH}-\text{CH}-$ which should be formed in the coupling reaction are located in 2-2,5 ppm region and overlap with the other CH_2 and CH of the PS chain.

Concerning product F coming from quaternization of terminal Br atom, no peak relative to the tertiary amine is observed in the expected area 4,7-5,2 ppm.

GPC analysis of compound **M14** and that of the product of the coupling reaction **B10** are shown in Figure 4.2. After coupling, $M_n = 24000 \text{ g. mol}^{-1}$ was measured with a polydispersity index $\text{PDI} = 2,26$. The starting monobromopolystyrene had $M_n = 12400 \text{ g. mol}^{-1}$ with $\text{PDI} = 1,75$.

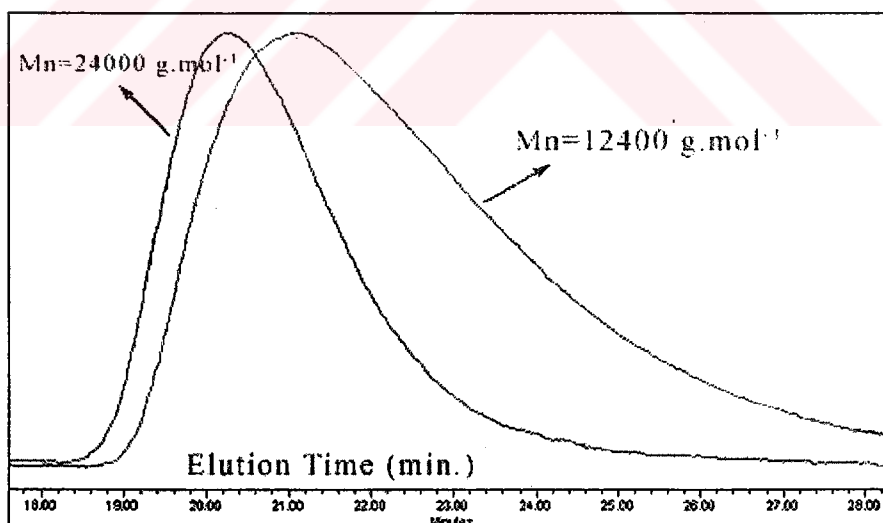
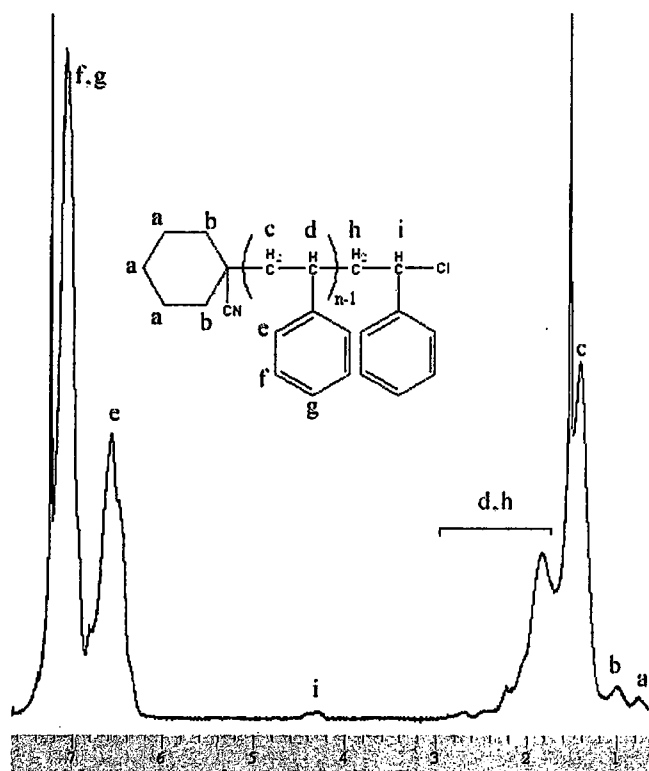
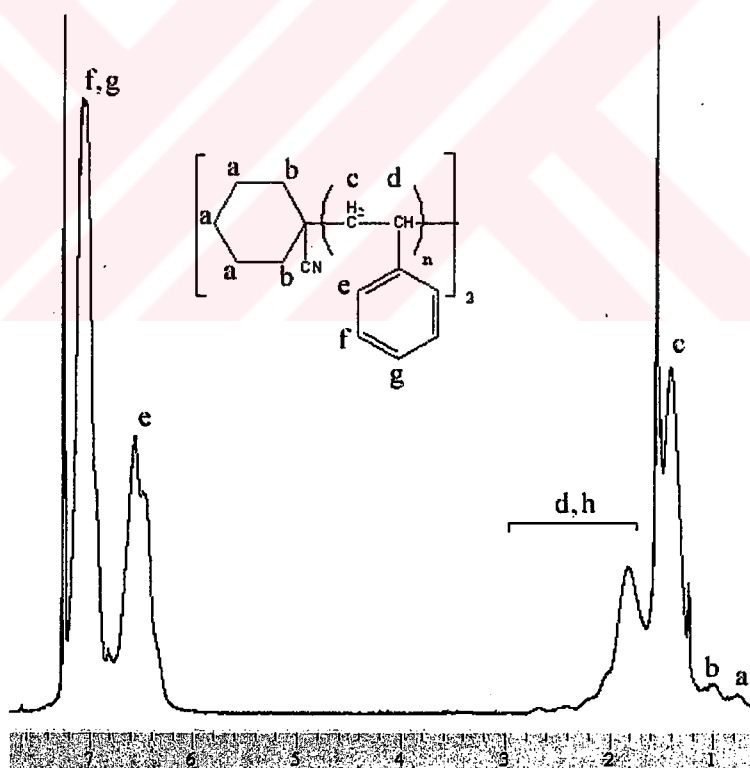


Figure 4.2: GPC traces of monofunctional PS and corresponding telechelic polymer **M14** and **B10**.



(a)



(b)

Figure 4.3: ¹H NMR spectra (CDCl₃) of (a) monotelechelic PS M20 and (b) telechelic PS B14.

^1H NMR of monobrominated polymer of styrene **M20** and ^1H NMR of the obtained telechelic polymer **B14** are shown in Figure 4.3. It reveals the signal at 4,3 ppm due to the methine protons in α -position to the bromine atom. a and b protons coming from initiator absorb at 0,9 and 1,0 ppm. It is seen in Figure 4.3(b), ^1H NMR shows essentially complete disappearance of the signal i located at 4,3 ppm corresponding to the CH at α -position to the bromine atom, confirming the efficient coupling reaction of the Br-terminated chains. Protons $-\text{CH}-\text{CH}-$ which should form in the coupling reaction are located in 2-2,5 ppm region and overlap with the other CH_2 and CH of the PS chain. Concerning product F coming from quaternization of terminal Br atom, no peak relative to the tertiary amine is observed in the expected area 4,7-5,2 ppm.

GPC analysis of compound **M20** and that of the product of the coupling reaction **B14** are shown in Figure 4.4. After coupling, $M_n = 4200 \text{ g. mol}^{-1}$ was measured with a polydispersity index $\text{PDI} = 1,45$. The starting monobromopolystyrene had $M_n = 2600 \text{ g. mol}^{-1}$ with $\text{PDI} = 1,48$.

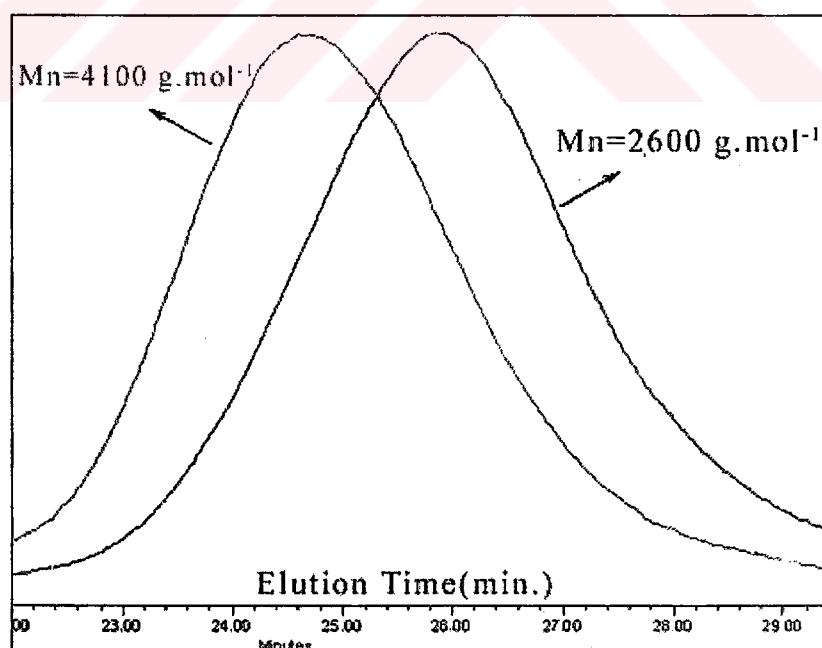
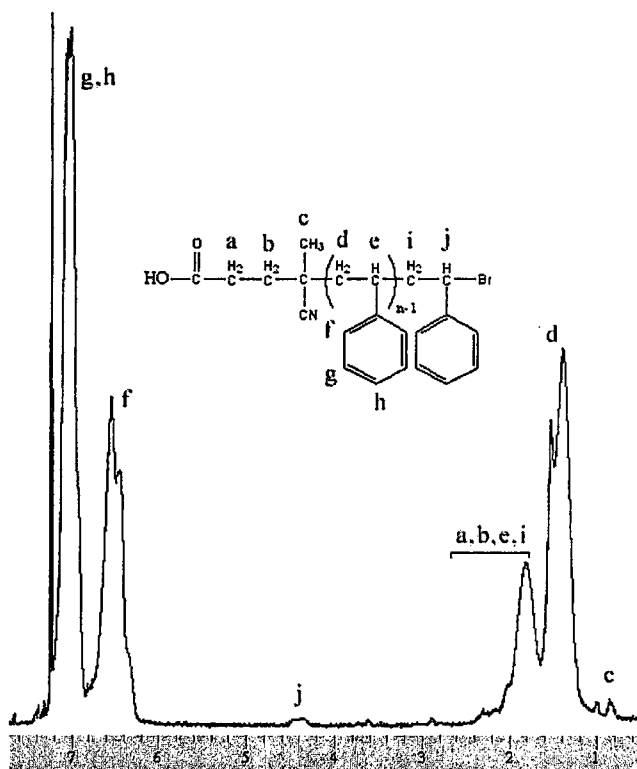
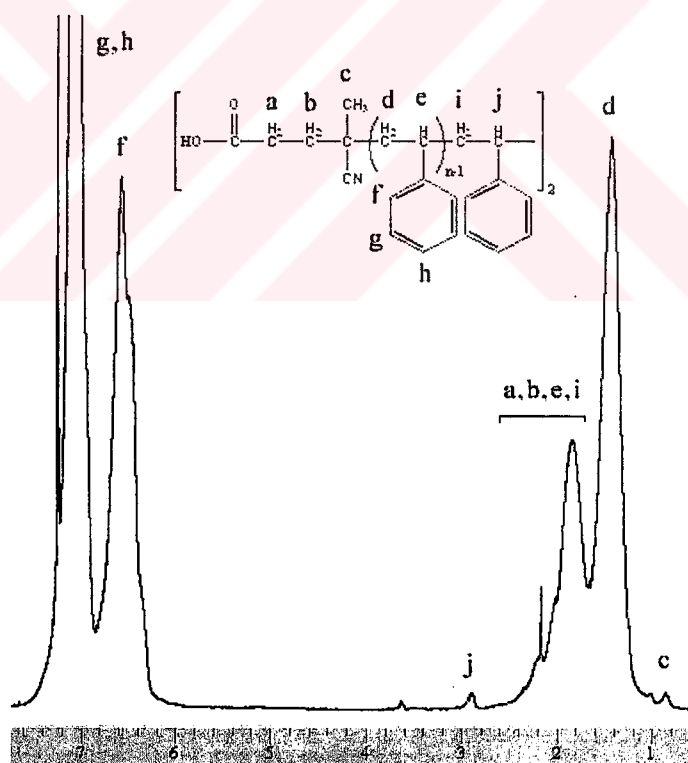


Figure 4.4: GPC traces of monofunctional PS and corresponding telechelic polymer **M20** and **B14**.



(a)



(b)

Figure 4.5: ^1H NMR spectra (CDCl_3) of (a) monotelechelic PS M16 and (b) telechelic PS B16.

Figure 4.5 (a) shows the ^1H NMR spectra of monobrominated PS **M16**. It reveals the signal at 4,3 ppm due to the methane protons in α -position to the bromine atom. Two CH_2 groups of initiator a and b absorb at 3,4 and 3,0 ppm. CH_3 groups of initiator absorb at 0,9 ppm. The signal at 5,5 ppm might belong to both OH and NH protons.

^1H NMR of the obtained telechelic PS **B16** is presented in Figure 4.5(b). ^1H NMR shows essentially complete disappearance of the signal *i* located at 4,3 ppm corresponding to the CH at α -position to the bromine atom, confirming the efficient coupling reaction of the Br-terminated chains. Protons $-\text{CH}-\text{CH}-$ which should be formed in the coupling reaction are located in 2-2,5 ppm region and overlap with the other CH_2 and CH of the PS chain.

GPC analysis of compound **M16** and that of the product of the coupling reaction **B16** are shown in Figure 4.6. After coupling, $M_n = 12800 \text{ g. mol}^{-1}$ was measured with a polydispersity index $\text{PDI} = 1,26$. The starting monobromopolystyrene had $M_n = 8600 \text{ g. mol}^{-1}$ with $\text{PDI} = 1,33$. Sholder in the GPC trace of resulting telechelic polymer **B16** might be coming from unreacted starting monotelechelic PS.

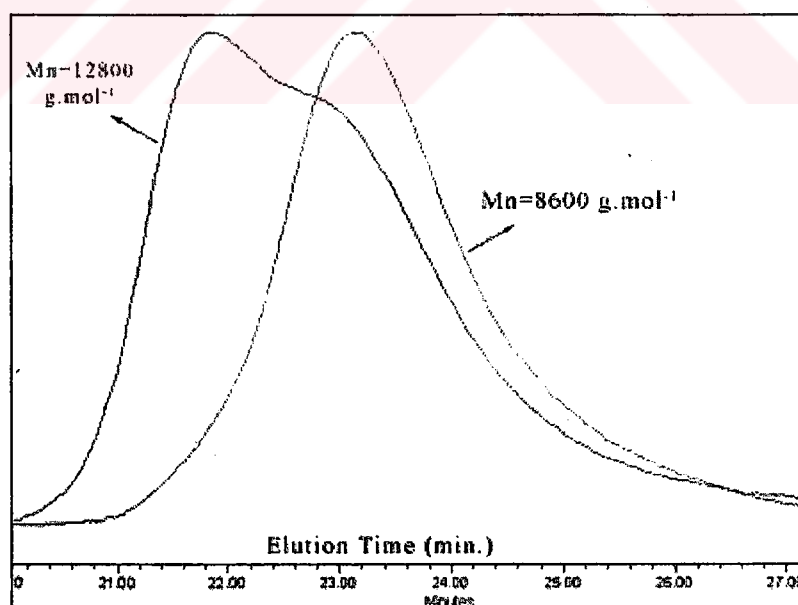


Figure 4.6: GPC traces of monofunctional PS and corresponding telechelic polymer **M16** and **B16**.

5. CONCLUSIONS

The aim of this study was the synthesis of telechelic polymers of styrene using RATRP in a first step, followed by ATRC of obtained monotelechelic polymers. Various initiating systems were applied in conjunction with several functional azo-initiators in RATRP for the preparation of monofunctional polystyrenes.

Although RATRP experiments with $\text{FeX}_3/\text{PPh}_3$ initiating system gave the best results for initiator efficiencies with low molecular weight polymers (which was a required property for preparing telechelic polymers) the system was not well-controlled with broad polydispersities.

$\text{CuX}_2/\text{PMDETA}$ initiating system was the most convenient system with higher conversions and narrow polydispersities despite the low initiator efficiencies.

α,ω -Telechelic polymers were then synthesized successfully by coupling of monofunctional RATRP products. Both of monofunctional and bifunctional telechelic polymers were characterized by ^1H NMR and GPC.

Although RATRP experiments gave satisfactory results with $\text{FeCl}_3/\text{PPh}_3$ initiating system, the corresponding ATRC process yielded polymers with low functionality which may result from the participation of residual Fe species in the subsequent redox reaction.

For the overall process, the best results were obtained with copper-mediated systems for both RATRP and ATRC. ^1H NMR analysis showed nearly complete disappearance of the signals of methane proton in α -position to halogen atom. GPC analysis showed that molecular weights almost doubled in comparison with those of the monohalogenated polymers.

Although the latter method seems to be less convenient, it can be useful for preparing link-functionalized materials as precursors for star type polymers.

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XIX. National Congress of Chemistry
Kuşadası, Turkey, 30 September- 4 October, 2005

She is co-author of the following chapter.

- Editor: J.P. Fouassier, A. Yildirim, **B. Aydogan**, B. Gacal, N. Yönet, Y Yüksel Durmaz, Y. Yagci, "Photochemistry and UV Curing: New Trends", Research Signpost.