İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

POLYMERIZATION OF CHALCONE FUNCTIONAL POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

M.Sc. Thesis by

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Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JUNE 2008

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Date of submission : 5 May 2008

Date of defence examination : 9 June 2008

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Tezin Savunulduğu Tarih : 9 Haziran 2008

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Doç.Dr. Yeşim HEPUZER GÜRSEL

HAZİRAN 2008

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to my thesis supervisor, Professor Ayşen Önen for her guidance, advices, encouragement, courtesy and endless patience throughout this study. I am grateful to her insightful comments and constructive suggestions.

I would like to thank to Professor Filiz Şenkal for her invaluable help, sharing her knowledge and experiences with me generously throughout this research.

I would also like to thank to my friends Betül Türel , Müfide Karahasanoğlu and Tuğba Çakır for their support in all possible ways and for helpful attitudes during my laboratory works.

Finally, I would like to extend thanks to my family, especially to my parents for their endless support, encouragement and unconditional love. Without the help and love of my family, this work could never have been possible.

June 2008 Remzi GÜRBÜZ

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LIST OF ABBREVIATIONS

ATRP	**:** Atom Transfer Radical Polymerization
ATRA	: Atom Transfer Radical Addition
MMA	: Methylmethacrylate
SFRP	**:** Stable Free Radical Polymerization
RAFT	**:** Reversible Addition-Fragmentation Chain Transfer
TMC	: Transition Metal Catalyzed
PRE	: Persistent Radical Effect
AIBN	: 2,2'-azobis(2-methylpropanenitrile)
PMDETA	: N, N, N, N', N''-pentamethyldiethylene triamine
HMTETA	: 1,1,4,7,10,10-hexamethyltriethylenetetramine
	tris[2- (dimethylamino)ethyl]amine (Me6TREN)
TEMPO	: 2,2,6,6-tetramthyl-1-piperidinyl-1-oxy
NMP	: Nitroxide Mediated Polymerization
THF	: Tetrahydrofuran
TEA	**:** Triethylamine
NMR	**:** Nuclear Magnetic Resonance
GPC	**:** Gel Permeation Chromatography
UV	**:** Ultra-Violet
IR	**:** Infrared Spectroscopy
GC	**:** Gas Chromatography
AABF	**:** 2-acetyl- 3-amino-benzofuran-2-yl
APPO	**:** 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one
CFI	: N-[(3-benzofuran-2-yl)-3phenyl prop-2-en-1-one]2-bromo
	asetamid
PDI	: Polysidpersity index

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LIST OF SYMBOLS

σ - : Sigma Bond
kt : Rate Constant of Termination
kp : Rate Constant of Propagation
$k_{act.}$: Rate Constant of Activation
k_{deact}• : Rate Constant of Deactivation
Mw/Mn : Molecular Weight Distribution
DPn : Degree of Polymerization
δ : Chemical Shift

POLYMERIZATION OF CHALCONE FUNCTIONAL POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

SUMMARY

Synthesis of polymers carrying reactive functional groups have been an active field of research in polymer science in recent years. Atom Transfer Radical Polymerization (ATRP) is a particularly successful Controlled Radical Polymerization (CRP) method and has attracted commercial interest because of its easy experimental setup, use of readily accessible and inexpensive catalysts (usually copper complexes formed with aliphatic amines or imines, or pyridines, many of which are commercially available), and simple initiators (often alkyl halides). ATRP is probably the most robust and efficient CRP and well-defined polymers with controlled topology, composition and functionality are readily prepared.

The aim of this work involves the synthesis and characterization of photoactive polymers containing α, β-unsaturated carbonyl groups namely chalcone groups at the chain ends.

For this purpose, a functional initiator having chalcone groups and halide in the same structure, N-[(3-benzofuran-2-yl)-3phenyl prop-2-en-1-one]2-bromo asetamid (Chalcone functional initiator-CFI), was synthesized by the amidation reaction of 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one (APPO) with bromoacetylbromide. The structure of CFI was identified by FT-IR, ^{1}H-NMR and UV spectroscopy.

In the second stage, Atom transfer radical polymerization of methylmethacrylate (MMA) was performed by utilizing CFI in the presence of copper (I)bromide, PMDETA as a ligand and anisole as solvent, polymers were characterized by spectroscopic techniques. The polymerization reaction was followed by gas chromatography (GC) and polymerization kinetics were studied.

KALGON FONKSİYONALİTESİNE SAHİP POLİMERLERİN ATOM TRANSFER RADİKAL POLİMERİZASYONU YÖNTEMİ İLE POLİMERİZASYONU

ÖZET

Fonksiyonel grup içeren polimerlerin sentezi son yıllarda polimer kimyasında önemli bir yer kapsamaktadır. Atom transfer radikal polimerizasyonu başarılı bir kontrollü radikal polimerizasyon yöntemidir ve kolay deneysel kurulumu, kolaylıkla ulaşılan ve ucuz kataliz kullanımı (çoğu ticari kullanımı mümkün alifatik aminler, iminler yada piridinlerden oluşan bakır kompleksleri) ve basit başlatıcı kullanılabilirliği (genellikle alkil halojenürler) yönleri ile ticari olarak da ilgi çekmektedir. Atom transfer radikal polimerizasyonu en verimli kontrollü radikal polimerizasyon yöntemi olarak bilinmektedir ve istenilen topoloji, bileşim ve fonksiyonalitede polimerler rahatlıkla üretilir.

Bu çalışmada uç grup olarak doymamış α, β karbonil grupları (kalgon grupları) içeren polimerlerin sentezi ve karakterizasyonu amaçlanmıştır.

Bu amaca yönelik olarak ilk aşamada kalgon ve halojen gruplarını içeren fonksiyonel başlatıcı, N-[(3-benzofuran-2-yl)-3phenyl prop-2-en-1-one]2-bromo asetamid (CFI), 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one (APPO) ile bromoasetilbromür arasındaki amidleşme reaksiyonu ile sentezlenmiştir. Bu başlatıcının yapısıFT-IR, 1H-NMR and UV spekroskopisi ile aydınlatılmıştır. Metilmetakrilat'ın (MMA) atom transfer radikal polimerizasyonu CFI'nin bakır (I) bromür, PMDETA(ligant), anisol (solvent) ile birlikte reaksiyonu ile başlatılmış ve sentezlenen polimerler spekroskopik yöntemler ile karakterize edilmiştir. Polimerizasyon reaksiyonu gaz kromatografisi ile takip edilerek polimerizasyon kinetiği incelenmiştir.

1. INTRODUCTION

Polymerization of vinyl monomers is of enormous industrial importance. These vinyl polymers are mostly thermoplastics and they are used in a wide variety of applications. Many vinyl monomers are polymerized by free radical, ionic, and coordination polymerization mechanism. For several reasons, radical polymerization has significant advantages over ionic and coordination polymerizations. The reaction conditions are usually not as demanding, they exhibit a tolerance of trace impurities, and it is possible to polymerize a variety of monomers by radical polymerization. As a consequence of these characteristics, it is possible to prepare high molecular weight polymers without removing the stabilizers present in commercial monomers, in the presence of trace amounts of oxygen, in solvents that have not been rigorously dried, or even in aqueous media. Today, free radical polymerization accounts for a large portion of mass-produced polymers.

Despite the limitations of ionic systems, they were easier to bring under control because of the number of influential variables available (solvent polarity, counter ions, etc.) that can be manipulated. However, these same variables are either unattainable or ineffective at modulating the reactivity of radicals, hence historically it has been difficult to control these polymerizations, which is the main deficiency of conventional free radical polymerization.

2. THEORETICAL PART

2.1 Controlled/"Living" Radical Polymerization

The first report of controlling radical polymerization was made in 1969 by Borsig, et al. They used bulky diaryl and triaryl ester groups on methacrylate monomers and observed during their polymerization, an increase of molecular weight with conversion and the formation of block copolymers [1]. However, the relationship between molecular weight and conversion was not linear, initiation efficiencies was low, and polydispersities of the product polymers were always relatively high. This could result from a slow but continuous initiation of the bulky organic radicals. This system was later extensively investigated by Braun [2], and improved by Crivello [3] and Otsu [4]. However, reports of work on this system have been rare in recent years.

The use of term "living radical polymerization was coined by Otsu, et al. during his work on the iniferter mechanism in 1982 [5]. In this article, they proposed calling the organic disulfide initiator with chain transfer and termination as initiation - transfer agent - terminator (iniferter). They used tetraethylthiuram disulfide in the thermal or photo polymerization of styrene and MMA, and obtained α, ω-functionalized polymers having initiator fragments and the chain termini. Later, they also found that S-alkyl dithiocarbamate groups undergo reversible photo dissociation to a reactive alkyl radical and an inert dithiocarbamate radical [6]. They exploited this property of the dithiocarbamates in the formation of block and graft copolymer by irradiating a monomer in the presence of a suitable initiator. However, the use of dithiocarbamates has the drawback of decomposition, which leads to a loss of the living nature of the chain end. For example, dithiocarbamate polymer chain ends can decompose to CS_2 and dialkyl amino radical, and this radical can initiate further polymerization at slow rate [7].

In 1995 two research groups independently reported a similar controlled radical polymerization technique, the atom transfer radical polymerization (ATRP) method.

They were based on catalytic systems used for atom transfer radical addition reaction (ATRA), or the well-known Kharasch reaction, an efficient method of forming carbon-carbon bonds between organic halides and alkenes.[8] The first reported by Sawamoto et al., uses $RuCI_2(PPh_3)_3/Al(O\text{-}iPr)_3$ as a catalyst system in the polymerization of MMA initiated by CCl_4 [9]. The second system reported by Matyjaszewski, et al., is the polymerization of styrene catalyzed by CuCI/2,2'-bipyridine (bpy) in the presence of 1-phenylethyl chloride as an initiator[10]. Since these first reports, there have been many reports on ATRP of styrene, acrylate, methacrylate, and acrylonitrile by using various transition metal complexes, including nickel, iron, palladium, and rhodium. Compared with other controlled radical polymerization methods, ATRP is very versatile. This method provides control in the polymerization of many different monomers under various reaction conditions, and makes it possible to prepare polymers having a wide range of architectures including blocks, grafts, gradient copolymers [11], stars, combs, branched, and hyper branched (co)polymers [12].

2.1.1 Types of Controlled Radical Polymerization

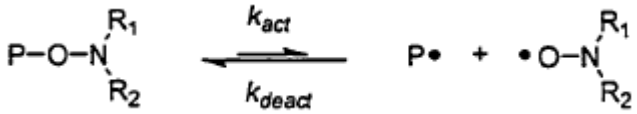
Three types of controlled radical polymerization are reviewed here: (i) nitroxide-mediate stable free radical polymerization, which employs stable nitroxyl radicals; (ii) reversible addition-fragmentation chain transfer polymerization, which uses dithioesters together with a free radical initiator; and (iii) atom transfer radical polymerization, which uses complexes of transition metals in conjunction with alkyl halides.

2.1.1.1 Nitroxide-Mediated Stable Free Radical Polymerization (SFRP)

Most controlled radical polymerization methods, including the nitroxide-mediated SFRP, employ the basic strategy of achieving control by establishing equilibrium, having very low equilibrium constant, between dormant and active species. In radical reactions, termination is the most important chain breaking process. Because termination reactions are second order in active radical concentration, and propagation reactions are first orders, the ratio of termination over propagation reaction decreases with decreasing concentration of active radicals. Although termination reactions cannot be eliminated completely, the contribution of termination can be significantly lowered by this approach, and it becomes possible to control the polymer architectures. The

concept of employing equilibrium between dormant and active species was first used in the cationic ring-opening polymerization of tetrahydrofuran [13] This idea has subsequently been successfully used in carbocationic polymerizations [14], although a "pseudo cationic mechanism",[15] "invisible species" [16], and "stretched-covalent bonds" [17] were all postulated initially.

Various compounds have been reported as trapping agents of active radicals to form the dormant species. Among them, the SFRP method uses stable persistent radicals for this purpose, and most of these are nitroxide radicals (eq 2.1).

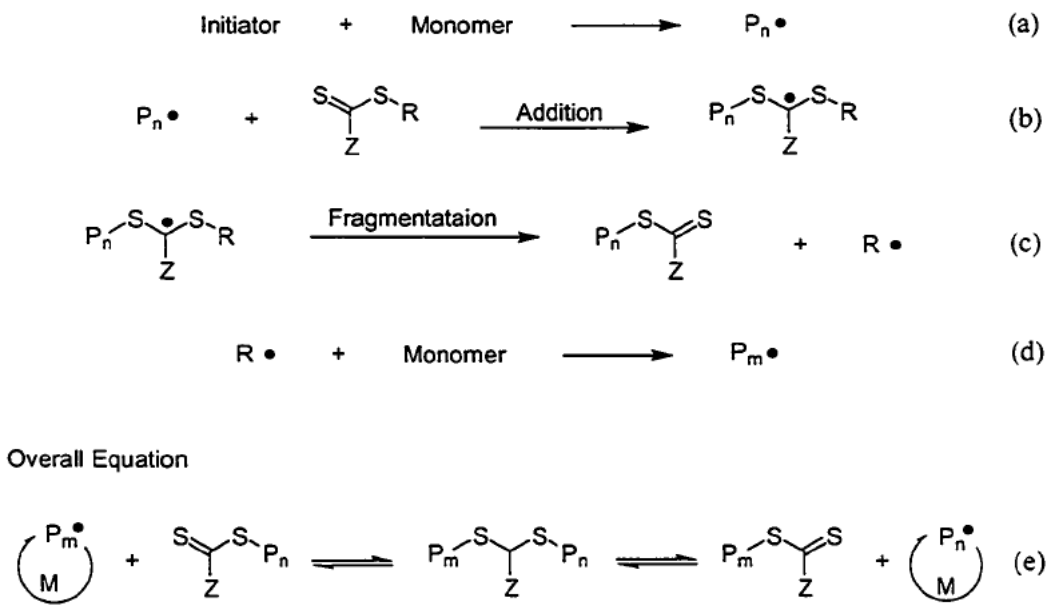


(2.1)

The ability of nitroxides to trap carbon-centered radicals has been known for some time, and nitroxides have been used as scavengers to inhibit polymerization or polymer degradation [18]. The stable nitroxide radicals do not initiate the growth of any extra polymer chains, but they react with organic radicals very fast at near diffusion-controlled rates. On the other hand, the alkoxyamine C-O bond is also known to be relatively unstable. [19] Upon heating, it readily cleaves homolytically to yield a carbon-centered radical species and a nitroxide. In the beginning of this process, the relative weak bond formed by the coupling of the primary radical and nitroxides breaks at high temperatures, and the monomer adds to the carbon based radical soon after. Eventually, the propagating radical is reversibly trapped by the nitroxide radical. These reactions can repeat until all the monomer is consumed. During this process, a very small instantaneous concentration of propagating free radicals produced by reinitiation is moderated by the nitroxides and leads to the stepwise growth of the chains. Consequently, termination reactions are minimized, and polymers with narrow polydispersities are obtained.

2.1.1.2 Reversible Addition-Fragmentation Chain Transfer Process (RAFT)

RAFT is a special case of degenerative transfer. The RAFT process involves the combination of monomer, a good solvent for both monomer and polymer, an azo- or peroxy- initiator, and the essential reversible transfer agent. A simplified mechanism is given in Scheme 2.1. The transfer agent (dithioester) reacts with the propagating radical (Pn•) to give another transfer agent and the species R•, which reinitiates polymerization (b and c). The living behavior involves a reversible addition-fragmentation sequence between the active and dormant species with the S=C(Z)S- chain transfer moiety (e).



Scheme 2.1: Mechanism of RAFT

The RAFT process has distinct advantages over other controlled free-radical living processes (e.g., nitroxide-mediate SFRP, reversible atom and group transfer) in that it can be used for a wide range of monomers, including N-isopropylacrylamide, methacrylic acid, styrenesulfonic acid sodium salt, 2-hydroxyethyl methacrylate, 2-(dimethylamino)ethyl methacrylate, and most importantly, vinyl acetate. These monomers can be polymerized in a wide range of

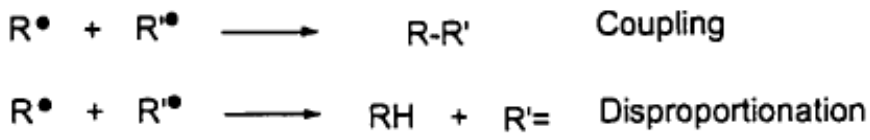
solvents under a wide range of experimental conditions. The products, whether homopolymers, random copolymers, gradient, or block copolymers, are of controlled molecular weight and generally have very narrow polydispersities (usually PDI < 1.2, and sometimes < 1.1).

In order for a dithioester compound to be effective as a RAFT agent, it needs to meet the following requirements; (i) both rates of addition and fragmentation must be fast relative to the rate of propagation, and (ii) the expelled radical (R•) must be capable of reinitiating polymerization. The first requirement ensures the rapid consumption of the initial RAFT agent and fast equilibration of the dormant and active species, while the second ensures the continuity of the chain process. By changing the substituents of dithioester compounds (Z and/or R in Scheme 2.1), it is possible to prepare chain transfer agents fulfilling these requirements in the polymerizations of various monomers, and consequently, to prepare polymers with controlled molecular weight and low polydispersity. The RAFT process is simple like nitroxide-mediate and does not require any metal catalyst. The advantage of RAFT is illustrated by the fact that the greatest number of monomers can be polymerized in controlled way compared to other controlled radical polymerization methods. A potential disadvantage of RAFT and degenerative transfer polymerization methods in general, is that a concentration of low molecular weight radicals is always present and available for unwanted termination reactions.

2.1.1.3 Atom Transfer Radical Polymerization

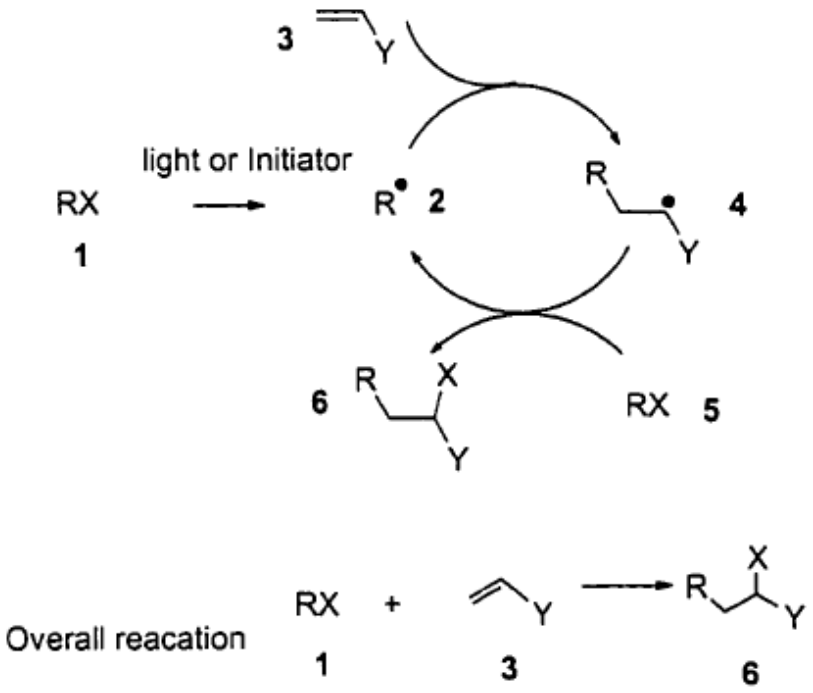
Addition of free radicals to alkenes is a fundamental reaction in organic and polymer synthesis. [20, 21, 22] This reaction in most cases is highly exothermic and rapid since one σ - bond is formed with the loss of one π-bond. The fast rate of radical addition as well as its tolerance to many functionalities, makes the radical addition reaction an attractive synthetic pathway. Therefore, it has been widely utilized for the synthesis of a variety of compounds ranging from complex natural products to commodity polymers.

Concurrently, the radical addition reaction possesses intrinsic side reactions, in particular, diffusion controlled radical-radical reactions through coupling or disproportionation. (Scheme 2.2.) Since these side reactions are extremely fast and unselective, they are difficult to control, and thus the radical addition reaction often becomes a non-exacting method to targeted products. This predicament is more pronounced in the polymerization process, where the addition reaction must be repeated many times, and the precise control of the reaction is even more important. Frequently, the polymers obtained from the radical process do not have well defined structures in terms of molecular weight, molecular weight distribution and functionalities. Therefore the precise control of radical polymerization has been one of the main challenges in polymer synthesis. [23]



Scheme 2.2: Radical Addition Reaction

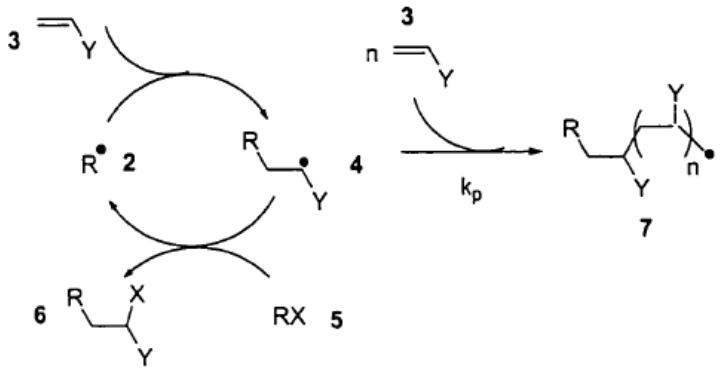
Fortunately, the side reactions between radicals can be minimized by decreasing the radical concentration ([R*]). While radical - radical reactions are second order in [R*], the addition of radical to alkene is first order in [R*]. A decrease in [R*] suppresses the radical-radical reaction effectively with a smaller reduction in addition rate. In organic synthesis, there have been several useful methods to maintain low radical concentrations, mostly based on chain reactions. . [20, 21] (Scheme 2.3.) In the chain reactions, only a catalytic amount of radicals is required since the radical is regenerated in the reaction cycle.



Scheme2.3. An example of radical chain reactions- atom transfer radical addition

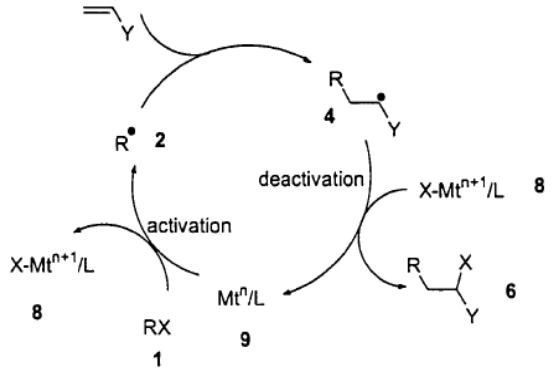
One such method is atom transfer radical addition (ATRA) or Kharasch reaction. [24, 25, 26, 27] (Scheme 2.3.). In ATRA, the chain reaction is initiated by the formation of radicals 2 from non-radical species 1, promoted either by light, or thermally labile compounds such as AIBN or peroxide. The reaction cycle is composed of addition and transfer reactions. In the addition step, the produced radicals 2 attack alkenes 3 to form adducts 4. The addition should be a fast reaction, in which less reactive radicals 2 are converted to more reactive radicals 4. These reactive radical adducts 4 rapidly abstract atom (or group) X from substrates 5, to form targeted products 6 and to regenerate radicals 2 in the transfer step. Continuous cycles of this chain reaction achieve the addition of 1 across the double bond of 3 to yield mono-addition products 6 while the radical concentration is kept low, which minimize the radical - radical reactions, termination (k_t) (Scheme 2.3).

In ATRA, there is another important side reaction, which is the formation of oligomeric or polymeric species, namely, the propagation reaction. Before the radical adducts 4 converts to desired product 6 through atom transfer, radicals 4 can escape from the reaction cycle and add to one or more alkenes 3 to yield oligomers / polymers 7 (Scheme 2.4.). This side reaction becomes more significant for alkenes with a higher propagation rate constant, kp (i.e. radically homopolymerizable alkenes). The low radical concentration cannot effectively reduce the propagation rate which is also first order in [R*] as the addition reaction is. Instead, the propagation can be suppressed by the correct choice of the alkenes / RX or the increasing the ratio of RX to alkenes.



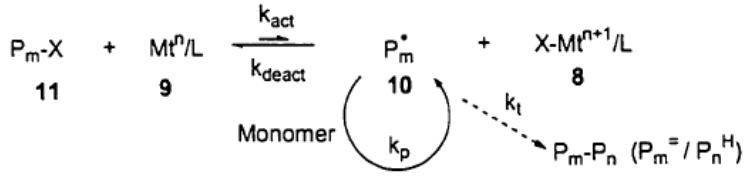
Scheme 2.4. Propagation reaction in ATRA

The use of a transition metal complex can be an alternative to expedite transfer relative to propagation. [28] Transition metal complexes 8 accelerate transfer of X to 4 without altering the rate of propagation so as to favor the formation of the mono addition product 6. (Scheme 2.5.) This process is referred to as deactivation, since unreactive products 6 are generated from reactive radicals 4. Transition metal complexes also abstract X from 1 to provide radicals 2 to the reaction cycle, in the activation step. The cycle does not need to be initiated by light or thermal initiator since the activation reaction in the catalytic cycle generates its radicals. The whole reaction cycle in Scheme 2.5 will be called transition metal catalyzed atom transfer radical addition (TMC ATRA) to distinguish it from non-metal mediated ATRA or Kharasch reaction.



Scheme 2.5. Transition metal catalyzed atom transfer radical addition

The recent adaptation of TMC ATRA to polymerization processes resulted in a new living radical polymerization method, namely, atom transfer radical polymerization (ATRP).[29,30] Similar to TMC ATRA, ATRP employs transition metal complexes 9 to catalyze atom transfer between radicals 10 and alkyl halides 11 where 10 and 11 can be either monomeric or polymeric species. (Scheme 2.6.) The atom transfer from alkyl halides 11 to transition metal complexes 9, produces the corresponding alkyl radicals 10 and oxidized metal complexes 8 with the activation rate constant, k_{act}. The reverse reaction yields 11 with reduction of 8, the deactivation rate constant, k_{deact}.



Scheme 2.6. Atom transfer radical polymerization

These activation and deactivation processes are reversible in ATRP, resulting in the reversible formation of radicals 10. The concentration of stationary radical 10 is low since the equilibrium between the activation and deactivation processes is shifted to left hand side, which reduces the termination reactions. The broken arrow in Scheme 2.6. represents the small contribution by the termination reactions with k, The addition of monomer with the propagation rate constant, kp,

proceeds in a controlled fashion for all chains through these reversible activation and deactivation cycles, and well-defined polymers with predetermined molecular weights and narrow molecular weight distributions can be produced.

It is important to note the concentration of 8 during the reaction (i.e. transition metal complex in higher oxidation state). In radical reactions, the radical - radical termination cannot entirely be eliminated, and their small contribution still exists even in the chain reactions of TMC ATRA / ATRP. This means that oxidized metal complexes 8 in Scheme 2.5. and 2.6. are continuously generated throughout the reaction. At some point, the increased concentration of 8 further decreases the radical concentration and slows down the termination reactions and generation of 8. The role of this self-regulating system was first explained by Fischer [31] and later named as the "persistent radical effect (PRE). [32] The persistent radical refers to stable radicals which only react with transient radicals (e.g. 2 and 4 in Scheme 2.5. and 10 in Scheme 2.6.) and do not react with other species including themselves. Now, it is believed that many of the transition metal catalyzed radical reactions are subject to the PRE and it is the persistent radical that may alter the kinetics of the process as well as the distribution of the products. Therefore, it would be useful to reinterpret some of the previous studies carried out and explained without considering the PRE.

In both TMC ATRA and ATRP, a key for success is the correct choice of the transition metal complex since the rate of reaction and the distribution of products are affected by the transition metal complex. It provides an opportunity toward further optimization of current systems and development of new systems. On the other hand, the understanding of the role of transition metal catalysts has been a central question in TMC ATRA and ATRP. The transition metal catalysts may complicate the systems and necessitate more detailed mechanistic and kinetic studies than those for non-metal catalyzed radical reactions.

Components of ATRP

In order to fully understand the ATRP technique, one must understand the roles of the various components. The ATRP system consists of monomer, initiator with a transferable halogen, and a catalyst system composed of a transition metal species and a suitable ligand. Solvent, reaction temperature, and additives are also important. As with any reaction, the conditions under which a particular reaction is to be performed must be optimized to achieve the desired results. Figure 2.1 shows that the relationship between Mw/Mn, Mn with conversion.

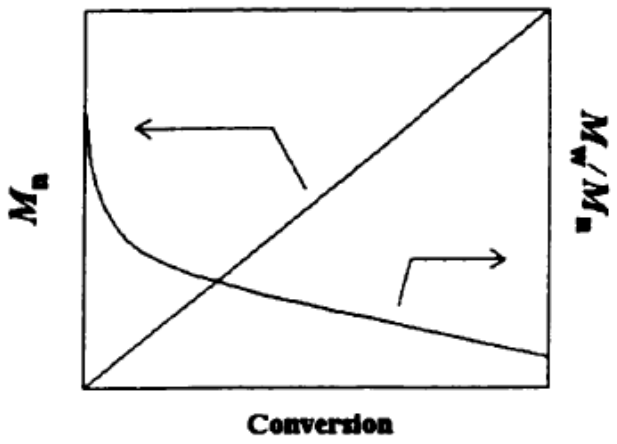


Figure 2.1 Representation of Molecular Weights and Polydispersities with Conversion for a Living Radical Polymerization

Monomers

A wide variety of monomers have been successfully polymerized by ATRP. These includestyrenes, [33,34] acrylates, [35,36] methacrylates, [37,41] vinylpyridine, [42] and acrylonitrile.[43] To be polymerizable via ATRP, the monomer must have stabilizing groups (e.g. phenyl or carbonyl) next to the carbon radical in order to have a sufficiently large atom transfer equilibrium and the monomer must not have groups (e.g. acids) that interfere with the catalyst system. The radical polymerization rate is unique to each monomer so that the concentration of propagating radicals and the rate of deactivation need to be adjusted for each particular system in order to maintain control. The overall equilibrium of the reaction depends on the radical (monomer) and the dormant species as well as on the amount and reactivity of the transition metal catalyst added.

Initiators and Halogen Exchange

ATRP is typically initiated by an alkyl halide, which contains an activating substituent on the α-carbon, stabilizing the resulting radical. The initiation step proceeds by the same process as propagation, and the role of the initiator is to determine the number of growing polymer chains and to provide the head group of the polymer chain. If initiation is fast and transfer and termination reactions are negligible, the number of growing chains is constant and equal to initiator concentration. The theoretical molecular weight or degree of polymerization increases inversely with initial initiator concentration and is given by equation [2.2]:

$$M_n = \frac{\text{moles monomer}}{\text{moles initiator}} \qquad (2.2)$$

To achieve control of molecular weight and narrow molecular weight distributions, the halide group must rapidly and selectively migrate between the growing chain and catalyst complex. Molecular weight control has been the most successful when the halogen is either chlorine or bromine. [44] Mixed halide

initiation systems (i.e. R-X/Cu-Y (X,Y=C1 or Br)) have also been investigated to obtain better control in ATRP of MMA. [45]

Solvents

ATRP has been successful in bulk, in solution, and in a heterogeneous system (for example, emulsion or suspension). A good solvent for ATRP will allow minimal chain transfer to solvent and solvent assisted side reactions. Polymerizations are typically carried out in organic non-polar media such as toluene or anisole although a wide range of solvents (e.g. diphenyl ether, ethylene carbonate, water, dimethylformamide, acetone, alcohols) have been effectively employed in various ATRP systems. Rate enhancement in polar media (e.g. using ethylene carbonate as solvent) has been observed and is attributed to a structural change in the copper complex.[46] Polar media also help to dissolve the catalyst.

Catalysts

The ideal ATRP catalyst should be highly selective for atom transfer and should not participate in other reactions. The catalyst determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. In order to be an efficient catalyst for ATRP, the metal must have at least two readily accessible oxidation states separated by one electron, have reasonable affinity toward a halogen, have an expandable coordination sphere upon oxidation to accommodate the halogen, and be strongly complexed to a ligand. To differentiate ATRP from redox-initiated polymerization, the oxidized transition state should rapidly deactivate the propagating polymer chains to form the dormant species, resulting in a controlled process. Although a variety of metals have been used such as Fe (II), [47] Ru (II), [48-50] and Ni (II) [51, 52] this work focuses on ATRP catalyzed by copper, which is superior to other metals in versatility and cost.

Ligands

The ligand serves to solubilize the catalyst in ATRP. Nitrogen ligands, which have been used in copper- and iron-mediated [53] .Multidentate ligands, are the ligands of choice and a variety have been developed. Some examples are shown in Figure 2.6. Derivatives of 2, 2'-bipyridine (bipy) are one example of ligands used in Cu-catalyzed ATRP.[54] The most common bipy ligand is the derivative with solubilizing nonyl groups in the 4, 4' position: 4, 4'-di(5-nonyl)-2, 2'-bipyridine. Haddleton et al.[55-57] reported use of π accepting, chelating imine-based ligands. Other aliphatic multidentate amines such as N, N, N, N', N''-pentamethyldiethylene triamine (PMDETA) 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), and tris[2-(dimethylamino)ethyl]amine (Me6TREN) [58] have also been reported.

Electronic and steric effects of the ligands affect ligand behavior in ATRP [59,60] Catalytic activity is reduced when there is excessive steric bulk around the metal center or the ligand possesses strongly electron-withdrawing substituents. Activity also decreases with a decrease in coordinating sites and as the number of linking carbons increases. Although the catalyst/ligand species in ATRP may be a complex structure, the generally accepted complex is two bidentate ligands complexed to one copper bromide molecule.[61,62] The order of decreasing activity for the various types of nitrogen ligands is as follows: R_2N- > Pyridines > R-N= > Ph-N= > Ph-NR-. Aliphatic amine ligands cause faster polymerization rates due to their poorer π-accepting ability, which results in less stabilization of the copper (I) species. [58] Altering the σ-donating and π-accepting properties of the ligand changes the redox potential for the copper oxidation and thereby increases the atom transfer equilibrium constant. [62]

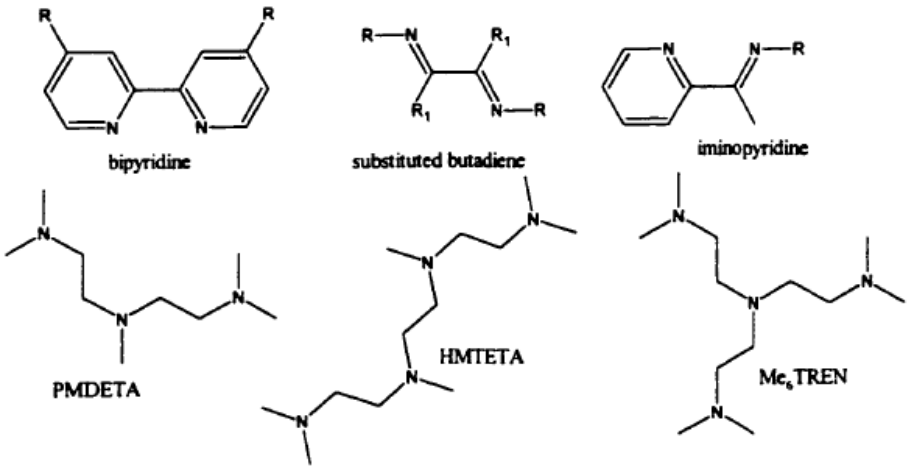


Figure 2.2: Examples of ATRP Ligands

Proper choice of ligand for the particular ATRP system is very important. Both heterogeneous and homogeneous catalytic systems have been used. Early ATRP experiments comparing bipy ligands with and without solubilizing alkyl groups showed that the soluble catalyst systems resulted in lower polydispersities, similar initiator efficiencies, and slower overall polymerization rates as compared to the heterogeneous bipy systems [63] The increased control is attributed to the better solubility of the copper (II) species which causes deactivation. Homogeneous systems also offer the advantage of allowing for detailed kinetic and mechanistic studies of the polymerization. [64,65] Mülhaupt and coworkers[66] have studied ATRP of styrene with various bipy and diimine ligands with CuBr catalyst and showed that ligand designs and steric constraints have an important effect on catalyst activity, which manifests itself either as incomplete initiation, slow deactivation, or a combination of both. Figure 2.2 shows that some ATRP ligands.

Additives

Additives to ATRP reactions have been investigated as ways to affect the reaction rate and control in the polymerization. Significant rate enhancements were observed using zerovalent metal as an additive. For example, when a small amount of copper (0) (copper powder) is added to styrene and methacrylate polymerizations, polymerization rates increase.[67] Copper (0) is said to reduce "excess" copper (II)

forming copper (I). Removal of small amounts of copper (II) enhanced the rate yet left a sufficient amount to maintain control of the polymerization. Addition of $CuBr_2$ has been used as a way to increase the rate of deactivation, in order to shift equilibrium to form the dormant species, which will in turn minimize side reactions and termination.

2.1.2 Comparison of Various Methods of Controlled Radical Polymerization

ATRP has been used successfully for the largest range of monomers, although the direct polymerization of vinyl acetate and acrylic acids has not yet been successful. ATRP has been carried out in bulk, solution, dispersion and emulsion at temperatures ranging from - 20 ˚C to 130 ˚C. Some tolerance to oxygen has been reported in the presence of zero-valent metals [68]. The catalyst complex is based on a transition metal that regulates both polymerization rate and polydispersity furthermore since the catalyst must be available for the reaction to occur both oxidation states should be sufficiently accessible in the reaction medium. The catalyst can be selected to facilitate cross-propagation for the synthesis of difficult block copolymers, and can scavenge some oxygen through in situ formation of the deactivator, but in homogeneous systems it should be removed or recycled from the final polymerization product since the concentration of the transition metal complex is generally higher than desired in most products. In some supported or hybrid catalyst systems the concentration of transition metal in the final product may be acceptably low [69]. Perhaps the biggest advantage of ATRP is the readily accessible inexpensive initiators whose active end group, normally consists of simple halogens. This is especially important for lower molecular weight polymers due to the high proportion of the end groups. Additionally, there is a multitude of commercially available macro initiators for ATRP. Moreover, the halogen end groups can be easily displaced with other useful functionalities using S_N2, S_N1, radical or other chemistries [70].

Most of the work reported in the open literature has used Schlenk techniques for the polymerizations but this reflects a desire to obtain reproducible kinetics and the use of monomers stored long term under normal laboratory conditions, rather than indicating a need for excessive purification of commercially available materials. It is expected that in commercial scale operations use of standard industrially

available radically polymerizable monomers would not require any pretreatment of the reaction medium prior to initiation of the controlled polymerization.

Degenerative transfer can potentially be used for any radically polymerizable monomer. However, reactions of vinyl esters are apparently more difficult and RAFT polymerization of vinyl benzoate requires very high temperatures (T ~ 150 ˚C). It may be difficult to assure an efficient cross-propagation for some systems [71]. In principle, all classic radical systems can be converted to RAFT, or to another degenerative transfer process, in the presence of efficient transfer reagents. With the current systems the end groups are alkyl iodides, methacrylates or thioesters. The latter are colored and can provide some odor for low molar mass species and require radical chemistry for removal and displacement. Methacrylate oligomers are efficient only for the polymerization of methacrylates. No transition metal catalyst is needed for activation in degenerative transfer since that role is fulfilled by addition of a standard radical initiator however this results in the incorporation of some undesired end groups. The amount of termination is governed by the amount of decomposed initiator. A potential disadvantage of degenerative transfer is that there is always a low molecular weight reactive radical available for termination reactions, in contrast to the ATRP and TEMPO systems where as conversions increase only reactive radicals associated with longer chains exist, and termination reactions occur more slowly.

Thus, the prime advantage of the nitroxide mediated system is the absence of any metal. ATRP may be especially well suited for low molar mass functional polymers due to the low cost of end groups and easier catalyst removal from low viscosity systems. It may be also very suitable for the synthesis of ‘difficult’ block copolymers and some special hybrids with end functionalities. However, it requires catalyst removal or the use of a supported catalyst. Degenerative transfer, and especially RAFT, should be successful for the polymerization of many less reactive monomers and for the preparation of high molecular weight polymers. It is likely that the search for new efficient transferable groups will continue due to some color and odor limitations of the sulfur containing compounds currently employed.

2.1.3 New Materials by Controlled/Living Radical Polymerization

After all this discussion about radical polymerization and new methods to develop processes to obtain better control of the polymerization, the question remains: Why? Why should one use these novel methods to polymerize vinyl monomers? The answer that first comes to mind is supplementation of anionic and cationic polymerization as the primary means of obtaining well-defined (co)polymers, in these cases by radical polymerization processes which are more tolerant of impurities, functional groups and are applicable to a wider range of monomers. This increased level of control over radical polymerization will allow industry to tailor a material to the requirements of a specific application using the most robust polymerization process available, ensuring the polymers have the optimal balance of physical and chemical properties for a given application.

Well-defined (co)polymers are generally recognized as polymers with molecular weights defined by DPn =Δ[M]/[I]o, and with low polydispersities, say, Mw/Mn < 1.3 (an arbitrary figure). However, such homopolymers are of little interest commercially; in some instances, materials with broad molecular weight distributions are desired for various rheological reasons. What controlled/living polymerizations offer is the ability to prepare entirely new polymers with a myriad of compositions, architectures, and functionalities (Figure 2.3)with each polymer chain in the bulk material having the same microstructure (composition, architecture and functionality) and not a distribution of composition and properties from chain to chain.

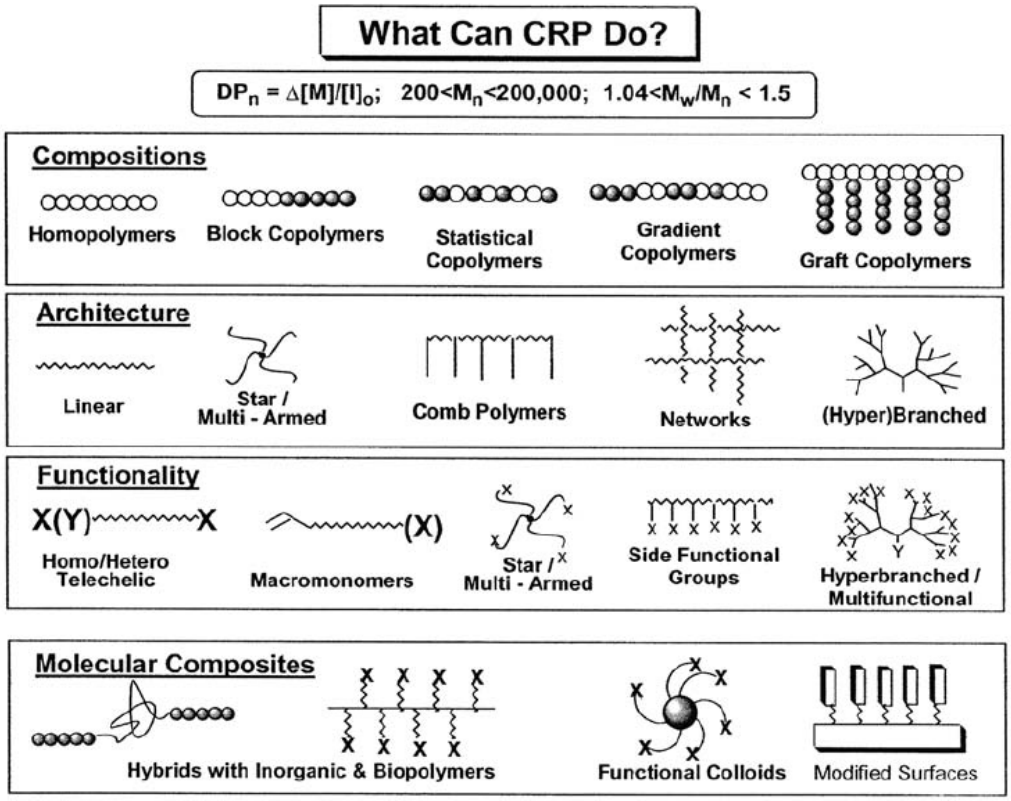


Figure 2.3: Molecular structures possible with controlled/living polymerizations.

Functional Polymers

There is an ever increasing demand for polymers for specific end-use properties such as enhanced resistance to fire or environmental attack or, in some cases, enhanced degradability. Development of new polymeric materials to meet this challenge has involved the use of a multidisciplinary approach involving chemistry, physics, and engineering. Every decade since the middle of 20th century seems to have witnessed an additional dimension in the thrust of development research in polymer science: the 1950s saw serious advances in polymer chemistry, the 1960s in polymer physics, the 1970s in polymer engineering, and the 1980s in functional polymers.[72] We are currently witnessing the emergence of high performance polymeric materials such as alloys and blends and advanced composites (so-called polymer abc) being developed through the application of polymer physics and engineering. In this discussion, we focus attention on functional polymers.

Functional polymers may be considered in broad terms as those polymers whose efficiency and characteristics are based on a functional group. A specific functional group is usually carefully designed and located at a proper place on the polymer chain. The functional groups may be dispersed along the polymer main chain (including chain ends) or attached to the main chain either directly or via spacer groups. The main objective of the introduction of special functional groups into the polymer backbone or side chains is to give the polymers special features. Functional groups are, therefore, typically chemical units that are chemically reactive, biologically active, electro active, mesogenic (liquid crystals), photoactive, and, more commonly, ionic, polar, or optically active.[72] There are two general techniques used for the preparation of functional monomers:[73]

• Polymerization or copolymerization of functional monomers

• Chemical modification of preformed polymers

The use of functional monomers permits ready control of the content and sometimes the distribution of units along the polymer chain; this procedure gives more latitude concerning the physical properties of the final product. On the other hand, chemical modification of an existing polymer, when possible,

enables the choice of molecular weight and the dispersity of the polymer. It also allows the synthesis of polymers inaccessible by direct route. [74]

Cross-linking, vulcanization, and grafting are some of the polymer reactions that take place on functional or reactive groups located in the polymer main chain.

2.1.4 Applications

Some existing markets targeted by materials prepared by CRP are:

- Adhesives
- Sealants
- Emulsifiers
- Polymer blend compatibilizers
- Coatings
- Toners
- Dispersants
- Lubricants
- Curable sealing compositions
- Elastomeric materials
- Drug delivery
- Cosmetics
- Materials comprising specific bulk physical properties

Although this has been but a brief review of novel materials prepared using controlled radical polymerizations, one can easily see that, regardless of the type of controlled radical polymerization employed, these methodologies open the door to a wide range of novel polymers with unique properties. Indeed control over polymer sequence distributions continuously expanding and recently multi-block heteropolymer chains with up to 100 blocks in an ordered sequence and controllable block lengths have been reported [75]. Only time will tell, but undoubtedly the question is not if such materials will find commercial uses, but one of when and how.

Radical polymerizations are widely used in industrial processes, accounting for the synthesis of nearly 50% of all polymeric materials. The widespread use of radical polymerization is due to its unique ability to easily and readily prepare high Mw polymers from a variety of monomers, under relatively mild reaction conditions.

To extend the usefulness of radical polymerization, various systems have been developed to allow for the 'control' of the polymerization such that termination and transfer processes can be avoided, or at least minimized. Towards this end, three systems have shown some ability to solve this problem; these are the nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and radical addition-fragmentation transfer (RAFT). All three have their benefits and deficiencies, but each may be particularly suited for certain applications, i.e., high molecular weight polymers vs. low molecular weight telechelic oligomers, etc.

It has been demonstrated that polymers with novel compositions, architectures, and functionality can be readily prepared by using these methods. Although some terminal functionality of the chains is lost due to unavoidable termination reactions, these materials may provide unique properties that will be good enough, or significant enough, to be used in new applications.

3. EXPERIMENTAL WORK

3.1 Materials

3.1.1. Purification of Materials

3.1.1.1 Monomers

Methylmethacrylate (MMA) (Fluka)

Washed with aq. NaOH 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure.

3.1.1.2. Solvents

Tetrahydrofuran (THF) (J:T:Baker)

Dried and distilled over CaH_2 then it was let mixing over sodium /benzophenon ketyl, and was distilled prior to use.

Chloroform (Lab Scan)

Shaken with several portions of conc. H_2SO_4 washed throughly with water and dried with $CaCl_2$ before filtering and distilling (61 ºC / 760 mmHg)

Methanol-(LabScan)

It was used without further purification.

Anisole (Lab Scan)

It was used without further purification.

3.1.1.3. Other Chemicals and Reagents

Acetonitrile (Aldrich)

It was used without further purification.

Triethylamine (TEA) (Acros)

It was used without further purification.

Copper (I) Bromide (Aldrich)

It was used without further purification.

N',N''-pentamethyl diethylenetriamine (PMDETA) (Acros)

It was used without further purification.

Bromoacetyl bromide (Aldrich)

It was used without further purification.

Hydroxybenzonitrile (Aldrich)

It was used without further purification.

Chloroacetone (Aldrich)

It was used without further purification.

Benzaldehyde (Aldrich)

It was used without further purification.

3.2. Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analysis were recorded on a Bruker 250 MHz Spectrometer.

3.2.2. Gel Permeation Chromatography (GPC)

GPC analysis were carried out with a set up consisting of agilent pump and refractive-index detector (Model 1100) and four Waters Columns (HR 5E, HR 4E , HR 3, HR 2).

THF was used as the eluent at a flow rate of 0.3 ml/min at 30 ºC. The molecular weights of polymers were calculated with the aid of poly MMA standards.

3.2.3 Photo Reactor

A merry-go-round type photo reactor, with 16 Philips 8W / 06 lamps were used.

3.2.4 Ultra-Violet Spectrophotometer (UV)

UV spectra were measured by Shimadzu Instrument type UV-1700, with a slit width of 1.0 nm.

3.2.5 Infrared Spectroscopy (IR)

Infrared spectra were recorded on KBr with a jasco model FT-IR – 5300 Fourier transform spectrophotometer.

3.2.6 Gas Chromatography (GC)

For kinetic calculations, ATI Unicam 610 model GC with packed column was used.

3.3Synthesis of Chemical Compounds

3.3.1 Preparation of 2-acetyl- 3-amino-benzofuran-2-yl (AABF)

13.8 g (0.1 mol) of K_2CO_3 in 200 mL of acetonitrile was added to 11.9 g (0.1 mol) of 2-hydroxybenzonitrile. The mixture was heated at 60 °C for 1 h. 9.25 g (0.1 mol) of chloroacetone was added to this mixture portion wise. The reaction was proceeded at room temperature for 4 h and was refluxed for 6 h. Reaction content was poured into water. The precipitated product was filtered and washed with excess of water and was dried at 40 °C under vacuum. The product was crystallized from ethanol. Yield: 80 %.

3.3.2 Synthesis of 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one (APPO)

Into a three-necked 500 mL flask equipped with magnetic stirring were placed 17.5 g of amino benzofuran (0.1 mol) dissolved in 60 mL of ethanol and 6 g of NaOH (0.15 mol) was dissolved in 40 mL of distilled water. Then 15 mL of benzaldehyde in 50 mL ethanol was added dropwise at 10 °C for 1 h. The mixture was stirred for 12 h at room temperature. The precipitated solid product was filtered, washed with excess of ice cold water, dried and re-crystallized from ethanol to get yellow crystals. Yield: 91%, melting point: 208 °C.

3.3.3. Synthesis of N-[(3-benzofuran-2-yl)-3phenyl prop-2-en-1-one]2-bromo asetamid (Chalcone Functional Initiator-CFI)

Under nitrogen, 4,56 mmol of 2-bromoacetyl bromide was added drop wise to a stirring mixture of 1,9 mmol of 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one(2) and 4,56 mmol of triethylamine in 50 ml of $CHCl_3$ in an ice bath for 30 min. After complete addition of the 2-bromoacetyl bromide , the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3×150 mL) and then dried over $MgSO_4$.After filtration, the evaporation of $CHCl_3$ gave a yellowish, greasy product. It was dissolved and crystallized in ethanol, filtered, and dried under vacuum. Yield: %75

3.3.4. General Polymerization Procedure for ATRP of MMA

To a schlenk tube equipped with magnetic stirrer , vacuum and dry nitrogen was applied five times, ($2{,}6x10^{-5}$ mol) chalcone functional initiator, ($2{,}6x10^{-5}$ mol) copper (I)bromide, ($5{,}2x10^{-5}$ mol) ligand (PMDETA) ,and ($3{,}12x10^{-3}$ mol) monomer (MMA) were added under nitrogen respectively. Anisole (0,2 ml) was used as a solvent. The reaction solution was bubbled by nitrogen to remove dissolved gasses and then tube was immersed in an oil bath and held by a thermostat at constant temperature. The polymerization was performed for a determined time and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The polymer solution was passed through a short alumina column to remove copper and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The polymer was dried under vacuum at room temperature for 24 h.

4. RESULT AND DISCUSSION

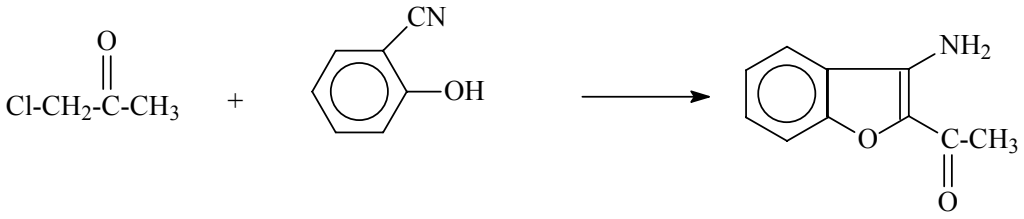
In this thesis a new chalcone containing initiator was synthesized and was used in ATRP of MMA. For this purpose, a functional initiator having chalcone groups and halide in the same structure was synthesized by the amidation of APPO with bromoacetylbromide.

This initiator has a fascinating character due to the presence of Br that could be employed in atom transfer radical polymerization and photosensitive chalcone group that could be activated photochemically.

Methylmethacrylate was polymerized via ATRP by using this initiator to obtain methacrylate polymers having chalcone groups at the chain ends.

4.1. Synthesis of 2-acetyl- 3-amino-benzofuran-2-yl (AABF)

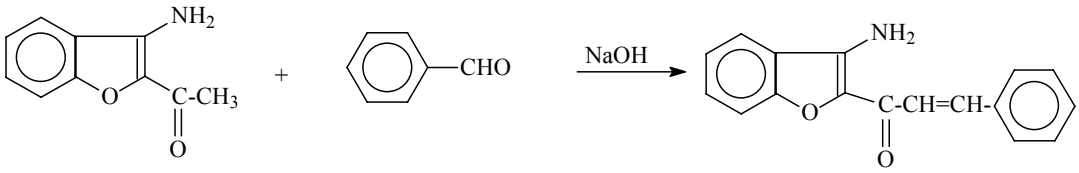
The preparation of the aminobenzofuran was performed according to previously reported procedures (Scheme 4.1) by the reaction of 2-hydroxybenzonitrile and chloroacetone yielding 80% product melting at 139 ^{0}C [76].



Scheme 4.1 Synthesis of AABF

4.2 Synthesis of 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one (APPO)

APPO was synthesized by the reaction of AABF and benzaldehyde according to the Claisen-Schmidt method (Scheme 4.2) [77] yielding 91% of product melting at 208°C.



Scheme 4.2 Synthesis of APPO

The structure of product was characterized by FT-IR and ^{1}H-NMR spectrum.The FT-IR spectrum of APPO in Figure 4.1 exhibits characteristic peaks to the structure at ν=3411 cm^{-1} (NH_2 stretching) and 3298 cm^{-1} (N-H stretching), 1608 cm^{-1} (C=O), 1582 cm^{-1} (aliphatic, CH=CH), 1575 cm^{-1} (aromatic, C=C stretching).

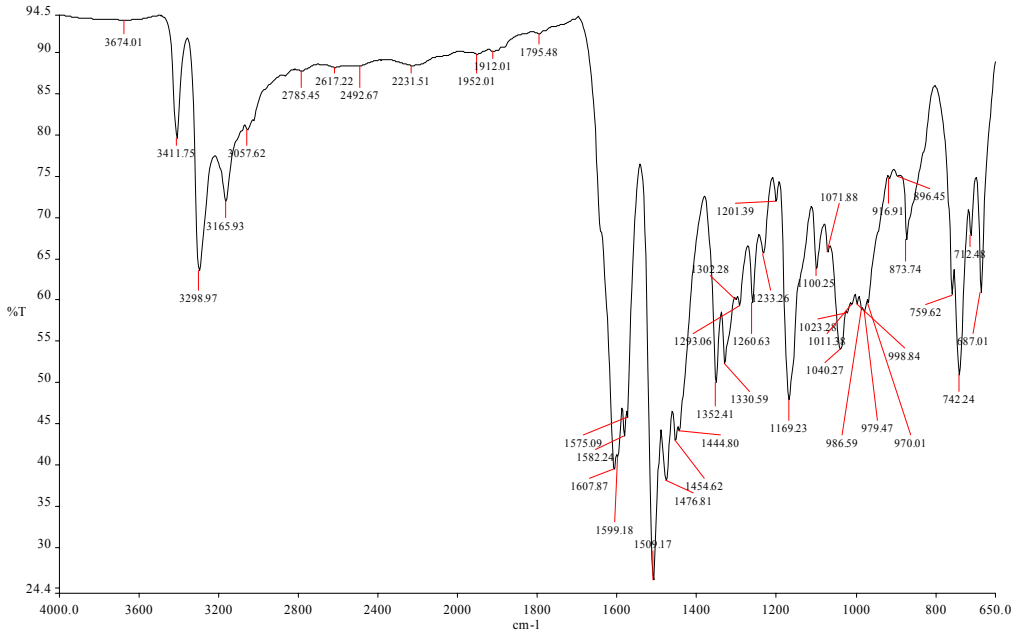


Figure 4.1 The FT-IR spectrum of APPO

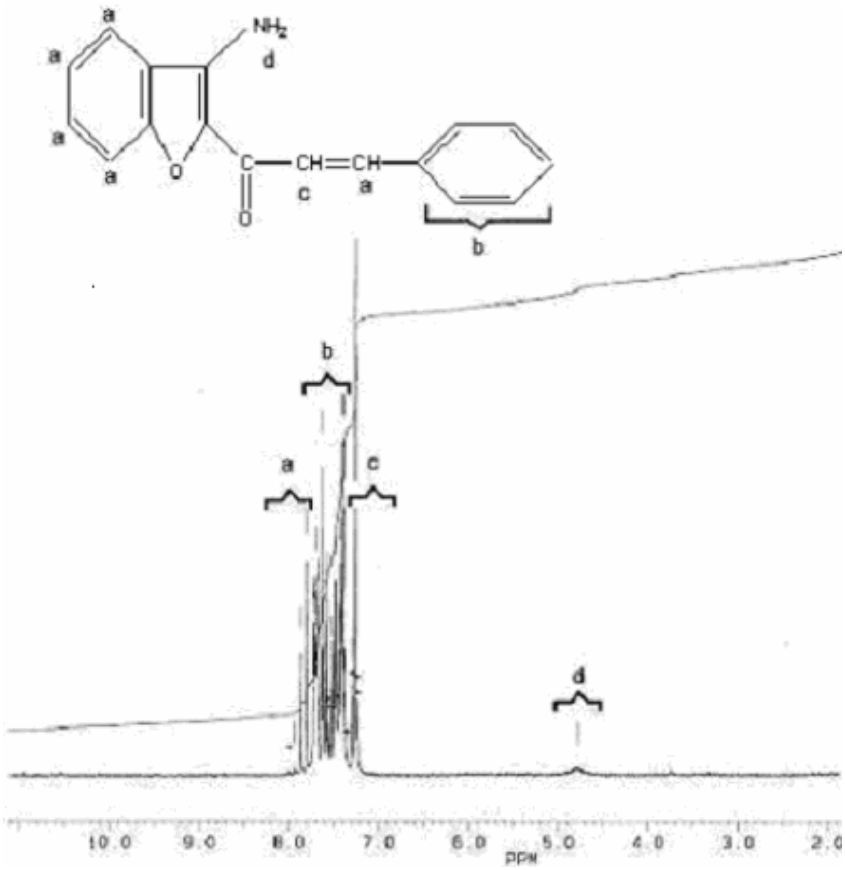


Figure 4.2 ^{1}H-NMR spectrum of APPO recorded in $CDCl_3$.

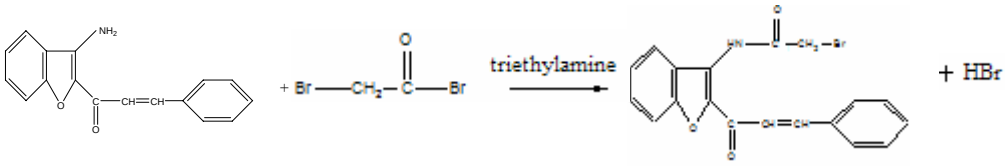
The formation of the product was also confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy (Figure4.2.)

^{1}H-NMR (DMSO-d6, ppm): δ=8.07-7.31 (m, ^{11}H, Ar-H and aliphatic, CH=CH), 4.78 (NH_2).

^{13}C-NMR (DMSO-d6, ppm): δ=177.94 (-C=O), 140.61 (-CH), 122.70 (-CH), 154.23, 135.37, 134.69, 130.62, 130.56, 129.44, 128.77, 122.70, 121.67, 112.74 (-C-aromatic and C-benzofuran).

4.3. Synthesis of N-[(3-benzofuran-2-yl)-3phenyl prop-2-en-1-one]2-bromo asetamid (Chalcone functional initiator-CFI)

Chalcone functional initiator (CFI) was prepared according to the modified method of Paik et al [78]. Amidation reaction of 1-(3-amino-1-benzofuran-2-yl)-3-phenyl prop-2-en-1-one with Bromoacetyl bromide yielded 75 % of CFI melting at 163 ^{o}C. (Scheme 4.3)



Scheme 4.3 Preparation of CFI

UV spectrum of CFI (Figure 4.3.) shows characteristic peaks for chalcone moieties at about 380-400 nm.

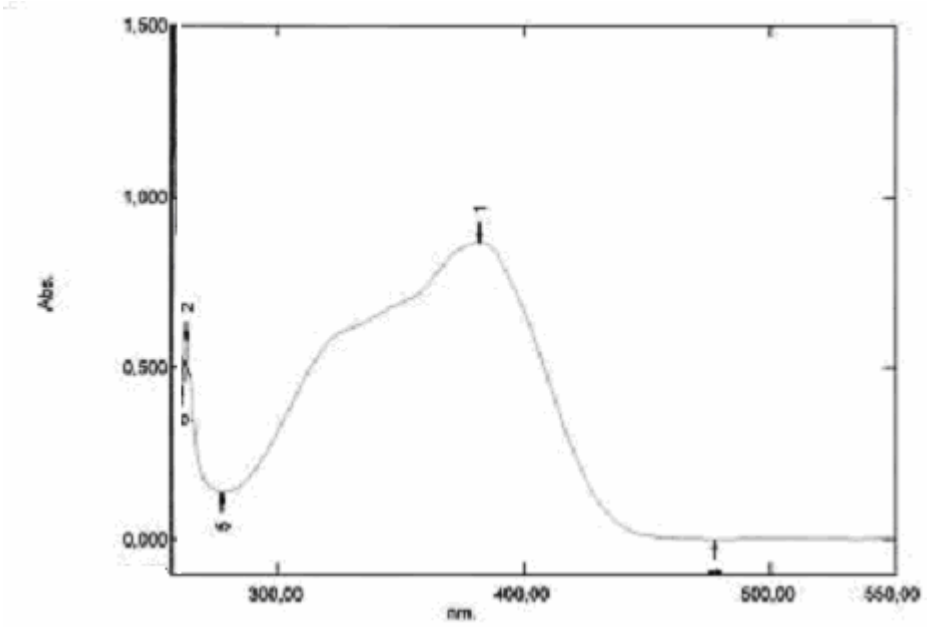


Figure 4.3 Absorption spectra of the chalcone functional initiator in $CHCl_3$

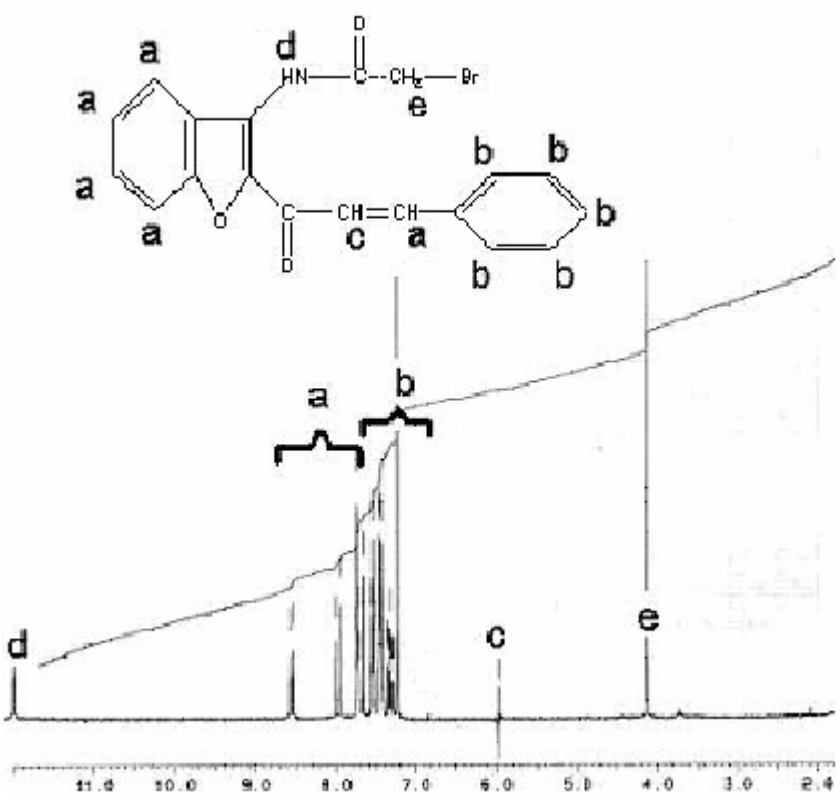


Figure 4.4 ^{1}H-NMR spectrum of the initiator (Chalcone functional initiator) in $CDCl_3$

^{1}H-NMR spectrum (Figure 4.4) of the CFI shows characteristic protons of the structure at δ= 11.89 ppm (amide protons) and δ= 4.07 ppm (-CH_2-Br).

The FT-IR spectrum of CFI (Figure 4.5) also shows characteristic peaks at 3298 cm^{-1} (N-H stretching), 1608 cm^{-1} (C=O), 1582 cm^{-1}(aliphatic, CH=CH), 1575 cm^{-1} (aromatic, C=C stretching), C-Br stretching 550 cm^{-1}

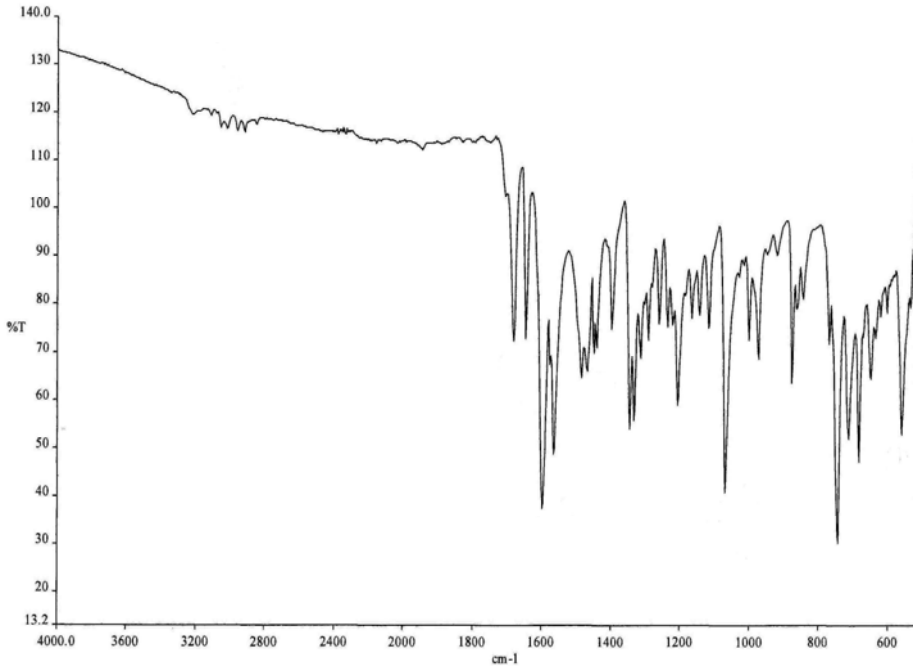
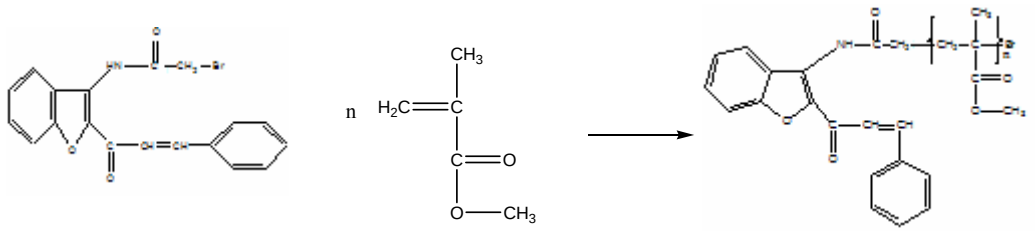


Figure 4.5 FT-IR Spectrum of the initiator (Chalcone functional initiator)

4.4. Preparation of Chalcone Functional Polymers by ATRP

Atom transfer radical polymerization of MMA was performed by utilizing CFI in the presence of copper (I) bromide, and PMDETA as a ligand and anisole as solvent Scheme (4.4). Polymerization conditions and results were collected in Table 4.1.



Scheme 4.4 Synthesis of chalcone functional polymers

This initiation mechanism suggested a bromine containing chalcone based functional group in the polymer chain ends. The incorporation of chalcone groups into the polymer was evidenced by ^{1}H NMR spectra of a PMMA.

The ^{1}H NMR spectra of the purified polymer Figure (4.6) sample clearly showed weak aromatic proton signals in the about 7.0–7.5 ppm range. This evidence established the proposed initiation mechanism.

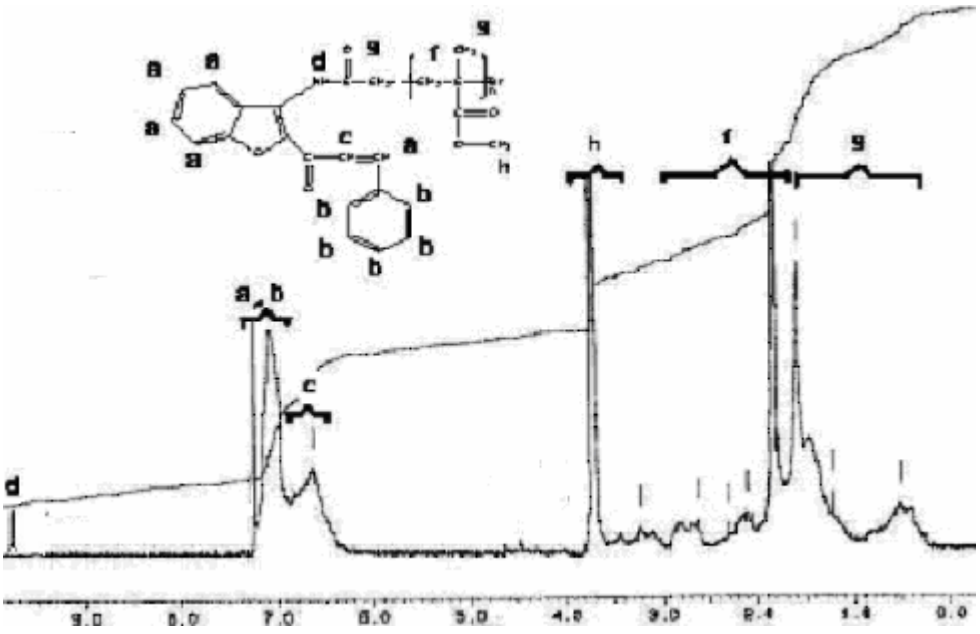


Figure 4.6 ^{1}H NMR spectra of the polymer

4.5 Polymerization Kinetics of the MMA

The polymerization reaction was monitored by gas chromatography (GC). The kinetics of the reaction was followed by aliquots taken at appropriate time intervals. The percentage-conversion data and GPC traces are presented in Table 4.1.

The MMA polymerizations gave linear $\ln(M_0/M)$ (where M_0 and M are the monomer contents at the beginning and at any time, respectively) versus time plots (Figs. 4.9)

The rate constant obtained from the slope was $k=1.83\times10^{-4}\ s^{-1}$ at $90\ ^{0}C$.

Polymerization kinetics were examined at different temperatures to obtain activation energy.

Table 4.1. ATRP of MMA in the presence of CFI

Time (Minute)	Conv. %	Mn(theo)a	Mn(GPC)b	Mw/Mn
10	10,49	1642	2105	1.495
20	17,84	2523	3101	1.387
30	26,81	3600	5762	1.306
60	55,9	7473	8177	1,239
120	60,6	7616	9547	1,196

(a) Mn, theo = $\{(\text{conversion x } [MMA]_0/[\text{initiator}]_0)\text{x } M_{MMA}\} + M_{\text{initiator}}$.

(b)GPC in THF, calibrated with PMMA standards.

[I]o/ [CuBr]o/[PMDETA] /[M]o: 1 /1 /2 /120 :0,0509 (Mol/liter)

[M]o :6,098 (Mol/liter)

T:90°C

The molecular weight conversion data gave linear relationships (Fig,4.7) as expected. Also corresponding conversion versus time data gave linear relationship. (Figure 4.8)

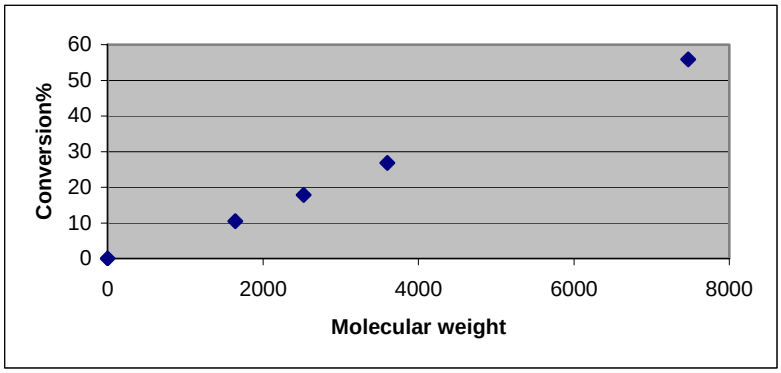


Figure 4.7 Conversion versus Molecular Weight plots

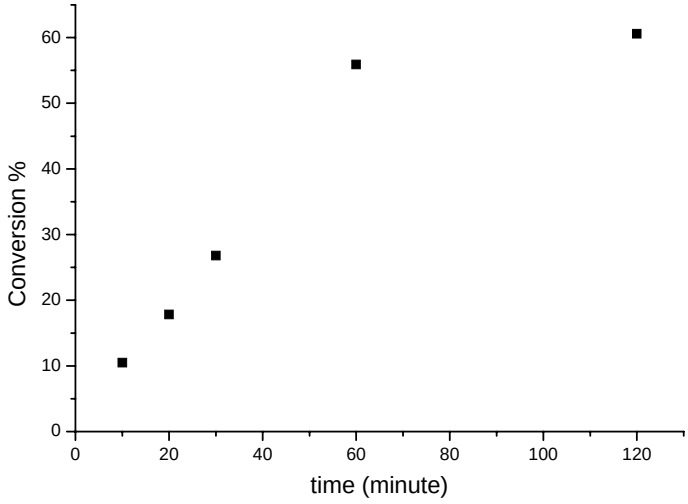


Figure 4.8 Conversion versus time plots

The polymerization reaction was carried out different temperature (table 4.2) to determine activation energy by using Arrhenius equation ($k=A.\ e^{-Ea\ /\ RT}$).

Table 4.2 ATRP of MMA with our initiator

t	T:90°C ln(Mo/M)	T:90°C convers.	T:105°C convers.	T:105°C ln(Mo/M)	T:120°C convers.	T:120°C ln(Mo/M)
0	0	0	0	0	0	0
10	0,11	10,49	12,33	0,131	14,38	0,155
20	0,196	17,84	20,03	0,2235	22,02	0,248
30	0,312	26,81	29,78	0,3535	32,14	0,387
60	0,818	55,90	56,93	0,8423	57,85	0,863
90	0,9137	59,90	60,03	0,917	60,05	0,917
120	0,933	60,60	60,60	0,931	60,7	0,934

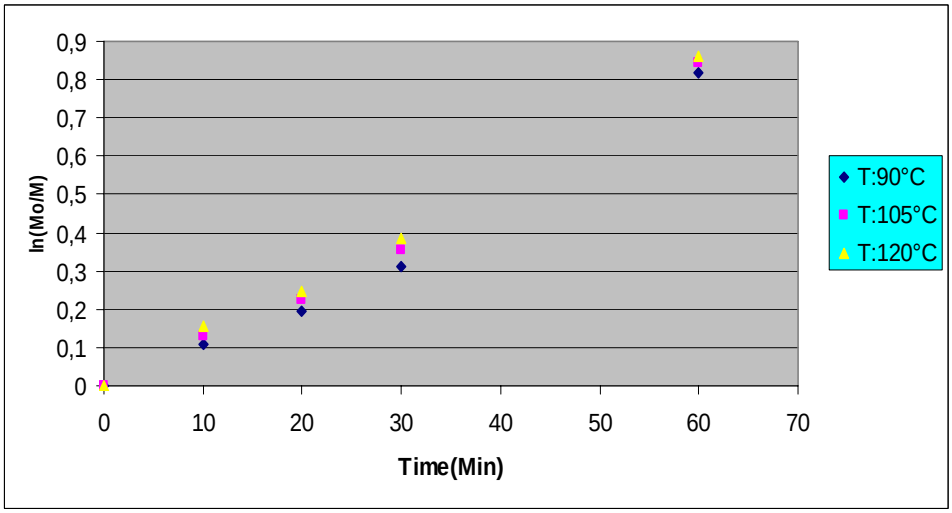


Figure 4.9 ln(M_0/M) versus time plot

The activation energy value was calculated from the slope of the Figure 4.10 (lnk versus 1 / T plot). This value was found as 10.93 kj / mol.

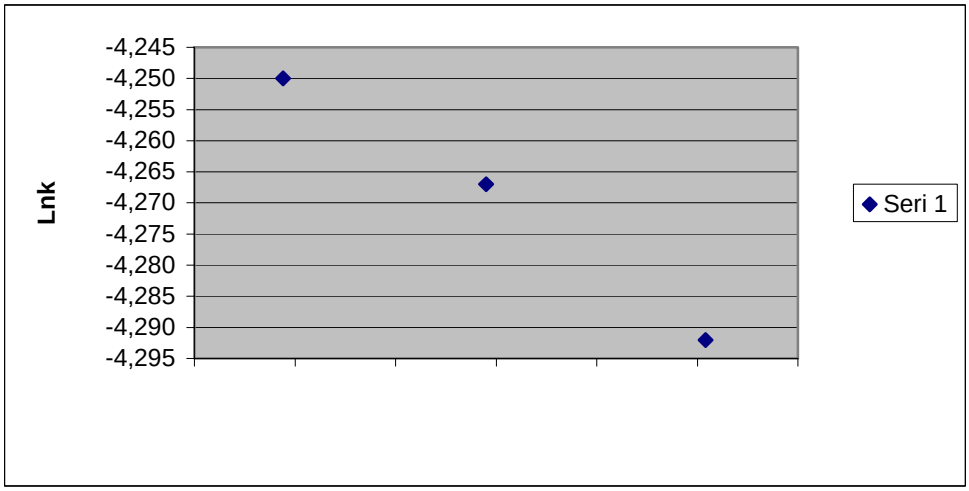
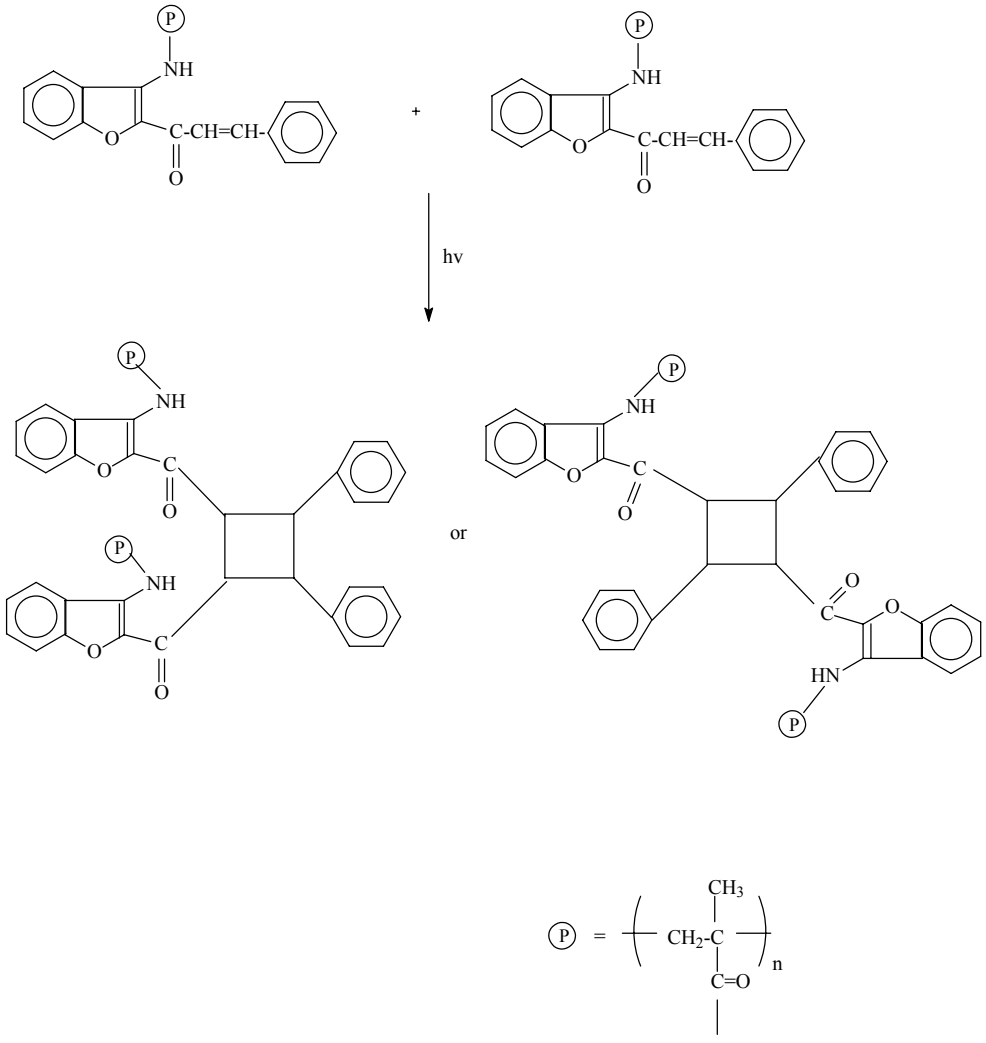


Figure 4.10. Arrhenius plot.

4.6 Chain Extension

To test the chalcone functional character of PMMA:

Upon irradiation chalcone moieties react to form cyclobutane ring and this reaction can be confirmed by fast decay of C=C bond of chalcone units [79]. In our case upon irradiation of chalcone functional polymers, chalcone moieties should also react to form cyclobutane ring thus extending the chain length of polymer [Scheme 4.5].



Scheme 4.5 Irradiation of chalcone moieties

To test the chalcone functional character of synthesized PMMAs, 5 mg/ml PMMA with molecular weight of 24000 (Figure 4.11. (a)) was dissolved in THF and irradiated for 1 hour at merry go round type photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at 350 nm at 25^{o}C. GPC chromatogram of resulting polymer showed significant (Mn: 40000 g/mol) (Figure 4.11. (b)) increase in comparision with initial polymer. Figure 4.11 shows GPC chromatograms of polymers before and after irradiation.

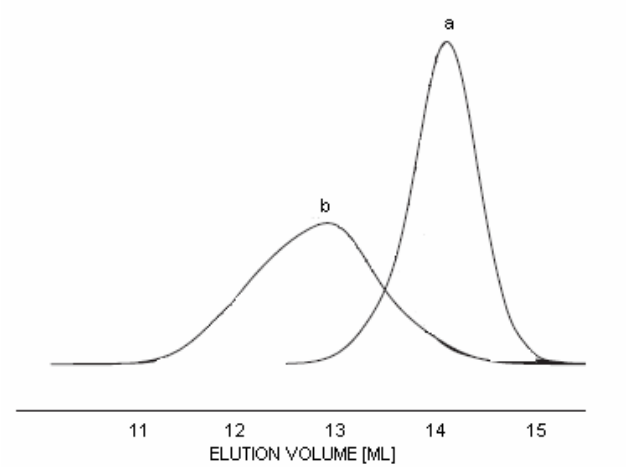


Figure 4.11 GPC Result of PMMA, a:Mn=24000 ; b:Mn=40000

5.CONCLUSIONS

In this study, a new chalcone functional initiator was synthesized and characterized by using spectrophotometric methods. This initiator was used in atom transfer radical polymerization (ATRP) of MMA. Polymerization kinetics and activation energy result were obtained from experimental values. Also Chain extension experiments were performed by using UV lamp at 350 nm to observe chalcone functionality disappear.

This result was also observed from GPC result. Molecular weight of PMMA measured after irradiation. The obtained result was shown chain extension.

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