ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ACTIVATOR FORMATION IN ATOM TRANSFER RADICAL POLYMERIZATION IN REACTION MEDIA

M. Sc. Thesis by
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Department : Polymer Science and Technology

Programme: Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ATOM TRANSFER RADİKAL POLİMERİZASYONUNDA REAKSİYON ORTAMINDA AKTİVATÖR OLUŞUMU

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymers
M_w	: Weight average molecular weght of polymers
M_w/M_n	: Molecular weight distribution of polymers
MWD	: Molecular weight distribution of polymers
St	: Styrene
***n*-BA**	: *n*-Butyl acrylate
MMA	: Methyl methacrylate
PMMA	: Poly (methyl methacrylate)
PS	: Polystyrene
PMDETA	: Polymethyl methacrylate
THF	: Tetrahydrofuran
k_a, 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
k_t	: Rate constant of termination
I, M	: Initiator and monomer respectively
DP	: Degree of Polymerization
GPC	: Gel Permeation Chromatography
NMR	: Nuclear Magnetic Resonance Spectroscopy
UV	: Ultra Violet Spectrophotometer
MALDI-TOF MS	: Matrix Assisted Laser Desorption Ionization Time-of-flight Mass Spectrometry

ACTIVATOR FORMATION IN ATOM TRANSFER RADICAL POLYMERIZATION IN REACTION MEDIA

SUMMARY

There has been a conspicuous growth in the development of living controlled radical polymerization techniques in the past few years. ATRP is one of the controlled/'living' polymerization methods has been the subject of many scientific researches. Transition metal complexes comprise the most important part of the multicomponent system ATRP. Major drawback of ATRP is using lower oxidation state metal salts due to high cost, early oxidation. This can be overcome by electron transfer from electron transfer agents to higher oxidation state metal salts (deactivator) and forming lower oxidation state metal salt *in situ*. This new method has all the benefits of a normal ATRP process plus the benefit of being able to add the catalyst complex in its more stable higher oxidation state to the reaction mixture. One requirement for the catalyst activation is that the oxidatively stable transition metal complex should be quickly and efficiently reduced to the desired degree by a nonradial forming reducing agent.

In the present work, the controlled polymerization of styrene and *n*-butyl acrylate in the presence of electron transfer agents (such as fructose and ascorbic acid) were carried out in anaerobic conditions and polymerization kinetic was investigated. The block copolymers of styrene and methyl methacrylate were synthesized via macroinitiator technique**.** Novel octa-functional initiator 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis-(2-bromopropionyloxi)calix[8]arene synthesized and used in the preparation of polystyrene and poly (styrene–*b*-methyl methacrylate). The monomodal shapes of the GPC (Gel Permeation Chromatography) traces and ^{1}H-NMR spectrum showed that the octa-arm and linear block copolymers were successfully synthesized in the presence of electron transfer agents via ATRP.

ATOM TRANSFER RADİKAL POLİMERİZASYONUNDA REAKSİYON ORTAMINDA AKTİVATÖR OLUŞUMU

ÖZET

Son yıllarda kontrollü/'yaşayan' radikal polimerizasyon yöntemlerinde büyük gelişmeler gözlenmiştir. Kontrollü/'yaşayan' radikal polimerizasyon yöntemlerinden olan atom transfer radikal polimerizasyon (ATRP) bir çok bilimsel araştırmaya konu olmuştur. Geçiş metal kompleksleri çok bileşenli bir sistem olan ATRP'unun en önemli parçasını oluşturmaktadır. Polimerizasyonda düşük oksidasyon basamağındaki metal tuzlarının (aktivatör) kullanılması yüksek maliyete ve erken oksidasyona sebep olmaktadır. Bu da ATRP'nin önemli dezavantajlarındandır. Bu engel, elektron transfer bileşiklerinden yüksek oksidasyon basamağındaki metal tuzuna (deaktivatör) elektron transferiyle aktivatörün (Cu(I)) *in situ* oluşturulması yöntemi ile ortadan kaldırılabilir. Normal ATRP'unun bütün yararlarını kapsamasının yanı sıra yüksek oksidasyon basamağındaki metal tuzunun (deaktivatör) kullanılması da bu yeni metodun avantajlarındandır. Katalizör aktivasyonunun sağlanması için bu yöntemin tek gereksinimi yüksek oksidasyon basamağındaki metal kompleksini istenilen dereceye hızlı ve etkili bir şekilde indirgeyen ve radikal oluşturmayan indirgen bileşiklerin bulunmasıdır.

Bu çalışmada, elektron transfer bileşikleri varlığında (fruktoz ve askorbik asit) stiren ve n-bütil akrilatın kontrollü polimerizasyonları anaerobik koşullarda gerçekleştirilmiş ve polimerizasyon kinetiği incelenmiştir. Makro başlatıcı tekniği ile lineer stiren-metil metakrilat blok kopolimerleri sentezlenmiştir. Ayrıca sekiz fonksiyonlu bir başlatıcı olan 5,11,17,23,29,35,41,47-okta-*tert*-butil-49,50,51,52,53,54,55,56-oktakis-(2-bromopropioniloksi)kaliks[8]aren sentezlenip, makro başlatıcı tekniği ile stiren-metil metakrilat blok kopolimeri sentezlenmiştir. GPC (Jel Geçirgenlik Kromotografisi) ve ^{1}H-NMR spektrumlarından elde edilen sonuçlar sekiz kollu ve lineer poli(stiren-*b*-metil metakrilat) kolimerlerinin elektron transfer bileşikleri varlığında gerçekleştirilen ATRP tekniğiyle başarıyla sentezlenebileceğini göstermiştir.

1. INTRODUCTION

Free-radical polymerization plays an important role in the industrial preparation of a wide variety of polymeric materials, especially statistical copolymers. However, the main drawback is the lack of control over macromolecular structure and molecular weight distribution. Recently, the concept of 'living'/controlled free-radical polymerization has gathered considerable interest due to the potential control over molecular weight, chain ends, and macromolecular architecture provided. Several methods have been developed to achieve this control. One of the approaches is the transition metal catalyzed atom transfer radical polymerization (ATRP).

Atom transfer radical polymerization (ATRP) is one of the most efficient controlled radical polymerization (CRP) systems. ATRP employs a reversible transfer of the halogen atom between growing chains and a redox-active transition metal catalyst. ATRP is a very versatile process, judging from the large number of monomers, catalysts and initiators that can be used to prepare polymeric materials with a great range of compositions, topologies and functionalities [1].The recent development of new catalytic systems for atom transfer radical polymerization (ATRP) enables the better control of chain functionalities, architectures and compositions as well as the extension to new monomers and new reaction conditions.

There are several requirements for an efficient catalytic system: chemoselectivity, solubility and stability of the catalyst, the position of the equilibrium constant and dynamics of exchange being most important. High chemoselectivity is needed for an efficient atom transfer process without outer sphere oxidation/reduction chemistry, hydrogen abstraction or formation of organometallic species. Sufficient solubility is required to assure a necessary concentration of both activator and deactivator in the polymerization mixture. Catalyst stability is related to the metal affinity toward the ligand, since the dissociation of the ligand may affect both solubility and chemoselectivity (side reactions). The position of the equilibrium defines the required amount of catalyst and the dynamics of exchange is directly related to polydispersity and control of the end group. All of these parameters depend strongly

on the metal and ligands used. Of all the transition metals investigated, copper appears to be the most promising in terms of price and versatility. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical. The rate of polymerization is also affected by the relative solubilities of the activating and the deactivating species of the catalyst. Any shift in the redox potential affects the electron transfer and the activation-deactivation equilibrium.

Considering the toxic alkyl halide and easy oxidized transition metal complex in a low oxidation step, new methods have been required. One of the approaches is the activator generated by electron transfer (AGET) ATRP. To reach the ATRP equilibrium instead of employing Cu(I), reducig agent is used to react with Cu(II) complex to generate activator. The procedure relies on electron transfer; therefore, this method is called AGET ATRP [2].

In this thesis, AGET ATRP process was used to demonstrate the effects of different ligand and reducing agent concentrations on polymerization of styrene in the presence of Cu(II) halide as catalyst. Additionally, linear and star block copolymers were also synthesized in order to focus on utility and convenience of this type of polymerization.

2. THEORETICAL PART

2.1 Controlled/Living Radical Polymerizations

Controlled/living radical polymerization (CRP) has been the focus of numerous studies during the past years, with the goal of obtaining well-defined polymer compositions (homo, random, gradient, block, graft), topologies (linear, star, comb, hyperbranched), or functionalities (end groups, side groups) [3]. Recent progress in controlled/'living' radical polymerizations (CRP) not only accomplishes the same task but also opens the door to many novel materials with various well-defined compositions and architectures, owing to a larger range of monomers available for radical than for ionic polymerizations, [4, 5], as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers [6]. 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), 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 [7].

Living polymerization was first defined as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide for molecular weight control and narrow molecular weight distributions (MWD). Additional prerequisites to achieve these goals are that the initiator should be consumed at early stages polymerization and that exchange between species of various relativities is fast in comparison with propagation. If these additional criteria are met, a controlled polymerization will

result. Polymerization can also be defined as controlled if side reactions occur, but only to an extent which does not considerably disturb the control of the molecular structure of the polymer chain.

Three types of radical polymerization have been called living;

Polymerizations where the normal termination process of radical-radical reaction is slow or absent because of the physical nature of the reaction medium or the immediate environment of the reactive chain end. Systems in this class include precipitation polymerization, certain template polymerizations and polymerizations in inclusion complexes. Unfortunately these systems have little generality and do not have application in the synthesis of high purity block copolymers.

Systems with reversible termination where the bond formed by primary radical termination or chain transfer are stable. The aim of the first polymerization step is to synthesize a macro-initiator serving as precursor to a block co-polymer. Narrow polydispersity is not available by these techniques.

Systems with reversible termination where the bond formed by free radical termination or chain transfer is kinetically unstable under the reaction conditions. These polymerizations should be considered as true living polymerizations.

The controlled/living systems are quite 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 [8]. Currently three systems seem to be most efficient: Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes such as RAFT [5]. Each of the CRPs has some limitations and some special advantages and it is expected that each technique may find special areas where it would be best synthetically suited. For example, NMP carried out in the presence of bulky nitroxides can not be applied to the polymerization of methacrylates due to fast β-H abstraction. ATRP cannot 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 the chain end [9]. RAFT can be applied to the polymerization of many unreactive monomers, such as vinyl acetate [10].

Well-controlled system should provide:

• Linear kinetic plot in semi logarithmic coordinates ($\ln([M]_0/[M])$ vs. time) if the reaction is first-order with respect to the monomer conversion. Acceleration on such a plot may indicate slow initiation, whereas deceleration may indicate termination of deactivation of the catalyst. Straight lines indicate only a constant number of active sites and will also be present under steady-state conditions. The transfer step should have no effect on kinetics.

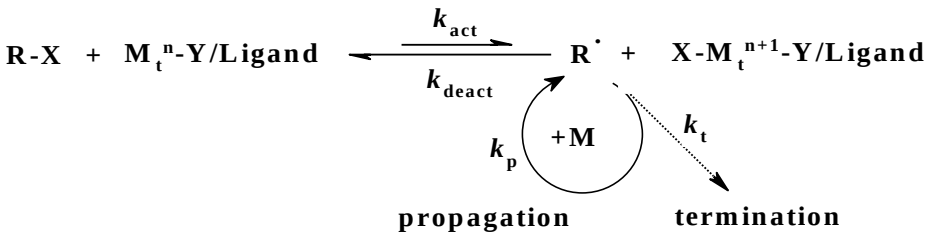
• Linear evolution of Mw with conversion. Mw lower than predicted by $\Delta[M]/[I]_0$ ratio indicates transfer, while Mw higher than predicted by $\Delta[M]/[I]_0$ either inefficient initiation or chain coupling. Straight lines indicate only a constant number of all chains and can not detect unimolecular termination.

• Polydispersity (M_w/M_n) should decrease with conversion for systems with slow initiation and slow exchange. Polydispersities increase with conversion when the contribution of chain breaking reactions becomes significant.

• End functionality should not affect by slow initiation and exchange but is reduced when chain breaking reactions become important.

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 [11]. A general mechanism for ATRP is given below.

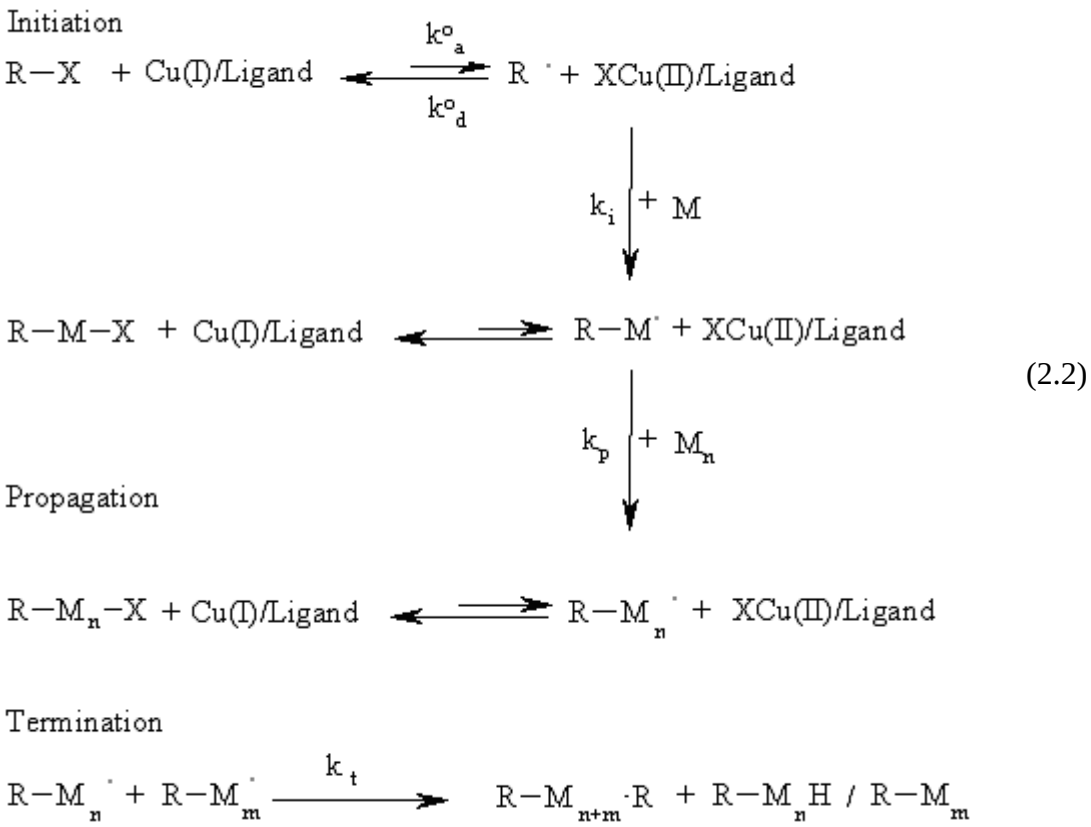


(2.1)

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, successfully polymerizing styrenes, various (meth)acrylates, acrylonitrile and other monomers [12, 13].

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-M_t^{n+1}, as persistent radicals to reduce the stationary concentration of termination [14]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_{deact}, and also with the concentration of deactivator. The molecular conversion and the amount of initiator used, DP = $\Delta[M]/[I]_0$; polydispersities are low, $M_w / M_n < 1.3$ [15].



(2.2)

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

2.2.1 Monomers

A variety of monomers have been successfully 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 if the equilibrium constant is too small. If it is too large then the equilibrium constant will lead to a large amount of termination because of high radical concentration [16].

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 theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization.

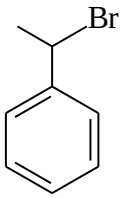
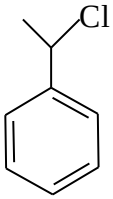
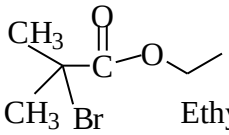
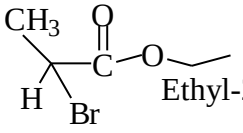
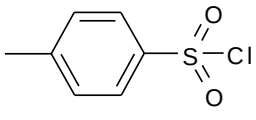
$$\mathbf{DP = [M]_0 / [I]_0 \times Conversion} \qquad (2.3)$$

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 [16].

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

Table 2.1: The most frequently used initiator types in ATRP systems

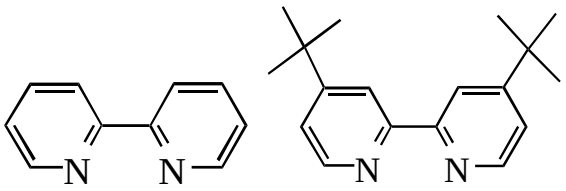
Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methyl methacrylate
 Ethyl-2-bromo propionate	Methyl acrylate and styrene
 p-toluene sulphonyl chloride	Methyl methacrylate

Two parameters are important for a successful ATRP initiating system; first, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized [16].

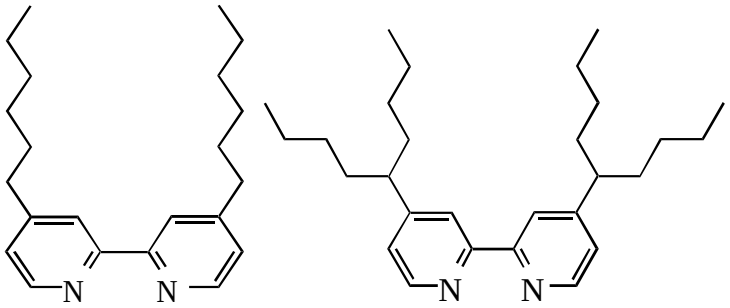
2.2.3 Ligands

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical.

Ligands, typically amines or phosphines, are used to increase the solubility of the complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. So far, a range of multidentate neutral nitrogen ligands was developed as active and efficient complexing agents for copper-mediated ATRP, including, bipyridines [17-18] (2.4), terpyridines [20,21], phenantrolines[22], picolyl amines [21,23], pyridinemethinamines [24-28] and tri [17,20,29-31] or tetradentate aliphatic amines [32-35] including linear and branched amines (2.5). Tridentate and tetradentate ligands generally provide faster polymerizations than bidentate ligands, while monodentate nitrogen ligands yield redox-initiated free radical polymerization. In addition, ligands with an ethylene linkage between the nitrogens are more efficient than those with a propylene or butylene linkage [36].

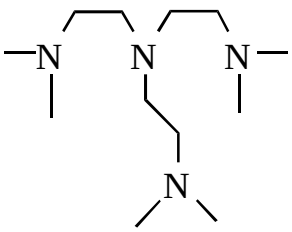


Bpy **dTbpy**



(2.4)

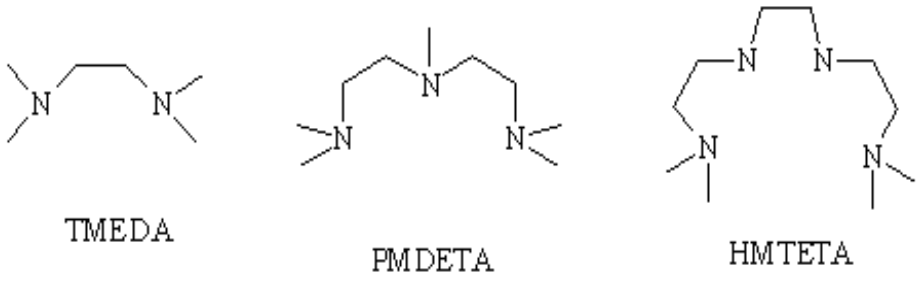
dHbpy **dNbpy**



(2.5)

Me_6TREN

Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (2.6) were synthesized and examined for ATRP as ligands [17]. Reasons for examining of these type of ligands are, they are cheap, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bpy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.



(2.6)

Solubility of the ligand and its metal complexes in organic media is of particular importance to attain homogeneous polymerization conditions. The rate of polymerization is also affected by the relative solubility of the activating and the deactivating species of the catalyst. In heterogeneous systems, a low stationary concentration of the catalyst species allows for a controlled polymerization, but the polymerization is much slower than in homogeneous systems [36]. The ligand with a long aliphatic chain on the nitrogen atoms provides solubility of its metal complexes in organic solvents. However, the increasing length of the alkyl subsistent induces steric effects and can alter the redox potential of the metal center. Any shift in the redox potential affects the electron transfer and the activation–deactivation equilibrium [21].

2.2.4 Transition Metal Complexes

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible 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 accommodate a (pseudo)-halogen. Fourth the ligand should complex the metal relatively strongly.

The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

2.2.5 Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer.

2.2.6 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 is usually negative first order with respect to the deactivator ($X\text{-}M_t^{n+1}$/Ligand).

The rate equation of copper-based ATRP is formulated in discussed conditions and given in (2.7).

$$\mathbf{Rp= k_{app}\,[M]= k_p\,[R\bullet]\,[M]= k_p\,K_{eq}\,[I]\,([CuX]/[CuX_2])\,[M]} \qquad (2.7)$$

Figure 2.1 shows a typical linear variation of conversion with time in semi logarithmic coordinates (kinetic plot). Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. However, since termination occurs continuously, the concentration of the Cu(II) species increases and deviation from linearity may be observed [37]. For the ideal case with chain length independent from termination, persistent radical effect [38, 40] kinetics implies the semi logarithmic plot of monomer conversion vs. time to the 2/3 exponent should be linear. Nevertheless, a linear semi logarithmic plot is often observed. This may be due to an excess of the

Cu(II) species present initially, a chain length dependent termination rate coefficient, and heterogeneity of the reaction system due to limited solubility of the copper complexes. It is also possible that self-initiation may continuously produce radicals and compensate for termination. Similarly, external orders with respect to initiator and the Cu(I) species may also be affected by the persistent radical effect [40].

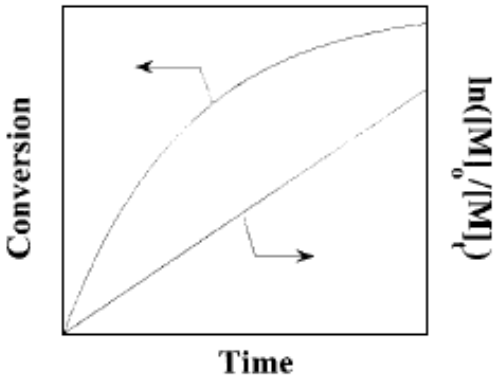


Figure 2.1: Kinetic plot and conversion vs. time plot for ATRP

Results from kinetic studies of ATRP for styrene (St) [41], methyl acrylate (MA) [42] and methyl methacrylate (MMA) [19, 43] under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations. These observations are all consistent with the derived rate law.

It should be noted that the optimum ratio can vary with regard to changes in the monomer, counter ion, ligand, temperature, and other factors [19, 44, 45]. The precise kinetic law for the deactivator CuX_2 was more complex due to the spontaneous generation of Cu(II) via the persistent radical effect [38, 40 , 41]. In the atom transfer step, a reactive organic radical is generated along with a stable Cu(II) species that can be regarded as a persistent metallo-radical. If the initial concentration of deactivator Cu(II) in the polymerization is not sufficiently large to ensure a fast rate of deactivation (k_d[Cu(II)]), then coupling of the organic radicals will occur, leading to an increase in the Cu(II) concentration.

Radical termination occurs rapidly until a sufficient amount of deactivator Cu(II) is formed and the radical concentration becomes low enough. Under such conditions, the rate at which radicals combine (k_t) will become much slower than the rate at which radicals react with the Cu(II) complex in a deactivation process and a

controlled polymerization will proceed. Typically, a small fraction (~5 %) of the total growing polymer chains will be terminated during the early stage of the polymerization, but the majority of the chains (>95 %) will continue to grow successfully. The effect of Cu(II) on the polymerization may additionally be complicated by its poor solubility, by a slow reduction by reaction with monomers leading to 1,2-dihaloadducts, or from the self-initiated systems such as styrene and other monomers.

If the deactivation does not occur, or if it is too slow ($k_p >> k_{deact}$), there will be no control and polymerization will became classical redox reaction therefore 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 (2.8).

$$\mathbf{M_w/M_n = 1 + ((}k_d\mathbf{[RX]_0)/(}k_p\mathbf{[X\text{-}M_t^{n+1}])) \times ((2/p)\text{-}1)} \quad (2.8)$$

p = polymerization yield

$[RX]_0$ = concentration of the functional polymer chain

$[X\text{-}M_t^{n+1}]$ = concentration of the deactivators

k_d = rate constant of deactivation

k_p = rate constant of activation

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 polydispersity are expected to be obtained because the smaller chains include little activation-deactivation steps and also the chain length difference is higher for small polymer chains resulting in little control of the polymerization.

b) For the higher ratios of k_p/k_d, higher polydispersity (molecular weight distributions) are usually obtained resulting in the little control of polymerization.

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

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control

over the molecular weights and the molecular weight distributions of the resulting polymers. Additionally, since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

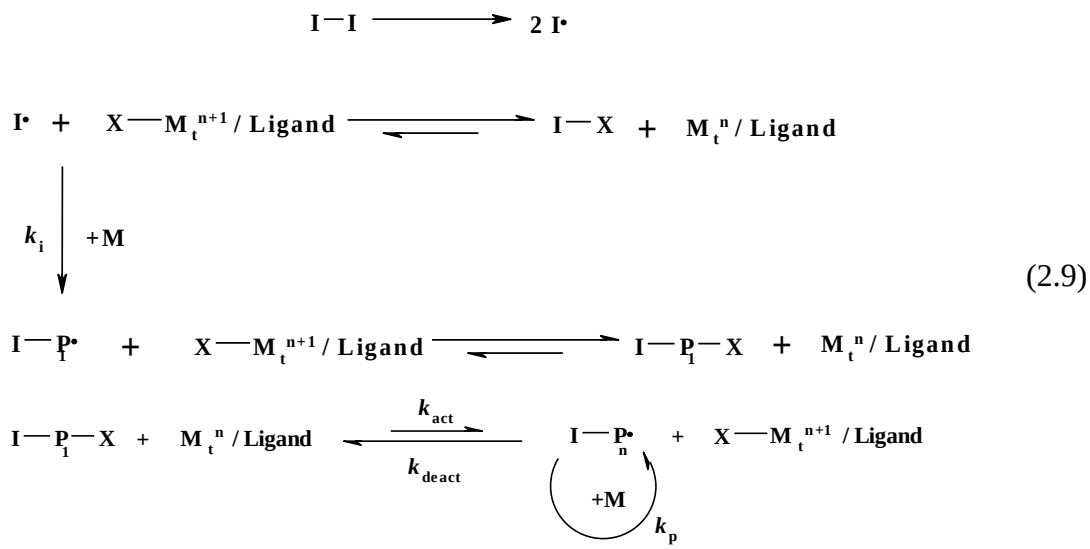
Although the above-mentioned conventional ATRP method is an efficient way to maintain living radical polymerization of various vinyl monomers, it has two major problems: the halide species RX are toxic, and the catalysts M_t^n/LX are easily oxidized by air. Since ATRP initiated by a redox reaction between an initiator with a radically transferable atom or group and a catalyst complex comprising a transition metal compound in a lower oxidation state (Scheme 2.1), the transition metal complexes can be easily oxidized to a higher oxidation state. Therefore, to obtain consistent results, special handling procedures are required, and the preformed catalyst must be stored under an inert atmosphere. Oxygen or other oxidants should be removed from the system prior to addition of the catalyst in the lower oxidation state; therefore, the process of catalyst complex handling can be challenging.

2.3 Reverse ATRP

To overcome the drawbacks of ATRP process, the use of conventional radical initiators, such as 2,2'-azobisisobutyronitrile (AIBN) in the presence of complexes of transition metals in their higher oxidation state, have been reported and referred to as "reverse" or "alternative" ATRP by Matyjaszewski et al. and Teyssie´ et al.,[46] respectively. This type of ATRP approaches the same type of equilibrium as a conventional ATRP starting from conventional radical initiators such as peroxides or diazo compounds. Several monomers, including St, MMA, and MA, were successfully polymerized via this process.

In a typical ATRP, the initiation system consists of a suitable alkyl halide such as a primary/secondary benzyl halide, an R-haloester, Rhaloketone, R-halonitrile, or sulfonyl Halide and a transition metal compound in its lower oxidation state such as Cu(I), Fe(II), Ru(II), or Ni(II). According to Scheme 2.1 the alkyl halide and M_t^n species reversibly form alkyl radicals and X-M_t^{n+1} species. It is also possible to

approach the same type of equilibrium starting from conventional radical initiators such as peroxides or diazo compounds and X-M_t^{n+1} species (Scheme 2.9).



(2.9)

This process was applied to an aqueous dispersed system with a high expectation of success for two reasons: first, many water-soluble initiators used in conventional emulsion polymerization could be utilized, and, second, the initial system was easy to handle because Cu(II) species, which are stable in air, were used in place of Cu(I) species. Reverse ATRP has been employed successfully in homogenous and in heterogeneous conditions. However, as more active catalyst complexes were developed, a limitation inherent in reverse ATRP became clear. The transferable atom or group (X) is added to the reaction as a part of the copper salt, and therefore highly active catalysts should still be used in the amount comparable to concentration of radical initiator. Therefore, complex concentration can not be independently reduced and block copolymers can not be formed.

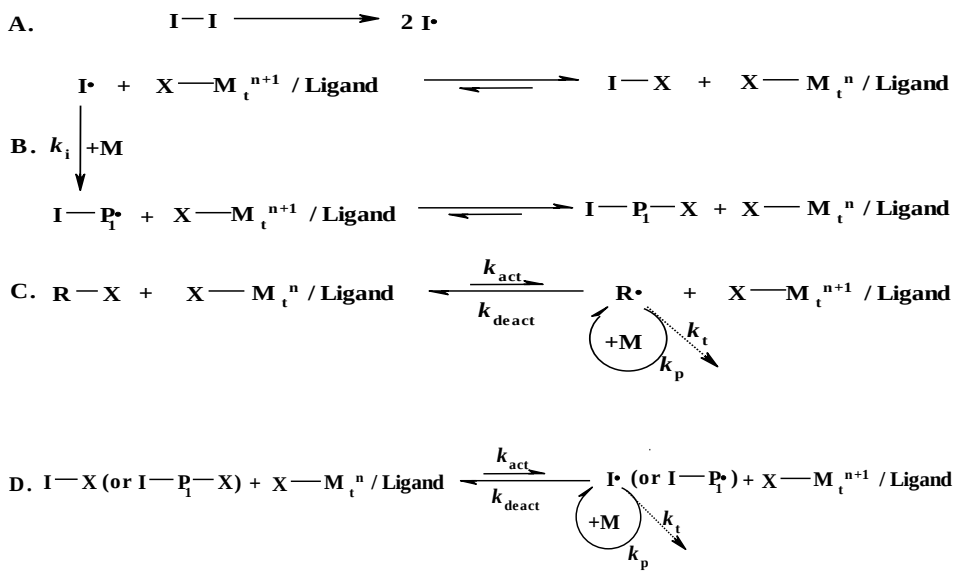
In the past, only two kinds of initiators, such as azo and peroxide compounds, were employed as the initiator in the reverse ATRP system. It is well known that the decomposition of conventional initiators is irreversible, which makes the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature, and it is also difficult to realize living radical polymerization for some high reactivity monomers. For example, the AIBN/$CuCl_2$/ bipy initiation system was successfully used for the living/controlled radical polymerization of St via a reverse ATRP process, but it was uncontrolled for

(meth)acrylate monomers. The development of new type initiators for reverse ATRP, using carbon–carbon bond initiator instead of azo or peroxide ones, is of interest. At the same time this new type initiator (an iniferter) could provide the initiation step of reverse ATRP, in which the iniferter reversibly decomposes to primary radicals, unlike other conventional initiators (AIBN or BPO) having an irreversible decomposition step, resulting in suitable amounts of primary radicals being generated.

2.4 Simultaneous Normal and Reverse Initiation (SR&NI) ATRP

As the thermal radical initiator (e.g., AIBN) is the sole free radical source, reverse ATRP can only readily produce linear homopolymers or linear copolymers. In addition, the concentration of copper complex in the system cannot be independently reduced for a given targeted degree of polymerization, particularly when using highly active catalyst systems, due to the intimate correlation between the initial concentration of deactivator (CuII complex) and normal radical initiator in the formulation.

A newly developed simultaneous reverse and normal initiation (SR&NI) process provides a way to produce well-defined (co)polymers with various composition and architectures and reduce the initial concentration of the added CuII complex without sacrificing control over the polymerization. SR&NI was demonstrated by conducting a fully controlled ATRP starting with a small amount of highly active catalyst in its higher oxidation state (e.g., CuX_2/ligand) and a dual initiator system consisting of a small amount of free radical initiator and a large amount of alkyl halide. Proposed mechanism for SR&NI in ATRP process is shown in Scheme 2.10.



(2.10)

As illustrated in Scheme 2.10, the initiation (step A and B in Scheme 2.10) begins with deactivation reaction between the small amount of CuX_2/ligand and radicals (I• or I-P_1 •) that are produced from the free radical initiator, I-I. Upon the generation of the activating transition metal complex, CuX/ligand, the large majority of alkyl halide (R-X), along with a minor concentration of newly formed halogenated chains (I-X or I-P_1-X), can initiate the polymerization concurrently via a normal ATRP process (steps C and D in Scheme 2.10). Since a highly active transition metal complex was employed, the catalyst usage was significantly reduced to 5-10 times lower than in a typical reverse ATRP process [47].

SR&NI ATRP comprises a dual initiation system: standard free radical initiators and initiators comprising a transferable atom or group in conjunction with the stable precursor of an active catalyst complex. This initation system can be used to prepare any type of polymer that can be prepared by normal ATRP, and it can be conducted in bulk, solution, emulsion, miniemulsion, and heterogeneous polymerization from surfaces.

A newly developed simultaneous reverse and normal initiation (SR&NI) provides a way to produce well-defined (co)polymers with various composition and architectures and reduce the initial concentration of the added Cu(II) complex without sacrificing control over the polymerization.

There are, however, some limitations to SR&NI ATRP. Since a standard free radical initiator is still added to the polymerization mixture to form radicals that reduce the

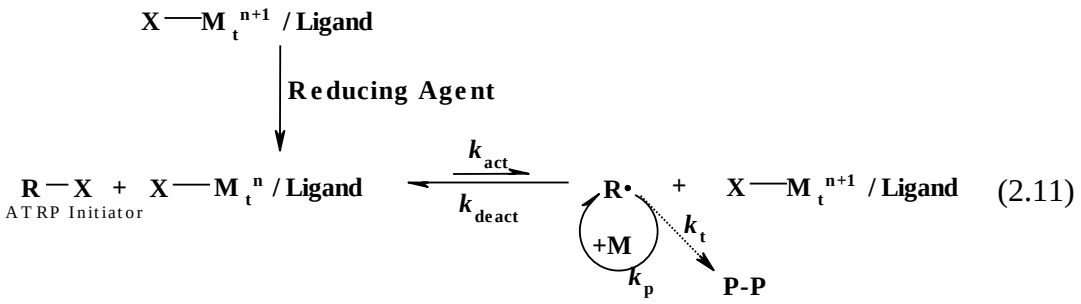
Cu(II), chains initiated by these radicals are always present. These chains derived free radical initiator lead to a partial loss of control over functionality and topology.

2.5 Activator Generated By Electron Transfer (AGET) ATRP

To overcome the problem of unavoidable formation of small amount of homopolymers previously reported reverse and SN&RI ATRP, a new method was developed for activation of the catalyst complex. This new procedure has been termed 'activator generated by electron transfer'. Instead of employing a conventional radical initiator, a reducing agent is used to react with Cu(II) complex and to generate to activator without an involvement of organic radicals which could initiate new chains.

This new method has all the benefits of a normal ATRP process plus the benefit of being able to add the catalyst complex in its more stable higher oxidation state to the rection mixture. One requirement for the catalyst activation is that the oxidatively stable transition metal complex should be quickly and efficiently reduced to the desired degree by a nonradical forming reducing agent. If this condition is fulfilled, the reduction can be conducted *in situ*.

Matyjaszewski and coworkers reported the use of electron transfer reaction to generate Cu(I) as activator employing tin(II) 2-ethylhexanoate ($Sn(EH)_2$) and ascorbic acid as reducing agents [2, 50]. Recently, it was reported that phenols in conjunction with Cu (II) / *N, N, N', N', N''*- pentamethyldiethylenetriamine (PMDETA) complex are successfully used in AGET ATRP of MMA, St, and MA in the presence of limited amount of air [48]. Recently it was reported that, Copper catalyzed LRP of styrene (St) was conducted using the silica gel supported $CuCl_2$/N, N, N', N', N''-pentamethyldiethylenetriamine PMDETA (SG-$CuCl_2$/PMDETA) complex as catalyst. This novel approach is based on *in situ* generation and regeneration of Cu(I) via electron transfer reaction between phenols and Cu(II). Sodium phenoxide or p-methoxyphenol was used as a reducing agent of Cu(II) complexes in LRP [49]. The proposed mechanism for this novel procedure was shown in Scheme 2.11.



(2.11)

2.6 Star Polymers

The synthesis of well-defined star polymers is a challenging task usually achieved following a "living" polymerization route. Branched polymers of controlled architecture have been designed in order to get a better understanding of the relationship between their topology and their unique solution and bulk properties, as compared to linear polymers. Among the branched structures, star polymers represent the most elementary way of arranging the subchains since each star contains only one branching point. There are essentially two methods to get access to star polymers: either by linking a given number of linear chains to a central core ("arm first" method) or by growing branches from an active core ("core-first" method) [51, 52]. To yield stars that would exhibit a precise number of arms, the core-first methodology requires that structurally well-defined plurifunctional initiators be used.

The first report of the core-first technique described the hexakis(bromomethyl)benzene-initiated ATRP of St, methyl acrylate, and methyl methacrylate, but its use was rather limited due to poor solubility in the reaction media [53].

Sawamoto [54] and Gnanou [55] also discussed the use of modified calixarenes as initiators for ATRP. Sawamoto studied the synthesis of homo and block star copolymers. Similarly Gnanou used an octafunctional calixarene composed of 2-bromopropionate moieties in the copper bromide/bipyridyl promoted ATRP of styrene.

To overcome the drawbacks of ATRP as mentioned previously and to show the advantages of AGET ATRP over normal ATRP, this study was carried out. The current work describes the polymerization of St via AGET ATRP applying fructose or ascorbic acid as reducing agents and addresses mechanistic issues such as the parameters affecting the polymerization rate, the molecular weight control etc. Efforts were also made to achieve a better understanding of the utilities of AGET ATRP, well-defined linear and star-shaped block copolymers were synthesized using halogenated ATRP macroinitiator via AGET ATRP.

3. EXPERIMENTAL PART

3.1 Materials

Styrene (St) (Acros, 99%) and *n*-butyl acrylate (*n*BA) (Aldrich, 99%) were purified by passing through a column filled with basic alumina to remove inhibitor, or antioxidant, dried over calcium hydride and distilled under reduced pressure to provide consistent kinetics. Methyl methacrylate (MMA) was obtained from Acros (99%) and purified by passing through a column filled with basic alumina and dried over calcium hydride and distilled under reduced pressure. N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%) was distilled over NaOH under reduced pressure. 4-*tert*-Butylcalix[8]arene (5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene) (TBC-8) (Acros, 97%), triethylamine (Merck, 99%), 2-bromopropionyl bromide (Aldrich, 97%), 1-chloro-1-phenyl ethane (1-PECl) (Acros, 97%), ethyl-2-bromoisobutyrate (EiBr) (Aldrich, 98%), anisole (Acros, 99%), copper(II) chloride ($CuCl_2$) (Fluka, 97%), copper(II) bromide ($CuBr_2$) (Acros, 99%), D-fructose (Merck, 98.5%), L-ascorbic acid (Merck, 99%), ethylene carbonate (EC) (Aldrich, 98%), tetrahydrofuran (THF) (J.T.BAKER, 99.5%), methanol (Technical grade) were used as received. Toluene (Aldrich, 99.5%) was distilled over metallic sodium and stored under nitrogene.

3.2 General Reaction Procedure for Kinetic Studies

Monomer (styrene or *n*-butyl acrylate), ligand, CuX_2 (X: Cl or Br) as a catalyst were added to a 25 mL Schlenk flask equipped with a magnetic stirring bar, and stirred for 5-10 minutes, then fructose or ascorbic acid (used as reducing agents), anisole (as an internal standard for GC), and initiator (1-PECl or EiBr) were added respectively. The first sample was taken for GC before applying freeze-pump-three thaw cycles. Then the reaction flask was charged with argon, immersed in an oil bath thermostated at the

appropriate temperature. The samples were removed from the mixture via syringe in a time interval under inert atmosphere. When the conversion was in the range of 75-85% reaction was stopped by exposing it to air. The kinetic samples were diluted with THF and purified by passing through neutral alumina to remove the copper salt and filtered through polytetrafluoroethylene (PTFE) filter (0.2 lm pore size) prior to GC and GPC measurements.

3.2.1 Effects of Reducing Agent on AGET ATRP

Investigation of AGET ATRP conditions for St polymerization was carried out with two different reducing agents such as fructose and ascorbic acid used several concentrations. To demonstrate the effects of different fructose concentrations on AGET ATRP of St different initiator/catalyst systems (1-PECl/$CuCl_2$ or EiBr/$CuBr_2$) were applied by means of kinetic experiments. The experimental mole ratios of $[St]_0$: $[1\text{-}PECl]_0$: $[CuCl_2]_0$: $[PMDETA]_0$ system were 100 : 1 : 0.5 : 1 with varying fructose ratios in the range of 0.125 and 0.25 with respect to initiator. Similarly, kinetic experiments were applied using fructose with three different concentrations which were 0.05, 0.125, and 0.25 for $[St]_0$: $[1\text{-}PECl]_0$: $[CuCl_2]_0$: $[PMDETA]_0$ system (100 : 1 : 0.5 : 5). The polymerizations were carried out bulk and reaction temperatures were kept constant at 110 ^oC.

Additionally, instead of using 1-PECl/$CuCl_2$ system, EiBr/$CuBr_2$ system was employed in order to better understand the effects of reducing agent concentration on kinetics using fructose with two different ratios (0.05 and 0.125) for $[St]_0$: $[EiBr]_0$: $[CuBr_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ system (30 : 1 : 0.5 : 1 : ***X***). The polymerizations were carried out in toluene (50/50, v/v) and reaction temperatures were kept constant at 110 ^oC.

Similarly, to examine the effects of different ascorbic acid concentrations on AGET ATRP of St two different mole ratios of ascorbic acid ($[1\text{-}PECl]_0$: [Ascorbic acid] = 0.125 and 0.25) were employed for $[St]_0$: $[1\text{-}PECl]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Ascorbic\ acid]_0$ (100 : 1 : 0.5 : 1 : ***X***) system. The polymerizations were carried out in bulk and reaction temperatures were kept constant at 110 ^oC.

The results of these kinetic experiments were represented in Section 4.2.

3.2.2 Effects of Different Ligand Ratios on AGET ATRP

To investigate the effects of different ligand concentrations on AGET ATRP of St employing fructose as a reducing agent, different initiator/catalyst systems (1-PECl/$CuCl_2$ and EiBr/$CuBr_2$) were applied by means of kinetic experiments. PMDETA was used as a ligand. Three different set was prepared with the ratios of ($[M]_0$: $[1\text{-PECl}]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ = 100 : 1 : 0.5 : ***X*** : 0.25) 1, 2.5, and 5 in order to investigate the effects of the amount of PMDETA in AGET ATRP systems. The polymerizations were carried out in bulk and reaction temperatures were kept constant at 110 ^oC. Using ethyl-2-bromoisobutyrate and $CuBr_2$ as initiator and catalyst, respectively, the effects of different PMDETA mole ratios ($[I]_0$:$[L]_0$ = 1 and 5) were also investigated for $[St]_0$: $[EiBr]_0$: $[CuBr_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ (= 30 : 1 : 0.5 : ***X*** : 0.05) system. The polymerizations were carried out in toluene (50/50, v/v) and reaction temperatures were kept constant at 110 ^oC.

Also to investigate the effects of different ligand concentrations on AGET ATRP of St using ascorbic acid as a reducing agent, two different concentrations of ligand were used for $[St]_0$: $[1\text{-PECl}]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Ascorbic\ acid]_0$ (= 100 : 1 : 0.5 : ***X*** : 0.125) system with the ratio of 1and 5 with respect to initiator. The polymerizations were carried out in bulk and reaction temperatures were kept constant at 110 ^oC.

The results of these kinetic experiments were represented in Section 4.2.

3.2.3 Catalyst Effect on AGET ATRP

To examine the effects of the different copper salts on AGET ATRP of *n*-BA in EC, kinetic experiments were applied using fructose as a reducing agent. Either $CuCl_2$ or $CuBr_2$ was used as a catalyst for $[n\text{-BA}]_0$: $[EiBr]_0$: $[CuX_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ system with the ratio of 100 : 1 : 0.25 : 0.5 : 0.5. The reaction temperatures were kept constant at 70 ^oC.

3.3 Synthesis of the Octafunctional Initiator 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis-(2-bromopropionyloxy)calix[8]arene, (1)

It was synthesized by a procedure similar to reported in literature [55]. In a 250 mL two-neck flask, equipped with a magnetic stirrer, 3 g (2.3 mmol) of TBC-8 was suspended in 30 mL of dry THF. Then 7.7 mL of triethylamine (55.2 mmol) was added and the mixture became homogenous upon stirring. The solution was cooled to 0 °C and 5.7 mL (55.2 mmol) of 2-bromopropionyl bromide dissolved in 30 mL of THF were added dropwise over a period of 1h. And then the reaction mixture was stirred at room temperature for 63 h. The solution was concentrated and precipitated in ice cold water. The crude solid compound thus obtained was dissolved in diethyl ether and washed succesively with dilute K_2CO_3 water solution and dried over anhydrous $MgSO_4$. Ether was removed and the concentrate precipitated from a mixture of methanol/water (90/10, v/v). The precipitation was repeated two more times to obtain a white powder of **1** in 82 % yield. ^{1}H-NMR ($CDCl_3$), δ: 7.01 (s, 2H, aromatic protons), 4.34 (s, 1H, −CHBr−), 3.69 (s, 2H, $-CH_2-$), 1.54 (s, 3H, CH_3-), 1.16 (s, 9H, *tert*-butyl).

3.4 Preparation of Linear and Octa-arm Polystyrene (PS) Macroinitiator

3.4.1 Preparation of Linear Polystyrene (PS) Macroinitiator for Block Copolymerization via AGET ATRP Applying Fructose as a Reducing Agent

Into a 25 mL Schlenk tube equipped with a magnetic stirring bar 5mL of styrene (43.6 mmol), 303 μL of PMDETA (1.46 mmol), 163 mg of $CuBr_2$ (0.73 mmol) were added in the order mentioned and stirred for 10 minutes. Then 13 mg of Fructose (0.073 mmol), 5 mL of toluene and last 213 μL of Ethyl-2-bromoisobutyrate (EiBr, 1.46 mmol) were added, respectively. The reaction mixture was subjected to three freeze-pump-thaw cycles. The tube was then placed in an oil bath set at 110 °C for 100 minutes. At the end of this time, the reaction mixture was cooled to room temperature and the contents were dissolved in THF and passed through a column of neutral alumina to remove the copper catalyst from the polymer. The excess of THF was evaporated under reduced pressure. The polymer was precipitated by adding into methanol. The solid product were dried

under vacuum, yielding the desired polymer ($M_{n,\ theo}$ = 1650, $M_{n,\ GPC}$ = 1650, f = 1, M_w/M_n = 1.11 at 52% conversion). The conversion was determined gravimetrically.

3.4.2 Preparation of Linear Polystyrene (PS) Macroinitiator for Block Copolymerization via AGET ATRP Applying Ascorbic Acid as a Reducing Agent

PS macroinitiator was prepared in a separate experiment. St (32 mL, 280 mmol), PMDETA (292 μL, 1.4 mmol), and $CuBr_2$ (156 mg, 0.7 mmol) were added in given order to a reaction flask equipped with a magnetic stirring bar and stirred for 10 min. Then, ascorbic acid (31 mg, 0.18 mmol) and EiBr (204 μL, 1.4 mmol) were added. The mixture was degassed by conducting three FPT cycles and the flask was immersed into an oil bath at 110 °C. After polymerization for 80 min., the mixture was diluted with THF and catalyst was removed by filtration. The resulting polymer was precipitated into excess methanol ($M_{n,\ GPC}$ = 3350, f = 0.94, M_w/M_n = 1.13 at 15% conversion). The conversion was determined gravimetrically.

3.4.3 Preparation of Octa-arm Polystyrene (PS) Star Macroinitiator for Block Copolymerization via AGET ATRP Applying Fructose

Styrene (14.5 mL, 126 mmol), PMDETA (70 μL, 0.34 mmol), $CuBr_2$ (38 mg, 0.17 mmol) were added in the order mentioned into a 25 mL Schlenk flask equipped with magnetic stirring bar and stirred for 10 minutes. Then Fructose (6 mg, 0.034 mmol) and octa-functional initiator (0.1g, 0.042 mmol), (**1**), were added into the reaction mixture, the flask was degassed by freeze-pump-thaw cycles three times to remove dissolved gases. Then the reaction mixture was placed in an oil bath heated at 110 ^oC for 40 minutes. The purification procedure was the same as that used for the above linear PS macroinitiator ($M_{n,\ theo}$ = 14900, $M_{n,\ GPC}$ = 17300, $M_{n,\ NMR}$ = 23850, M_w/M_n = 1.17 at 4% conversion). The conversion was determined gravimetrically.

3.5 Preparation of Linear and Octa-arm PS-*b*-PMMA

3.5.1 Preparation of Linear PS-*b*-PMMA via AGET ATRP Applying Fructose

MMA (3.2 mL, 30 mmol), PMDETA (12 μL, 0.06 mmol), $CuCl_2$ (4 mg, 0.03 mmol) were added were added in given order to a reaction flask equipped with a magnetic

stirring bar and stirred for 10 min. Then, fructose (3 mg 0.015 mmol), toluene (3.2 mL), and linear prepared macroinitiator PS-Br (0.1 g, 0.06 mmol) were added and the mixture was degassed by conducting three FPT cycles. The flask was immersed into an oil bath at 90 ºC. After polymerization for 22 h, the mixture was diluted with THF and catalyst was removed by filtration. The resulting polymer was precipitated into excess methanol. The solid product was dried under vacuum, yielding the desired polymer. ($M_{n,\ theo}$ = 38200, $M_{n,\ GPC}$ = 54950, f = 0.7, M_w/M_n = 1.26 at 73% conversion) The conversion was determined gravimetrically.

3.5.2 Preparation of Linear PS-*b*-PMMA via AGET ATRP Applying Ascorbic Acid

MMA (4.8 mL, 45 mmol), PMDETA (48 μL, 0.23 mmol), $CuCl_2$ (6 mg, 0.045 mmol) were added were added in given order to a reaction flask equipped with a magnetic stirring bar and stirred for 10 min. Then, ascorbic acid (4 mg 0.023 mmol), toluene (4.8 mL), and linear prepared macroinitiator PS-Br (0.3 g, 0.09 mmol; $M_{n,\ GPC}$ = 3350) were added and the mixture was degassed by conducting three FPT cycles. The flask was immersed into an oil bath at 90 ºC. After polymerization for 20 h, the mixture was diluted with THF and catalyst was removed by filtration. The resulting polymer was precipitated into excess methanol ($M_{n,\ theo}$ = 45400, $M_{n,\ GPC}$ = 64400, f = 0.71, M_w/M_n = 1.16 at 84%conversion). The solid product was dried under vacuum, yielding the desired polymer. The conversion was determined gravimetrically.

3.5.3 Preparation of Octa-arm PS-*b*-PMMA Star via AGET ATRP Applying Fructose

MMA (11.84 mL, 111 mmol), PMDETA (12 μL, 0.056 mmol), $CuCl_2$ (4 mg, 0.028 mmol) were added were added in given order to a reaction flask equipped with a magnetic stirring bar and stirred for 10 min. Then, fructose (1 mg, 0.006 mmol), toluene (11.84 mL), and 8-arm prepared macroinitiator (PS-Br star) (0.12g, 0.005mmol; $M_{n,\ GPC}$ = 17300, M_{NMR} = 23850) were added and the mixture was degassed by conducting three FPT cycles. The flask was immersed into an oil bath at 90 ºC. After polymerization for 4h, the mixture was diluted with THF and catalyst was removed by filtration. The resulting polymer was precipitated into excess methanol ($M_{n,\ GPC}$ = 155000, $M_{n,\ theo}$ = 200100, $M_{n,\ NMR}$ = 237400, f =0.84, M_w/M_n = 1.16 at 8% conversion). The solid product

was dried under vacuum, yielding the desired polymer. The conversion was determined gravimetrically.

3.6 Hydrolysis of the Octa-arm PS Star

The prepared octafunctional star polymer ($M_{n,\,GPC}$ = 17300, $M_{n,\,NMR}$ = 23850, M_w/M_n = 1.17), 0.15 g, was dissolved in 15 mL of THF in a 100 mL round-bottomed flask fitted with a condenser and N_2 inlet. Then 10 mL of KOH (1 M solution in ethanol) was added and the charge refluxed for 96 h. The solution was evaporated to the dryness, dissolved in THF, and finally precipitated in methanol and dried.

3.7 UV–vis Measurements

The preparation of a stock solution was given as follows: into a 10 mL of volumetric flask, PMDETA (0.455 mL, 2.18 mmol), $CuCl_2$ (0.0293 g, 0.218 mmol), Fructose (0.0196 g, 0.109 mmol) and water were added. From this homogenous mixture, 0.5 mL of aliquot was diluted to 5 mL and spectrum was immediately measured. A stock solution is then transferred to a 25 mL of flask. The flask was degassed by freeze-pump-thaw cycles three times and charged with nitrogen. The reaction mixture was placed in a thermostated oil bath at 85 ºC. 0.5 mL of aliquots were taken and diluted to 5 mL for UV– vis measurements at given time intervals.

3.8 Characterization

Molecular weights were determined with GPC system (Agilent Model 1100) consisting of a pump and refractive index and UV detectors and four Waters styragel columns (HR5E, HR4E, HR3, and HR2) in series. GPC measurements were conducted using THF as the eluent (flow rate 0.3 mL/min 30 °C). Calibration curve based on polystyrene and polymethylmethacrylate standards were applied for the determination of molecular weights of polymers.

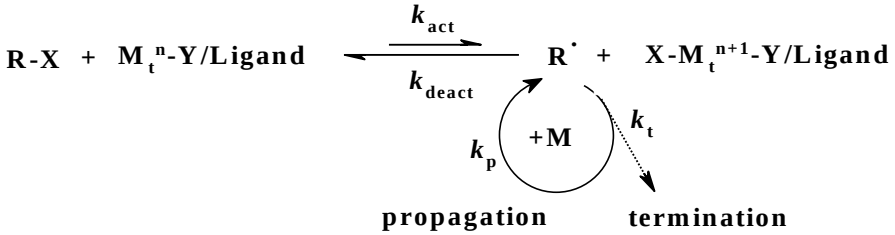
Conversion of monomers was measured using a Unicam 610 gas chromatography with a FID detector equipped with a T&W scientific 15 m DB WAX Wide-bore capillary column. The chromatographic conditions: Injector and detector were kept constant at 280 °C and 285 ºC, respectively. Initial column temperature is 40 ºC, finally reaching up to 120 ºC at a heating rate of 40 ºC/min.

The ^{1}H-NMR spectra was recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard.

UV visible spectra were recorded on a Perkin Elmer λ-2 UV–vis spectrophotometer.

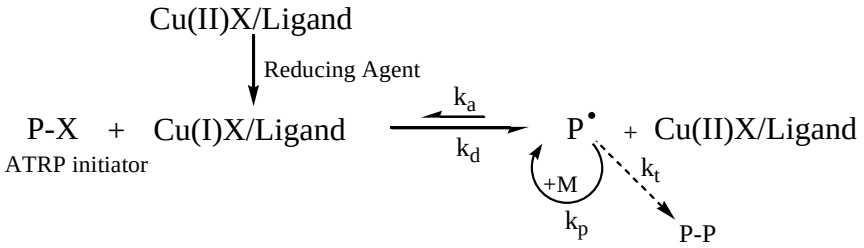
4. RESULTS and DISCUSSION

ATRP is based on the reversible transfer of an atom or group from a dormant polymer chain to a transition metal catalyst (Mt^n) to form a radical species that is able to propagate ($R^{\bullet}$) and oxidize the metal to $X\text{-}Mt^{n+1}$. The growing radicals react reversibly with the oxidized metal complex, $X\text{-}Mt^{n+1}/L$ (deactivator), to re-form the dormant species and the activator [Scheme 4.1].



Scheme 4.1 Mechanism of ATRP

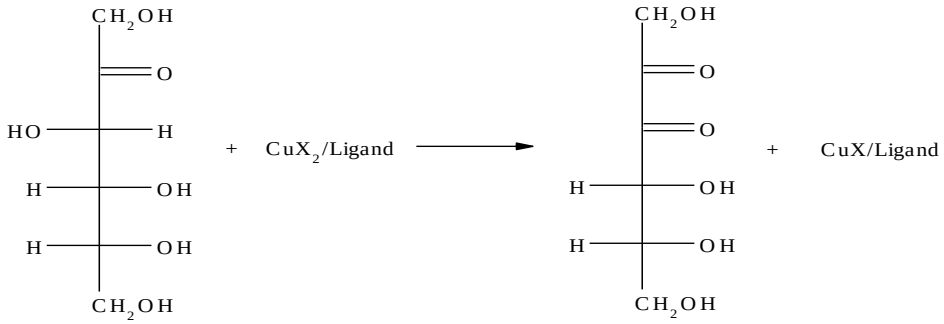
Although ATRP has the usual advantages of radical polymerization, it has some limitations. Since ATRP is initiated by a redox reaction between an initiator with a radically transferable atom or group and a catalyst complex comprising a transition metal compound in a lower oxidation step, the transition metal complexes can be easily oxidized to a higher oxidation step. Therefore, to obtain consistent results, some new methods are required. One of these methods is AGET ATRP which forms the basic concept of this work. Because the ATRP activator is formed from the stable catalyst precursor, reduced by an agent which does not form radicals capable of initiation this new method has been termed "activator generated by electron transfer" ATRP (AGET ATRP) [Scheme 4.2]. This procedure has all benefits of typical ATRP process combined with the additional benefit of applying the catalyst complex to the reaction mixture in its more stable higher oxidation state. The use of oxidatively stable catalyst precursors can allow the more facile preparation, storage, and shipment of ATRP catalyst systems.



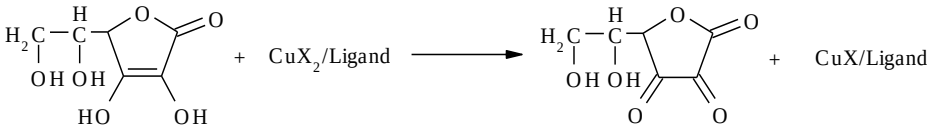
Scheme 4.2 Proposed mechanism AGET process in ATRP

In this study, fructose and ascorbic acid are two of the several possible reducing agents were applied for *in situ* generation of Cu(I) species. These agents can reduce Cu(II) to Cu(I), as shown by Scheme 4.3a-3b. These agents have a crucial role in AGET ATRP. During the *in situ* generation, stable transition metal complex abstracts an electron from fructose and fructose converts into diketone form. Similarly, ascorbic acid is oxidized to yield dehydroascorbic acid, so the required activator Cu(I) which is the key element of ATRP is formed. Kinetic investigations via ATRP reaction of several monomer/catalyst precursor systems were studied (styrene and *n*-butyl acrylate) applying these reducing agents. Additionally, linear and star block copolymers were also synthesized in order to focus on utility and convenience of this type of polymerization.

a.



b.



Scheme 4.3 Oxidation Mechanism of **(a)** Fructose **(b)** Ascorbic acid

A general reaction procedure for kinetic studies was carried out as explained in Section 3.2. The kinetic experiments were employed to demonstrate the effects of ligand and reducing agent (fructose or ascorbic acid) concentrations on AGET ATRP of styrene. Additionally, kinetic studies of *n*-butyl acrylate were applied to show the usage of several monomers in AGET ATRP. Consequently, on the basis of the prepared homopolymers (linear and star) and pure block copolymers, the success of this AGET technique was proved.

4.1 UV–vis Monitoring of Cu(II) Complex Consumption and Cu(I) Complex Formation

Firstly, in order to demonstrate *in situ* generation, UV-vis measurements were applied. UV-vis spectrum of $CuCl_2$/PMDETA/Fructose mixture in water shows a characteristic maxima in the region of 450-900 nm (curve a) in Figure 4.1. The absorption at 620 nm is attributed to d–d band of the Cu(II)-halide. Upon heating the mixture, the maxima gradually decreased (curve b, t = 5 min. later) and after 15 min. the absorption was not observed (curve c). This results pointed out a consumption of Cu(II), which consequently provided to monitor a new absorption at 290 nm (curve c). This is attributed to the characteristic peak of Cu(I)/PMDETA complex at 290 nm. When the reaction was proceeded the maxima at 290 nm gradually increased (curves c-f).

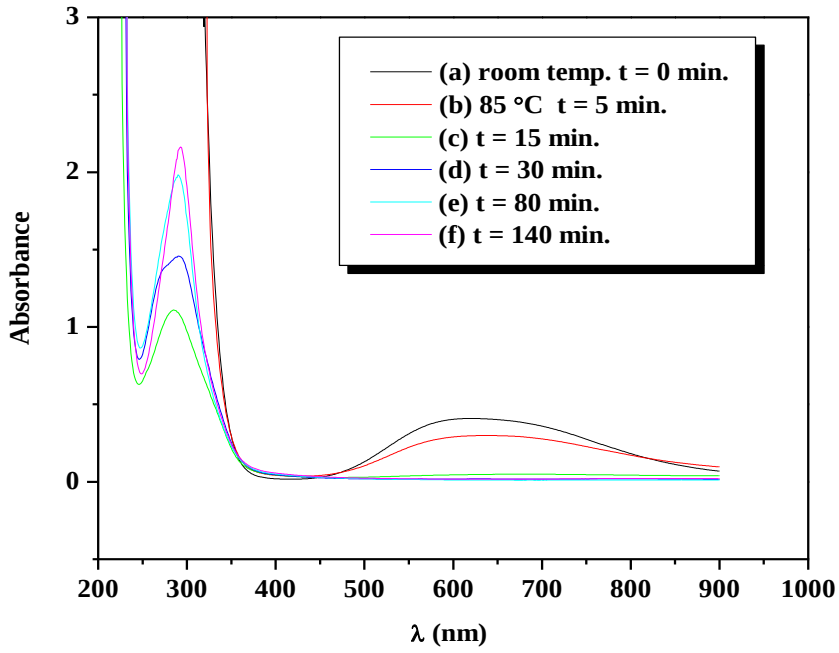


Figure 4.1 UV–vis spectrum of **(a)** $[CuCl_2] = 2.18\times10^{-4}$ M, $[CuCl_2]$: [PMDETA] : [Fructose] = 1 : 10 : 0.5 in water, at room temperature, t = 0; **(b)** t = 5 min. at 85 °C; **(c)** t =15 min.; **(d)** t = 30 min.; **(e)** t = 80 min.; **(f)** t = 140 min.

After *in situ* generation was proved via UV–vis measurements applying fructose as a reducing agent, the kinetic studies of St polymerization via AGET ATRP were started.

4.2 Kinetic Experiments

4.2.1 The Effects of Fructose Concentration on AGET ATRP of Styrene

As previously stated, reducing agent concentration plays an important role in AGET ATRP. In order to explore this parameter, kinetic studies were carried out ($[St]_0$: $[1\text{-}PECl]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ = 100 : 1 : 0.5 : 5 : ***X***) and three different fructose concentrations were applied while keeping all the other parameters constant. The amount of fructose, were varied to define conditions for better control of the polymerization. The amounts of fructose used were 0.05, 0.125, and 0.25 equiv. vs 1-PECl keeping all the other parameters constant. The semi-logarithmic kinetic plot ($ln([M]_0/[M])$ versus time) and number-average molecular weight and polydispersity as a function of conversion are shown in Fig. 4.2 and Fig. 4.3, respectively.

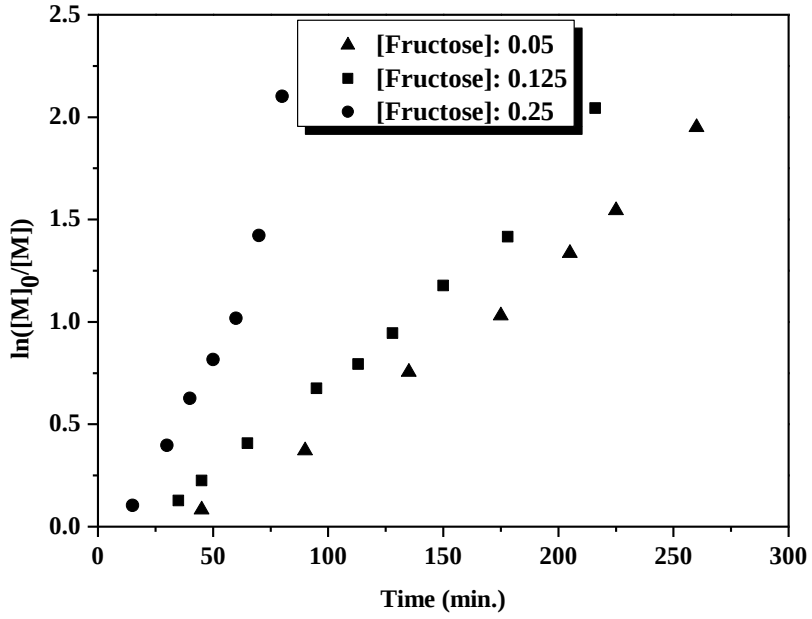


Figure 4.2 The first-order kinetic plot for the bulk polymerization of St in an AGET ATRP at 110 ºC using different concentrations of fructose as a reducing agent. $[St]_0$= 7.26 M; $[St]_0$: $[1\text{-}PECl]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ = 100 : 1 : 0.5 : 5 : ***X***.

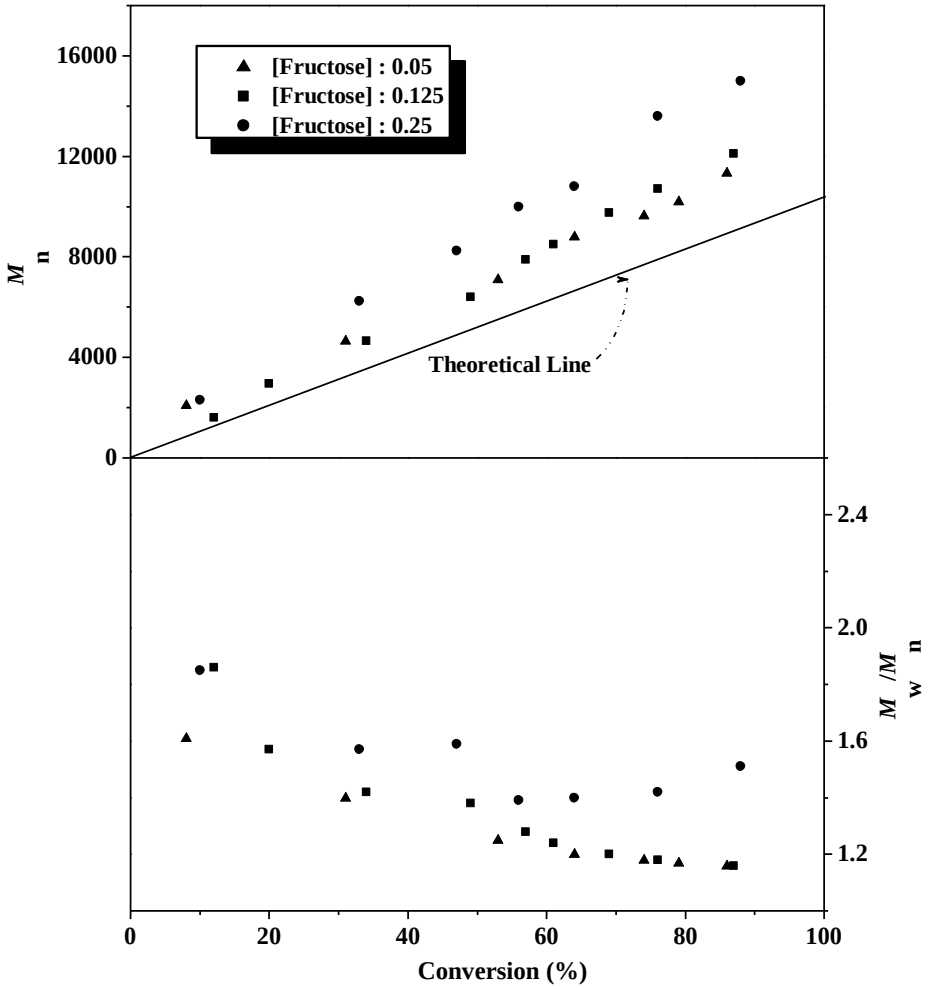


Figure 4.3 The dependence of molecular weight, M_n, and polydispersity, M_w/M_n, upon monomer conversion for the bulk polymerization of St in an AGET ATRP at 110 ºC (Experimental conditions as in **Fig. 4.2**).

All polymerizations were carried out at 110 ^oC. Meanwhile, fructose was completely soluble in the reaction mixture. Although excess amount of PMDETA was applied a green heterogeneous reaction media was observed, which indicated the formation of partially soluble $CuCl_2$/PMDETA complex. Upon heating, the solution gradually became dark green, due to the formation of CuCl/PMDETA complex. The first-order

kinetic plot (Figure 4.2) for the bulk polymerization of St revealed a linear semi-logarithmic relationship between monomer concentration and reaction time meaning that the concentration of the active species was constant during the polymerization. According to semi-logarithmic kinetic plot, one can easily say, increase in fructose concentration not only provides an increase in the rate of polymerization but also results in a decrease in induction period. Within experimental errors, the apparent rate constants (k_{app}) for the AGET ATRP of styrene were estimated from the slopes of the first-order kinetic curves which were 1.34×10^{-4} s^{-1}, 1.50×10^{-4} s^{-1} and, 3.8×10^{-4} s^{-1} with respect to [Fructose]/[1-PECl] ratios which were 0.05, 0.125, and, 0.25, respectively. The molecular weights and polydispersities were measured by GPC. Molecular weight and polydispersity evolutions as a function of conversion were depicted in Fig. 4.3. The molecular weights were higher than the values predicted by the ratio of starting monomer and initiator concentration (i.e., $M_{n,\,theo} = \Delta[M]_0/[I]_0\times MW(\text{of Styrene})$). These can be attributed to the incomplete initiation or some side reactions that take place at the early stages of polymerization. In summary, using high amount of fructose increased the rate of polymerization but it led to poor control over polymerization.

In previous kinetic studies PMDETA concentration was five fold excess compared to typical ATRP conditions. So we decreased the PMDETA concentration and again examine the effect of fructose concentration on the AGET ATRP of styrene, a series of polymerizations were performed for $[St]_0$: $[1\text{-PECl}]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ = 100 : 1 : 0.5 : 1 : ***X*** using two different [Fructose]/[1-PECl] ratios which were 0.125 and 0.25, respectively. The obtained results are shown in Figures 4.4 and 4.5, respectively.

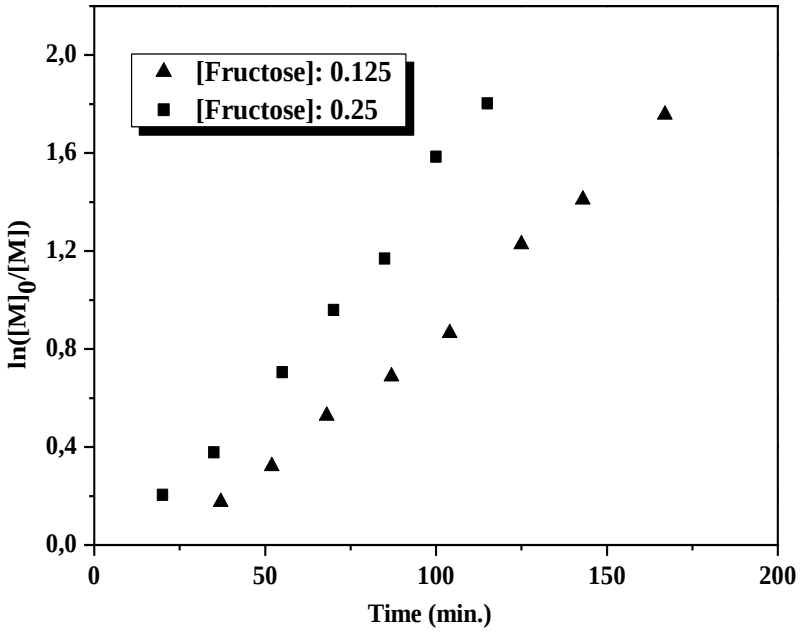


Figure 4.4 The first-order kinetic plot for the bulk polymerization of St in an AGET ATRP at 110 ºC applying different concentrations of fructose as a reducing agent. $[St]_0$= 7.73 M; $[St]_0$: $[1\text{-PECl}]_0$: $[CuCl_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ = 100 : 1 : 0.5 : 1 : ***X***.

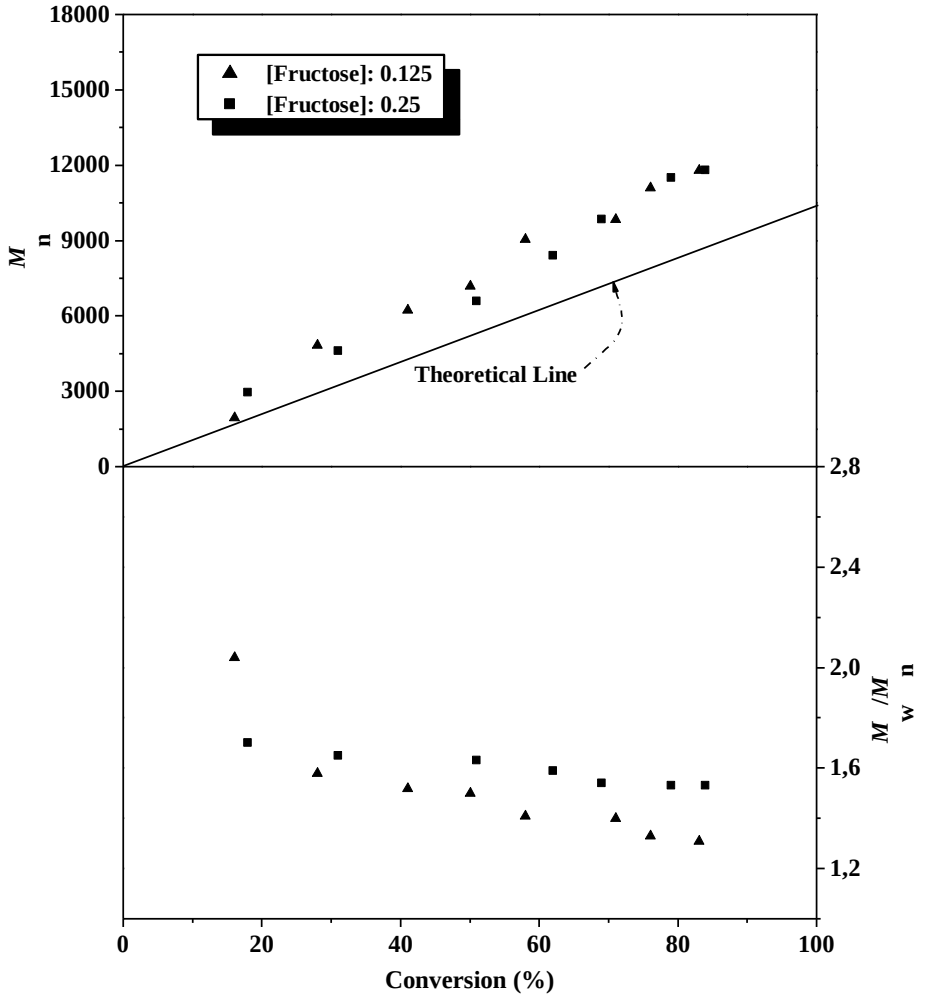


Figure 4.5 The dependence of molecular weight, M_n, and polydispersity, M_w/M_n, upon monomer conversion for AGET ATRP of St at 110 ºC in bulk (Experimental conditions as in **Fig. 4.4**)

As shown in these figures, $\ln([M]_0/[M])$ versus time plots are linear (Fig. 4.4), which indicated that the polymerization rate was first-order with respect to monomer concentration and the active center concentration was constant throughout the polymerization. A decrease in fructose concentration led to a decrease in the polymerization rate as presented in Fig. 4.4. Furthermore, apparent rate constants (k_{app})

for the AGET ATRP of styrene using [Fructose]/[1-PECl] ratios of 0.125 and 0.25 were calculated from the slopes of the $\ln([M]_0/[M])$ versus time plots as 1.73×10^{-4} s^{-1} and 2.76×10^{-4} s^{-1}, in the order mentioned. Also the linear increase in number average molecular weight versus conversion % plot (Fig. 4.5) confirmed that the number of growing chains remained constant during the polymerization. Indeed, determined M_n values were not significantly higher from the predicted theoretical ones at low conversion. However, M_n values deviated from the theoretical values at high conversion. The polydispersity tend to decrease in the case of using lower fructose concentration. On the contrary, polydispersity evolutions remained virtually unchanged when fructose was used at higher concentration.

In order to expand the investigation of AGET ATRP of St, different initiator/catalyst ($EiBr/CuBr_2$) system was applied using two different ratios of fructose with respect to initiator which were 0.05 and 0.125 for $[St]_0 : [EiBr]_0 : [CuBr_2]_0 : [PMDETA]_0 : [Fructose]_0 = 30 : 1 : 0.5 : 1 : \boldsymbol{X}$. Additionally, all the other conditions were kept constant. Both polymerizations were fulfilled in toluene (50/50, v/v) at 110 ºC. The results of these kinetic experiments are shown in Figures 4.6 and 4.7.

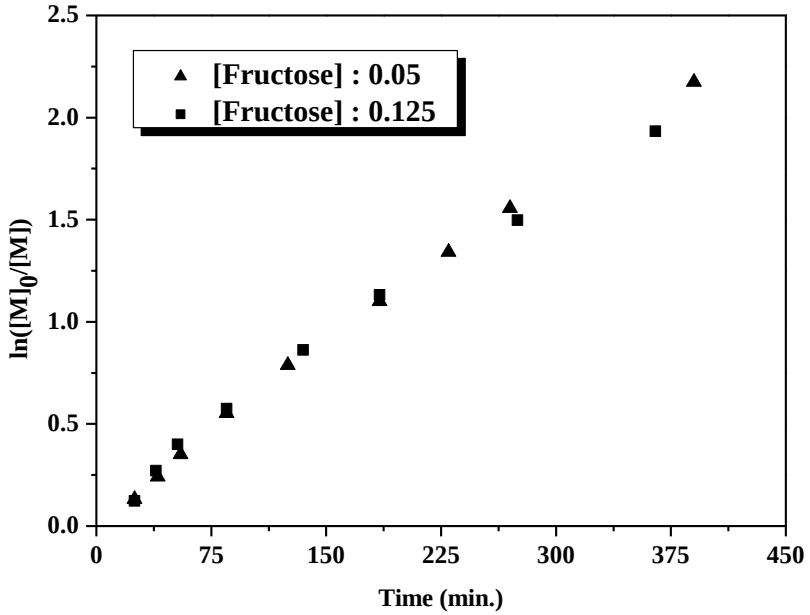


Figure 4.6 The first-order kinetic plot for the solution polymerization of St in an AGET ATRP at 110 ºC in toluene (50/50, v/v) using different concentrations of fructose as a reducing agent. $[St]_0$=3.96 M; $[St]_0$: $[EiBr]_0$: $[CuBr_2]_0$: $[PMDETA]_0$: $[Fructose]_0$ = 30 : 1 : 0.5 : 1 : ***X***.

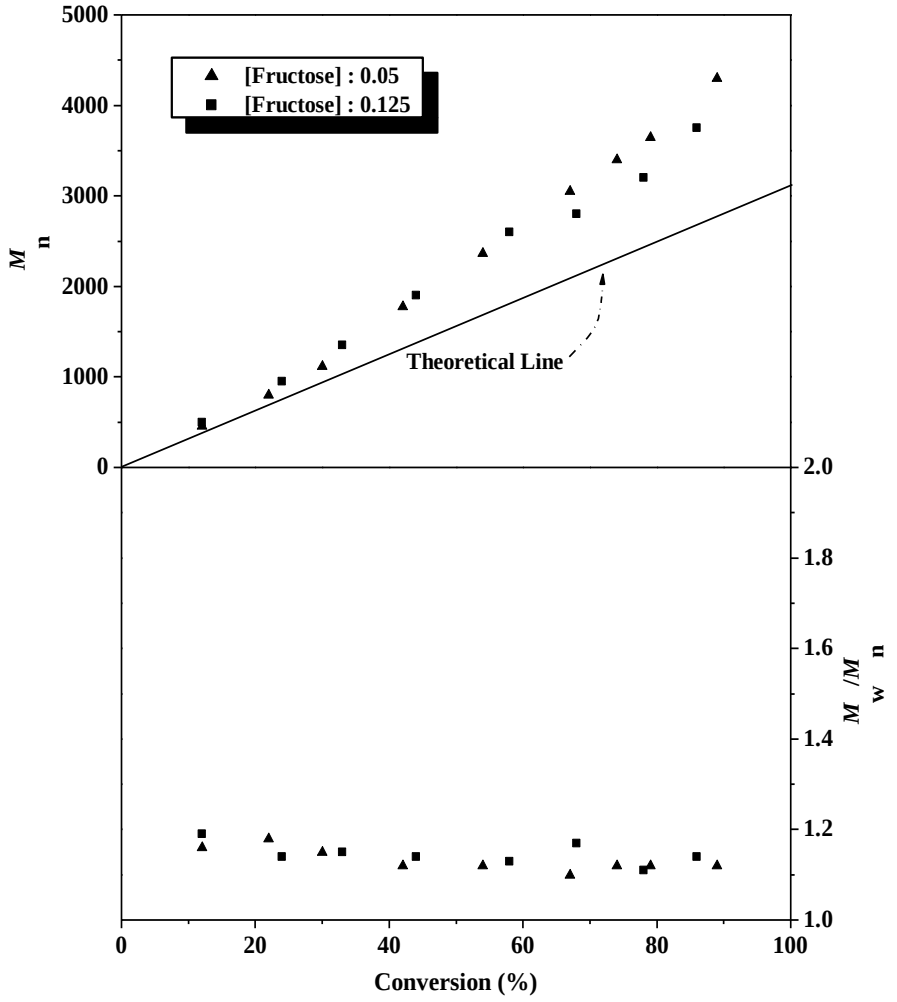


Figure 4.7 The dependence of molecular weight, M_n, and polydispersity, M_w/M_n, upon monomer conversion for AGET ATRP of St in solution at 110 ºC (Experimental conditions as in **Fig. 4.6**)

According to Fig. 4.6, plots of $\ln([M]_0/[M])$ versus time are linear, which confirmed that the polymerization rate was first-order with respect to monomer concentration. On the contrary the obtained results for 1-PECl/$CuCl_2$ system increase in polymerization rate and decrease in induction period was not observed even using more fructose. Apparent rate constants (k_{app}) for the AGET ATRP of styrene with the ratios of fructose 0.05 and 0.125 were calculated 1.08×10^{-4} s^{-1} and 1.03×10^{-4} s^{-1}, respectively. Also the linear

increase in number average molecular weight versus conversion % plot (Fig. 4.7) indicated that the radical concentration remained constant during the polymerization. Molecular weights tend to increase with conversion and the polydispersity remained narrow throughout for each polymerization ($M_w/M_n<1.2$).

4.2.2 The Effects of PMDETA Concentration on AGET ATRP of Styrene Using Fructose as a Reducing Agent

As mentioned in Section 2.2.3, concentration of the ligand is one of the most important parameters for ATRP. Ligands may act to accelerate the atom transfer process by solubilising the catalyst, or by altering redox potential of the catalyst system, or by both. In order to determine the effect of ligand concentration, kinetic studies were carried out applying three different ratios of PMDETA with respect to initiator that were 1, 2.5, and 5 for $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [Fructose]_0 = 100 : 1 : 0.5 : \boldsymbol{X} : 0.25$ while keeping other conditions constant. The results of these kinetic experiments are shown in Figures 4.8 and 4.9.

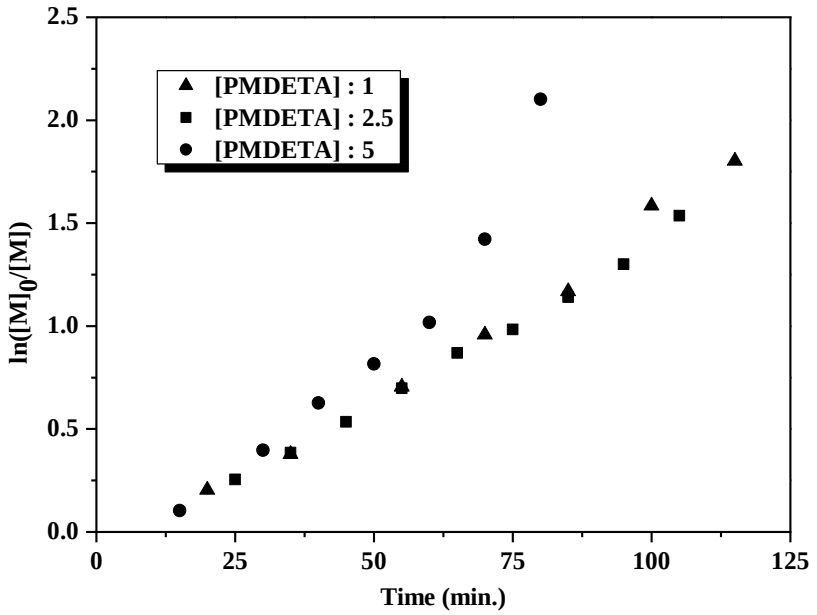


Figure 4.8 The first-order kinetic plot for the bulk polymerization of St in an AGET ATRP at 110 ºC in the presence of various amount of PMDETA. $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [Fructose]_0 = 100 : 1 : 0.5 : \boldsymbol{X} : 0.25$; (▲) 1, $[St]_0 = 7.73$ M; (■) 2.5, $[St]_0 = 7.54$ M; (●) 5, $[St]_0 = 7.26$ M.

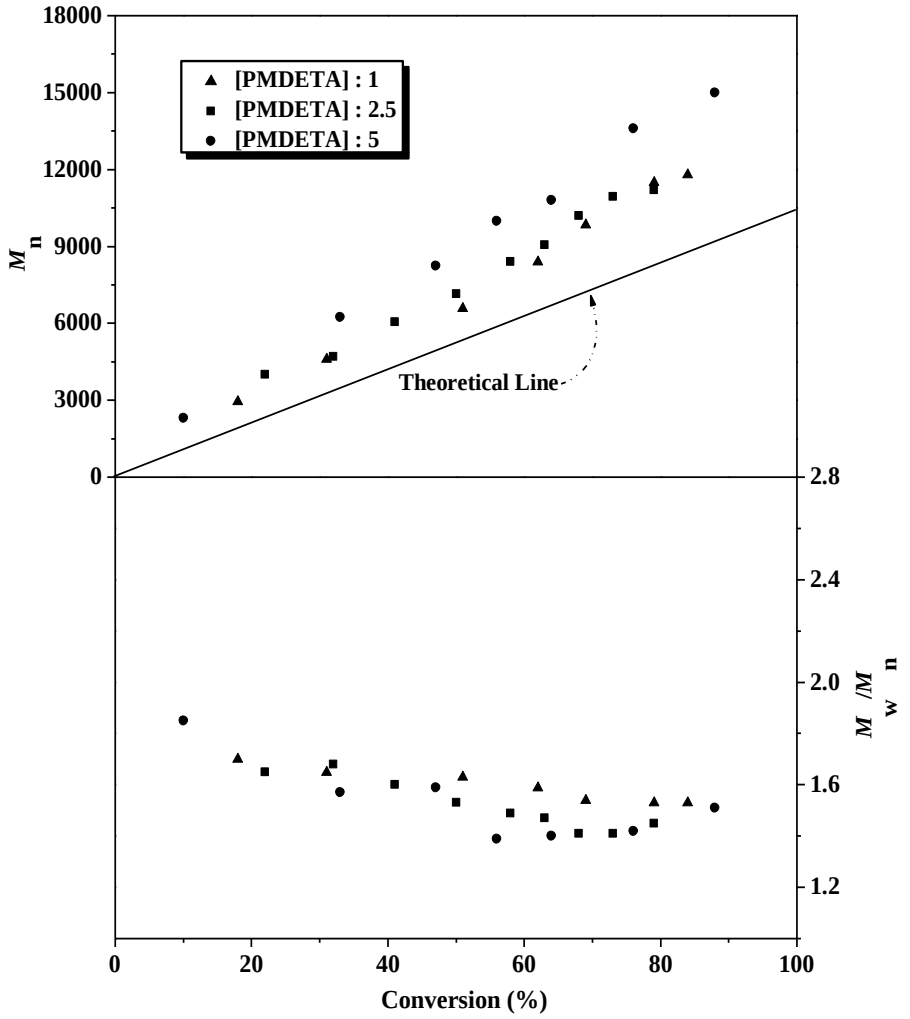


Figure 4.9 The dependence of molecular weight, M_n, and polydispersity, M_w/M_n, upon monomer conversion for AGET ATRP of St at 110 ºC in bulk (Experimental conditions as in **Fig. 4.8**)

Initially, the heterogeneous reaction media was observed and green in colour, which indicates the formation of partially soluble $CuCl_2$/PMDETA complex even in excess amount of PMDETA. Upon heating, the solution gradually became dark green, due to the formation of CuCl/PMDETA complex. Plots of $\ln([M]_0/[M])$ versus time are linear (Fig. 4.8), which confirmed that the polymerization rate was first-order with respect to

monomer concentration and the active center concentration was constant throughout the polymerization. According to Fig. 4.8 and the calculated apparent rate constants (k_{app}) for the AGET ATRP of styrene ([PMDETA]$_0$: 1, k_{app}: 2,76×10^{-4} s^{-1}; [PMDETA]$_0$: 2.5, k_{app}: 2,59×10^{-4} s^{-1}; [PMDETA]$_0$: 5, k_{app}: 3.8×10^{-4} s^{-1}), PMDETA concentration did not influence the rate of polymerization as well as fructose concentration. As shown in Figure 4.8 when the concentration of ligand was varied, k_{app} did not reach an appreciable value until a ratio of approximately 5:1 (ligand-to-initiator). Figure 4.9 shows how molecular weights (M_n) and polydispersity (M_w/M_n) varied throughout the polymerization when different PMDETA concentrations were applied. Molecular weights tend to increase with conversion. Furthermore, deviation from theoretical line was higher for the higher PMDETA concentration. The polydispersity remained high for each polymerization. This can be attributed to the usage of high amount of fructose leads to consumption of higher oxidation state metal salt which should be present in reaction media to maintain the reversible activation deactivation cycle.

Similarly, the amount of ligand, PMDETA, was varied to determine the better conditions in EiBr/$CuBr_2$ system. The amounts of PMDETA used were 1 and 5 equiv vs EiBr for [St]$_0$: [EiBr]$_0$: [$CuBr_2$]$_0$: [PMDETA]$_0$: [Fructose]$_0$ keeping all the other parameters constant. The results of these kinetic experiments are shown in Figure 4.10 and Figure 4.11.

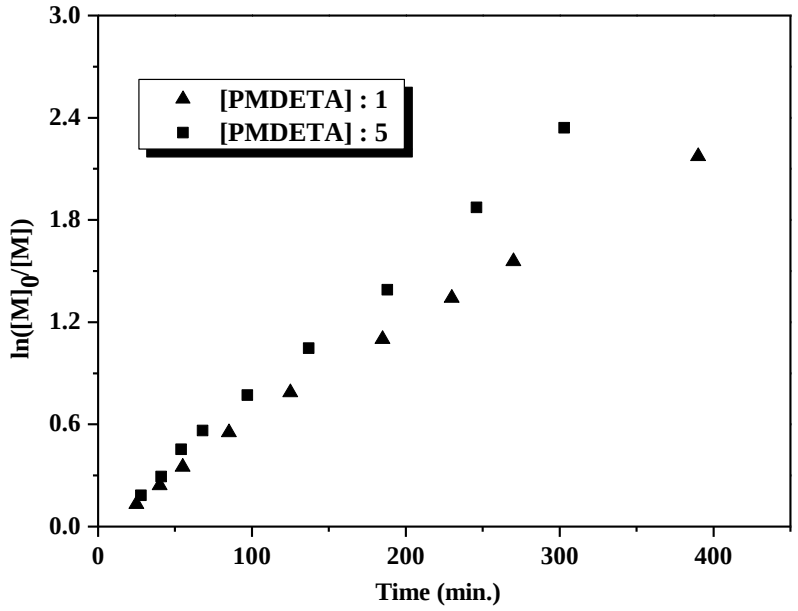


Figure 4.10 The first-order kinetic plot for solution polymerization of St in an AGET ATRP at 110 ºC in toluene (50/50, v/v) using variable amounts of PMDETA as ligand. $[St]_0 : [EiBr]_0 : [CuBr_2]_0 : [PMDETA]_0 : [Fructose]_0 = 30 : 1 : 0.5 : \boldsymbol{X} : 0.05$; (▲) 1, $[St]_0$= 3.96 M; (■) 5, $[St]_0$= 3.57 M.

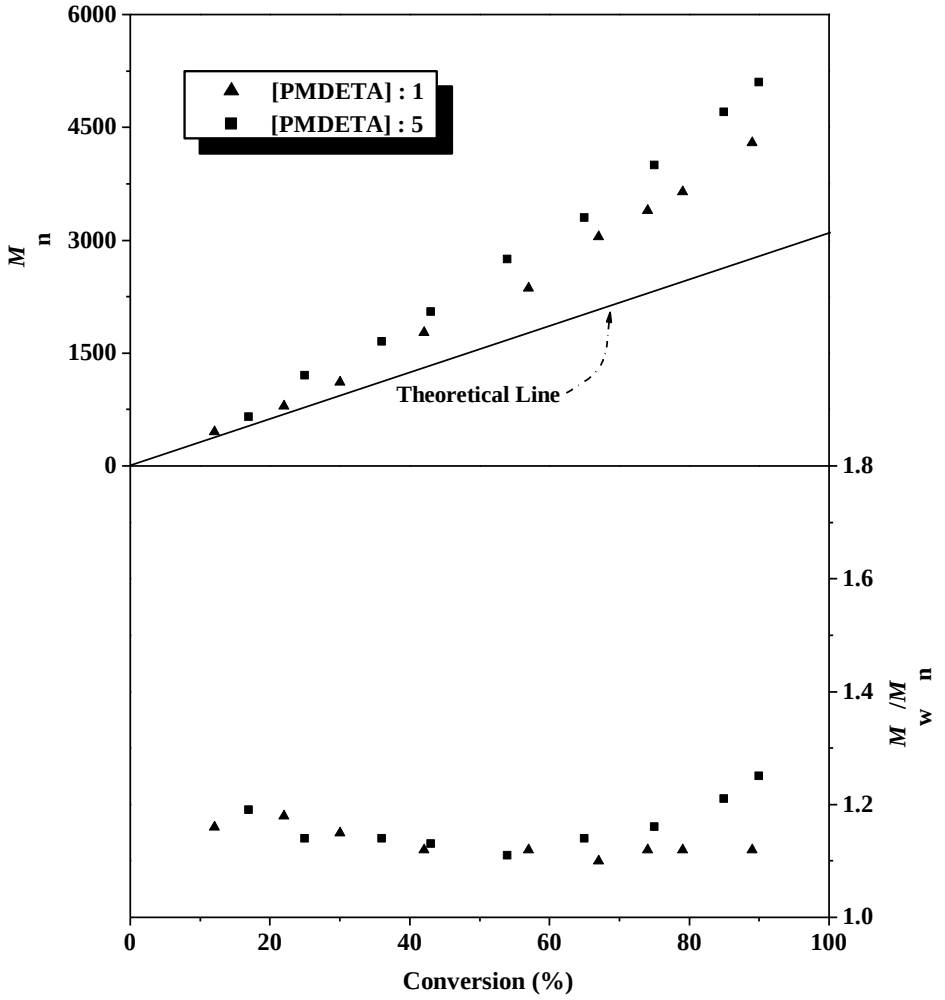


Figure 4.11 The dependence of molecular weight, M_n, and polydispersity, M_w/M_n, upon monomer conversion for AGET ATRP of St at 110 ºC in solution (Experimental conditions as in **Fig. 4.10**)

As shown in Figure 4.10, the obtained results are similar to that of 1-PECl/ $CuCl_2$; plots of $\ln([M]_0/[M])$ versus time were linear, which confirmed that the polymerization rate was first-order with respect to monomer concentration that the concentration of active center was constant throughout the polymerization. Additionally, a decrease in PMDETA concentration led to a decrease in reaction rate as presented in Fig. 4.10 and

the apparent rate constants (k_{app}) for the AGET ATRP of styrene were found 1.08×10^{-4} s^{-1} for $[PMDETA]_0$: 1 and 1.31×10^{-4} s^{-1} for $[PMDETA]_0$: 5. Figure 4.11 shows how molecular weights and polydispersity varied throughout the polymerization when different PMDETA concentrations were used. Molecular weights tend to increase with conversion. M_n values were highest for the highest PMDETA concentration. Similarly, polydispersity were highest for the highest PMDETA concentration.

4.2.3 The Effects of Different Catalysts on AGET ATRP of *n*-Butyl Acrylate

In order to show, AGET ATRP technique can be used for different monomers, kinetic experiments of *n*-BA was carried out. In addition, to examine the effects of the different copper salts on kinetics, two different Cu(II) salts were employed while keeping all the other conditions constant. The experimental conditions and the results of these studies were shown in Fig. 4.12 and Fig. 4.13.

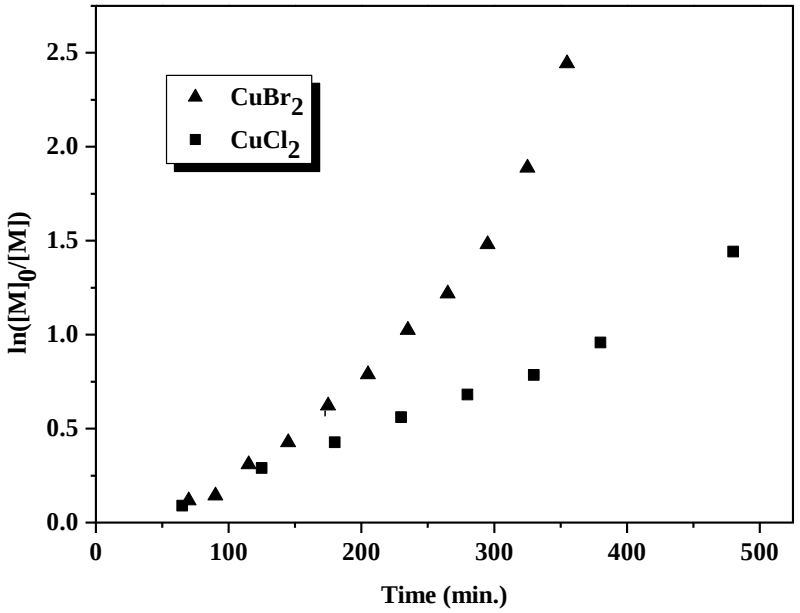


Figure 4.12 The first-order kinetic plot for solution polymerization of *n*-BA in an AGET ATRP at 70 ºC in ethylene carbonate (10/1, v/v) using different copper salts as catalyst. .$[n\text{-BA}]_0$= 5.73 M. $[n\text{-BA}]_0 : [\text{EiBr}]_0 : [\text{Cu}\boldsymbol{X}_2]_0 : [\text{PMDETA}]_0 : [\text{Fructose}]_0$ = 100 : 1 : 0.25 : 0.5 : 0.5.

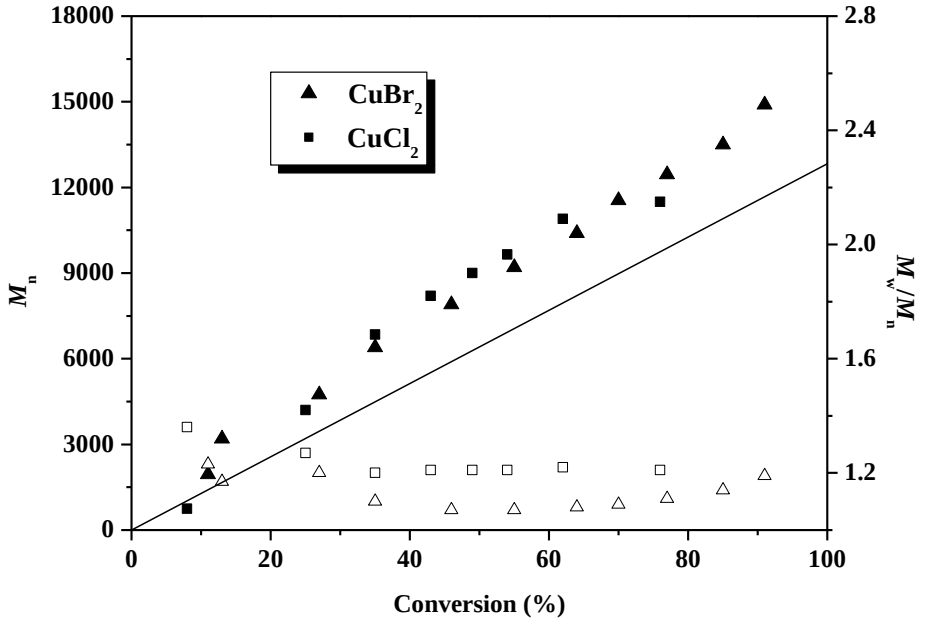


Figure 4.13 The dependence of molecular weight, M_n, and polydispersity, M_w/M_n, upon monomer conversion for AGET ATRP *n*-BA at 70 ºC in solution (Experimental conditions as in **Fig. 4.12**)

Ethylene carbonate (EC) was used as solvent for each polymerization. For both cases (using $CuBr_2$ or $CuCl_2$), the kinetic plots (Fig. 4.12) indicated that the polymerization was first-order with respect to monomer concentration within the experimental errors. The kinetic plot clearly shows that the rate of polymerization is faster when $CuBr_2$ was used as transition metal catalyst. This can be attributed to slower activation of C-Cl bond in comparison to C-Br. Apparent rate constants (k_{app}) for the AGET ATRP of *n*-BA were found 1.01×10^{-4} s^{-1} and 4.38×10^{-5} s^{-1} employing $CuBr_2$ or $CuCl_2$ as a catalyst, respectively. Fig. 4.13 shows how molecular weights (▲,■) and polydispersity(Δ, □) varied during the polymerization when different catalyst were used. The molecular weights also displayed a linear dependence on conversion and polydispersity remained low during the each polymerization ($M_w/M_n < 1.2$). Furthermore, when $CuCl_2$ was used as a catalyst polydispersity was significantly higher.

4.2.4 The Effects of Ascorbic Acid Concentration on AGET ATRP of Styrene

As mentioned before, reducing agents have a crucial role in AGET ATRP. So ascorbic acid was used which a well is known antioxidant. AGET ATRP of St polymerization employing ascorbic acid were carried out using two different ratios of ascorbic acid that are 0.125 and 0.25 (with respect to 1-PECl) for $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [Ascorbic\ acid]_0$ while keeping all the other parameters constant. The experimental conditions and the results of these studies were shown in Fig. 4.14 and Fig. 4.15.

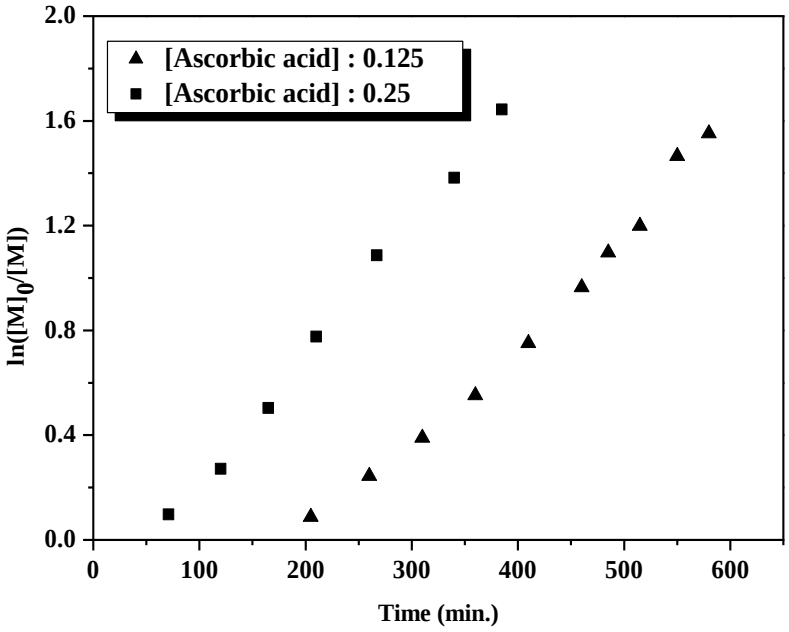


Figure 4.14. The first-order kinetic plot for bulk polymerization of St in an AGET ATRP at 110 ºC using various amounts of ascorbic acid as a reducing agent. $[St]_0$= 7.73 M; $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [Ascorbic\ acid]_0 = 100 : 1 : 0.5 : 1 : \boldsymbol{X}$.

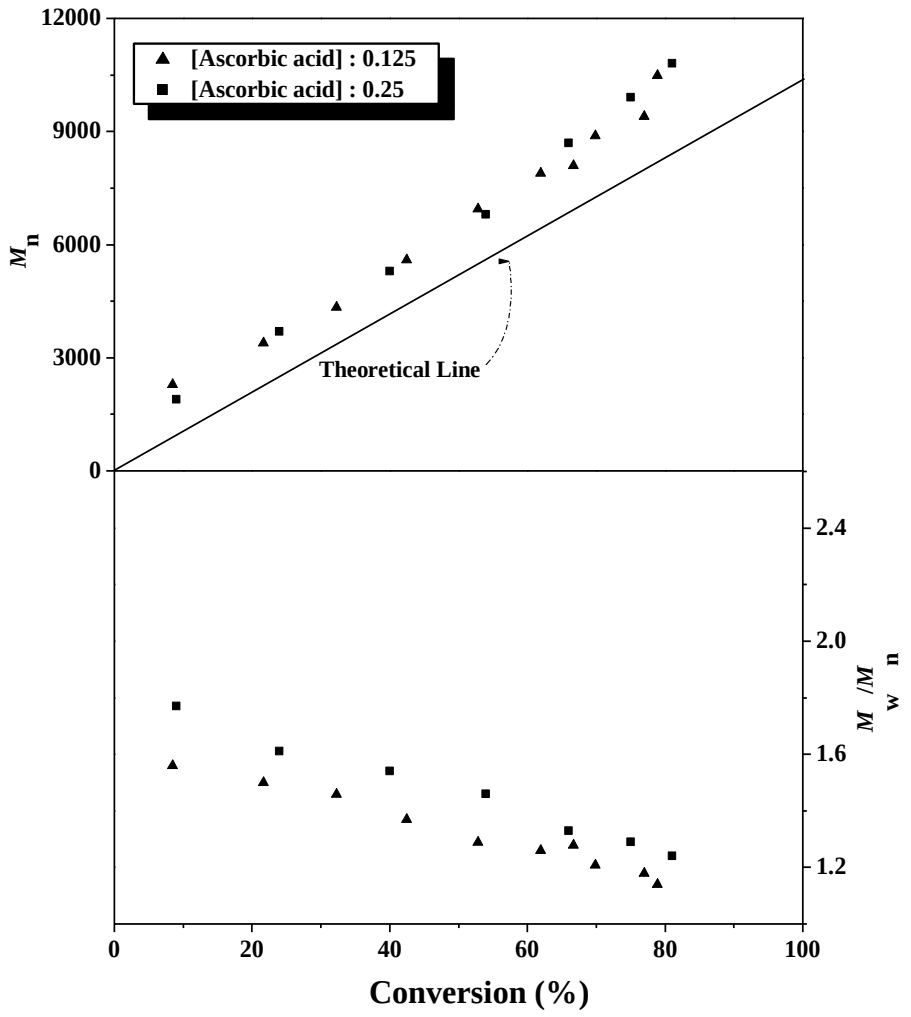


Figure 4.15 Number-average molecular weight and polydispersity evolutions as a function of conversion in an AGET ATRP of St in bulk at 110 ºC (Experimental conditions as in **Fig. 4.14**).

All of the reactions for ATRP of styrene were carried out at 110 ºC. Meanwhile, ascorbic acid was completely soluble in reaction mixture. The first-order kinetic plot (Fig. 4.14) for the polymerization of St revealed a linear semi-logarithmic relationship between monomer concentration and reaction time meaning that the concentration of the active species was constant during the polymerization. According to this result, one can easily say, increase in ascorbic acid concentration provided not only an increase in

polymerization rate but also a decrease in induction period. Apparent rate constants (k_{app}) for the AGET ATRP of styrene were found 5.9×10^{-5} s^{-1} and 8.25×10^{-5} s^{-1} with the ratios of ascorbic acid 0.125 and 0.25 (ascorbic acid to initiator) respectively. Molecular weight and polydispersity evolutions were represented in Figure 4.15. The molecular weights are slightly higher than the values predicted by the ratio of starting monomer and initiator concentration (i.e., $M_{n,\ theo} = \Delta[M]_0/[I]_0\times MW(\text{of St})$). Molecular weights increased linearly with conversion while the polydispersity values decreased during the polymerization. Additionally, a decrease in ascorbic acid concentration led to a decrease in the polydispersities, as presented in Figure 4. 15.

4.2.5 The Effects of PMDETA Concentration on AGET ATRP of Styrene Using Ascorbic Acid as a Reducing Agent

As previously mentioned, ligand concentration is one of the most important parameter for ATRP. In order to determine the effects of this parameter, kinetic studies were carried out with two different ratios that were [PMDETA]/[1-PECl]$_0$: 1 and 5 for [St]$_0$: [1-PECl]$_0$: [$CuCl_2$]$_0$: [PMDETA]$_0$: [Ascorbic acid]$_0$ while keeping other conditions constant. The experimental conditions and the results of these studies were shown in Fig. 4.16 and Fig. 4.17.

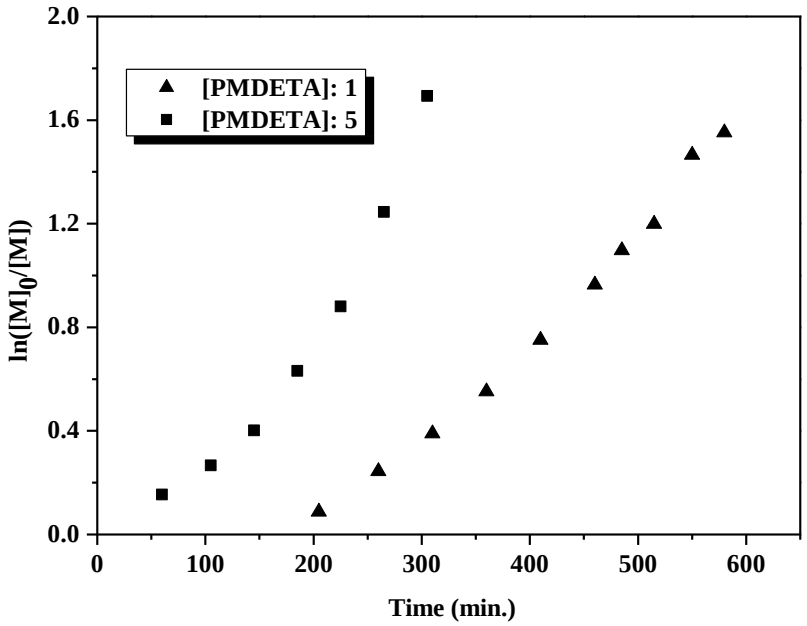


Figure 4.16 The first-order kinetic plot for bulk polymerization of St in an AGET ATRP at 110 ºC in the presence of various amounts of PMDETA as ligand. [St]$_0$: [1-PECl]$_0$: [$CuCl_2$]$_0$: [PMDETA]$_0$: [Ascorbic acid]$_0$ = 100 : 1 : 0.5 : ***X*** : 0.125; (▲) 1, [St]$_0$= 7.73 M; (■) 5, [St]$_0$= 7.26 M.

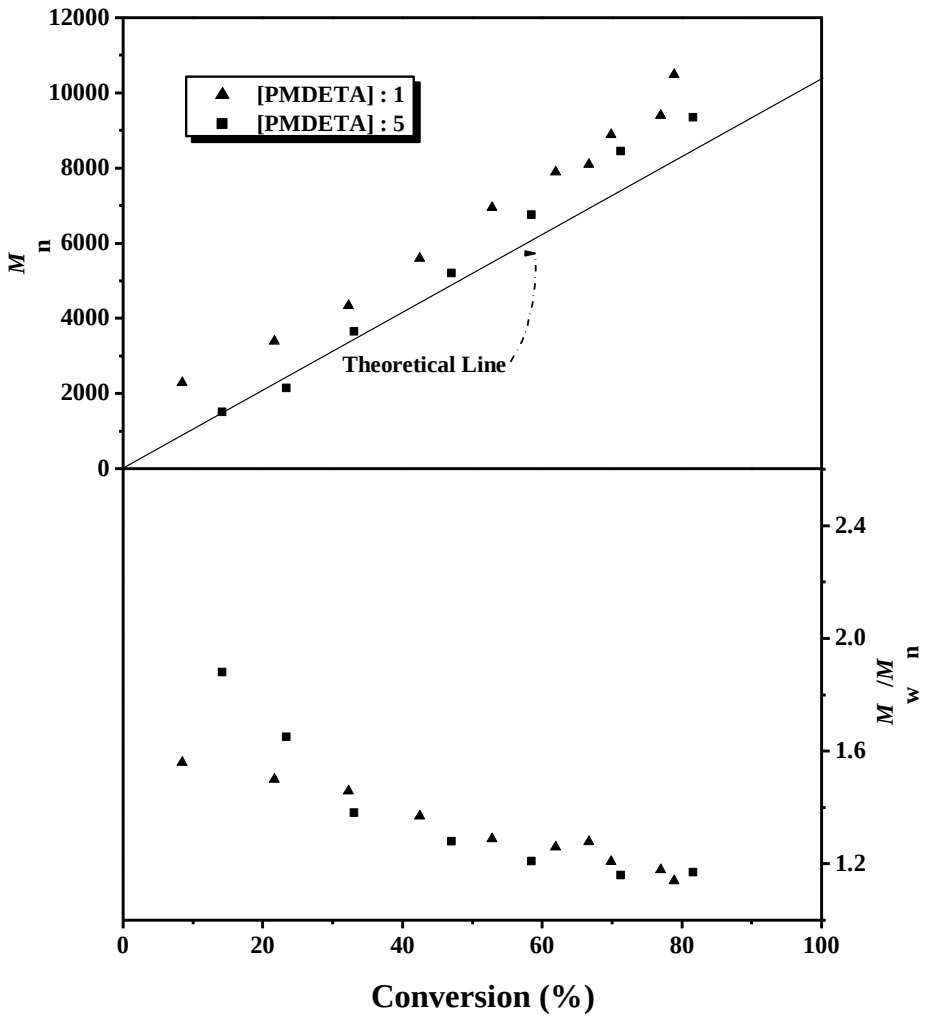


Figure 4.17 Number-average molecular weight and polydispersity evolutions as a function of conversion in an AGET ATRP of St in bulk at 110 ºC (Experimental conditions as in **Fig. 4.16**).

As shown in Figure 4.16, plots of $\ln([M]_0/[M])$ versus time were linear, which indicates that the polymerization rate was first-order with respect to monomer concentration that the active center concentration was constant throughout the polymerization. As predicted, decrease in PMDETA concentration led to a decrease in the polymerization rate and conversely an increase in induction period as presented in Figure 4.16. Additionally, apparent rate constants (k_{app}) for the AGET ATRP of styrene were

calculated 5.9×10^{-5} s^{-1} for the ratio of $[PMDETA]_0$: 1 and 1.2×10^{-4} s^{-1} for the ratio of $[PMDETA]_0$: 5. Figure 4.17 shows how molecular weights and polydispersity varied throughout the polymerization when different PMDETA concentrations were applied. Molecular weights increased with increasing monomer conversion implying that the number of growing chain is constant during the polymerization and polydispersities decreased as well.

4.2.6 Comparison the Efects of Fructose and Ascorbic acid on AGET ATRP of Styrene

Reducing agents have an important role in AGET ATRP which are used to react with Cu(II) complex to generate the activator and consequently to reach ATRP equilibrium. The results of the effects of different reducing agents on kinetic of St polymerization are represented in the range of Fig. 4.18-4.23.

Figure 4.18 and Figure 4.19 present the results of kinetic investigations of St polymerization applying either fructose or ascorbic acid for $[St]_0 : [1\text{-PECl}]_0 : [CuCl_2]_0 : [PMDETA]_0 : [\boldsymbol{X}]_0 = 100 : 1 : 0.5 : 1 : 0.125$ system. The other conditions were kept constant.

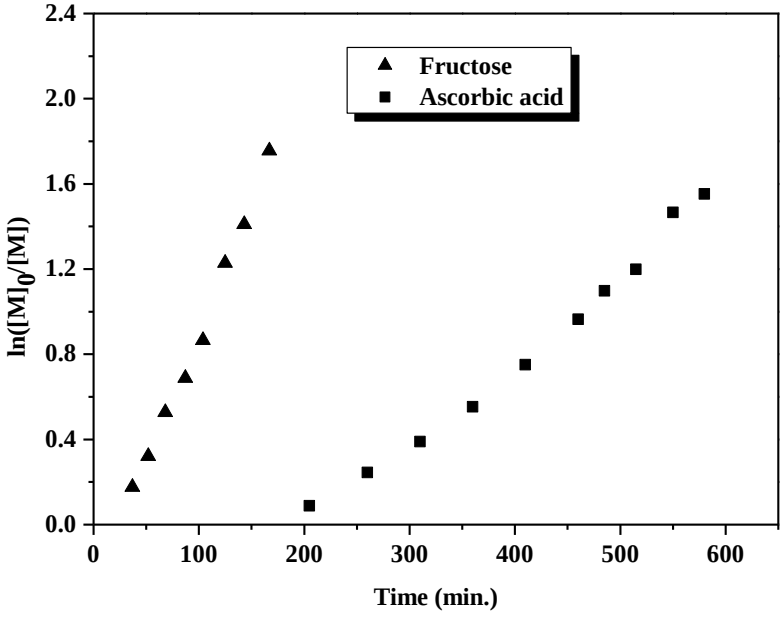


Figure 4.18 First-order kinetic plot of monomer conversion as a function of reaction time for AGET ATRP of styrene at 110 ºC in the presence of using different reducing agents. $[St]_0 : [1\text{-PECl}]_0 : [CuCl_2]_0 : [PMDETA]_0 : [\boldsymbol{X}]_0 = 100 : 1 :0.5 : 1 : 0.125$ $[St]_0$= 7.73 M.

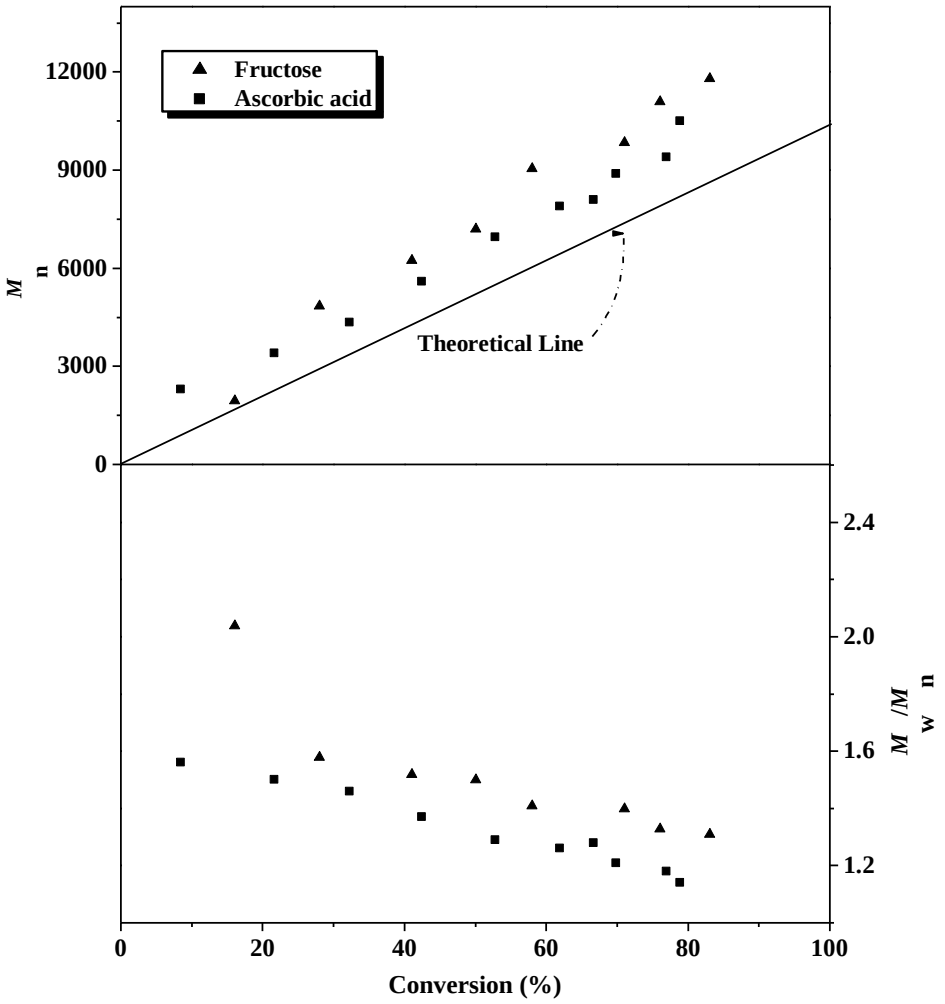


Figure 4.19 Number-average molecular weight and polydispersity as a function of conversion for the bulk polymerization of styrene at 110 ºC (Experimental conditions as in **Fig. 4.18**)

Figure 4.20 and 4.21 show the results of kinetic investigations of St polymerization using either fructose or ascorbic acid as a reducing agent. The ratio of $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [\boldsymbol{X}]_0$ was kept constant as 100 : 1 : 0.5 : 1 : 0.25.

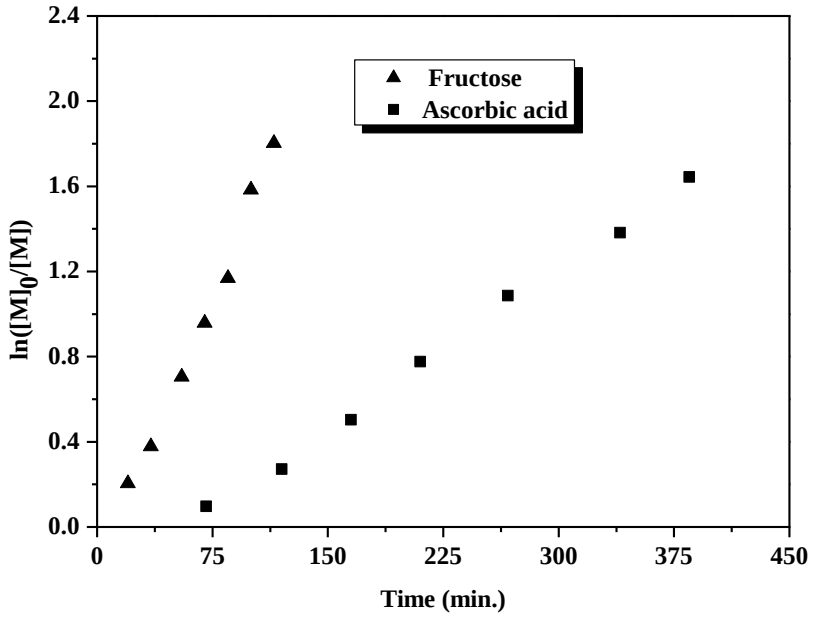


Figure 4.20 First-order kinetic plot of monomer conversion as a function of reaction time for AGET ATRP of styrene at 110 ºC in bulk in the presence of different reducing agents. $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [\boldsymbol{X}]_0$ = 100 : 1 : 0.5 : 1 : 0.25 $[St]_0$= 7.73 M.

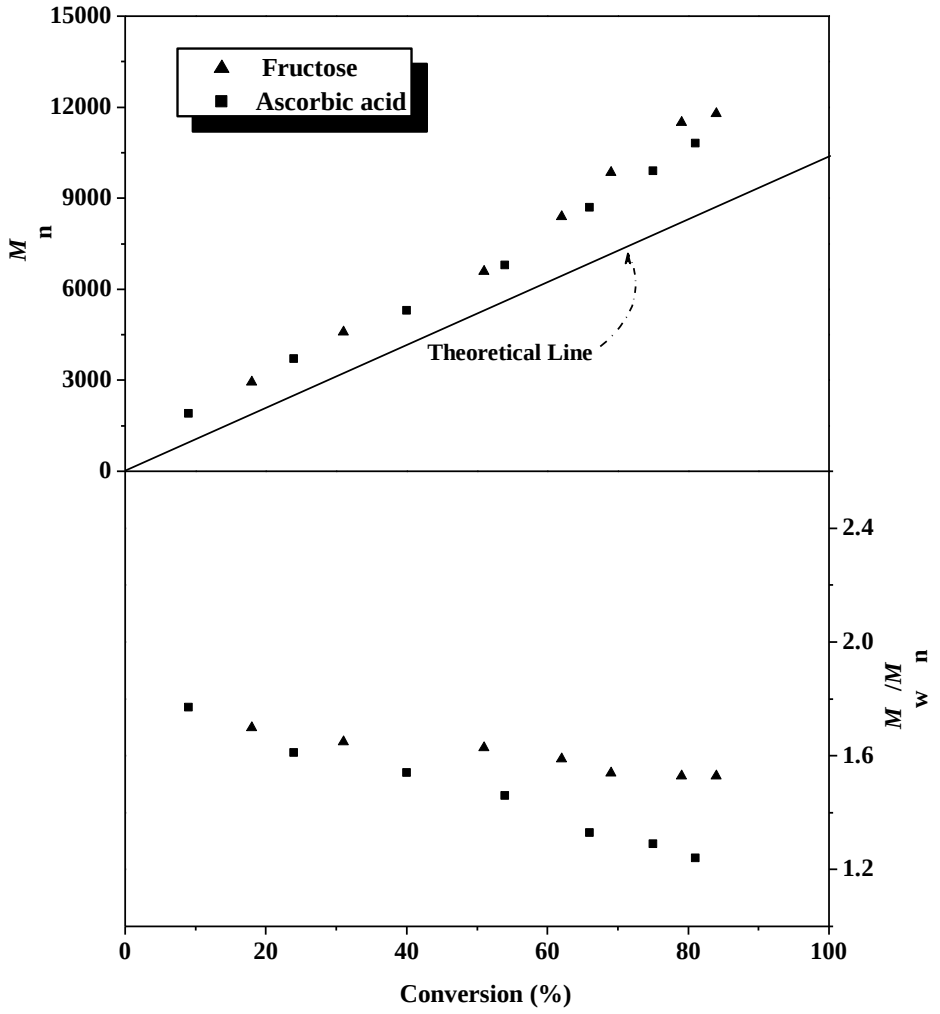


Figure 4.21 Number-average molecular weight and polydispersity as a function of conversion for the bulk polymerization of styrene at 110 ºC (Experimental conditions as in **Fig. 4.20**)

Figure 4.22 and 4.23 show the results of kinetic investigations of St polymerization using either fructose or ascorbic acid as a reducing agent. The ratio of $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [\boldsymbol{X}]_0$ was kept constant as 100 : 1 : 0.5 : 5 : 0.125.

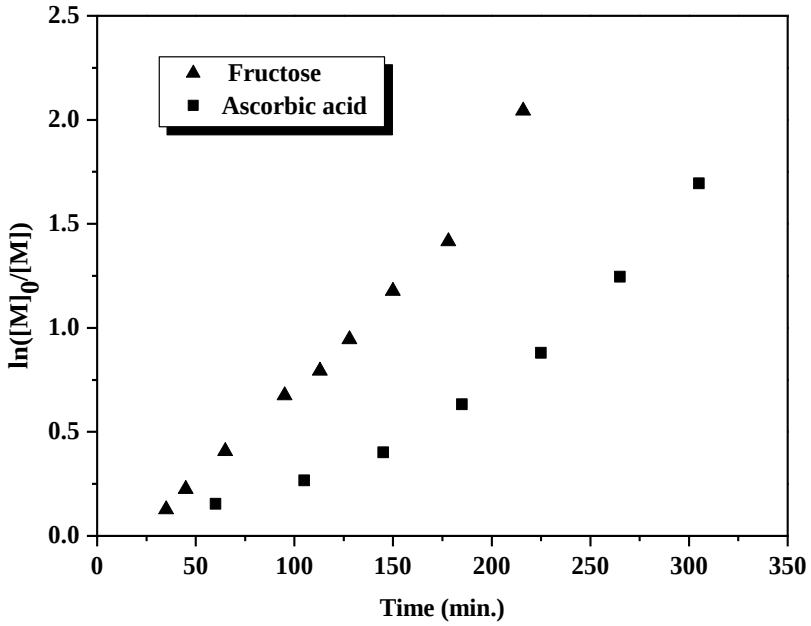


Figure 4.22 First-order kinetic plot of monomer conversion as a function of reaction time for AGET ATRP of styrene at 110 ºC in the presence of different reducing agents. $[St]_0$= 7.26 M; $[St]_0 : [1\text{-}PECl]_0 : [CuCl_2]_0 : [PMDETA]_0 : [\boldsymbol{X}]_0$ = 100 : 1 : 0.5 : 5 : 0.125.

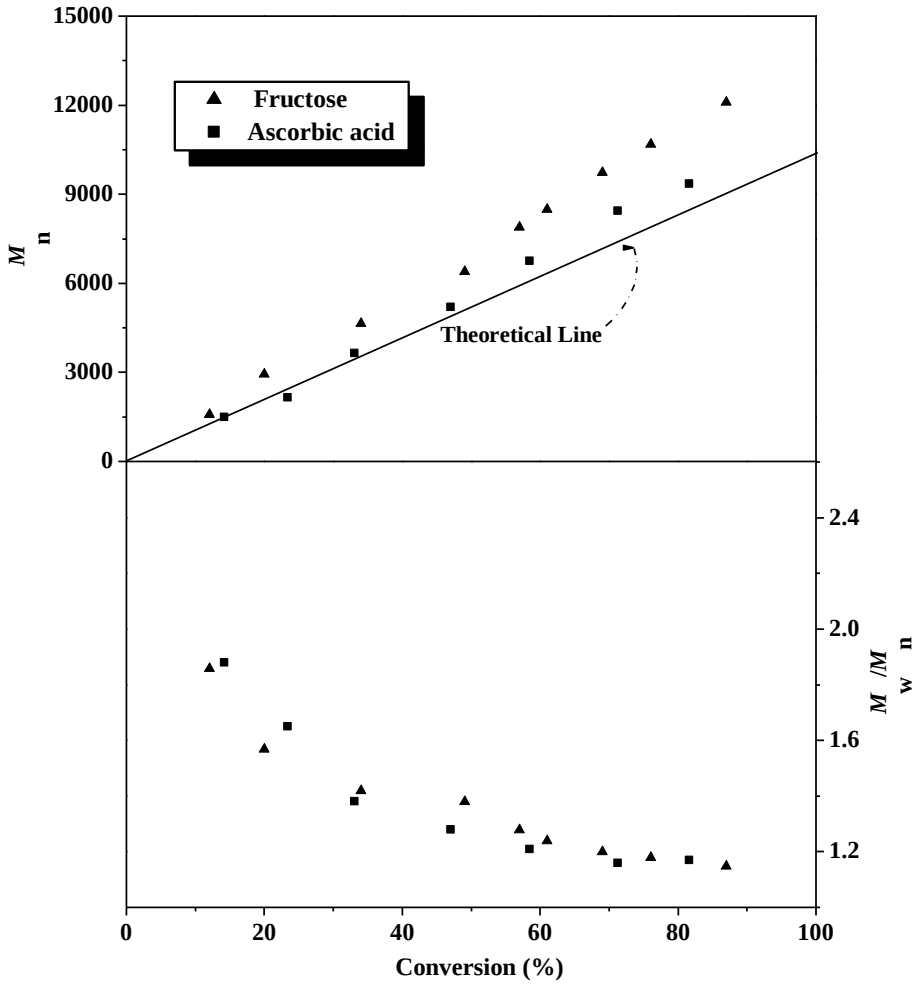


Figure 4.23 Number-average molecular weight and polydispersity as a function of conversion for the bulk polymerization of styrene at 110 ºC (Experimental conditions as in **Fig. 4.22)**

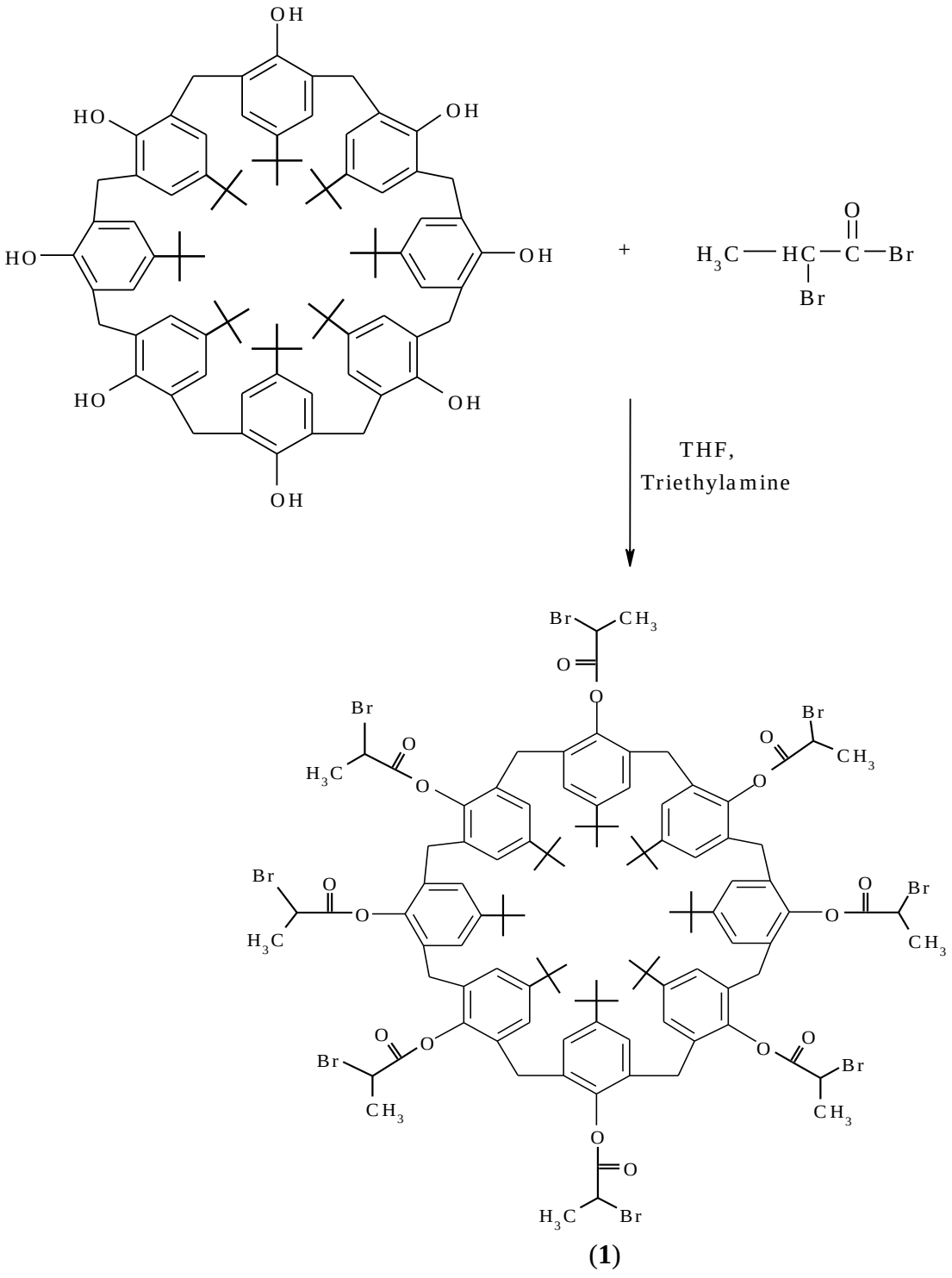
On the basis of Fig.18-20-22, plots of $\ln([M]_0/[M])$ versus time were linear, which indicated that the polymerization rate was first-order with respect to monomer concentration and the active center concentration was constant throughout the polymerization. Additionally, it can be seen from plots of $\ln([M]_0/[M])$ versus time (Fig.18-20-22) that fructose led to a more magnificent enhancement in the rate of polymerization than ascorbic acid. This may be the result of that fructose in general has a larger fraction of its acyclic form in equilibrium with its cyclic form in solution. This results in fructose being more reactive and therefore more effective in reducing the Cu^{2+} species to Cu^{1+}. Also the linear increase in number average molecular weight versus conversion % plot (Fig. 4.19, 4.21, and 4.23) that indicated radical concentration remained constant during the polymerization. Molecular weights tend to increase with conversion and the polydispersity tend to decrease throughout for each polymerizations.

In summary, ascorbic acid is a milder reducing agent compared to fructose, so higher polymerization rate and poor control over polymerization are obtained when fructose is used as reducing agent. This can be the result of the reduction of higher oxidation state metal salt (deactivator) and in the following increasing radical concentration.

4.3 Synthesis of Octafunctional Initiator

4.3.1 Synthesis of Octafunctional Initiator 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis(2-bromopropionyloxy)calix[8]arene (1)

It was synthesised by a procedure similar to this reported by Angot et. al.[55]. The octafunctional initiator, (**1**), was prepared from 4-*tert*-butylcalix[8]arene (TBC-8) and 2-bromopropionyl bromide in ca 82% yield. The obtained initiator, (**1**), was then characterized by ^{1}H-NMR. ^{1}H-NMR spectrum of the initiator showed no signal corresponding to residual phenolic protons of the starting TBC-8, indicating its quantitative esterification (Figure 4.24). ^{1}H-NMR ($CDCl_3$), δ: 7.01 (s, 2H, aromatic protons), 4.34 (s, 1H, −CHBr−), 3.69 (s, 2H, $-CH_2-$), 1.54 (s, 3H, CH_3-), 1.16 (s, 9H, *tert*-butyl).



(1)

Scheme 4.4 Synthesis of 5,11,17,23,29,35,41,47-Octa-*tert*-buty-49,50,51,52,53,54,55, 56-Octakis-(2-bromopropionyloxy)calix[8]arene, (**1**).

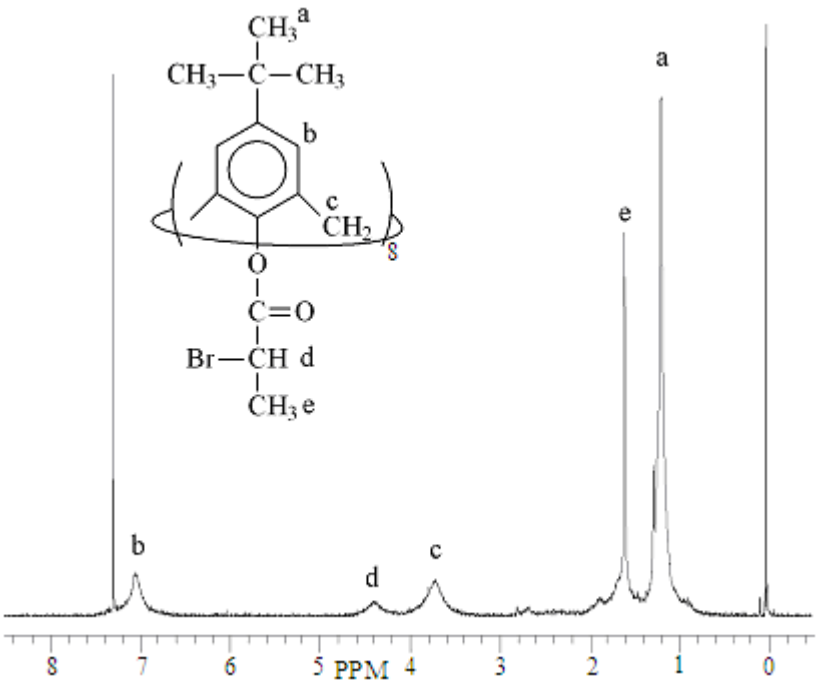


Figure 4.24 The ^{1}H-NMR spectrum of the initiator, (**1**), 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56- Octakis-(2-bromopropionyloxy)calix[8]arene in $CDCl_3$.

4.4 Preparation of Block Copolymers

4.4.1 Preparation of Linear PS Macroinitiators

Experimental conditions and the results of linear PS macroinitiators were represented in Table 4.2. PS macroinitiators were synthesized via AGET ATRP at 110 ºC using different reducing agent such as fructose or ascorbic acid initiated by ethyl 2-bromoisobutyrate.

The experimental number average molecular weights were determined by GPC based on linear PS standards and the theoretical ones were calculated as follows:

$$M_{n,\,theo}\mathbf{: ([M]_0/[I]_0 \text{ x conversion \% x MW(St))}}$$

The conversion was calculated gravimetrically by the following formula:

Conversion% = (W/M) x 100 where;

W: weight of the obtained polymer

M: weight of the monomer initially taken

Size exclusion chromatography (SEC) traces of the obtained polymers displayed narrow and monomodal polydispersity.

Both macroinitiators were synthesized in order to prepare PS-*b*-PMMA.

4.4.2 Preparation of Octa-arm PS Stars

Octa-arm PS stars were prepared by "activator generated by electron transfer" (AGET) ATRP of St using fructose as a reducing agent, and $CuBr_2$/PMDETA as a catalyst system and (**1**) as multifunctional initiator at 110 °C generally in bulk otherwise indicated. The results of these polymerizations are listed in Table 4.1. Consequently, the most appropriate one for synthesizing PS-*b*-PMMA star was chosen (Table 4.1 ,Run 4) from prepared octa-arm PS Stars.

Beyond 15-20% monomer conversion, the probability of occurrence of the irreversible coupling reactions of the growing radicals between different stars will be important. These coupling reactions between two different growing stars which is termed as "intermolecular termination" causes an increase in the molar mass and after one intermolecular termination between two growing stars the resulting polymer constitutes

of 14 branches instead of the expected octa-arm star. Concomitantly, a shoulder appears in the high molar mass side of the SEC traces of the stars which can be attributed to the irreversible coupling of the growing radicals between different stars.

The molecular weight distributions of the obtained polymers remained very low below 15-20% monomer conversion. The GPC traces based on PS standards were unimodal and the experimental number average molecular weights were not exactly in good agreement with the theoretical ones. This is due to the differences in hydrodynamic volume between star and linear polymers.

The theoretical number average molecular weights were calculated by the following formula:

$$M_{n,\,theo}: ([M]_0/[I]_0 \times conversion\% \times MW(St)) + 2378.85\ g/mol$$

Table 4.1 Preparation of Octa-arm PS Stars

Run	$[M]_0$ (mol/L)	$[M]_0/[I]_0$	$[Fructose]_0/[Cu]$	Time (min.)	Conversion (%)	$M_{n,\ theo}$	$M_{n,\ GPC}$	M_w/M_n	f
1	8.48	500	0.1	50	13	9150	8350	1.1	1.1
2	8.48	500	0.2	50	27	16450	22800	1.9	0.72
3	7.62	1000	0.2	45	3	5500	4600	1.03	1.2
4	8.67	3000	0.2	40	4	14900	17300[a]	0.86	1.17
5	8.67	3000	0.2	50	10	33650	29900	1.24	1.13
6	4.35	3000	0.1	100	10	33650	24250	1.48	1.39
7	8.71	6000	0.2	50	3	21150	18600	1.17	1.14

All of the polymerizations were carried out in the absence of air. Bulk polymerization of styrene at 110 °C except run 6, toluene (50/50, v/v) was used. Ligand: PMDETA, [Ligand]/[Cu]: 2, $[I]_0/[Cu]$: 0.25. $CuBr_2$ was used as a catalyst.

$M_{n,\ theo}$: ($[M]_0/[I]_0$ x conversion % x MW(St)) + 2378.85 g/mol. Molecular weights were calculated with linear PS standards. [a] Molecular weight was also calculated from ^{1}H-NMR found 23850.

4.4.3 Preparation of Linear and Octa-arm PS-*b*-PMMA Copolymers

Experimental conditions of linear and octa-arm PS-*b*-PMMA copolymers were represented in Table 4.2. Block copolymers were synthesized via AGET ATRP at 90 ºC applying reducing agents. The results of this copolymerization are listed in Table 4.2.

The synthesis of linear PS-*b*-PMMA copolymers was achieved with bromine-ended PS as macroinitiator via AGET ATRP of MMA employing either fructose or ascorbic acid as reducing agents and $CuCl_2$ as a catalyst. Both copolymerizations were performed at 90 ºC in toluene (50/50, v/v) (Run 8-9, Table 4.2). Figure 4.25 indicates the comparison of GPC traces of linear PS precursor and PS-*b*-PMMA copolymer employing fructose as a reducing agent. Figure 4.26 indicates the comparison of GPC traces of linear PS precursor and PS-*b*-PMMA copolymer employing ascorbic acid as a reducing agent.

Table 4.2 Block Copolymerization from PS to PMMA

Run	Polymer	$[M]_0$ (mol/L)	$[M]_0$:$[I]_0$:$[CuX_2]_0$:$[PMDETA]_0$:[Reducing Agent]$_0$	Time (min.)	Conv. (%)	$M_{n,\,theo}$	$M_{n,exp}$	M_w/M_n	f
8[a]	**PS**	4.15	30:1:0.5:1:0.05	100	52	1650	1650	1,11	1
9	PS-*b*-PMMA	4.67	500:1:0.5:1:0.25	1305	73	38200	54950	1.26	0.7
10[a, c]	**PS**	8.6	200:1:0.5:1:0.125	80	15	3150	3350	1.13	0.94
11[c]	PS-*b*-PMMA	4.65	500:1:0.5:2.5:0.25	1170	84	45400	64400	1.16	0.71
4[b]	**PS**	8.67	3000:1:4:8:0.8	40	4	14900	23850	1.17	0.63
12	PS-*b*-PMMA	4.67	22000:1:5.5:11:1.1	240	8	200100	237400	1.16	0.84

Bold entries describe ([a]) linear and ([b]) octa-arm PS macroinitiators. ([c])Ascorbic acid was used, in the others fructose was used as a reducing agent. [b] **(1)** was used as an initiator for preparing octa-arm PS macroinitiator. Linear macroinitiators were prepared using EiBr as an initiator. $M_{n,\,exp}$ values were calculated from ^{1}H-NMR for octa-arm PS macroinitiator and octa-arm PS-*b*-PMMA. $M_{n,\,exp}$ values were determined by GPC for linear polymers. Theoretical molecular weights were determined as follows: $M_{n,\,theo}$: ($[M]_0/[I]_0$ x conversion % x MW(St)) +MW(PS macroinitiator) for block copolymers.

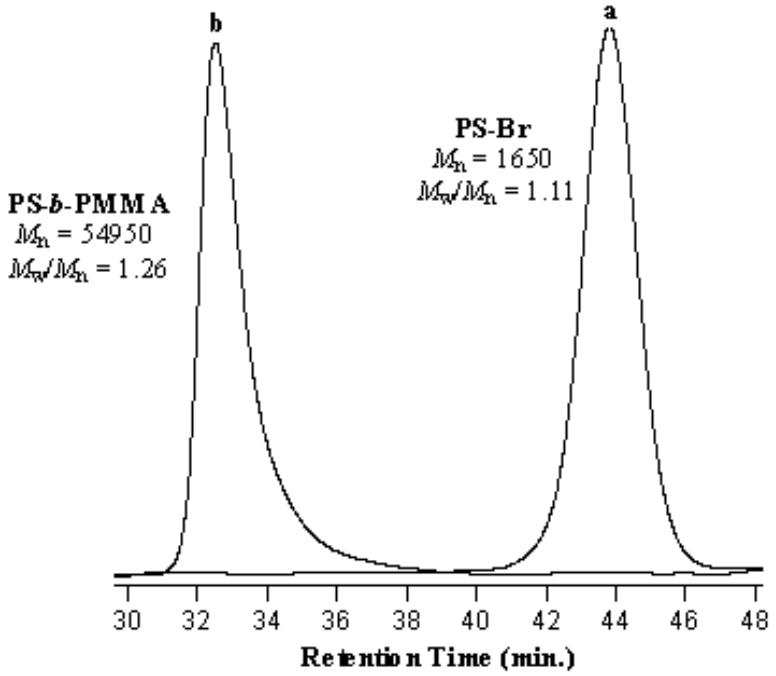


Figure 4.25 GPC traces for linear PS-Br macroinitiator (a, Table 4.2, run 8), and PS-*b*-PMMA (using fructose as a reducing agent) (b, Table 4.2, run 9).

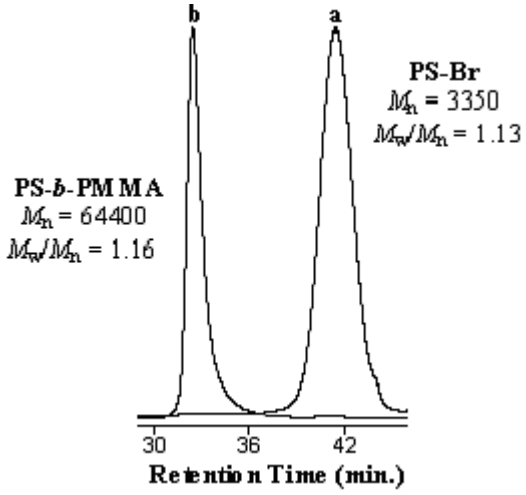


Figure 4.26 GPC traces for (**a**) linear PS-Br macroinitiator (Table 4.2, run 10), and (**b**) PS-*b*-PMMA (Table 4.2, run 11) (using ascorbic acid as a reducing agent).

Peaks corresponding to linear PS-*b*-PMMA copolymers (Fig. 4.25, Fig. 4.26) were clearly shifted to higher molecular weight region.

To obtain a well-defined octafunctional PS-*b*-PMMA copolymer at higher $[M]_0/[I]_0$ ratio (=22000) with lower monomer conversion, octa-arm PS macroinitiator was used

with $[M]_0/[I]_0$ ratio of 3000 and 4% monomer conversion (Table 4.1, run 4). PS-*b*-PMMA star with narrow molecular weight distribution could be synthesized by maintaining the monomer conversion below 15-20%. Figure 4.27 indicates the comparison of GPC traces of octa-arm PS precursor and PS-*b*-PMMA copolymer. The block copolymer contains 3.1% macroinitiator peaks on the GPC traces indicates that the macroinitiator was almost fully converted to block copolymers

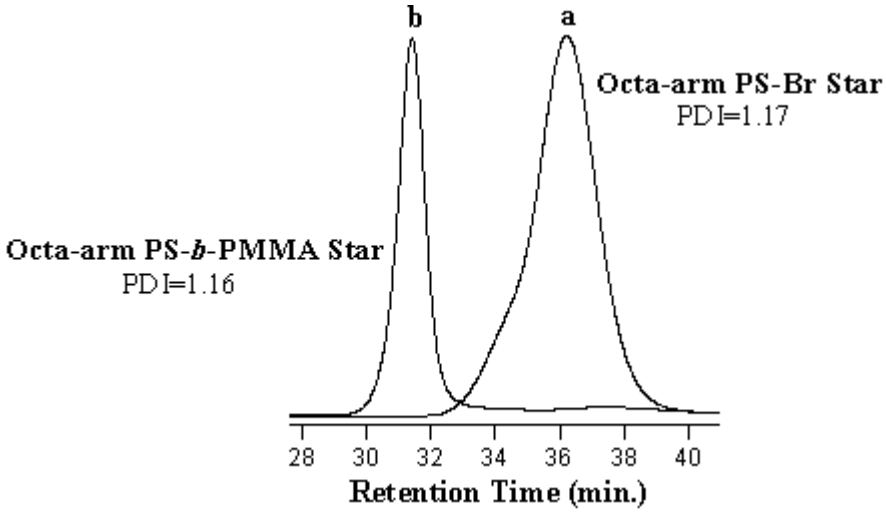


Figure 4.27 GPC traces of (**a**) octa-arm PS-Br star macroinitiator, (Table 4.2, run 4), and (**b**) octa-arm PS-*b*-PMMA star (Table 4.2, run 12).

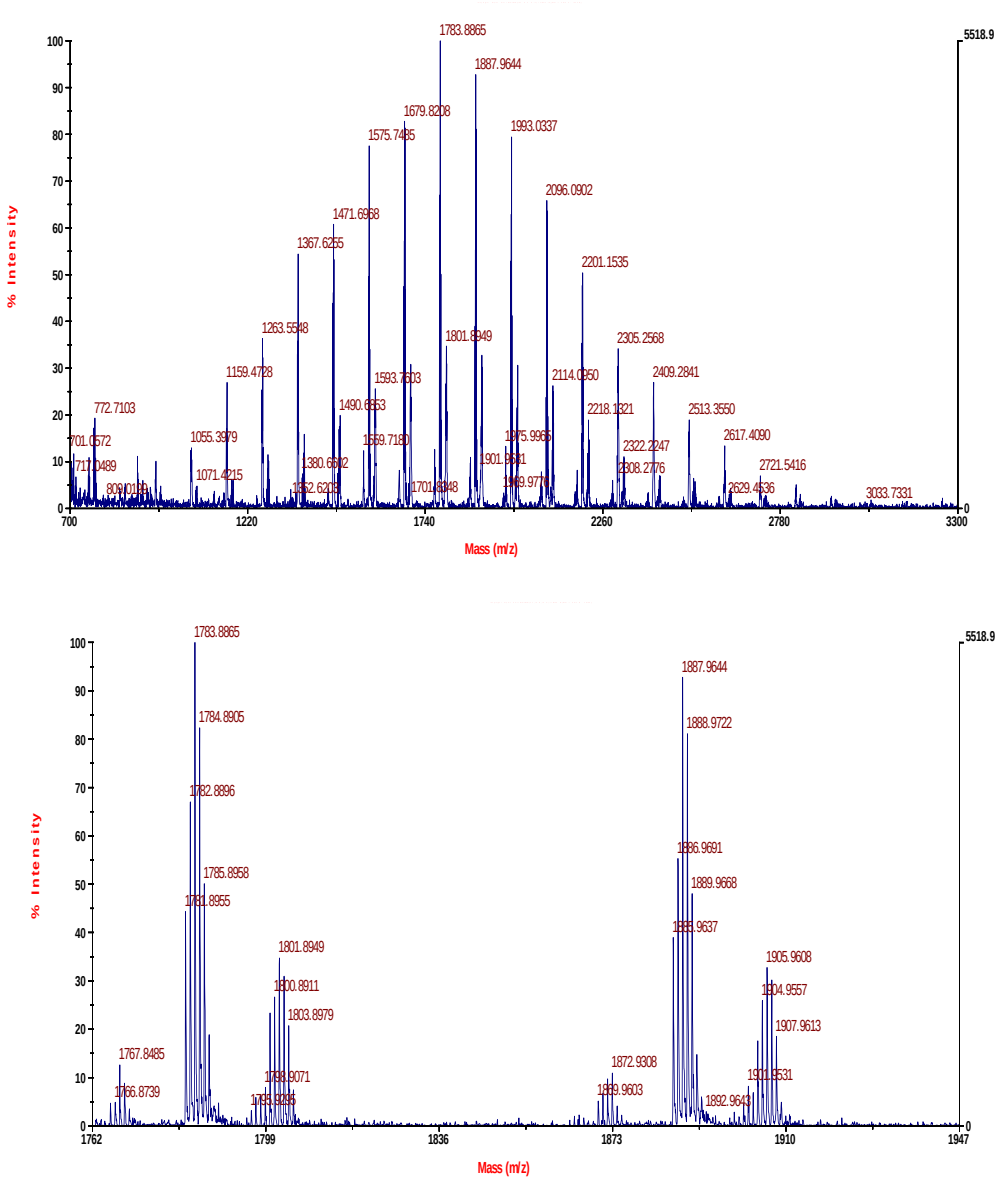
Peaks corresponding to octafunctional PS-*b*-PMMA copolymer (Fig. 4.27, b) were clearly shifted to higher molecular weight region.

According to GPC traces of prepared PS-*b*-PMMA copolymers, peaks corresponding to PS-*b*-PMMA copolymers clearly shifted to higher molecular weight region of the chromatogram indicating that both the chain end functionality of the macroinitiators and the blocking efficiency were high. The block copolymers prepared under these conditions were of low polydispersity and the GPC traces were monomodal. Also GPC traces showed the expected increase in molecular weight through the copolymerization for PS-*b*-PMMA copolymers.

4.5 Characterization of Synthesized Polymers

4.5.1 Characterization of Linear PS Macroinitiator

To confirm the molecular weight and polydispersity of linear PS macroinitiator (Table 4.2, run 8) MALDI-TOF MS was employed. Figure 4.28 shows a typical MALDI spectrum of PS with $M_{n,\,GPC}$ = 1650 and M_w/M_n = 1.11. M_n and M_w/M_n by MALDI are M_n = 1783 and PDI = 1.07, respectively.



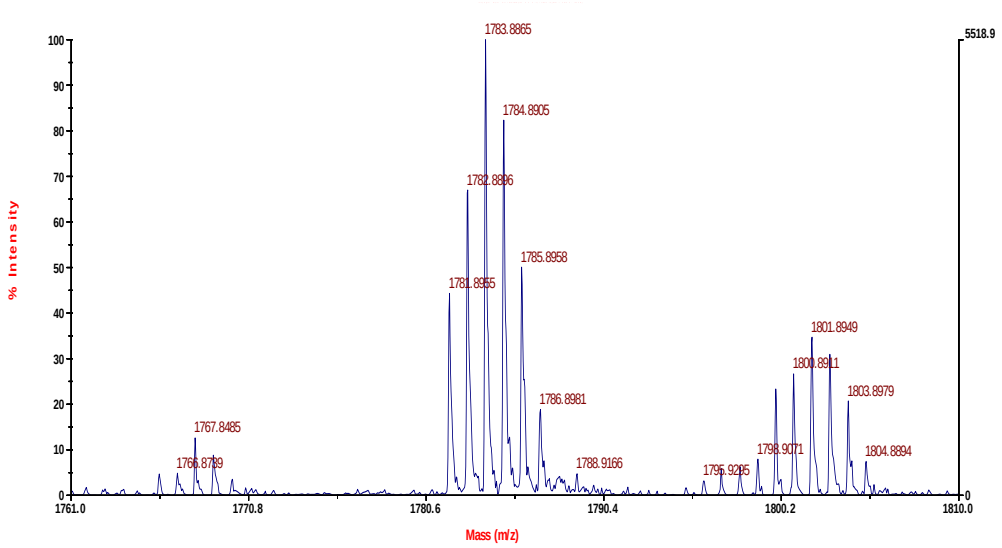


Figure 4.28 MALDI-TOF MS spectrum of linear PS macroinitiator

Molecular weight obtained via MALDI (the main serie) was comparable to obtained via GPC.

[MW(St) × DP (= 15)] + Ag + Br =1750

Two side series was observed with a molecular weight of about 18 dalton higher and a small one with a molecular weight of 16 Da less than the main serie.

4.5.2 Characterization of Octa-arm PS Macroinitiator and Octa-arm PS-*b*-PMMA Copolymer

The ^{1}H-NMR spectrum of the synthesized PS star polymer ($M_{n,\ NMR}$ = 23850) exhibit a signal at 4.5 ppm which can be assigned to the secondary bromine end group – $CH_2\underline{CH}(C_6H_5)Br$ (Fig. 4.29). As to the signal corresponding to the methine proton of the initiator, it has completely disappeared, indicating a quantative initiation. SEC molar masses of PS macroinitiator ($M_{n,\ GPC}$ = 17300) is lower than this obtained by ^{1}H-NMR which clearly demonstrates that the octa-arm PS star obtained from the calixarene-based initiator exhibit a branched structure. However, to better characterize this star and to determine their precise functionality, hydrolysis of this polymer was employed.

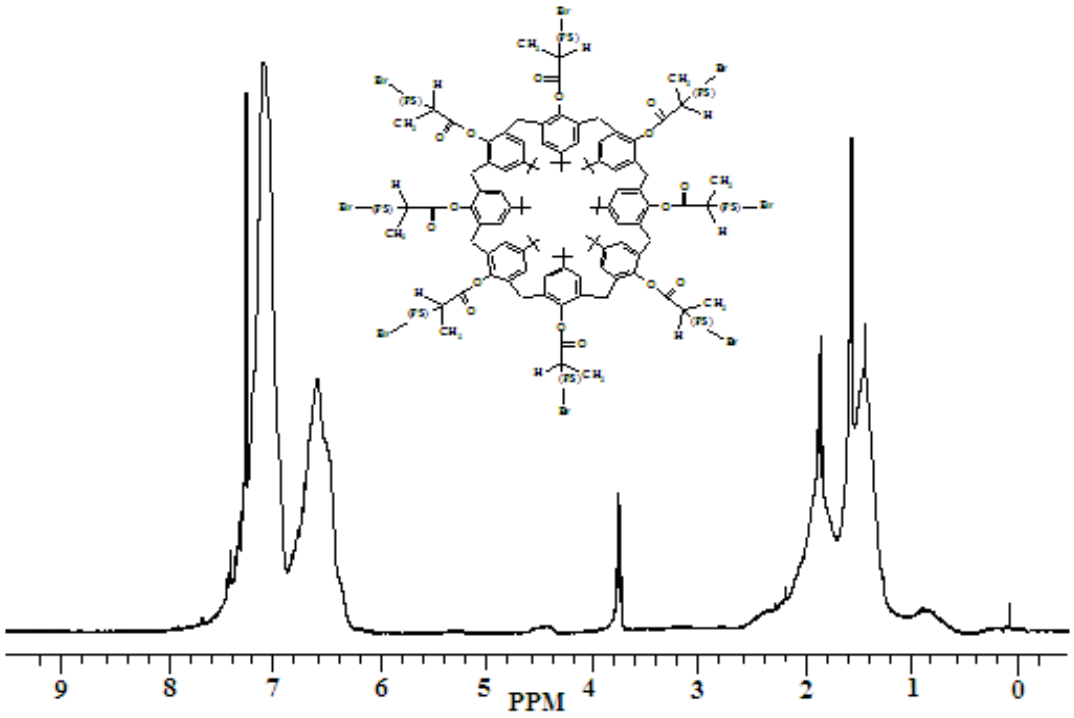


Figure 4.29 The ^{1}H-NMR spectrum of Octa-arm PS Macroinitiator in $CDCl_3$

The molecular weight of octa-functional PS-*b*-PMMA calculated by ^{1}H-NMR spectrum was found 237400. SEC molar masses of PS-*b*-PMMA ($M_{n,\,GPC}$ = 155000) is lower than this obtained by ^{1}H-NMR. The composition of PS-*b*-PMMA (9% PS, 91% PMMA) copolymer was elucidated by ^{1}H-NMR measurement. The ^{1}H-NMR spectrum of PS-*b*-PMMA copolymer (Fig. 4.30) exhibited the major peaks which are characteristic of St and MMA segments. The molecular weight calculated from the integration of signals at 6.5-7.0 ppm of St (5H, aromatic protons) and 3.58 ppm of MMA (3H, -OCH_3) (Fig. 4.25)

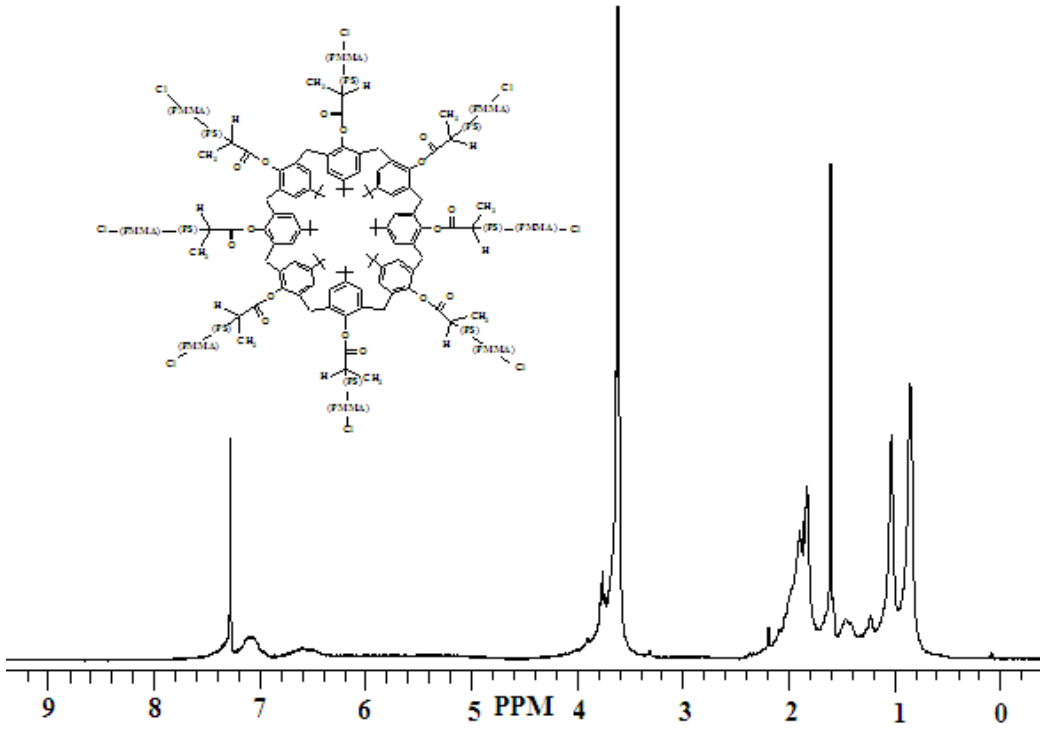


Figure 4.30 The ^{1}H-NMR spectrum of Octa-arm PS-*b*-PMMA in $CDCl_3$

4.5.3 Hydrolysis of the Octa-arm PS Macroinitiator

Core destruction is a useful method to determine the number of branches in star structure. The PS arms are attached to the calixarene core through an ester function that could be cleaved by hydrolysis under basic conditions yielding linear PS. By comparing the molar masses of stars before and after hydrolysis, one can obtain another proof for the star structure. Octa-arm PS star was hydrolyzed using KOH in a mixture of THF and ethanol, and the resulting hydrolyzed polymers were characterized by SEC. The representative SEC traces of the starting well-defined star and the corresponding hydrolyzed polymer are given in Figure 4.31. The SEC traces of the linear polymer obtained after hydrolysis is monomodal. The ratio between the molar masses obtained before ($M_{n,\,NMR}$ = 23850, M_w/M_n = 1.17) and after hydrolysis ($M_{n,\,GPC}$ = 3300, M_w/M_n = 1.44) was found to be close to 8, confirming that the synthesized star exhibit the expected functionality. It appears also that the polydispersity of the star polymer is lower than that of their individual arms.

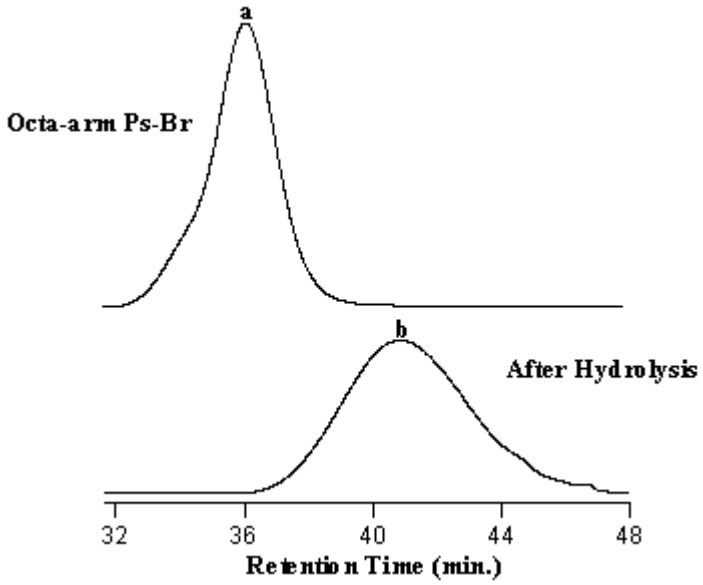


Figure 4.31 SEC traces of polystyrene star ($M_{n,\,NMR}$ = 23850) obtained using [M]/[**1**] of 3000 **(a)** before and **(b)** after hydrolysis of the ester function.

5. CONCLUSION

The universal character of AGET ATRP was investigated by polymerization of styrene with different initiator/catalyst system and different reducing agents: styrene with 1-PECl/$CuCl_2$ applying either fructose or ascorbic acid additionally with EiBr/$CuBr_2$ applying fructose. The kinetic experiments were employed to demonstrate the effects of ligand and reducing agent (fructose or ascorbic acid) concentrations on AGET ATRP of styrene. Additionally, kinetic studies of *n*-butyl acrylate applied with different catalyst systems was showed the usage of several monomers in AGET ATRP.

On the basis of kinetic experiment results, ascorbic acid is a milder reducing agent compared to fructose, so that higher polymerization rate and poor control over polymerization was obtained when fructose was used as reducing agent for styrene.

In addition, a novel calixarene-based octafunctional initiator, (**1**), was synthesized by an esterification reaction between p-*tert*-butyl-calix[8]arene and 2-bromopropionylbromide in one step and succesfully used in the preparation of the octa-arm star block copolymer.

Linear and Octa functional PS-*b*-PMMA copolymers were synthesised via AGET ATRP. Halogen exchange was employed to enhance the rate of cross propagating where well defined bromine ended PS was used as macroinitiator for methylmethacrylate polymerization. The observed molecular weights of homopolymers and block copolymers measured by GPC (Gel permeation chromatography) and ^{1}H-NMR spectroscopy. According to prepared homopolymers (linear and star) and pure block copolymers, the success of this AGET technique was proven.

This study is expected to contribute the development of AGET ATRP process in a positive way and then enable the manufacturing of the advanced technological materials with better mechanical and physical properties.

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