İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

LICA GEL SUPPORTED ATOM TRANSFER RADICAL POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF OXYGEN AND SODIUM PHENOXIDE

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Date of submission : 24 December 2003

Date of defence examination : 15 January 2003

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JANUARY 2003

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

METİL METAKRİLATIN OKSİJEN VE SODYUM FENOKSİT VARLIĞINDA SİLİKA JEL DESTEKLİ ATOM TRANSFER RADİKAL POLİMERİZASYONU

YÜKSEK LİSANS TEZİ

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Tezin Enstitüye Verildiği Tarih : 24 Aralık 2003

Tezin Savunulduğu Tarih : 15 Ocak 2003

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OCAK 2003

ACKNOWLEDGEMENT

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

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Ümit TUNCA and Prof. Dr. Gürkan HIZAL for offering invaluable help in all possible ways, continuous encouragement and helpful critisms throughout this research. Also I would like to thank to all of my professors in Polymer Science and Technology Department.

I would like to thank expecially to Şebnem İNCEOĞLU, Sermin ARAS for their friendship and never ending helps, to Recep UÇAN for his encouragement and to my colleagues Mine BARLAN, Çiğdem ÇELİK, Mustafa ÇIKILMAZKAYA, Hümeyra MERT, Alper ÜSTÜN for their helpful attitude during my laboratory works.

Finally, I would like to dedicate this thesis to my parents Gülseren and Hilmi ALOĞLU, my brother Tolga ALOĞLU and Cenk SEZGİN, for their patience, understanding and morale support during all stages involved in the preparation of this thesis.

January 2003 Tuğba ALOĞLU

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LIST OF ABBREVIATIONS

ATRP : Atom Transfer Radical Polymerization

MWD : Molecular weight distribution of polymers

MA : Methyl Acrylate

MMA : Methyl Methacrylate

PMMA : Poly (methyl methacrylate)

PMDETA : N, N, N, N'',N''-pentamethyldiethylenetriamine

DPE : Diphenylether

EIBr :2-bromo-ethyl isobutyrate

St : Styrene

Cat : Catalyst

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LIST OF SYMBOLS

M_n : Number average molecular weight of polymers

M_w : Weight average molecular weight of polymers

k_k, k_d : Rate constants of activation and deactivation steps of the initiation in radical polymerization.

K_{eq}, k_p : Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively

I, M : Initiator and monomer respectively

SILICA GEL SUPPORTED ATOM TRANSFER RADICAL POLYMERIZATION OF METHYLMETHACRYLATE, IN THE PRESENCE OF OXYGEN AND SODIUM PHENOXIDE

SUMMARY

Recently, controlled polymerization of vinylic monomers has been of considerable interest for the synthesis of well-defined narrow polydispersity polymers. Among them, atom transfer radical polymerization (ATRP) is one of the most widely used living free radical polymerization method for the polymerization of various types of vinylic monomers. However, against advantages of ATRP; such as its great tolerance to water and other protonic species, it also has some disadvantages such as high catalyst concentration needed and the removal of catalyst after the polymerization. This is not only costly and waste of time for commercial production of polymers. One of the solutions to this problem is to immobilize the catalyst onto a solid that can be recycled. Also, due to the radical nature of ATRP, the propagating radicals are inhibited by the free radical scavengers such as galvinoxy or diphenylpicrylhydrazyl (DPPH). Phenolic compounds are also free radical scavengers in radical polymerizations. However, studies on the mechanism of ATRP proved that, by using phenolic compounds, ATRP can be accomplished in the presence of certain amount of oxygen. In this study, living polymerization of MMA, using silica gel supported CuCl-PMDETA complex, in the presence of PhONa and definite amount of oxygen was developed. The supported catalysts were recycled; kinetics of the reaction and the activity of the recyled catalyst were investigated.

METİLMETAKRİLATIN OKSİJEN VE SODYUM FENOKSİT VARLIĞINDA, SİLİKAJEL DESTEKLİ ATOM TRANSFER RADİKAL POLYMERİZASYONU

ÖZET

Son yıllarda vinil monomerlerinin kontrollü polimerizasyonu, iyi tanımlanmış, dar molekül ağırlığı dağılımına sahip polimerlerin sentezi açısından büyük ilgi görmektedir. Bunların içinde, atom transfer radikal polimerizasyonu (ATRP), en sık kullanılan yaşayan serbest radikal polimerizasyon metodudur. Ancak, ATRP'nin su ve diğer protonik maddelerden etkilenmemesi gibi avantajlarının yanında dezavantajları da mevcuttur. Bunlar yüksek konsantrasyonda katelizör gereksinimi ve bu katelizörün proses sonrası ortamdan uzaklaştırılmasıdır. Labratuvar ortamında uygulanan yöntemler, hem zaman kaybı açısından hem de ekonomik olarak endüstriyel kullanıma uygun olmamaktadır.Bu soruna çözüm olarak katalizörün, reaksiyon ortamında tekrar kullanılabilecek bir katı üzerine sabitlenerek sonraki polimerizasyonlarda tekrar kullanılabilmesi düşünülebilir. Ayrıca ATRP, radikal karakterinden dolayı serbest radikaller ortamda istenmez. Bu nedenle ATRP, genellikle oksijensiz ortamda gerçakleştirilmektedir. Ancak yapılan çalışmalar, fenolik bileşiklerin, ATRP'nin sabit miktarda oksijen içeren ortamda, reaksiyon hızını arttırdığını göstermiştir. Bu çalışmada, metil metakrilatın, silikajel destekli CuCl-PMDETA kompleksi katelizör olarak kullanılarak, sodyum fenoksit ve belirli miktarda oksijen içeren ortamda atom transfer radikal polimerizasyonu incelenmiş ve reaksiyonun aynı katelizör ile tekrarlanması halinde, katelizörün aktivitesi ve reaksiyon kinetiği incelenmiştir.

1. INTRODUCTION

Recently, synthesis of polymers with well defined compositions has become an important aspect of polymer science. For this reason, various controlled living radical polymerization methods such as stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP) and reverse addition fragmentation transfer (RAFT) have been utilized for the synthesis of well defined narrow polydisperity polymers. Living radical polymerization mediated by a metal halide complex, ATRP is one of the most widely used living free radical polymerization method for the polymerization of styrene methylmethacrylate, acrylates and other vinylic monomers. ATRP is advantageous over other anionic, catonic and group transfer reactions due to its tolerance to water and other protonic species.

However, due to the radical nature of ATRP, the propagating radicals are inhibited by the free radical scavengers such as galvinoxy or diphenylpicrylhydrazyl (DPPH). Contradictory to the inhibitor role of phenolic compounds in radical polymerizations, studies on the mechanism of ATRP showed that, by using phenolic compounds, ATRP can be accomplished in the presence of certain amount of oxygen (using unpurified monomers). In this case, metal salts with their higher oxidation state and phenol derivatives were employed. Since Mt^nX is continously produced by the redox reaction between phenolic compound and $Mt^{n+1}X_2$, after the oxygen is consumed to form Mt^nX, controlled polymerization conditions are achieved. Such systems based on catalytic redox cycle of the metal complexes are also used in oxidative coupling polymerizations of phenols.

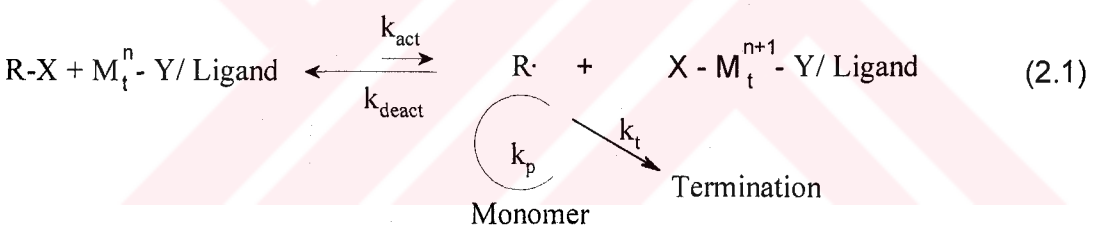
In commercial uses, challenge of ATRP is the high catalyst concentration needed and the purification of the polymer by removal of catalyst after the polymerization (usually by passing the polymer solution through silica gel or alumina). This is not only costly but also a waste of time. Against this challenge, catalyst can be supported onto a silica, crosslinked polystyrene beads,or attached to polymer chains, which can easily be removed and recycled.

In this study we investigated silica-gel supported CuCl-PMDETA complex for living polymerization of MMA in the presence of PhONa and definite amount of oxygen. The supported catalysts were recycled, kinetics of the reactions and the activity of the recyled catalyst were investigated.

2.THEORETICAL PART

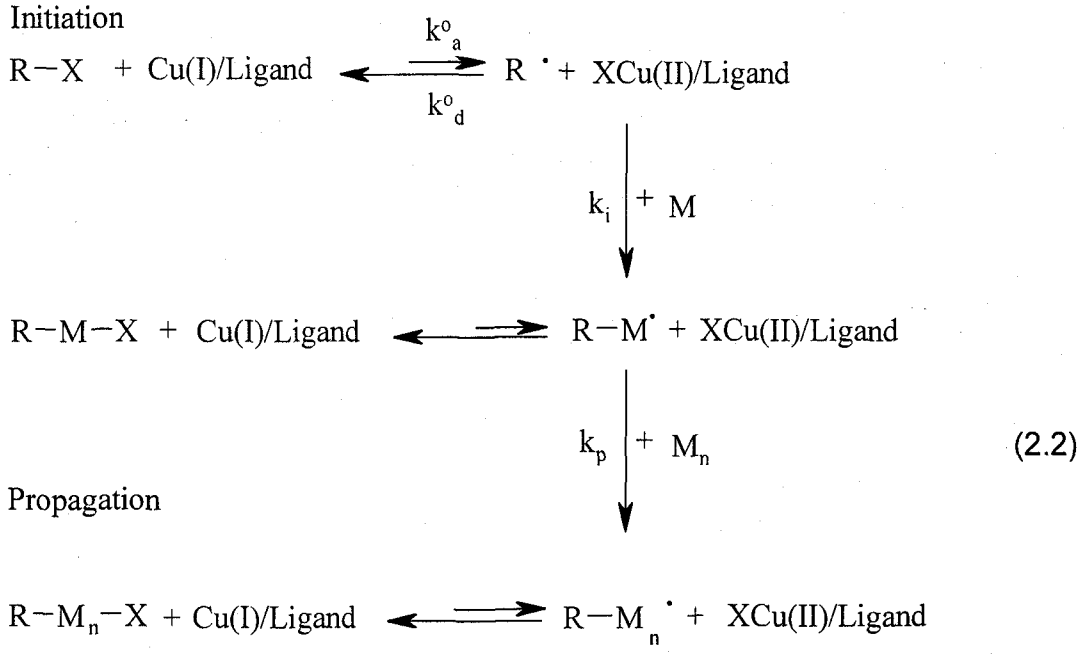
2.1 Atom Transfer Radical Polymerization (ATRP)

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal complexed with a suitable ligand). Both activating and deactivating components of the catalytic system must be present. Solvent, temperature, concentrations and solubility of all components, and sometimes the order of their addition must also be taken into consideration.



(2.1)

ATRP occurs as a repetitive addition of a monomer to a growing radicals generated from dormant alkyl halides by a reversible redox process catalyzed by transition metal compounds complexed by amine ligand. The equilibrium between the active and the dormant chains enables a low concentration of propagating radicals and thus reduces the probability of termination. Termination reactions can occur through radical coupling or disproportionation; however in a well controlled ATRP, only a few percent of polymer chains undergo termination. For a successful ATRP, also uniform growth of all the chains (accomplished through fast initiation and rapid reversible deactivation) is needed. The mechanism of ATRP is given in scheme (2.2).



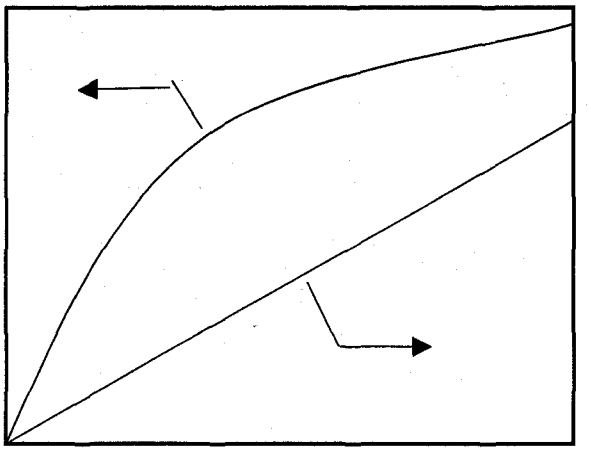
(2.2)

By using a proper catalyst (transition metal compound and a ligand), suitable initiator and providing the polymerization conditions, lower polydispersities and molecular weights increasing linearly with conversion (which are typical in living process) can be obtained. This allows us control the chain topology (stars, combs, branched), the composition (block, gradient, alternating etc), and the end functionality for a wide range of radically polymerizable monomers[1.2].

2.1.1 Basic Principles of ATRP

2.1.1.1 Kinetics of ATRP

In ATRP system, rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator (CuX_2 / Ligand)[3].



(2.3)

Results from the kinetic studies of ATRP under homogenous conditions indicate that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to the monomer (2.3). However, since termination occurs continuously, the concentration of the Cu(II) species increases and deviation from linearity may be observed. For ideal case with chain length independent termination, persistent radical effect kinetics implies the logarithmic plot of monomer conversion versus time to the 2/3 exponent should be linear. Nevertheless, a linear semilogarithmic plot versus time is often observed. This may be due to an excess of the Cu(II) species present initially, a chain length dependent termination rate coefficient, or heterogeneity of the reaction system due to limited solubility of copper complexes. It is also possible that self-initiation may continuously produce radicals and compensate for termination.

The rate equation of ATRP is obtained by the aid of some assumptions such that the contribution of termination on the rate of the polymerization is ignored, the initiating molecules are completely consumed in the initiation step and fast equilibrium, which is necessary for getting low polydispersities,. The rate law for ATRP is as follows

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

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[P\cdot][Cu(II)X]}{[Cu(I)][PX]} \quad (2.4)$$

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

2.1.1.2 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 (2.5)the polydispersity index in ATRP in the absence of chain termination and transfer is shown.

D: Deactivator

kp: Propagation rate costant

kd: Deactivation rate costant

p: Monomer conversion

$$M_w / M_n = 1 + [[RX]_o) k_p / k_d [D]] [(2 / p) - 1] \quad (2.5)$$

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)

2.1.2 Components Used

2.1.2.1 Monomers

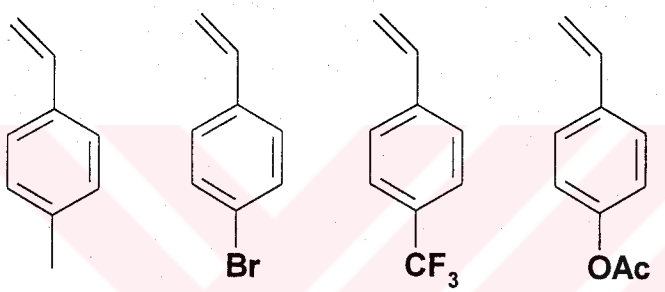
A variety of monomers can be polymerized using ATRP. These include styrenes, methacrylates, acrylates, acrylamides, methacrylamides, N-vinylpyrollidone, N-vinylpyridine, dienes and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Under same conditions each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. For each monomer, the product of equilibrium constant (k_{eq}) and the propagation rate constant determines the rate of polymerization. If k_{eq} is too small (e.g: less reactive monomers such as olefins, halogenated alkenes and vinyl acetate) then the reaction will occur slowly thus will not be very successful. If k_{eq} is too large , then termination reaction will increase due to the high radical concentration. This will be accompanied by production of a large amount of deactivating higher oxidation state metal complex, which will shift the equilibrium toward dormant species and again cause slower polymerization. Thus, for controlled polymerization, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted for a specific monomer. Also the amount and reactivity of the transition metal catalyst, temperature solvent and some additives effect the polymerization.

For monosubtituted alkenes, the equilibrium constants are lower. For α substitutents the equilibrium costants are in the following order: CN > Ph > C(O)OR > $C(O)NR_2$ > COC(O)R.

However two types of monomers which have not been very successful in ATRP systems. One of them is acidic monomers which protonate ligands and form carboxylate salts. By using basic ligands (e.g. oxygen and sulfur based ligands) we may prevent the loss of ligands. Also acids may also be used as ligands themselves (e.g. iron succinides or halides). The other group which have not been successfully polymerized is the halogenated alkenes, alkyl-substituted olefins and vinyl esters. These monomers have very small reactivity and very small equilibrium constant.

Catalysts with very high reactivity is needed to polymerize these monomers. But this may cause the reduction of the free radicals to carbanions and form organometalic species which prefer coordination reactions.

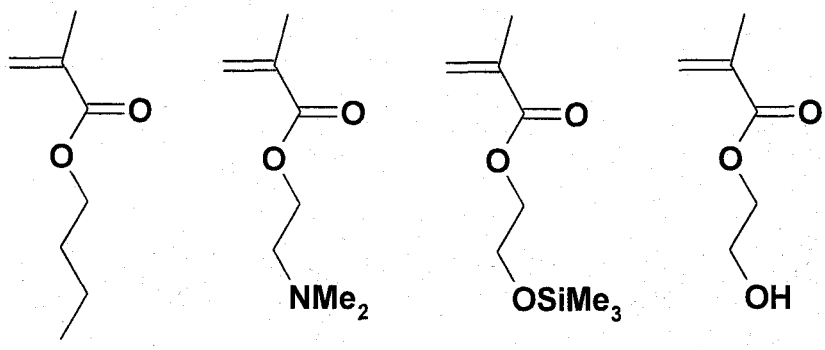
Styrene: In the ATRP of styrene, if Br is used as halogen, the reaction temperature should be 110 ^{0}C. If Cl is used then the temperature should be 130 ^{0}C. Phenyl ethyl halides, benzylic halides, halogenated alkanes, α-bromoesters and multisubstituted alkanes and arene sulfonylchlorides are are used as initiators. Since the halogen end groups are effected, usually nonpolar solvents are used in the ATRP of styrene. In the molecular weight of 1000-30000, molecular weight distribution of $(M_w/M_n)<1.1$,and over 30000, molecular weight distribution of $1.1< M_w/M_n<1.5$ is observed [4]. Some derivatives of styrene monomer are shown in Figure (2.6)



(2.6)

Methyl Methacylate: The reaction temperature is 90^{0}C and less copper is used compared to the polymerization with styrene. The rate constant of the MMA polymerization is higher than of the styrene. (k_p= 1.6x10^3 M^{-1} s^{-1} ,90^{0}C for MMA, k_p=8.95x10^2 M^{-1} s^{-1} ,90^{0}C for styrene).

Since the rate of initiation is higher than the rate of propagation, p-toluene sulfonyl chlorides, 2-bromo-2-methl malonate and α-bromo ester can be used as initiators. In the molecular weight of 1000-90000, molecular weight distribution of $(M_w/M_n)<1.1$,and over 90000, molecular weight distribution of $1.1< M_w/M_n<1.5$ can be obtained. Some derivatives of MMA monomer are shown in Figure(2.7).



(2.7)

Acrylonitrile: Since polyacrylonitryle is not soluble in its monomer, it is necessary to use solvent in the polymerization. DMF is a good solvent for acrylonitrile; however it may also complex with copper and deactivate the catalyst. Also polymerizations with ethylene carbonate in the presence of $CuBr(bpy)_2$ compex using α-bromopropionitrile as initiator at temperatures of 44-64°C has been successfull. Polymers with the molecular weight of 1000-10000 and molecular weight distribution of $M_w/M_n<1.05$ can be obtained.[5]

2.1.2.2 Initiators

In ATRP, the amount of the initiator determines the number of growing polymer chains and thus the molecular weight of the polymer. The initial initiator concentration will be constant if the initiation is fast and chain transfer and termination is negligible. In living radical polymerizations the initiator concentration increases reciprocally with the molecular weight and degree of polymerization (DP).

Two main parameters are important to obtain well defined polymers with narrow polydispersities: (1) the initiation rate should be should be faster than that of propagation. (2) the probability of side reactions should be predicted. The halide group of the initiator should rapidly and selectively migrate between the growing chain and the transition metal complex. In some cases R-X bond can be cleavaged heterolytically depending on the initiator structure and the catalyst, thus causes side reactions. The initiator (organic halides) usually, should have a structure homologous to the corresponding polymer end group. Also macroinitiators where initiating moiety is attached to a macromolecule can be used as initiators in ATRP.

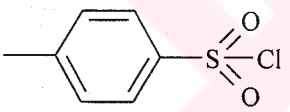
Alkyl halides with activating substituents on the α-carbon (such as aryl, carbonyl or allyl groups) or polyhalogenated compounds such as CCl4 or CHCl3 and compounds

with a weak R-X bond such as N-X, S-X, or O-X are used as initiators in ATRP [7, 8].

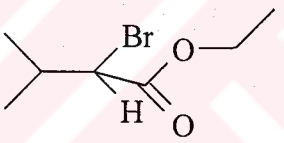
It has been observed that in MMA polimerization at 90^{O}C alkyl chloride is more successful than alkyl bromide because C-Cl bond has higher strength than C-Br bond. Ethyl-2-bromoisobutyrate/CuCl and ethyl-2-bromoisobutyrate/CuBr initiator/catalyst systems were investigated and it was observed that in Ethyl-2-bromoizobutyrate/CuCl systems, showed better control of the Mw [9].

In ATRP of MMA, p-toluene sulphonyl chloride, 2-bromo-ethyl isobutyrate, allyl bromide, tertbutyl-2-bromopropionate, 4-cyanobenzyl bromide or 2-bromo ethyl propionate initiators and in ATRP of styrene, 1-bromo-1-phenyl ethane, 1-chloro-1-phenyl ethane, hydroxyethyl-2-bromopropionate, tert-butyl-2-bromopropionate initiators are used.

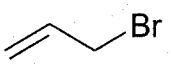
Initiators used for MMA:



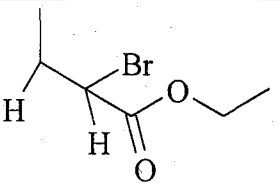
p-toluene sulphonyl chloride



2-Bromo ethyl isobutyrate

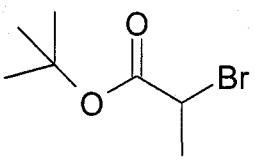


Allyl bromide

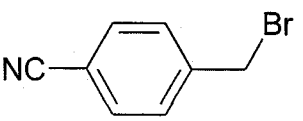


2-Bromo ethyl propionate

(2.8)

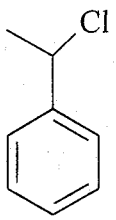


tert-butyl-2-bromopropionate

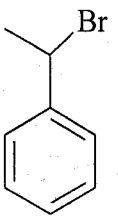


4-Cyanobenzyl bromide

Initiators used for styrene:

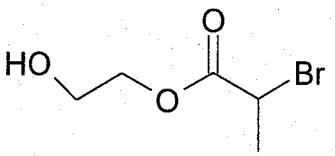


1-Chloro-1-phenyl ethane

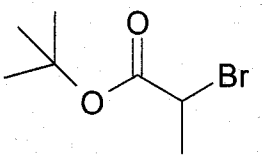


1-Bromo-1-phenyl ethane

(2.9)



Hydroxyethyl
2-bromopropionate



tert-butyl-2-bromopropionate

2.1.2.3. Transition metal catalysts

The importance of transition metals used as catalyst in ATRP system is due to its determining role for the atom transfer equilibrium and the dynamics of exchange between dormant and active species. There are several requirements for an effective transition metal catalysts.

Metal center should have at least two oxidation states separated by one electron. The metal should have high affinity toward halogen atom. , but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β -hydrogen elimination) and the formation of organometallic derivatives may be observed.

The equilibrium position, dynamics of exchange between dormant and active species is very important. The oxidized transition metal should rapidly deactivate the propagating polymer chains to form dormant species.These parameters are related to the redox cycle Mt^{n} / Mt^{n+1} but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus the thermodynamic ability defined by the equilibrium constant is not sufficient to define the utility of the catalyst. Thus a rearrangement and expansion of the inner coordination sphere of Mt^{n} is required to accommodate incoming halogen (ligand). Also the ligand should complex the metal center relatively strongly. Thus variety of transition metal

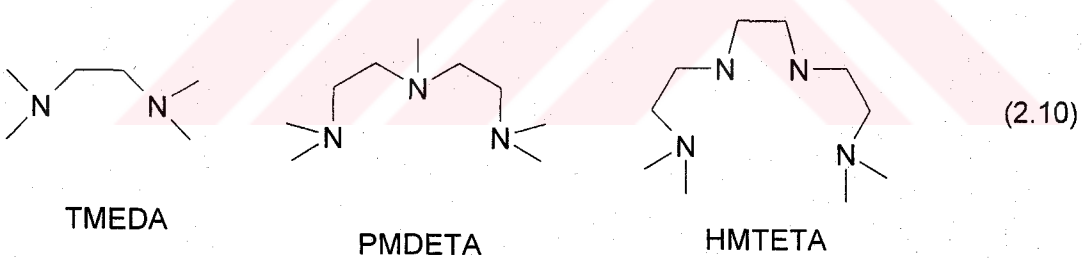
complexes with various types of ligands have been studied as ATRP catalysts.The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, Ni(II), Ru(II) / Al $(OR)_3$ and Fe(II) / $3PR_3$.

2.1.2.4 Ligands

In ATRP, ligands affect the redox chemistry by their electronic effects. They control the selectivity by steric / electronic effects and adjust the redox potential and halogenophilicity of metal center forming a complex with appropriate reactivity and dynamics for atom transfer. They also solubilize the transition metal catalyst in the organic media.

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10 hexamethyl triethylene tetraamine (HMTETA).

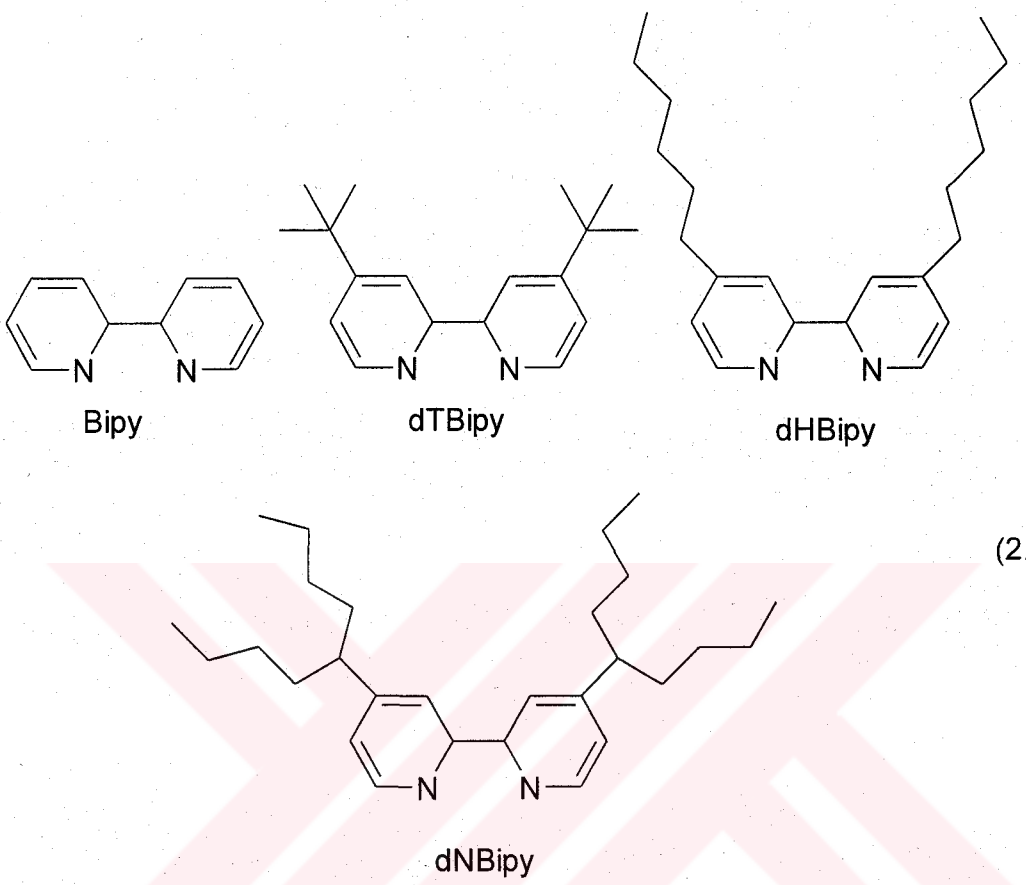
Nitrogen based ligands:



(2.10)

When bipy or TMEDA is used as ligand, copper(I) to ligand ratio is usually selected as 1:2 [7], while in the case of PMDETA is chosen as the ligand the ratio of 1:1 is sufficient to achieve maximum rates and control of polymerization [10]. The low polydispersities can be ascribed to the less sterically hindered copper (II)-PMDETA complex, which facilitates the deactivation process. When there is excessive steric hinderence around the metal center or the ligands have strongly electron – withdrawing substituents, catalytic efficiency is reduced [11].

Derivatives of 2,2-bipyridine:



(2.11)

Nitrogen based ligands have been used for copper and iron mediated ATRP successfully. Since the coordination complexes between copper and simple amines have lower redox potentials than the copper bipy complexes, the rate of polymerization increases [12].

2.1.2.5 Solvents

ATRP is usually bulk polymerizations, but it can be carried out in solution or in heterogenous systems like dispersion, emulsion or suspension. Even if the same amount of reactants are used, solution polymerization is slower than the bulk polymerization due to the effect of each components concentration to the reaction rate. Benzene, toluene, acetone, anisole, diphenylether, ethyl acetate, water, ethylene

carbonate, dipmetylformamide (DMF) can be used as solvent for ATRP systems. There are several requirements for selecting the suitable solvent. Chain transfer to solvent should be minimal. Potential interactions between solvent and catalytic system is also important. Polar solvents may poison the catalyst or may cause side reactions such as elimination of HX from polystyryl halide end groups . Solvent can also change the structure of the catalyst and thus change the efficiency of the catalyst [5].

2.1.2.6 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 Immobilization of Copper Catalyst in ATRP

ATRP is advantageous over other anionic, catonic and group transfer reactions due to its tolerance to water and other protonic species. However there are some challanges facing ATRP. The major problem facing ATRP is the high catalyst concentration needed due to the low catalyst efficiency and thus the purification of the polymer by removal of catalyst after the polymerization. In a typical ATRP procedure the ratio of initiator to catalyst is 1:1, which means one catalyst molecule mediate polymer chain. This causes high catalyst residual, coloring the polymer. Therefore additional purification is required to remove the catalyst from the polymer. In laboratory, the usual procedure involves precipitation or filtration of polymer solution through aluminium oxide column. The disadvantages of these techniques are the cost, difficulties in scaling up, loss of polymer and difficulties in separating catalyst from the functional polymers that interact with copper complexes. Catalyst can also be removed by treatment with MeOH, Na_2S or an ion exchange resin [13], but it is not useful for industrial productions.

A possible solution to this problem is to immobilize the catalyst on a solid support, thus provide a more efficient way of separating and recycling the catalyst. In recent literature there are some examples of successful immobilization of catalyst that maintains their activity on a solid support [14]. ATRP is feasible when multidentate nitrogen donor ligands [15] as well as Schiff base ligands are covalently bound to silica and crosslinked polystyrene supports [16]. Continious ATRP process was developed by packing silica gel supported copper bromide-hexamethyltriethylenetetramine (CuBr/HMTETA) into column reactor [17, 18]. The activity of the reactor decreased after 100 h, due to the catalyst loss from continous washing out of the reactor. The loss of the catalyst was ascribed to the physical adsorbtion on the silica gel. It was presumed that if the catalyst was covalently supported on the particles, it would be more stable. However, to date covalently supported systems for ATRP have not been successful. Haddleton et al.[16] supported copper halide via alkylpyridylmethanimine onto silica gel/crosslinked polystyrene particles to polymerize MMA but did not obtained a good control over Mw. Matyjaszewski et al. immobilized CuBr onto multidentate amine functionalized silica gel and crosslinked polystyrene particles to polymerize styrene, MMA and MA but did not obtain satisfactory results.

These systems offered limited control over the polymerizations of vinyl monomers, originating from the heterogenous nature of the process. The reason was the slow deactivation of the growing radicals resulting from slow diffusion of polymer chains toward metal center.Therefore insufficient deactivation occurs [19] To overcome this diffusion limitation, hybrid systems were investigated [20]. This process based on using majority of immobilized catalyst with minute amount of soluble more active catalyst. A small amount of the low molecular weight catalyst exists in the solution phase to accelerate the deactivation process of the growing radical and reduce the diffusion barrier.

There are also successful heterogenous systems such as ruthenium(II) catalyst supported onto amine-functionalized silica gel in the polymerization of MMA, copper bromide-hexamethyltriethylenetetramine (CuBr/HMTETA) complex for MMA[14, 21, 11], (dimethylamino) ethyl methacrylate (DMAEMA), styrene and MA. [22, 14]

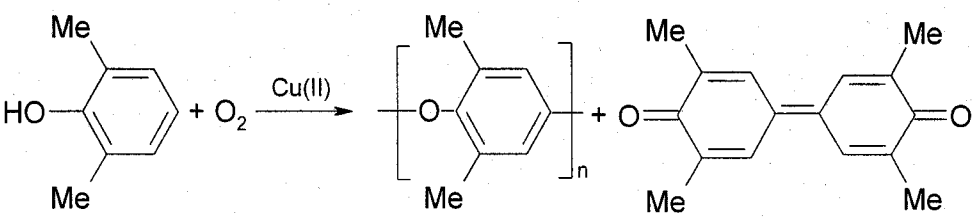
Shipping Zhu and co-workers supported onto silica gel by simple adsorption for ATRP [18]. Compared to grafting methods, this adsorption is much simplier and does not require special chemicals or tedious procedures. The supported catalysts were recycled two or three times with good retention of the catalyst activities.

Another approach to the catalyst recycling is regeneration of catalyst. Zhu and co-workers used excesssive amount of catalyst (CuBr/Initiator=1.5) to achieve living process because of the limited mobility of the supported catalyst. The recycled catalyst showed reduced catalytic activity due to the presence of Cu(II). After being regenerated by a reaction with Cu(0), the catalyst regained its activity and mediated a first-order polymerization with respect to the monomer. The molecular weights of PMMA from the regenerated catalyst were very close to the fresh catalyst [23].

In recent literature, there has been several successful studies on absorbing catalyst physically onto solid support. There has been several other approaches including the reversible adsorption of the catalyst using ion exchange resins, or using ligands whose solubility strongly depends on the temperature [13].

2.3 Oxidative Coupling Polymerization of Phenols

Oxidative coupling polymerization is the most widely used method for the synthesis of poly(phenylene oxide). The reaction was first reported by A. S. Hay in 1959 as copper catalyzed oxidation of 2,6-dimethylphenol to PPO [24]. Since then, a number of systems with different transition metal catalyzes or without catalyzes, have been reported.



(2.12)

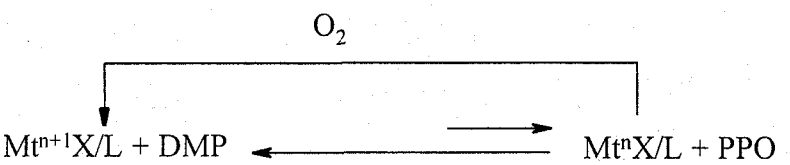
A variety of phenol derivatives, usually having substituents in two ortho positions, can be used in oxidative coupling polymerization reactions. Most phenols with ortho alkyl, aryl, chloro or bromo substituents produce poly(phenylene oxide) in high

yield. If the substituents are bulky, the diphenoquinone becomes the major product and the yield of the polymerization is low. Phenols with one ortho substituent and an open para position usually causes highly branched and colored products.

Catalysts for oxidative coupling polymerization of phenols are usually composed of a transition metal salt (eg: copper, manganese, cobalt) and a base. Molecular oxygen is normally the oxidizing agent. Most liquids that can dissolve the polymer, such as benzene or toluene can be used as solvents. A dessicant or a polar liquid is often added to prevent water, a by product of the polymerization, from forming a separate phase which may interact and poison the catalyst. Copper and manganese is usually used as transition metal in oxidative coupling polymeriztion. Copper catalyzed systems contain a copper halide and an amine (either heterocyclic or aliphatic). [24, 25, 26] These include N,N,N',N'-tetramethylethyleneamine (TMEDA), N,N'-Di-t-butyl-ethylenediamine (forms a catalyst with copper that is not easily hydrolized during polymerization), pyridine, 4-N,N-(dimethlamino)pyridine, polymeric amines, including poly(vinylpyridine), imidazole polymers, poly(iminotrimetylene) and oligomeric amines.

Reaction can also be achieved with none catalytic systems by using metal oxides and other inorganic compouds as the oxidizing agent (instead of moleculer oxygen) such as manganese dioxide [27], lead dioxide [28], silver oxide [29] and sodium bismuthate [30].

The chemistry of oxidative coupling polymerization of phenols is based on the catalytic cycle of copper- amine complexes [31].

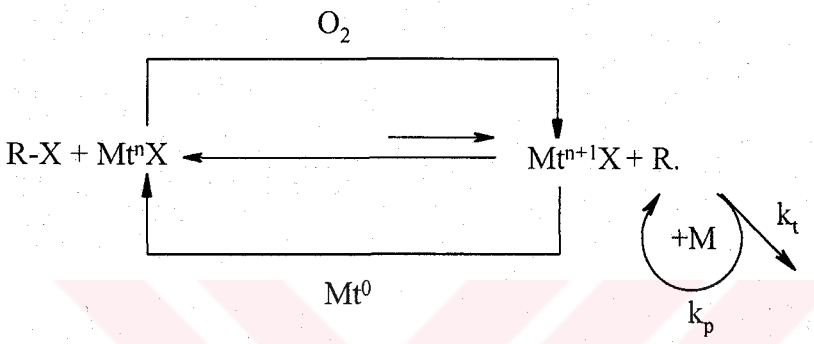


(2.13)

DMP = 2,6- dimethylphenol
PPO = Poly(phenylene oxide)
L = ligand (Amine)

Typical polymerization procedure is based on electron transfer reaction between phenol and Cu(II) to yield active phenolic species that react with other phenol molecule to give consequently the polymer. Moleculer oxygen is the oxidizing agent for Cu(I) to reproduce Cu(II) catalyst.

The similarity between oxidative coupling polymerization of 2,6-disubstituted phenols and ATRP is that, each system is based on redox couple of metal complexes. In both polymerizations, usually Cu(I) and Cu(II)- amine complexes were used as catalyst [32].



(2.14)

Due to the radical nature of ATRP, addition of free radical scavengers such as galvinoxy or diphenylpicrylhydrazyl (DPPH) inhibits the ATRP. [33, 34, 35] Haddleton and co-workers have observed that large excess of phenolic compounds increased the rate of MMA polymerization in ATRP system, contradictionary to their inhibitor role in radical polymerization [36]. Furthermore, Matyjaszewski et. al. reported that ATRP can be conducted in the presence of small amount of oxygen and using unpurified monomers containing phenolic inhibitors [37]. In this case, the mixture of their higher oxidation state and excess zero valent metals were employed. Since the Mt_nX is continously produced by the redox reaction between zero valent metal and Mt_{n+1} X_2 , after an induction period that can be attributed to the consumption of the oxygen, controlled polymerization conditions were achieved.

The similarity between two polymerization systems prompted us to investigate ATRP system in which oxygen and excess amount of phenolic compounds (sodium phenoxide) are present. We demonstrate that sodium phenoxide conjunction with Cu(II) or Cu(I)-PMDETA complexes can be used for the ATRP of MMA. Various

types of phenol derivatives give a possibility to use Cu(II) salts instead of Cu(I) analogs and reduces the amount of metal complexes in the polymerization system.

3. EXPERİMENTAL

3.1 Chemicals

a) Monomer

Methyl methacrylate (MMA, 99% Acros) was dried over CaH_2 and distilled under vacuum and stored at –15 °C before use.

b)Initiator

2-bromo-ethyl isobutyrate (EIBr ,Aldrich) was used directly.

c) Solvents

Tetrahydrofuran (THF, 99.8%, J.T. Baker HPLC grade)

Toluene (distilled over Na)

Diphenylether (DPE, 99%Acros) was used directly.

Methanol (technical grade) was used in precipitation of polymers.

d) Ligand

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

e) Catalyst

$CuCl_2$ and CuCl, (Merck) were used as received.

f) Other Chemicals

Silica gel with 40 mesh with avarage pore diameter of 0.070-0.23mm and 60 mesh with avarage pore diameter of 0.063-0.20mm was boiled in deionized water for 5h and then dried in the air and under vacuum.

PhONa is synthesized from a reaction of PhONa and slightly excess amount of NaH in dry THF.

3.2. Characterization

Gel permeation chromatographic (GPC) analysis were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and (four waters styragel columns (HR 5E, HR 4E, HR 3, HR 2). THF was used as the eluent at a flow rate of 0.3 mL/min. Molecular weight of the polymers was calculated with the aid of poly(methyl methacrylate) standards. Monomer conversion was determined by Unicam 610 Series gas chromatography (GC) instrument equipped with a FID detector using a J& W Scientific 15m DB Wax widebore injector. Detctor and injector tempertatures were kept constant at 285 and 280 respectively. Column temperature was started from 40°C to 160 ° C with a heating rate of 20 ° C/min, initiation time:1 minutes, upper time: 3 minutes.(For the polymerizations in DPE, upper temperature was 200 ° C). Residual copper amount was determined by Atomic Absorbtion instrument (Perkin Elmer 30303030 Zieman AA)

3.3 Procedure For the Polymerization of Methyl Methacrylate

To a 15 ml round bottom flask, anisole (as internal standart for GC), toluene, methyl methacrylate, silika gel, PMDETA, $CuCl_2$ were added and stirred for 5 minutes. When the stirring was stopped the blue silica particles settled to the bottom of the flask and the upper solution layer became colorless. PhONa was then introduced to the flask. Then it was closed with rubber septum and placed in thermostated oil bath at 90 °C. After stirring for 10 minutes, EIBr was addded with syringe. By adding the initiator, the color of the mixture turned to violet and later to dark green. At given time intervals, a small amount of reaction solution was taken with a syringe. While doing this, nitrogen was passed in order to get the samples easily and not to let air get in the flask. The samples were diluted with THF and the progress and the kinetics of the polymerizations were observed by giving the samples to GC and GPC instruments.

3.4 General Procedure for Catalyst Recycle

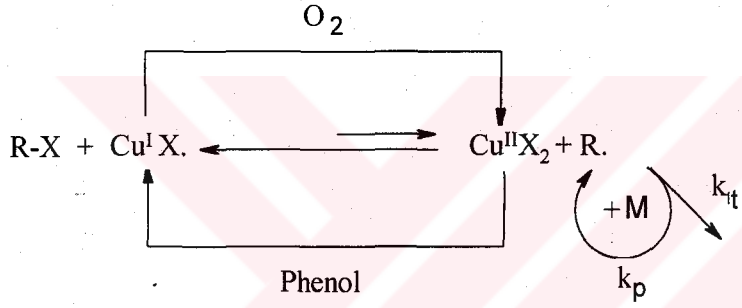
After completion of the polymerization, the flask was lifted from the oil bath, cooled and diluted with toluene. The remaining solid in the flask was washed with toluene and filtered through PTFE filter. Then the solid was charged into the flask and toluene was removed by drying under vacuum. In the following reaction, due to the weight of the remaining solid, given amounts of anisole, solvent, MMA, PMDETA, phONa and initiator were charged to the flask. The polymerization procedure was repeated.

3.5. Procedure for chain extension polymerization

The poly(methyl methacrylate) macroinitiator (M_n = 7700, M_w/M_n = 1,09) was prepared by the polymerization technique mentioned above. Poly(methyl methacrylate macroinitiotor (0.2 g), MMA (1.11mL, 10.4mmol), CuCl (0L00252 g, 0.026 mmol) and PMDETA (0.0055ml, 0.026 mmol) were added in a Schlenk flask. Oxygen was removed by three freeze-pump-thaw cycles. The reaction was stirred at 90 °C in an oil bath. The resulting polymer mixture was diluted with THF and passed through alumina column precipated into methanol. The polymer was dried in vacuum and molecular weights were determined by GPC.

4. RESULTS AND DISCUSSION

ATRP systems are usually carried out in degassed systems due to the deactivating effect of oxygen. We demonstrate that sodium phenoxide conjunction with Cu(II)-PMDETA complex can be used to initiate ATRP of MMA in the presence of certain amount of oxygen and tried to find the optimum amount of amine, needed for the second charge of the catalyst. In all reactions, we used Cu(II) at the beginning of the reactions contrary to typical ATRP. Scheme (4.1).



(4.1)

We assumed that the reduction of Cu(II) by electron transfer from phenol to Cu(II) would be the first step of the reaction. The Cu(I) formed can then react with organic halide to form propagating radical or it reacts with oxygen to form copper salt in its higher oxidation state which is then reduced to Cu(I) by excess sodiumphenoxide. At high ratios of phenol to Cu(II), fast and uncontrolled reaction was observed, which can be explained by the consumption of Cu(II) to Cu(I) by excess sodiumphenoxide and as a result it can not deactivate the polymerization.

Polymerizations were carried out in heterogenous systems, with a support of CuCl-PMDETAcomplex adsorbed on silica gel. Although we do not know the exact adsorbtion mechanism, we believe that the high polar CuCl- PMDETA complex has a high affinity for the –OH groups on the surface of silica gel particles.

4.1.Polymerization with first charge of catalyst

Reactions were performed in 15 ml round bottom flask unless indicated. Anisole (as internal standart for (GC), solvent, methyl methacrylate, silica gel, PMDETA, $CuCl_2$ were added in order and stirred for 5 minutes. When the stirring was stopped the blue particles settled to the bottom of the flask and the upper solution layer became colorless. PhONa and initiator (EIBR) were then introduced to the flask. At given time intervals, a small amount of reaction solution was taken with a syringe. While doing this, nitrogen was passed in order to get the samples easily and not to let air get in the flask. The samples were diluted with THF progress and the kinetics of the polymerizations were observed by giving the samples to GC and GPC instruments. The kinetic of the reaction was observed by GC, from the comparison of decrease in MMA to anisole concentration in the reaction. At given times small amounts of samples were taken with a syringe and diluted with THF. Colon temperature was started from 40°C to 160 ° C with a ramp of 20 ° C, initiation time was 1 minutes, upper time was 3 minutes.(For the polymerizations in DPE, upper temperature was 200 ° C)

As shown in the graphs, the linear behavior of the semilogarithmic kinetic plots of PMMA obtained with GC instrument and dependence of number average molecular weight calculated from gel permeation chromatography (GPC) on conversion supports the living character of the polymerization. Also reveals that the concentration of the propagating radicals were constant during the polymerization. In all polymerizations, molar concentrations of the monomer to initiator was Mo / Io =100(molar), Silica gel / $CuCl_2$ = 10 (g) ,and the temperature was 90 °C.

In the first reaction we used 40 mesh 0.070-0.23mm silica gel as support and DPE as solvent. The volume of the tube was 33.2 mL The ratios of the components were EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75. Initiator was added before the rubber septum was closed, then introduced into the termostated bath. The molecular weights were higher than the theoretical ones (Table4.1) . The calculated initiator efficiencies lowered throughout the polymerization.

Table 4.1 Polymerization of MMA in DPE at 90 °C. Mo / Io =100, EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75, Headspace volume =25.3mL, 1st charge of Silica gel (40 mesh 0.070-0.23mm)

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	f
1	30	20	1.24	1700	2000	0.22	1.1
2	55	37	1.21	3700	3700	0.46	1.01
3	80	59	1.23	5750	5850	0.89	1,01
4	105	68	1.19	8800	6800	1.13	0.77
5	130	82	1.17	11400	8200	1.69	0.72
6	155	88	1.22	12200	8800	2.08	0.72
7	180	92	1.11	15700	9200	2.47	0.59

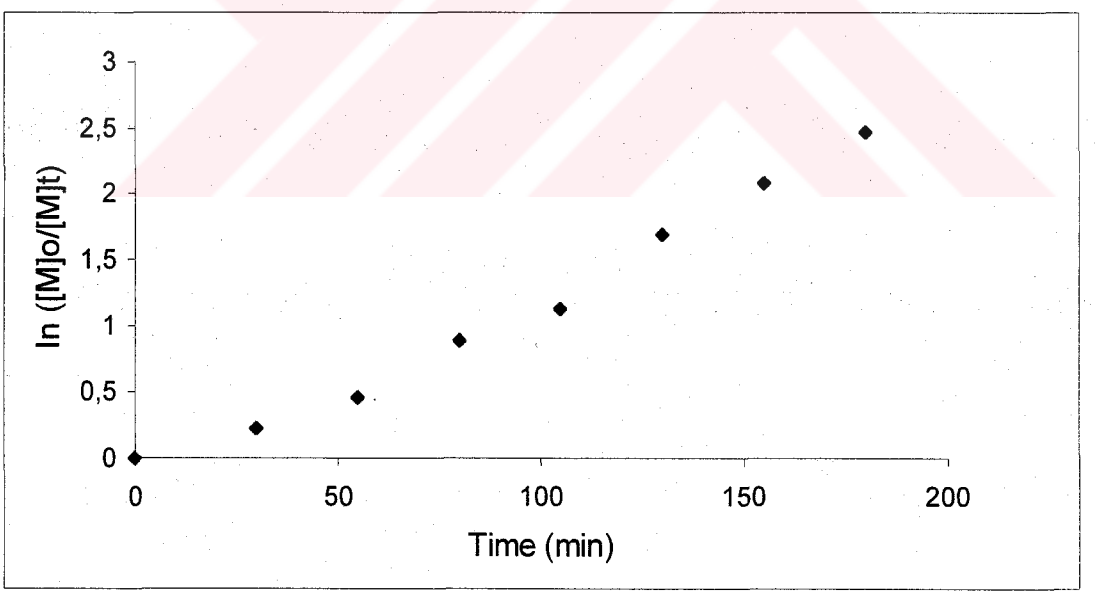


Figure 4.1 Comparison of the semilogarithmic kinetic plots of PMMA Polymerization of MMA in DPE; Mo / Io =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75;Headspace volume =25.3mL, 1st charge of Silicagel (40 mesh 0.070-0.23mm)

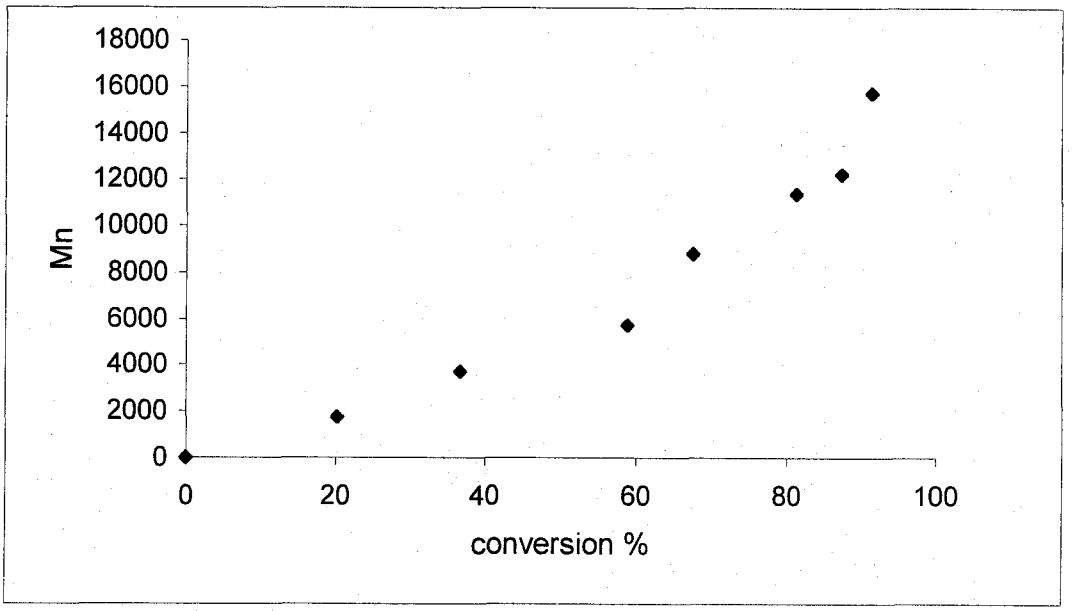


Figure 4.2 Dependence of number average molecular weight on conversion in polymerization of MMA in DPE; Mo / Io =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75, Headspace volume =25.3mL, 1st charge of silica gel (40 mesh 0.070-0.23mm)

In figure 4.1 an induction period of approximately 20 minutes was observed. This can be explained by the consumption of oxygen 25.3 (mL) in the tube. At the end of polymerization, the flask was lifted from the oil bath, cooled and diluted with toluene. The remaining solid in the flask was washed with toluene and filtered through PTFE filter. Then the solid was charged into the flask and toluene was removed by drying under vacuum. In the following reaction, we assumed that the remaining solid contained copper and silica gel. From the percentage of the solid we obtained to the total weight of the copper, amine and silica gel we used in the first reaction, we calculated the copper amount in the solid. Other contents were calculated from copper. Asuming that some amine was lost during filtration, half of the calculated PMDETA was added in the second charge of the reaction. The molar concentrations were EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75. $CuCl_2$ and silicagel was not added. The initiation efficiency and rate polymerization in the second charge of the silica gel was higher.(Table4.2) This may be due to the assumption we made for the calculation of second charge of catalyst.

Tableb 4.2 Polymerization of MMA in DPE at 90 °C. Mo / Io =100, EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75, Headspace volume =25.1mL, Second charge of silica gel (40 mesh 0.070-0.23mm)

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	*f*
1	20	4	1.17	1700	400	0,04	0.23
2	40	31	1.19	5100	3100	0,37	0.60
3	60	56	1.23	8100	5600	0,82	0.69
4	80	73	1.21	10100	7400	1,33	0.73
5	100	83	1.2	11500	8300	1,77	0.72
6	120	89	1.2	12200	8900	2,17	0.73
7	140	91	1.22	12800	9100	2,48	0.71

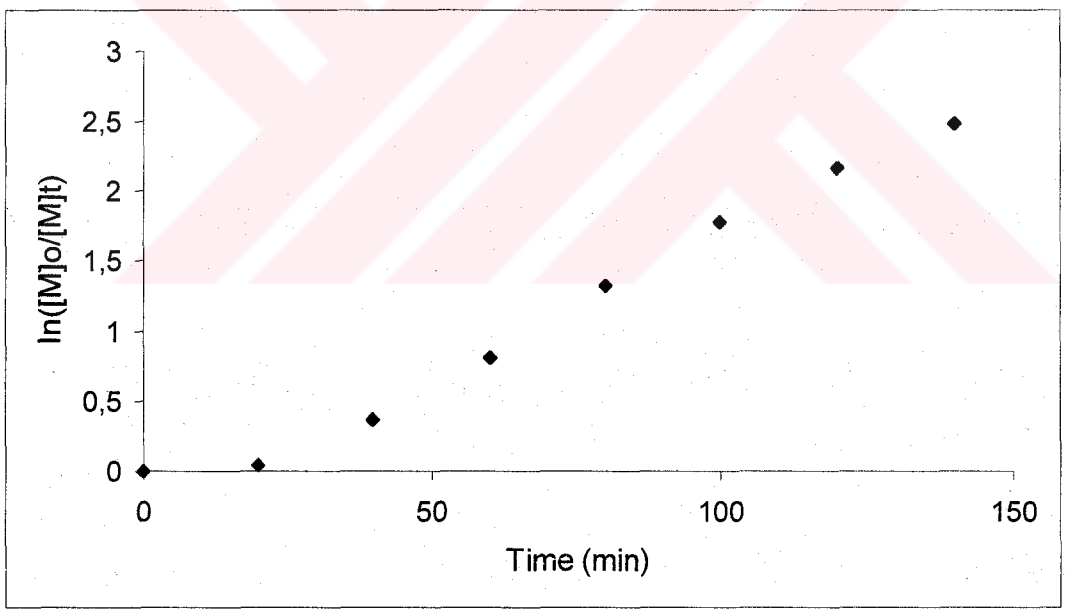


Figure 4.3 Comparison of the semilogarithmic kinetic plots of MMA polymerization of in DPE at 90 °C. [M]o /[I]o =100, EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75, Headspace volume =25.1mL, Second charge of silica gel (40 mesh 0.070-0.23mm)

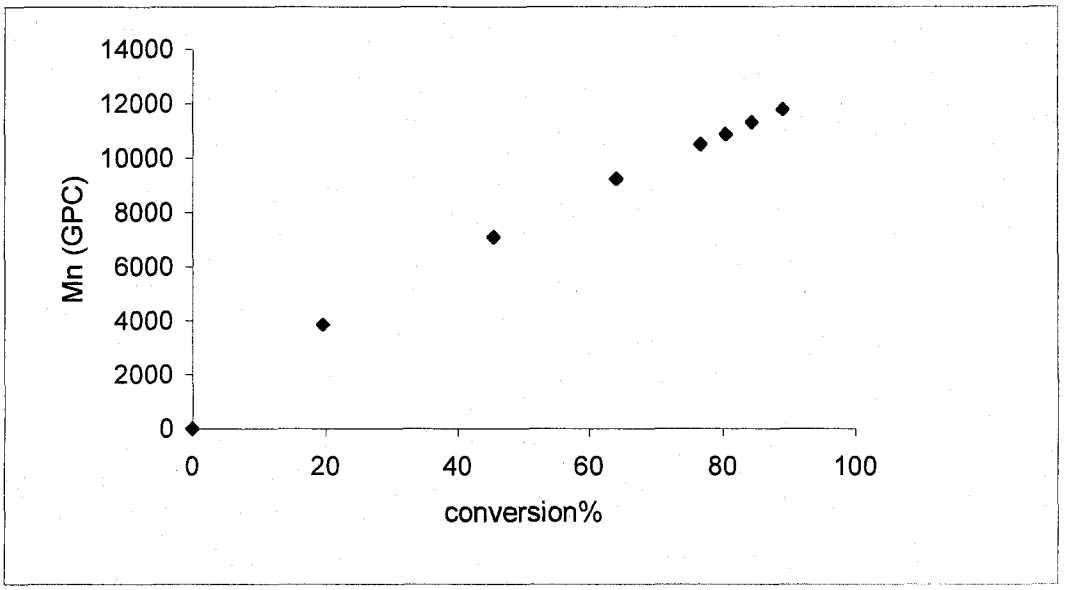


Figure 4.4 Dependence of number average molecular weight on conversion in polymerization of MMA in DPE, [M]o /[I]o =100, EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75, Headspace volume =25.1mL, Second charge of silica gel (40 mesh 0.070-0.23mm)

From our previous studies toluene and DPE were used as solvent and did not differ the polymerization conditions. In the reaction represented by table 3, we repeated the polymerization in Toluene without using silicagel. The same amounts of the components as in table 4.1 were used.

Table 4.3 Polymerization of MMA in toluene, without silica gel support [M]o /[I]o =100, EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75; Headspace vol =8mL

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	f
1	25	28.4	1.15	4900	2840	0.33	0.58
2	50	55	1.23	7100	5500	0.8	0.77
3	69	62.2	1.21	8550	6230	0.97	0.73
4	85	67.2	1.27	9240	6730	1.11	0.73
5	101	74.8	1.23	10440	7500	1.38	0.72
6	119	81.4	1.25	10700	8150	1.68	0.76
7	151	85.7	1.26	10850	8580	1.94	0.79
8	169	91.1	1.23	11500	9100	2.41	0.79

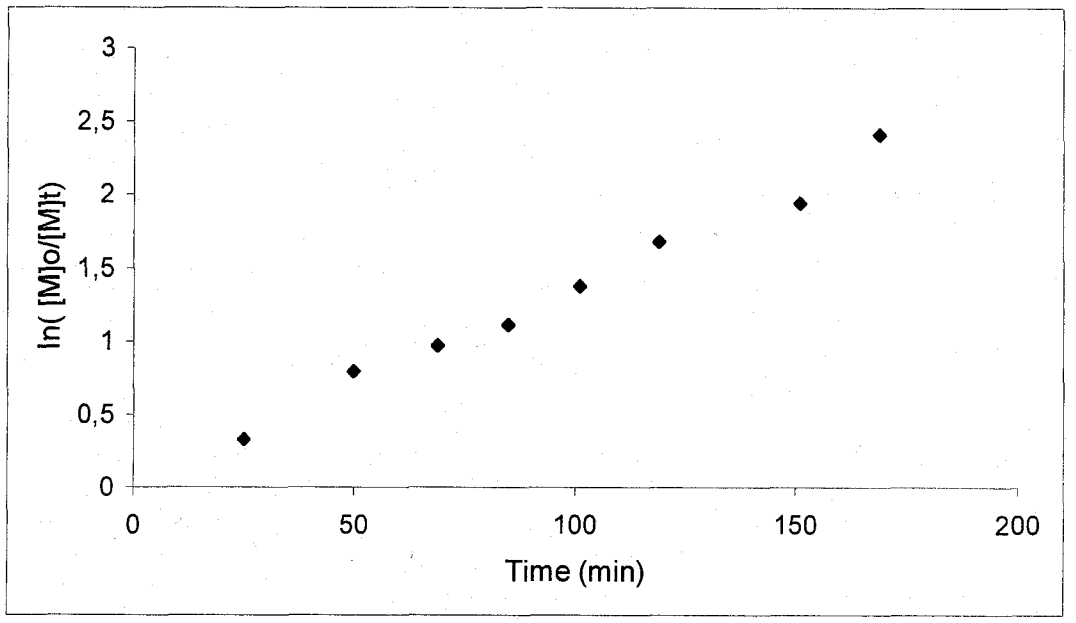


Figure 4.5 Semilogarithmic kinetic plots of PMMA at 90°C in toluene, without silica gel support [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75; Headspace volume =8mL

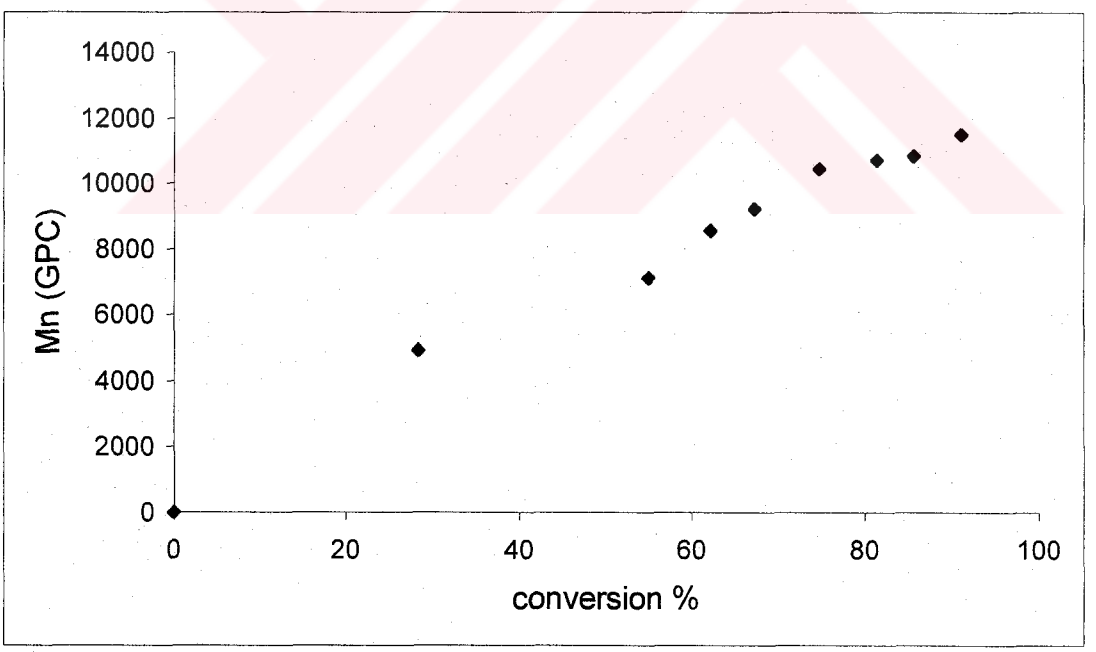


Figure 4.6 Dependence of number average molecular weight on conversion in of MMA in toluene at 90 °C without silica gel support [M]o /[I]o =100 (molar); EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 10 / 0.75; Headspace volume =8mL

The polymerization rate of the one without silica gel support was higher than the one with the first charge of silica gel. The experimental and theoretical molecular weights were closer than the silica gel supported polymerization, due to the higher initiation efficiency than in the silica gel supported one. (Table4.3, Table4.1)

In the following reaction we added the initiator with a syringe after other components were stirred in oil bath for 10 minutes, in order to annihilate the induction period and increase the initiation efficiency. We also reduced the molar ratio of the amine to EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75. The same silica gel (40 mesh 0.070-0.23mm) as in table 4.1, was used. The polydispersities were lower and the molecular weights were lower and closer to theoretical ones than in the polymerization in Table 4.1 and Table 4.3.

Table 4.4 Polymerization of MMA in toluene at 90 °C, [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75; Headspace volume =8,1mL; 1st charge of Silica gel (40 mesh 0.070-0.23mm)

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	f
1	18	20	1.18	3600	2000	0.18	0.56
2	38	43.5	1.15	5500	4350	0.57	0.79
3	53	54	1.11	6950	5400	0.78	0.78
4	73	68.4	1.16	7680	6850	1.15	0.89
5	93	78.7	1.14	8600	7870	1.54	0.92
6	113	87.1	1.15	9350	8720	2.05	0.93

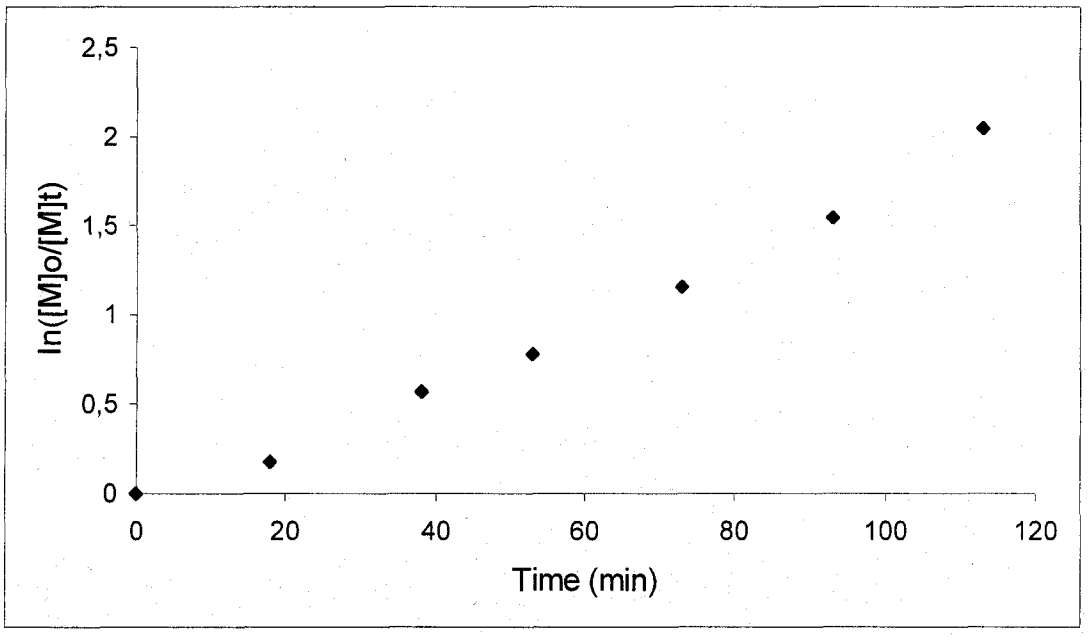


Figure 4.7 Semilogarithmic kinetic plots of PMMA at 90 °C in toluene. [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75; Headspace volume =8.1mL; 1st charge of Silica gel (40 mesh 0.070-0.23mm)

Both the semilogarithmic kinetic plot and graph of Mn vs conversion confirm better control over polymerization. The polymerization rate was higher than the previous ones.

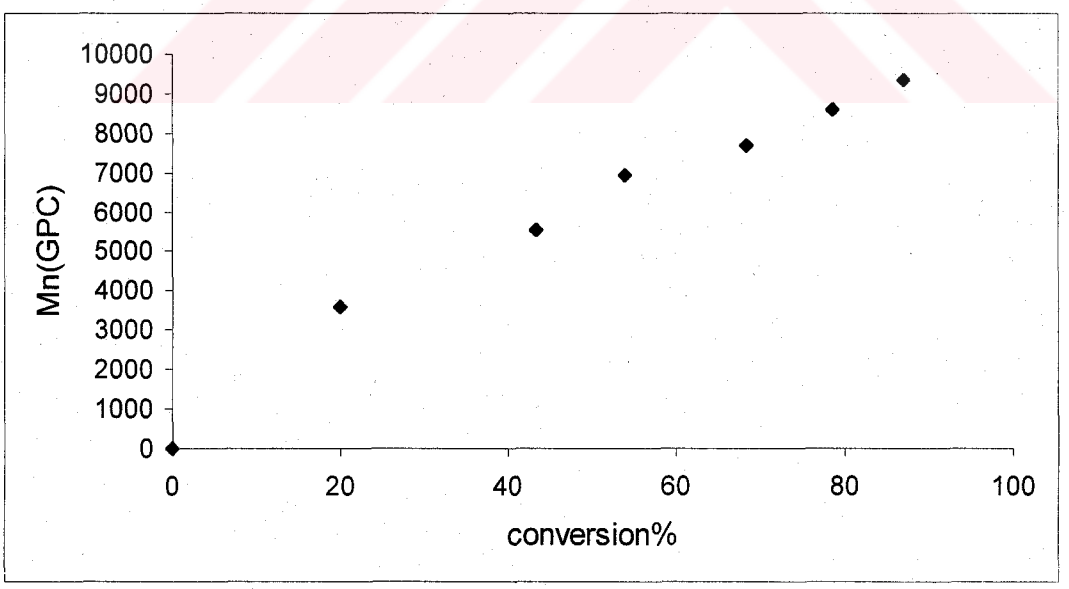


Figure 4.8 Dependence of number average molecular weight on conversion in of MMA in toluene. [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75; Headspace volume =8.1mL; 1st charge of silica gel (40 mesh 0.070-0.23mm)

In the second charge of this reaction in table4.5 the remaining solid was weighed and assumed that it contained Cu(II), PMDETA and silica gel. From the percentage of the solid we obtained to the total amount of copper, amine and silica gel in the first reaction, we calculated the copper amount in the solid. The charged amounts were calculated from the percentage of the copper we obtained from the previous reaction to the copper we used in the previous reaction. And compared to the first charge of the reaction (in table4.4), amine to initiator ratio was reduced to half. Molar ratios of the components were EIBr / CuC_{12} / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; $CuCl_2$. and and silica gel was not added. It was observed that the initiation efficiency dereased compared to the first charge (table4.5). This may be due to the assumption we made for the amount of copper. Semilogarithmic coordinates were still first-order kinetics in monomer (Figure 4.9) but the initiation efficiency and rate was lower than first charge of the reaction.

Table 4.5 Polymerization of MMA in toluene at 90 °C; [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; Headspace volume =8.8mL; 2nd charge of silica gel (40 mesh 0.070-0.23mm)

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	f
1	19	7	1.15	3600	700	0.08	0.19
2	35	30	1.2	5300	3000	0.36	0.57
3	50	34	1.27	6500	3400	0.42	0.52
4	65	53.4	1.15	8600	5400	0.76	0.63
5	90	63.2	1.13	10750	6300	1	0.59
6	140	80	1.2	12300	8000	1.63	0.65
7	165	84	1.13	13400	8400	1.81	0.63

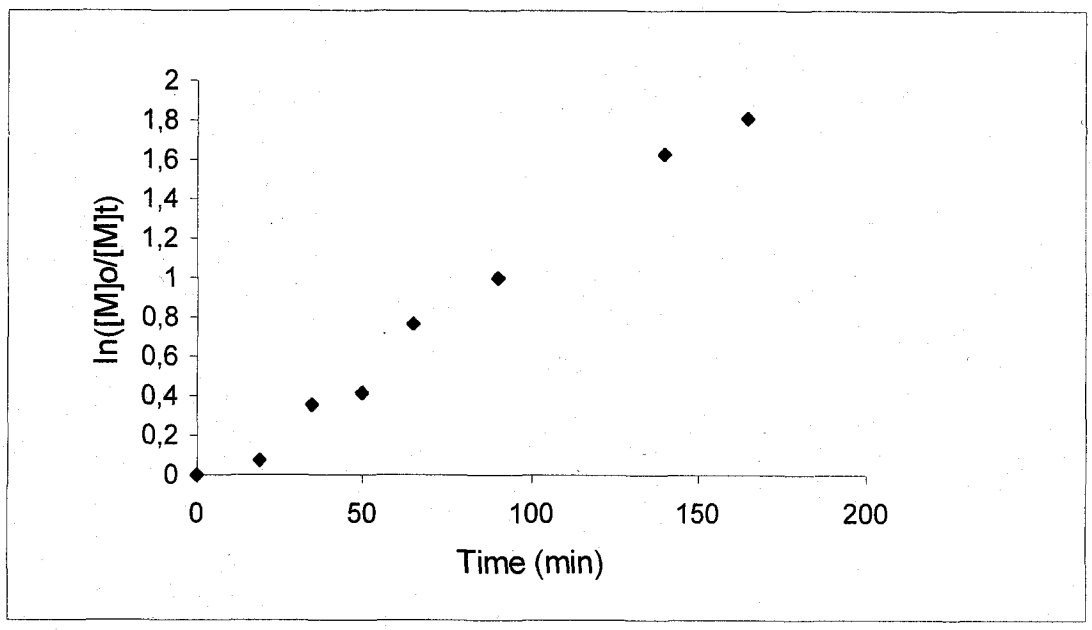


Figure 4.9 Semilogarithmic kinetic plots of PMMA at 90 °C in toluene. [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; Headspace volume =8.8mL; 2nd charge of silica gel (40 mesh 0.070-0.23mm)

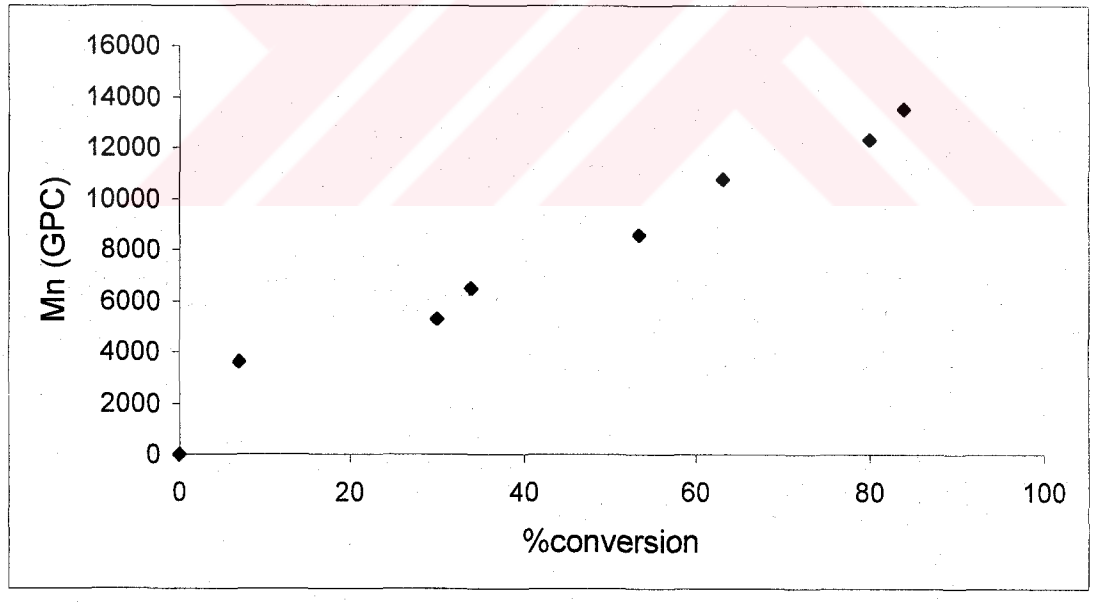


Figure 4.10 Dependence of number average molecular weight on conversion in of MMA in toluene; [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; Headspace volume =8.8mL; 2nd charge of silica gel (40 mesh 0.070-0.23mm)

In the first charge polymerization represented by table 4.6, the same ratios with the one in table 4.4 were used. The differance was the size of the silica gel (60 mesh 0.063-0.20mm). Molar ratios of the components were EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75. As in the reaction in table 4.4, the initiator was added after other components were stirred in oil bath for 10 minutes.

Table 4.6 Polymerization of MMA in toluene at 90 °C, [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75; Headspace volume =8.1mL; 1st charge of silica gel (60 mesh 0.063-0.20mm)

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	*f*
1	15	18	1.13	5500	1800	0.21	0.33
2	55	45.3	1.13	11600	4500	0.6	0.39
3	75	60.3	1.15	13200	6040	0.92	0.46
4	135	74.2	1.19	14800	7480	1.35	0.51
5	192	86	1.22	15700	8600	1.97	0.55
6	212	88.6	1.18	16800	8900	2.17	0.53
7	232	91.6	1.15	17400	9200	2.48	0.53
8	275	95.9	1.15	17800	9600	3.1	0.54

When we look at the Table 4.6 it can be seen that compared to 40 mesh 0.070-0.23mm silica gel, the polymers had higher molecular weight, were not in agreement with the theoretical ones and the initiation efficiency was low. This can be explained by the decrease in mobility of the catalytic species and decrase in homogenity of the system. The differances in the porous structure of the support effect the polymerization. Silica gel with porous structure and therefore has a larger surface area allow for condensation of more coupling agent during the same time as in the case of rather dense silica gel.

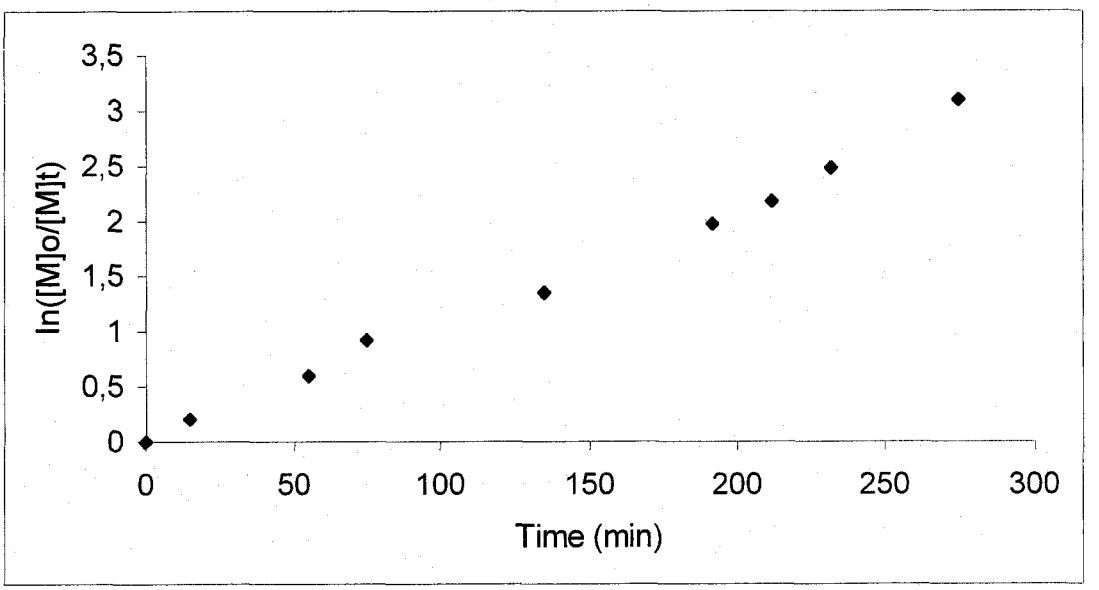


Figure 4.11 Comparison of the semilogarithmic kinetic plots of PMMA; [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75; Headspace volume =8.1mL; 1st charge of silica gel (60 mesh 0.063-0.20mm)

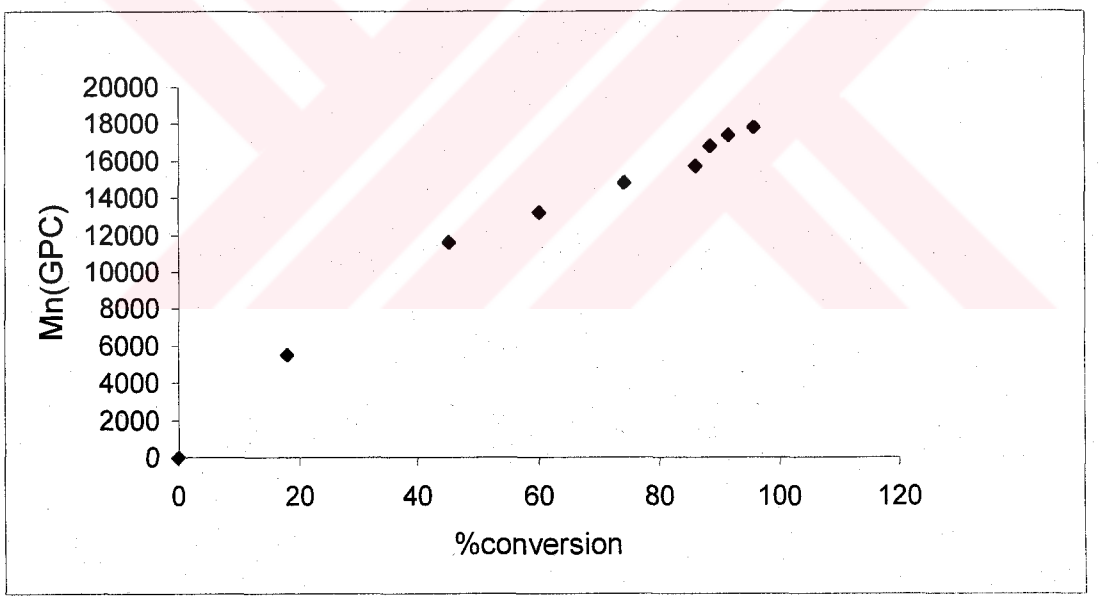


Figure 4.12 Dependence of number average molecular weight on conversion in polymerization of MMA in toluene at 90 °C, [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 5 / 0.75; Headspace volume =8.1mL; 1st charge of silica gel (60 mesh 0.063-0.20mm)

In the second charge, initiation efficiency was still low. The polymerization rate and also the molecular weights were nearly the same as the first charge.

Table 4.7 Polymerization of MMA in toluene at 90 °C, [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; Headspace volume =11.6 mL; Second charge of Silica gel (60 mesh 0.063-0.20mm)

Sample	Time(min)	Con %	PDI	Mn sec	Mn theo	ln ([M]o/[M]t)	*f*
1	22	21	1.06	4160	2100	0.24	0.51
2	35	31.5	1.2	5170	3150	0.38	0.61
3	55	40	1.17	9340	3980	0.51	0.43
4	75	54	1.14	11800	5420	0.78	0.46
5	95	67	1.17	14300	6700	1.1	0.47
6	115	73	1.19	15600	7320	1.31	0.47
7	145	82	1.23	16600	8200	1.71	0.49
8	175	89	1.19	17700	8900	2.2	0.50

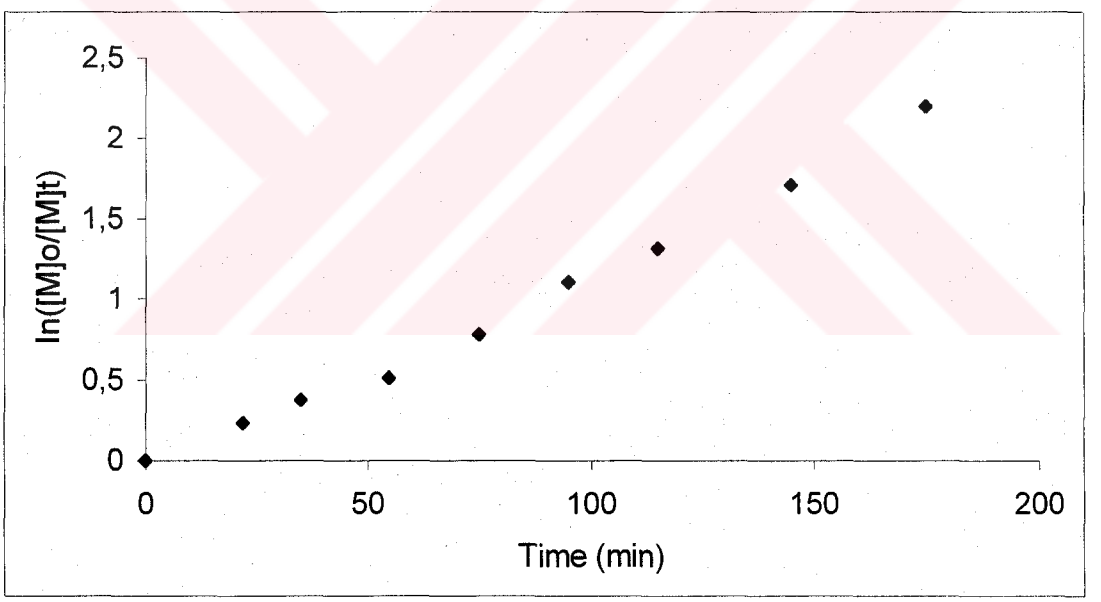


Figure 4.13 Comparison of the semilogarithmic kinetic plots of PMMA in toluene at 90 °C, [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; Headspace volume =11.6 mL; Second charge of silica gel (60 mesh 0.063-0.20mm)

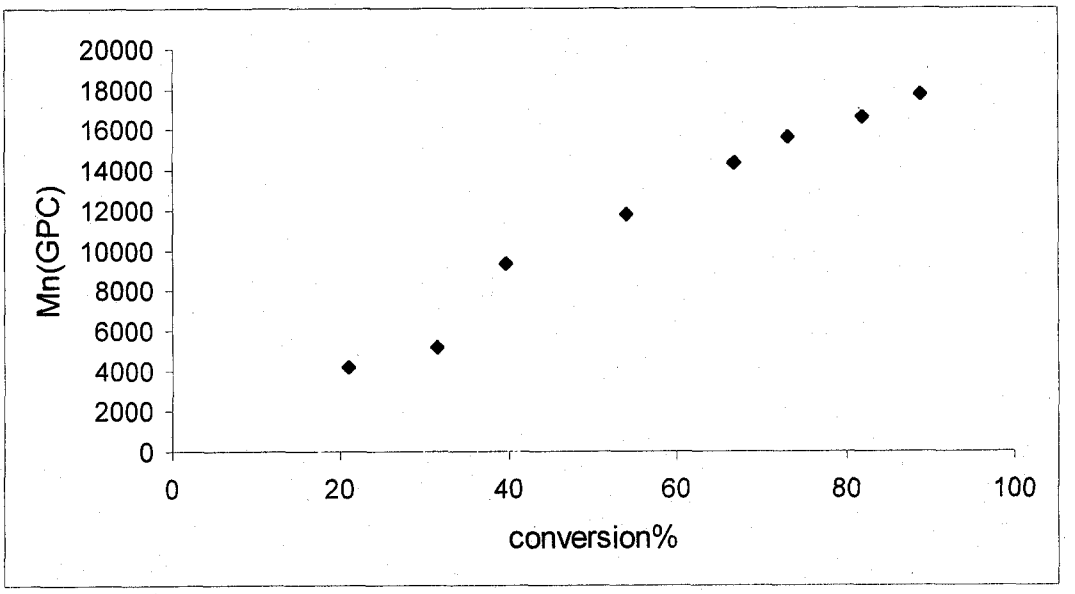


Figure 4.14 Dependence of number average molecular weight on conversion in polymerization of MMA in toluene at 90 °C, [M]o /[I]o =100; EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0.5 / 2.5 / 0.75; Headspace volume =11.6 mL; Second charge of silica gel (60 mesh 0.063-0.20mm)

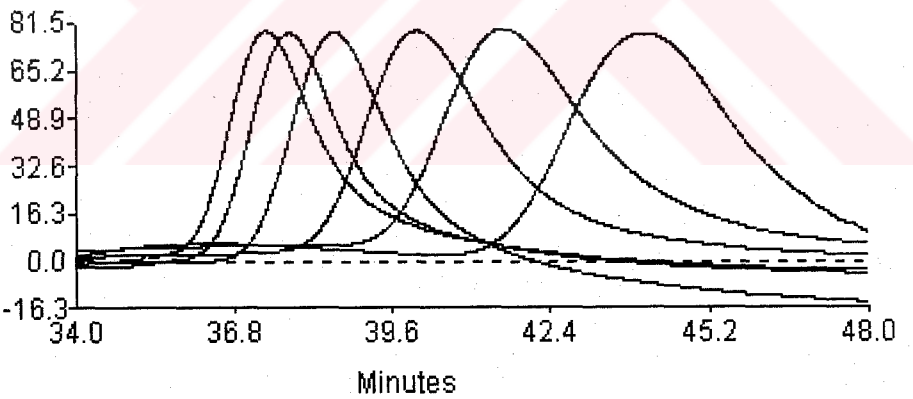


Figure 4.15 GPC chromatograms of the polymerization of MMA in DPE; [M]o /[I]o =100 (molar) catalyzed by $CuCl_2$-PMDETA supported onto silica gel; temp=90 °C EIBr / $CuCl_2$ / PMDETA / PhONa =1 / 0,5 / 10 / 0,75 (molar),Headspace volume =25.3mL, 1st charge of silica gel (40 mesh 0.070-0.23mm)

4.2. Chain Extension Polymerization

In order to demonstrate that the halogen is the end group of the obtained polymers, the chain extension polymerization was performed. The polymethylmethacrylate

macroinitiator (M_n = 7700, M_w/M_n = 1,09) was prepared by the polymerization technique mentioned above. Polymethyl methacrylate macroinitiotor (0,2 g), MMA (1,11ml, 10,4mmol), CuCl (0,00252 g, 0,026 mmol) and PMDETA (0,0055ml, 0,026 mmol) were added in a Schlenk flask. Oxygen was removed by three freeze-pump-thaw cycles.The reaction was stirred at 90 °C in an oil bath for 28 hours. The resulting polymer mixture was diluted with THF and passed through alumina column precipated into methanol. The polymer was dried in vacuum and molecular weights were determined by GPC.

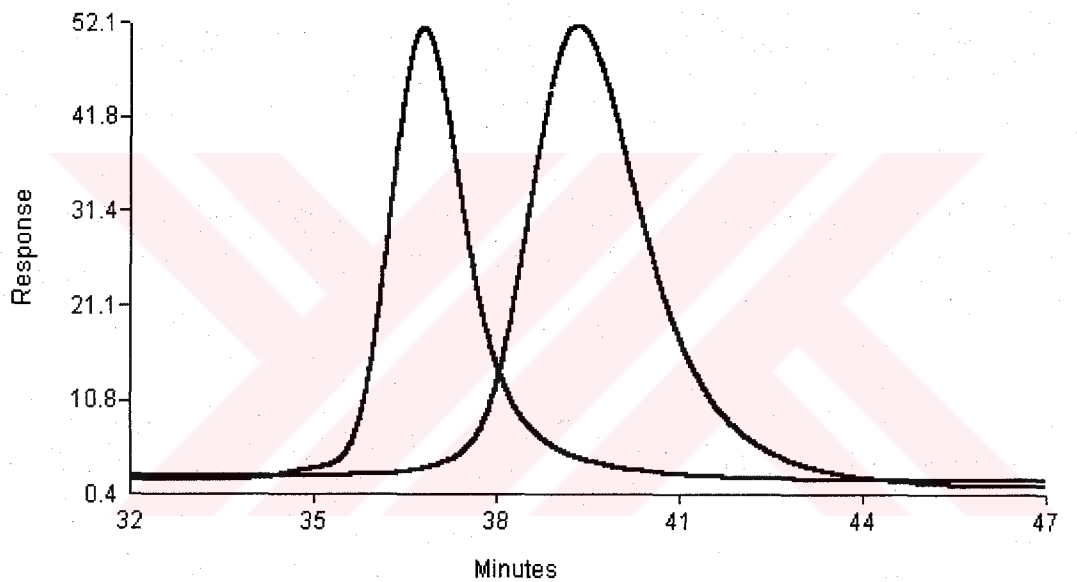


Figure 4.16. GPC Chromatograms of the PMMA macroinitiator a (Mw:7700; Mw/ Mn:1.09), Chain extended polymer b (Mw:33100; Mw/Mn: 1.103)

5. CONCLUSION AND RECOMMENDATİONS

In this work we demonstrate that ATRP of MMA can be accomplished in the presence of limited amount of oxygen and PhONa with silica gel supported catalyst. The redox cycle in the initiation step is proposed to be similar to oxidative coupling polymerization of phenols. Contrary to typical ATRP systems, we used higher oxidation state of copper to be reduced to Cu(I) by excess PhONa. The supported catalyst was prepared by simple adsorbtion of CuCl-PMDETA on silica gel yielding PMMA with very low polydispersity. The catalyst was recycled for subsequent polymerization of MMA with reduced amine amount. The apparent rate of polymerizations was found to be first-order with monomer concentration for the studied polymers. The inititor efficiency increased when the initiator was added after the thermal equilibrium is reached. Immobilized systems provided even better control over polymerization than the systems without silica gel support. In order to verify the active nature of the chain end of the obtained PMMA, the chain extension polymerization of MMA was carried out in classical ATRP process starting with PMMA (Mn= 7700; Mw/Mn= 1.1) as a macroinitiator. The absence of the PMMA macroinitiator peak in the GPC trace of the resulting polymer demonstrates that the macroinitiator was fully extended. The copper amount of the polymers, obtained by this process were found to be 9.8ppm. The applications of the supported catalyst for further reactions and the optimum amount of amine needed is under evaluation.

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