İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

TRICHLOROCYANURIC ACID INITIATED ATOM TRANSFER RADICAL POLYMERIZATION OF METHYL METHACRYLATE

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METİL METAKRİLATIN TRİKLOROSİYANURİK ASİT BAŞLATICILIĞINDA ATOM TRANSFER RADİKAL POLİMERİZASYONU

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymers
M_w	: Weight average molecular weght of polymers
M_n/ M_w	: Molecular weight distribution of polymers
PMMA	: Polymethyl methacrylate
k_{act}, k_{deact}	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
K_{eq}, k_p	: Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively
k_t	: Rate constant of termination
I, M	: Initiator and monomer respectively

TRICHLOROCYANURIC ACID INITIATED ATOM TRANSFER RADICAL POLYMERIZATION OF METYL METHACRYLATE

SUMMARY

In recent years, the development of controlled radical polymerization methods has been a major trend. Controlled/ living radical polymerizations enable the synthesis of well-defined polymers with narrow molecular weight distributions, and precisely controlled functionalities.

One such controlled/ living polymerization is atom transfer radical polymerization (ATRP). ATRP provides a number of aspects necessary to produce materials of variety of compositions with complex yet predetermined architectures. In ATRP, an alkyl halide generates radicals by the continuous redox reaction provided by a transition metal complex. Methods to attach these groups to small molecules or polymers are numerous leading to a variety of structural motifs. Among these is the synthesis of star polymers from small molecules composed of multiple initiating species.

In this work, the polymerization of methyl methacrylate (MMA) mediated by CuCl/ PMDETA catalyst, in the initiation of trichlorocyanuric acid (trifunctional initiator) with the ATRP system was studied. The conversions were calculated from the gas chromatography (GC) and the molecular weights of the polymers were obtained from the Gel Permeation Chromatography (GPC).

METİL METAKRİLATIN TRİKLOROSİYANURİK ASİT BAŞLATICILIĞINDA ATOM TRANSFER RADİKAL POLİMERİZASYONU

ÖZET

Son yıllarda, kontrollü radikal polimerizasyon yöntemlerinin geliştirilmesine yönlenilmiştir. Kontrollü/ yaşayan polimerizasyonlar düşük molekül ağırlığı dağılımına sahip iyi tanımlanmış polimerlerin doğru fonksiyonalite ile sentezini sağlamaktadırlar.

Kontrollü/ yaşayan polimerizasyonlara bir örnek olarak atom transfer radikal polimerizasyonu verilebilir (ATRP). ATRP, yapıları önceden belirlenmiş, çeşitli bileşimlerdeki maddelerin üretimine olanak sağlar. ATRP'da, alkil halojenürler bir geçiş metali kompleksi tarafından sağlanan sürekli redoks reaksiyonu ile radikal üretirler. Bu grupları küçük moleküllere ya da polimerlere eklemek için birçok yöntem vardır. Bunlardan birisi, birçok başlatıcı gruba sahip küçük moleküllerden yıldız tipli polimerlerin sentezidir.

Bu çalışmada, CuCl/ PMDETA katalizörlüğünde, trichlorocyanuric acid (üç kollu başlatıcı) başlatıcı olarak kullanılarak MMA'nın ATRP sistemi ile polimerizasyonu incelenmiştir. Dönüşümler gaz kromatografisi (GC) kullanılarak hesaplanmıştır. Polimerlerin molekül ağırlıkları ise, Gel Permeation Chromotography (GPC) kullanılarak belirlenmiştir.

1. INTRODUCTION

The ability to synthesize macromolecules with complex and controlled architectures is becoming an incresingly important aspect of polymer science.

Polymers derived from radical initiated polymerizations are of significant importance in industrial processes, since the polymerization process is simple and applicable to a wide range of monomers. However, the control of molecular weights and molecular weight distributions in classical free radical polymerization is poor, due to radical coupling and chain transfer reactions of the growing species. This lack of control has limited the applicability of radical polymerization techniques for the preparation of well-defined molecular architectures. In contrast to the development of controlled ("living") anionic and cationic polymerizations, progress in controlled radical polymerization is relatively recent. These living free radical polymerization techniques are based on the reversible end capping of growing chains during polymerization. This mediates the reactivity and minimizes radical dimerization and disproportionation [1]. Free radical polymerization is the most common method of making polymeric materials. Nearly 50 % of all polymers are made by free radical polymerization.

There have been several techniques aimed at controlling free radical polymerization including iniferters, nitroxide mediated polymerization, reversible addition fragmentation chain transfer (RAFT), and atom transfer radical polymerization (ATRP).

Atom transfer radical polymerization (ATRP) provides as number of aspects necessary to produce materials of a variety of compositions with complex yet predetermined structures. Since the initiation and propagation occur through activated alkyl halides, initiators must contain structures as α- haloesters, benzyl halides, trichloroalkanes, or substituted sulfonyl halides. Methods to attach these groups to small molecules or polymers are numerous leading to a variety of structural

motifs. Among these is the sythesis of star polymers from small molecules composed of multiple initiating species.

Star-shaped or star polymers have attracted much attention in research over the years due to their unique three-dimensional shape and highly branched structure. Among all branched structures that are known, star polymers have been certainly the most investigated architectures, attracting much experimental and theoretical interest. Indeed star polymers represent the simplest model of brached structures, involving only one central branching unit per macromolecule. The best defined among them containing a precise number of arms of equal length. Such species have been useful in providing further insight into how branching affects the overall properties of polymers in solution or in melt.

ATRP is the most efficient CRP (controlled radical polymerization) methods which can be succesfully applied to the synthesis of star polymers. Star polymers can principally be synthesized in two different ways. One possibility consists of attaching growing polymer chains to a multifunctional molecule, which becomes the core of the star. This type of reaction is known for anionic polymerization and occurs when molecules bearing multiple electrophilic substituents are allowed to react with living polymer chains. However, anionic polymerizations are usually unsuitable for industrial purposes, and this method has another significant disadvatage: As the polymer chains grow, the reaction of several chains wiht the same quencher molecule becomes increasingly difficult because of steric hindrance. This problem may lead to stars with missing arms. A second possibility involves the use of multifunctional initiators. In this route, the core molecule reacts only with monomers, which are sterically much less demanding than polymer chains. Furthermore, these steric problems diminish as the chains grow and the distances between the reactive centers increase. However, this route is limited in the case of anionic polymerization, because of the necessity of multiply charged initiator molecules, which are usually poorly soluble. Similar restrictions apply to cationic polymerization. But with controlled/living radical polymerizations it is possible to avoid these problems. In this regard, atom transfer radical polymerization (ATRP) has proven to be very versatile [2].

1. THEORETICAL PART

2.1. Controlled / Living Radical Polymerizations

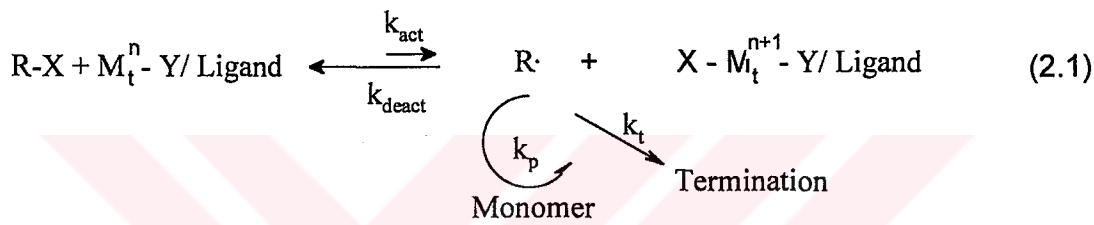
The development of controlled / living radical polymerization (CRP) methods has been a long standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers [3]. The advent of controlled / living radical polymerization (CRP) enables preparation of many new materials such as well defined components of coatings (with narrow MWD, precisely controlled functionalities and reduced VOC s), non ionic surfactants, polar thermoplastic elastomers, entirely water soluble block copolymers (agents for crystal engineering), gels and hydrogels, lubricants and additives, surface modifiers, hybrids with natural and inorganic polymers, various biomaterials and electronic materials. This is very important since free radical polymerization is the most common method of making polymeric materials [4].

The controlled / living systems are quiete similar to the conventional ones, however, the radical formation is reversible. Similar values for the equilibrium constants during initiation and propagation, ensure that the initiator is consumed at the early stages of the polymerization, generating chains which slowly and continuously grow, like in a living process [5]. Currently three systems seem to be most efficient: Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes such as RAFT [6]. Each of the CRP s has some limitations and some special advantages and it is expected that each technique may find special areas where it would be best synthetically suieted. For example, NMP carried out in the presence of bulky nitroxides cannot be applied to the polymerization of methacrylates due to fast β-H abstraction. ATRP can not yet be used for the polymerization of the acidic monomers, which can protonate the ligands and complex with copper. RAFT is very slow for the synthesis of low molecular weight polymers due to trapping of growing radicals by the intermediate radicals. At the same time each technique has some special advantages. Terminal alkoxyamines

may act as additional stabilizers for some polymers. Atom transfer radical polymerization enables the synthesis of special block copolymers by utilizing a halogen exchange and has an inexpensive halogen at hte chain end [7]. RAFT can be applied to the polymerizaiton of many unreactive monomers, such as vinyl acetate [8].

2.2. Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [9]. A general mechanism for ATRP is given in (2.1).



(2.1)

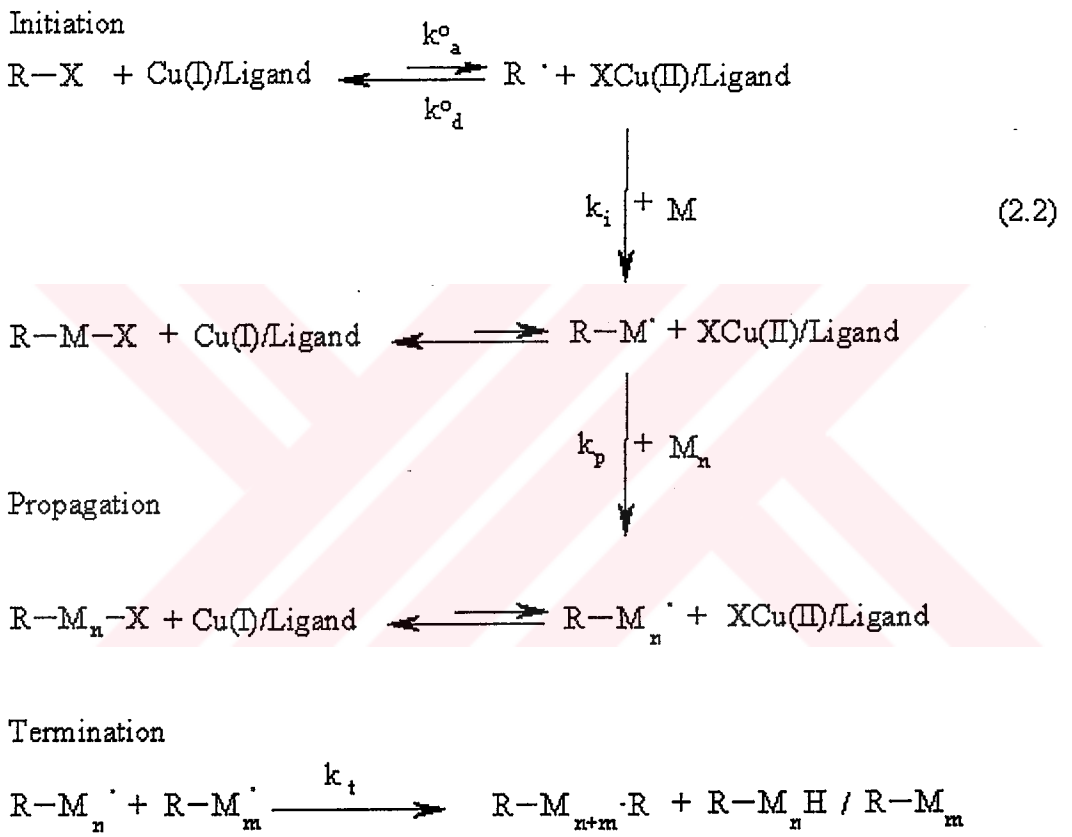
ATRP is based on the reversible transfer of an atom or group from a dormant polymer chain (R-X) to a transition metal (M_t^n / Ligand) to form a radical (R•), which can initiate the polymerization, and a metal-halide whose oxidation state has increased by one (X-M_t^{n+1} / Ligand); the transferred atom or group is covalently bound to the transition metal. A catalytic system employing copper (I) halides (M_t^n / Ligand) complexed with substituted 2,2'-bipyridines (bpy) has proven to be quite robust, succesfully polymerizing styrenes, various (meth)acrylates, acrylonitrile and other monomers [10-11].

This process occurs with a rate constant of activation, k_{act}, and deactivation, k_{deact}. Polymer chains grow by the addition of the intermediate 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.

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 polymerization. This process generates oxidized metal complexes, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of termination [12]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_{deact}, and also with the concentration of deactivator [5]. The molecular conversion and the amount of initiator used, $DP = \Delta [M] / [I]_0$; polydispersities are low, $M_w / M_n < 1,3$ [13].

The shematic representation of the mechanism of ATRP is given in (2.2).



(2.2)

The ATRP system is consisting of the monomer, initiator, catalyst- composed of transition metal species with any suitable ligand.

2.2.1. Monomers

A variety of monomers have been succesfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile, and other monomers which contain substituents that can stabilize the

propagating radicals. Even under same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant determines (k_{eq} = k_{act}/ k_{deact}) the polymerization rate. ATRP will not occur very slowly if the equilibrium constant is too small. In contrast, too large an equilibrium constant will lead to a large amount of termination because of high radical concentration [14].

2.2.2. Initiators

The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multifunctional initiators may provide chain growth in several directions. The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoritical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization.

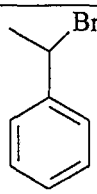
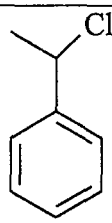
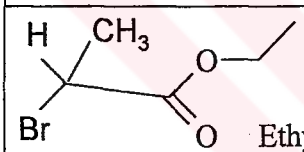
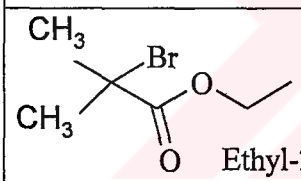
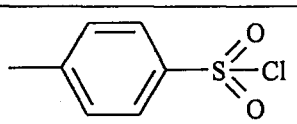
$$DP = [M]_0 / [I]_0 \text{ x conversion} \qquad (2.3)$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group X, must rapidly and selectively migrate between the growing chain and the transition-metal complex.

Initiation should be fast and quantitative with a good initiator. In general haloganated alkanes, benzylic halides, α-haloesters, α-haloketones, α-halonitriles and sulfonyl halides are used as ATRP initiators [14].

The most frequently used initiator types used in the atom transfer radical polymeriztion systems are given in Table 2.1.

Table 2.1 Types of initiators used in ATRP systems

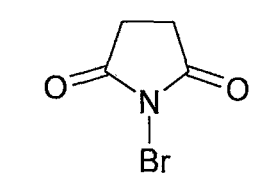
Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo propionate	Methylmethacrylate
 Ethyl-2-bromo isobutyrate	Methacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

Two parameters are important for a succesful ATRP initiating system; first, initiation shoul be fast in comparison with propagation. Second, the probability of side reactions should be minimized [14].

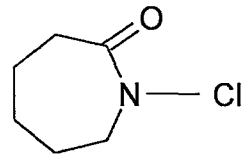
The only class of initiators that provide much higher rate of initiation than propagation with methacrylates, styrenes, acrylates and acrylonitrile is based on functional alkyl and aryl sulfonyl chlorides [15,16]. The N-centered radical

chemistry is not well understood except for some classic reactions such as Hoffmann-Lofller [17,18] or benzylic (allylic) halogenations [19]. Some of the N-halogenated derivatives used as initiators for the living radical polymerization of methyl methacrylate are given in (2.4).

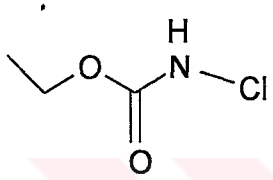
(2.4)



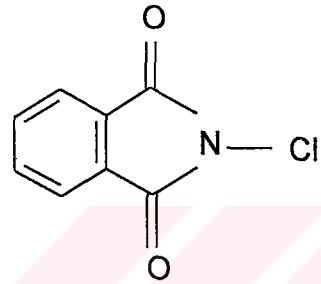
N-bromo succinimide
(NBS)



N-chlorocaprolactam
(NCC)



N-chloro urethane
(NCU)



N-chloro phatalimide
(NCPh)

2.2.3. Transition Metal Complexes

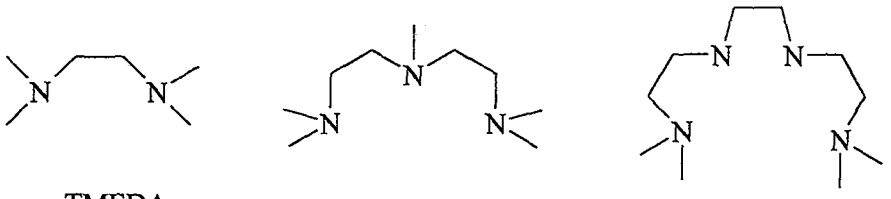
Catalyst is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prequisities for an efficient transition metal catalyst. First, the metal center must have at least two readily accesible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accomodate a halogen. Fourth, the ligand should complex the metal relatively strong. The most important catalysts used for ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3/Al(OiPr)_3$.

2.2.4. Ligands

The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer [20]. They control the selectivity by

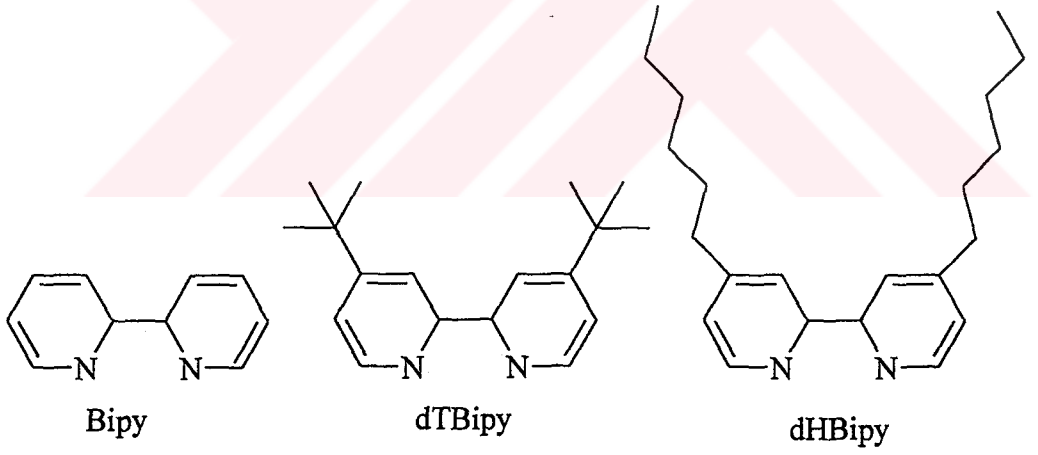
steric / electronic effects. The mostly used ligands for the ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N",N" pentamethydiethylenetriamine (PMDETA), tetramethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetramine (HMTETA), tris[2-(dimethylamino)ethyl]amine (Me-TREN) and alkylpyrdylmethanimines.

Nitrogen based ligands:

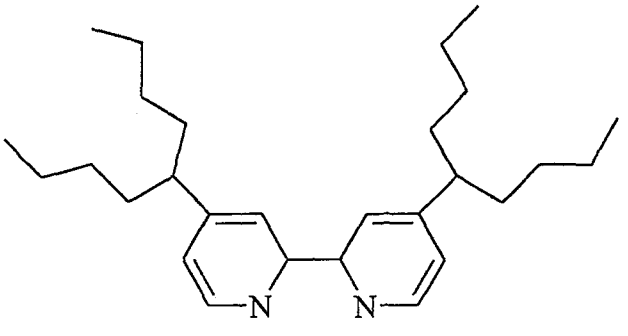


TMEDA PMDETA HMTETA (2.5)

Derivatives of 2,2-bipyridine:



Bipy dTBipy dHBipy



dNBipy (2.6)

2.2.5. Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system. Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethylacetate, acetone, dimethylformamide (DMF), ethylene carbonate, alcohol, water, carbondioxide, and some others, are being used for different kinds of monomers. A solvent is sometimes necessary when the obtained polymer is insoluble in its monomer. Chain transfer to solvent shoul be minimum.

2.2.6. Temperature and reaction time

The rate of polymerization also determines the rate of polymerization by effecting both propagation rate costant and the atom transfer equilibrium constant. The k_p/k_t ratio increase as a result of higher temperature, thus enables us better control over the polymerization. However this may also increase the side reactions and chain transfer reactions. The increasing temperature also increases the solubility of the catalyst. Against this, it may also poison catalyst by decomposition. Determining the optimum temperature; monomer, catalyst and the targeted molecular weight should be taken into consideration.

2.2.7. Molecular weight and molecular weight distribution

We can determine the average molecular weight of the polymer by the ratio of consumed monomer and the initiator as in a typical living polymerization ($DP_n=\Delta[M]/[I]_o$, DP=degree of polymerization) while there is a narrow molecular weight distribution ($1.0 < Mw / Mn < 1.5$).

The molecular weight distribution or polydispersity Mw / Mn is the index of the polymer chain distribution. In a well controlled polymerization, Mw / Mn is usually less than 1.1. In the equation (2.7)the polydispersity index in ATRP in the absence of chain termination and transfer is shown.

D: Deactivator

k_p: Propagation rate costant

k_d: Deactivation rate costant

p: Monomer conversion

$$M_w / M_n = 1 + [[RX]_o) k_p / k_d [D]] [(2 / p) - 1] \quad (2.7)$$

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

i) Polydispersities (molecular weigh distributions) decrease, if the catalyst deactivates the chains faster (smaller k_p / k_d)

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

iii) Polydispersities (molecular weigh distributions) decrease as the concentration of the deactivators decreases. (For example, the addition of a small amount of Cu(II) halides in copper-based ATRP decreases the reaction rate thus leads to better controlled polymerizations)

2.2.8. Kinetic of ATRP

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

The rate equation of ATRP is formulated in discussed conditions and given in (2.8).

$$R_p = k_{app} [M] = k_p [P.][M] = k_p K_{eq} [I]_0 \frac{[Cu(I)]}{[Cu(II) X]} [M] \quad (2.8)$$

Results from kinetic studies of ATRP for styrene, methyl acrylate (MA), and methyl methacrylate (MMA) under homogeneous conditions indicate that the rate of

polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations.

If the deactivation does not occur, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in (2.9).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d [RX]_0}{k_p [XCu^{II}]} \right) \left(\frac{2}{p} - 1 \right) \qquad (2.9)$$

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

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

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

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

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

2.2.9. Materials Made By ATRP and Other CRP Techniques

The most important benefit of controlled/living polymerizations is that they allow to prepare new macromolecules with novel topologies (linear, star, comb, (hyper)branched, networks, etc.), varying compositions (homopolymers, random,

periodic, block, graft ang gradient copolymers), and functionalities placed at different parts of macromolecules or various combinations of these [21].

2.3. Star Shaped Polymers

Synthesis of star-shaped and comb-shaped polymers of narrow molecular weight distribution provide further examples of the versatility of the living-polymer technique in preparative polymer chemistry. A star-shaped polymer molecule possesses a number of arms radiating from a common center [22]. Star polymers have different hydrodynamic properties and higher degrees of chain end functionality compared to linear polymers of similar composition. Methods toward making star polymers fall into two broad classes. The first method is the "arm first" approach and the second class of star polymers are synthesized by the "core first" approach.

The applicability of controlled radical polymerization techniques toward the synthesis of star polymers has been demonstrated. For the "arm first" approach diviniylbenzene was used to produce microgels in the radical polymerization of styrene [24,25]. The first report of the "core first" technique described the hexakis(bromomethyl)benzene initiated, ATRP of styrene, methylacrylate, and methylmethacrylate [26], but its use was rather limited due to poor solubility in the reaction media. Therefore, other hexafunctional initiators were explored such as, hexakis(4-(2-bromopropionyloxymethyl)phenoxy)cyclotriphosphazene, 6BrPr. In one case, a macroinitiator of star poly(methylacrylate) synthesized from 6BrPr was used in the ATRP of isobornylacrylate, thereby yielding a star-block copolymer [27].

A number of studies have described the use of ATRP in the synthesis of star-branched macromolecules. Pugh et. all used a trifunctional initiator for the synthesis of the three-arm polyacrylates for investigations of liquid crystalline polymers [28]. Sawamoto and co-workers also made three-arm star polymers of methyl methacrylate using trifunctional initiators bearing trichloroacetate moieties [29].

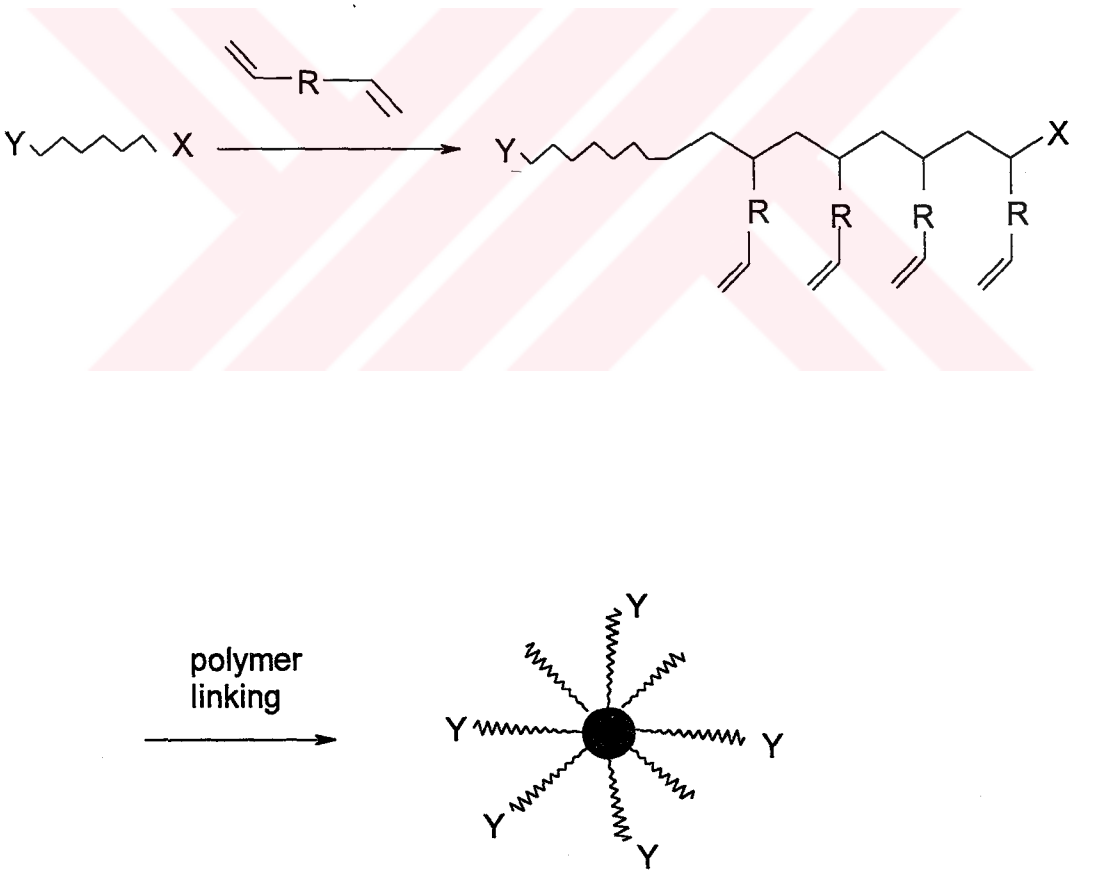
2.3.1. Star Shaped Polymers by the "Arm First" Approach

In the "arm first" approach, monofunctional, living linear macromolecules are initially synthesized. Star formation then occurs in one of two ways: a difunctional

comonomer is used to provide cross-linking through propagation or a multifunctional terminating agent is added connecting a precise number of arms to a central core molecule. The former, microgel, technique produces macromolecules with a large, often heterogeneous, number of arms while in the latter case separation techniques are used to isolate stars from uncoupled linear polymers [23].

An original study based on the "arm first" approach was reported by Fraser and colleagues [30], who synthesized 2,2-dipyridiyl-carrying PS and PMMA chains by ATRP, which they managed to chelate onto a hexadendate Fe(II)- based complex to form corresponding starlike polymers, thus containing a metallic core.

The most recent studies on star synthesis by this convergent approach are described below.



Scheme 2.1 Star polymer synthesis through the use of a divinylic compound

To derive their PS stars, Matyjaszewski and colleagues [25] used a performed PS macroinitiator obtained by ATRP that was allowed to react with various divinylic monomers, in the presence of CuBr / dipyridyl in anisole at 110 °C. A ratio of 5:15 between divinyl benzene and PS macroinitiator was found to be optimal for the star formation. Other experimental parameters such as the choice of solvent, the addition of Cu(II), and the reaction time were found to be crucial for the efficient star formation.

2.3.2. Star Shaped Polymers by the "Core First" Approach

This way includes the use of multifunctional initiators. The core molecule reacts with the monomers. Multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Furthermore, the reaction consists solely of stars in the absence of linear polymers. However, in some cases the multifunctional must be presynthesized, and limited studies have been documented using this method due to the poor solubility of multiply charged species needed to initiate ionic polymerizations [31,32]. Conventional free-radical polymerization, however, may possibly lead to crosslinked materials due to radical recombination reactions. Controlled or living radical polymerization techniques provide a solution to some of these problems. Star polymers have been synthesized via atom transfer radical polymerization (ATRP) with multifunctional initiators [26]. Some of multifunctional initiators that have been used so far for the synthesis of star polymers via controlled radical polymerization arre hexophenyl benzene hexasulfonyl chloride and multifunctional initiators deriving from cyclotriphosphazenes, cyclosiloxanes, and organic polyols [23].

Some examples for the "core first" approach can be given. Matyjaszewski and colleques [25], reported the synthesis of star polystyrene (PSt) and poly(methylacrylate) (PMA) using either organic or siloxane and cyclotriphosphazane-derived inorganic multifunctional initiators [27]. Sawamoto and co-workers reported the synthesis of star poly(methylmethacrylate) (PMMA) by ruthenium mediated ATRP using tri-, tetra-, hexa- and octafunctional dichloroacetate initiators [28,33]. Similarly, Gnanou and co-workers reported the synthesis of star PSt using octafunctional calixarene derivatives [34].

3. EXPERIMENTAL PART

3.1. Chemicals Used

a)Monomer

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

b) Solvent

Tetrahydrofuran (THF, 99,8%, J.T. Baker HPLC grade) was dried and distilled over lithium aluminium hydride.

c) Ligand

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

d) Initiator

Trichlorocyanuric acid (95%, Fluka)

3.2. Synthesis of Poly(methyl metacrylate) under argon in bulk

A flask equipped with a magnetic stirring bar was closed with a rubber septum. The nitrogen-bubbled monomer, ligand, catayst, initiator and anisole were added in the order mentioned. Anisole was added as an internal standart for the gas chromatography (GC) measurements. Vacuum-argon was applied to the reaction medium several times and then the flask was immersed into a thermostated oil bath at 90°C. Samples were taken at given time intervals under nitrogen in order to determine the monomer conversion. Samples were diluted with THF, then conversion was measured by gas chromatography. After the polymerization the

reaction mixture was cooled and diluted with THF, and then passed through a column of neutral alumina to remove the metal salt. The excess of THF was evaporated under reduced pressure and the polymer sample was precipitated in methanol, filtered and dried in vacuum oven at 25°C for overnight.

3.3. Synthesis of Poly(methyl metacrylate) under vacuum in bulk

In a schlenk tube equipped with a magnetic stirring bar, the nitrogen bubbled monomer, ligand,catalyst and the initiator were added. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed into a thermostated oil bath at 90 °C. After the polymerization the reaction mixture was cooled and diluted with THF, and then passed through a column of neutral alumina to remove the metal salt. The excess of THF was evaporated under reduced pressure and the polymer sample was precipitated in methanol, filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined gravimetrically.

3.4. Characterization

Monomer conversion was determined using a Unicam 610 Series Gas Chromotograph equipped with a FID detector using a J&W Scientific 15 m DB WAX Widebore. Injector and detector temperatures were kept constant at 280°C and 285°C, respectively. Initial column temperature is 40°C, finally reaching up to 120°C with a heating rate of 20°C / min.

Molecular weight and molecular weight distributions were determined by a gel permeation chromatography (GPC) instrument. An Agilent Model 1100 consisting of a pump, a refractive index detector and four Waters Styragel columns HR 5E, HR 4E, HR 3, HR 2; and THF was used as eluent at a flow rate of 0.3ml/min at 30°C. Molecular weights were calibrated using polymethylmethacrylate standarts.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis of poly(methyl methacrylate) under argon in bulk

Synthesis of poly(methyl methacrylate) is illustrated is Scheme 4.1.

Initiation

$$R{-}X + Cu(I)/Ligand \underset{k^{o}_{d}}{\overset{k^{o}_{a}}{\rightleftharpoons}} R^{\bullet} + XCu(II)/Ligand$$

$$\downarrow k_i \; + M$$

$$R{-}M{-}X + Cu(I)/Ligand \rightleftharpoons R{-}M^{\bullet} + XCu(II)/Ligand$$

$$\downarrow k_p \; + M_n$$

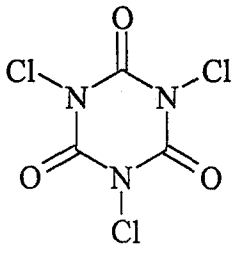
Propagation

$$R{-}M_n{-}X + Cu(I)/Ligand \rightleftharpoons R{-}M_n^{\bullet} + XCu(II)/Ligand$$

Termination

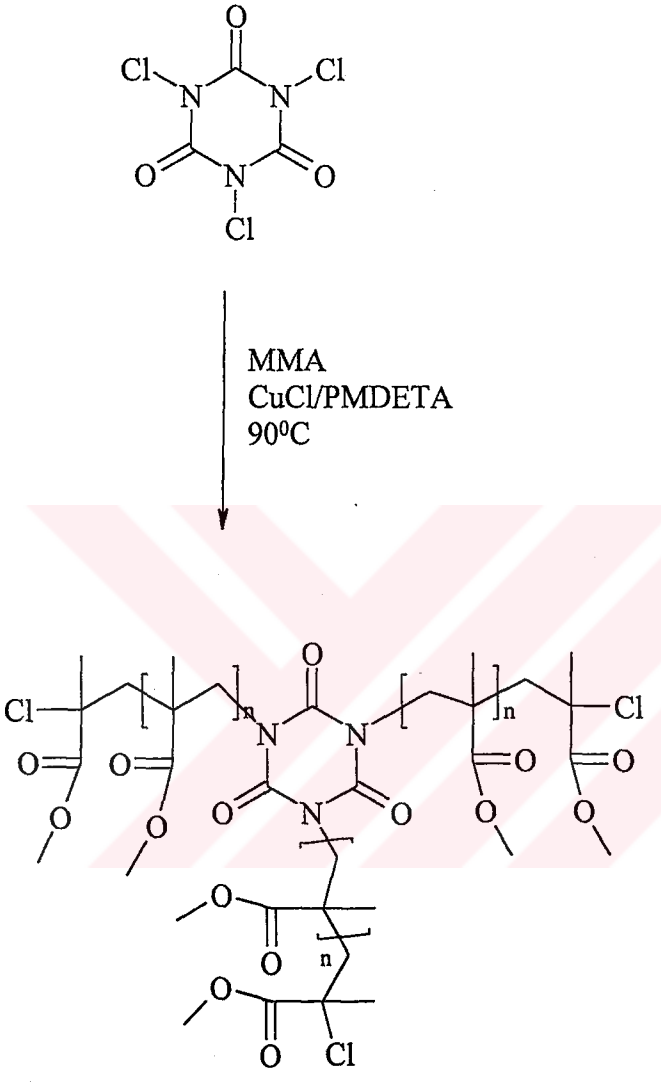
$$R{-}M_n^{\bullet} + R{-}M_m^{\bullet} \xrightarrow{k_t} R{-}M_{n+m}{-}R + R{-}M_nH \,/\, R{-}M_m$$

Where R-X is the initiator; trichlorocyanuric acid;



Ligand: PMDETA; Monomer: methyl methacrylate

Scheme 4.1. Atom transfer radical polymerization (ATRP), and trichlorocyanuric acid as a schematic representation.



Scheme 4.2. The schematic representation of the polymerization of MMA

The polymerization of MMA was carried out in bulk using trichlorocyanuric acid **(1)** as an initiator / CuCl / PMDETA system. $[MMA]_o/[I]_o = 400$ and CuCl / PMDETA = 3:3 in mole ratio, at 90°C. M_n vs. % conversion (Fig.4.1) and $\ln([M]_o/[M]_t)$ vs. time (Fig.4.2) are established to monitor whether the polymerization proceeds in a controlled manner.

Table 4.1. Polymerization of MMA in bulk at 90°C with the ratio of; $[MMA]_o/[I]_o$ = 400, $[I]_o$: [CuCl]: [PMDETA] = 1:3:3

Run	Time	Mn_{theo}	Mn_{GPC}	%conversion	PDI	*f*
1.1	30	7200	16700	18	1,07	0,43
1.2	60	15210	27900	38	1,15	0,54
1.3	90	17220	34800	43	1,15	0,49
1.4	120	28400	43300	71	1,15	0,65
1.5	150	29200	51200	73	1,07	0,57
1.6	180	30400	53000	76	1,33	0,57

The initiator efficiency (*f*) is defined as the molar ratio of polymer chains obtained to the one expected. It is simply deduced by the formula $f = pM_r/M_n$, where p denotes the conversion ratio, M is the molecular weight of the monomer weight of the monomer, M_n is the number-average molecular weight from GPC traces, and r is the molar ratio of the monomer to the initiator [35].

The number average molecular weights were determined by GPC based on linear PMMA standarts. The theoretical molecular weights are calculated from the formula; $M_{n,theo} = [M]_o / [I]_o$ x conversion % x M_w.

The conversions in this experiment were determined by gas chromatography.

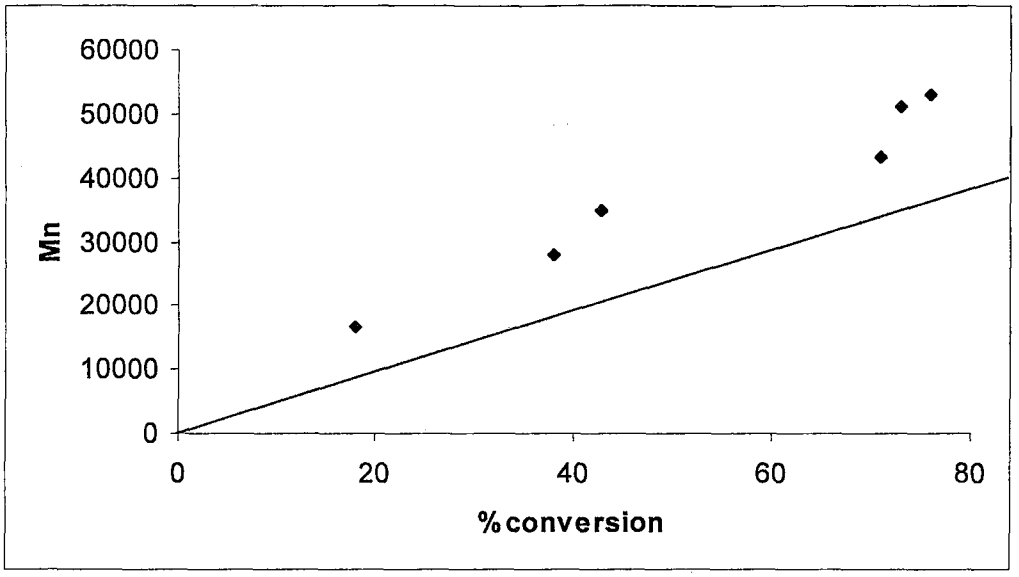


Figure 4.1. Dependence of number average(M_n) molecular weight versus conversion in bulk polymerization of MMA at 90°C, $M_{n,theo}$ (—).

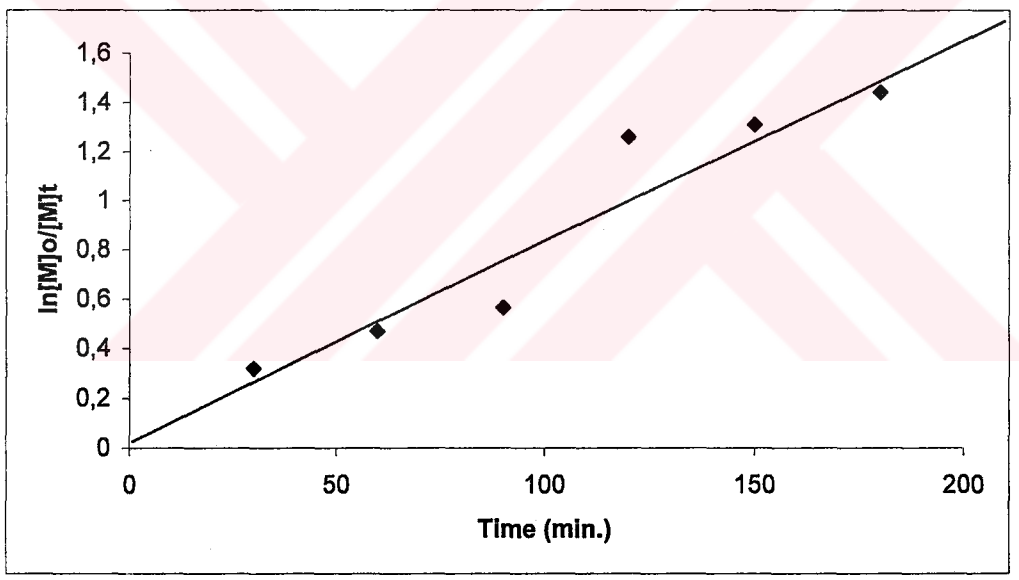


Figure 4.2. Plot of $\ln[M]_o/[M]_t$ versus time for the polymerization of MMA in bulk at 90°C.

In the plot of $\ln[M]_o/[M]_t$ versus time as shown in Figure 4.2, a straight line is observed indicating that the kinetics is first order with respect to the monomer concentration for the polymerization.

Evolution of molecular weights with conversion is shown in Figure 4.3. Molecular weights obtained from GPC are higher than the theoretical values. The curves are

normalized, and the molecular weight distribution of the polymer shifted to higher molecular weight with increasing conversion.

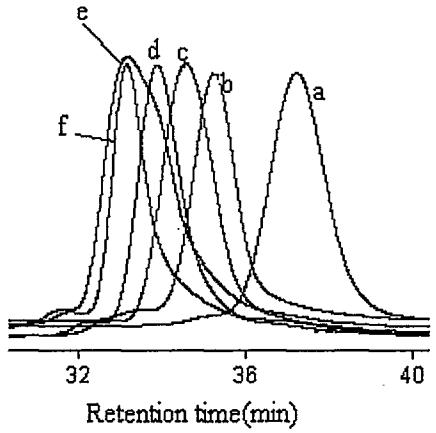


Figure 4.3. GPC traces from the polymerization of methyl methacrylate in bulk at 90°C with $[MMA]_o/[I]_o = 400$, $[I]_o$: [CuCl]: [PMDETA] = 1:3:3. (a) 18 %conversion, (b) 38 %conversion, (c) 43 %conversion, (d) 71 %conversion, (e) 73 %conversion, (f) 76 %conversion.

4.2. Synthesis of Poly(methyl methacrylate) under vacuum in bulk

The polymerization of MMA was carried out in bulk using trichlorocyanuric acid **(1)** as an initiator / CuCl / PMDETA system. $[MMA]_o/[I]_o = 400$ and CuCl / PMDETA = 3:3 in mole ratio, at 90°C. The plots of M_n vs. % conversion and $\ln([M]_o/[M]_t)$ vs. time demonstrated a controlled polymerization behaviour (Fig 4.4 and Fig 4.5).

The experimental molecular weights were determined by GPC based on linear PMMA standarts. The theoretical molecular weights are calculated from the formula; $M_{n,theo} = [M]_o / [I]_o$ x conversion % x M_w.

The conversions in this experiment were calculated gravimetrically by the following formula;

% conversion = (W/M)x 100

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

Table 4.2. Polymerization of MMA in bulk at 90°C with $[MMA]_o/[I]_o$ = 400, $[I]_o$: [CuCl]: [PMDETA]= 1:3:3

Run	Time	Mn_{theo}	Mn_{GPC}	%conversion	PDI	*f*
1.7	15	870	9030	2,2	1,14	0,09
1.8	30	5600	22400	14	1,13	0,25
1.9	60	9790	32700	25	1,12	0,29
1.10	120	13600	65500	34	1,35	0,20
1.11	240	18000	65570	45	1,30	0,27
1.12	360	22000	95000	55	1,35	0,23

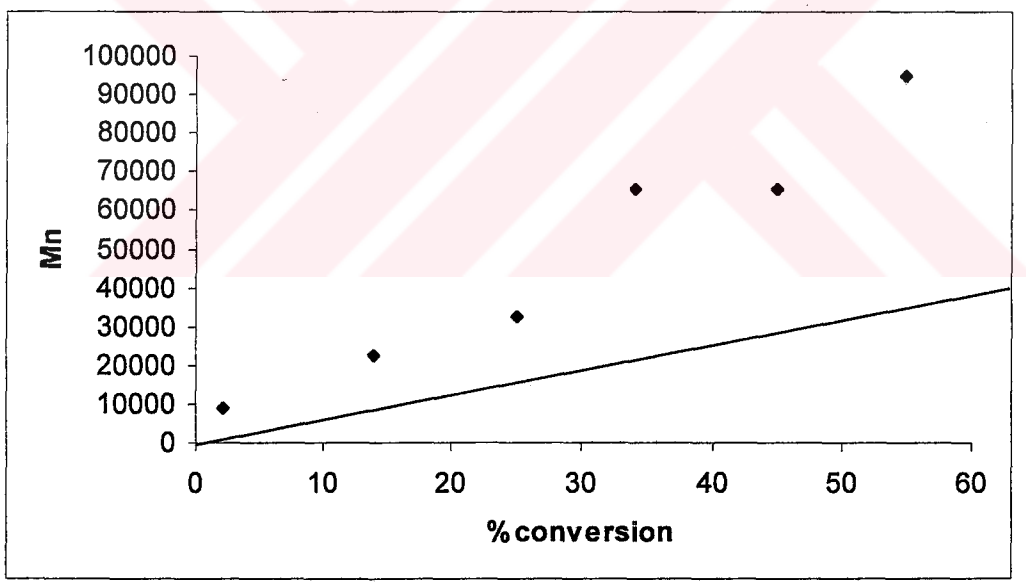


Figure 4.4. Dependence of number average(M_n) molecular weights versus conversion in bulk polymerization of MMA at 90°C, $M_{n,theo}$ (—).

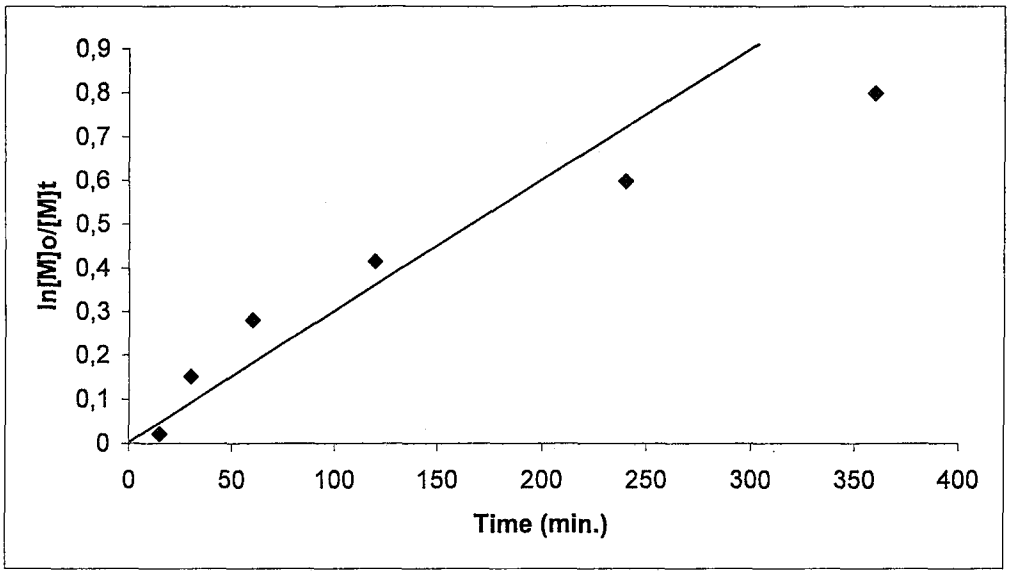


Figure 4.5. Plot of $\ln[M]_o/[M]_t$ versus time for the polymerization of MMA in bulk at 90°C.

In the plot of $\ln[M]_o/[M]_t$ versus time as shown in Figure 4.5, a straight line is observed indicating that the kinetics is first order with respect to the monomer concentration for the polymerization.

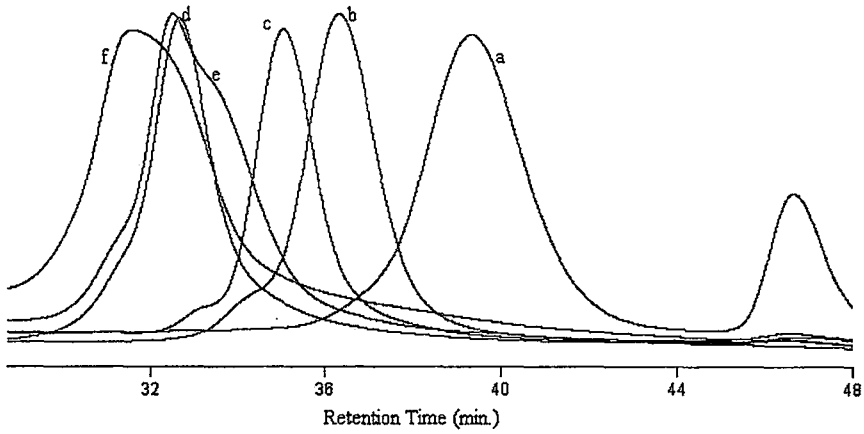


Figure 4.6. GPC traces from the polymerization of methyl methacrylate in bulk at 90°C with $[MMA]_o/[I]_o$ = 400, $[I]_o$: [CuCl]: [PMDETA] = 1:3:3. (a) 2,2 %conversion, (b) 14 %conversion, (c) 25 %conversion, (d) 34 %conversion, (e) 45 %conversion, (f) 55 %conversion.

The ^{1}H-NMR spectrum of PMMA can be seen in Figure 4.7. The metoxy protons detected at 3,58 ppm belongs to MMA. The N-CH_2 protons could not be detected around 2,5-3 ppm, as expected.

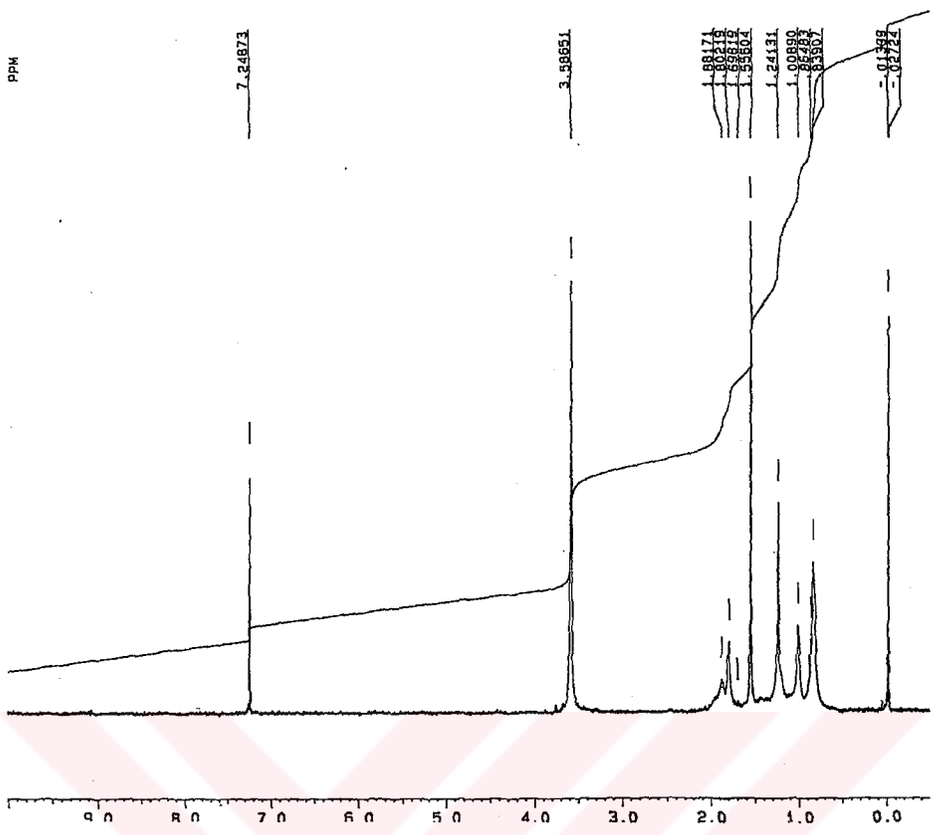


Figure 4.7. The ^{1}H-NMR spectrum of PMMA.

We attempted to apply the same polymerization conditions for other monomers as well. The polymerization of styrene and tert-butyl acrylate failed, although the solutions were clear and homogeneous like in the methyl methacrylate polymerizations.

5. CONCLUSION

In this study, we have reported that a new trifunctional initiator (trichlorocyanuric acid) was utilized in atom transfer radical polymerization of MMA. The bulk polymerization of MMA was conducted using CuCl / PMDETA as catalyst in 90°C.

The monomer conversion was determined by using two different methods. In the first method, monomer consumption was followed by GC, and in the second method monomer conversions were calculated gravimetrically. Dependence of number average molecular weights versus conversion and the $\ln[M]_o/[M]_t$ versus time plots were linear for both of the polymerizations. These results indicate that both of the polymerizations obey the first order kinetic and the radical concentration remains constant during the polymerizations. The molecular weights of the polymers were obtained by GPC measurements. They were higher than the theoritical molecular weights. The initiation efficiencies were calculated and found to be in the range of 0,09-0,64. This may be attributed to some side reactions taken place at the early stages of polymerizations.

It was demonstrated that ATRP of MMA can be carried out by using trichlorocyanuric acid as initiator. Hence, well-defined star PMMAs with low polydispersity (M_w/M_n<1,4) were obtained.

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AUTOBIOGRAPHY

She was born in 1979 in İstanbul. In 1997, she graduated from Kalamış Private High School and completed her undergraduate study in the Chemistry Department of İstanbul Technical University in 2002. After that she was accepted as an M.Sc. student to the same university, to the programme of Polymer Science and Technology, which she is about to graduate.