İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF BLOCK COPOLYMERS OF ETHYLENE GLYCOL AND GLYCIDYL METHACRYLATE FOR EXTRACTION OF MERCURY IONS FROM AQUEOUS SOLUTION

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

Programme : Polymer Science and Technologies

JANUARY 2009

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JANUARY 2009

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

CİVA İYONLARININ SULU ÇÖZELTİLERDEN UZAKLAŞTIRILMASI AMACIYLA ETİLEN GLİKOL ve GLİSİDİL METAKRİLAT KOPOLİMERİN HAZIRLANIŞI

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OCAK 2009

FOREWORD

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January 2009

Gülşah GÖKAY

Polymer Science and Technology

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ABBREVIATIONS

PEG	: Polyethylene glycol
FT-IR	: Fourier Transform Infrared
GMA	: Glycidyl methacrylate
ATRP	: Atom Transfer Radical Polymerization
bpy	: Bipyridine

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PREPARATION OF BLOCK COPOLYMERS OF ETHYLENE GLYCOL AND GLYCIDYL METHACRYLATE FOR EXTRACTION OF MERCURY IONS FROM AQUEOUS SOLUTION

SUMMARY

Removal of inorganic pollutants from wastewater is a tedious process compared to the removal of organics because most of the latter can be removed relatively simply by activated carbons without much regard to their origin. Inorganic pollutants, however, need to use sorbents with ligating groups able to bind to them by forming chemical bonds.

Mercury is used in a wide variety of industries such as electrical paints, fungicides, chlor-alkali, paper and pulp, pharmaceutical, etc. Because of the high toxicity of all mercury compounds, the extraction of mercuric ions from aqueous wastes and drinking water are special environmental importance. The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles and reviews.

In this study, commercial PEG-400 was modified with chloroacetyl chloride to obtain macroinitiator.

Block copolymerization reaction of glycidyl methacrylate (GMA) was carried out by atom transfer radical polymerization (ATRP) method using PEG macroinitiator. (Figure 2.).

Conversion-time plot of the block copolymerization of GMA was given in Figure 1.

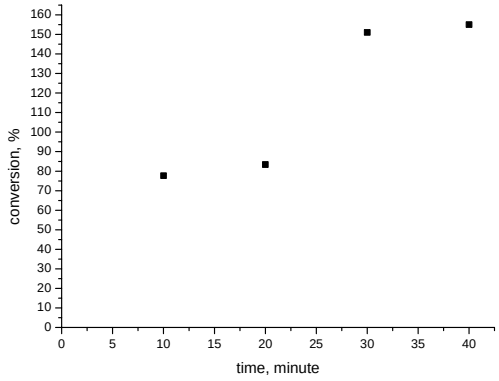


Figure 1. : Conversion of the block copolymerization of glycidyl methacrylate at 65 ^{0}C [GMA] = 7.2 mol/L; [PEG-Cl]= 0.17 mol/L; [CuBr]= 1 mol/L, [bpy]=1mol/L

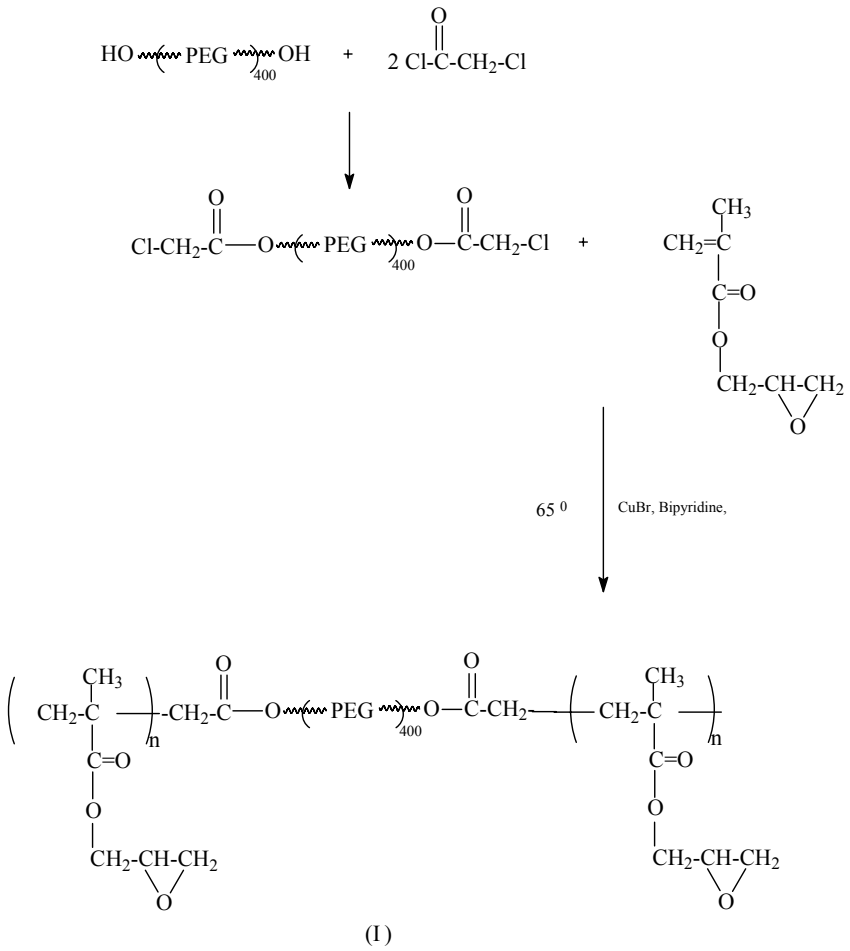


Figure 2. : Block copolymerization reaction of GMA by ATRP method.

1. Sulfonamidation of the copolymer

Reaction with excess of ammonia was given a primary amine containing polymer with 3,33 mmol g^{-1} amine functions (Figure 3.).

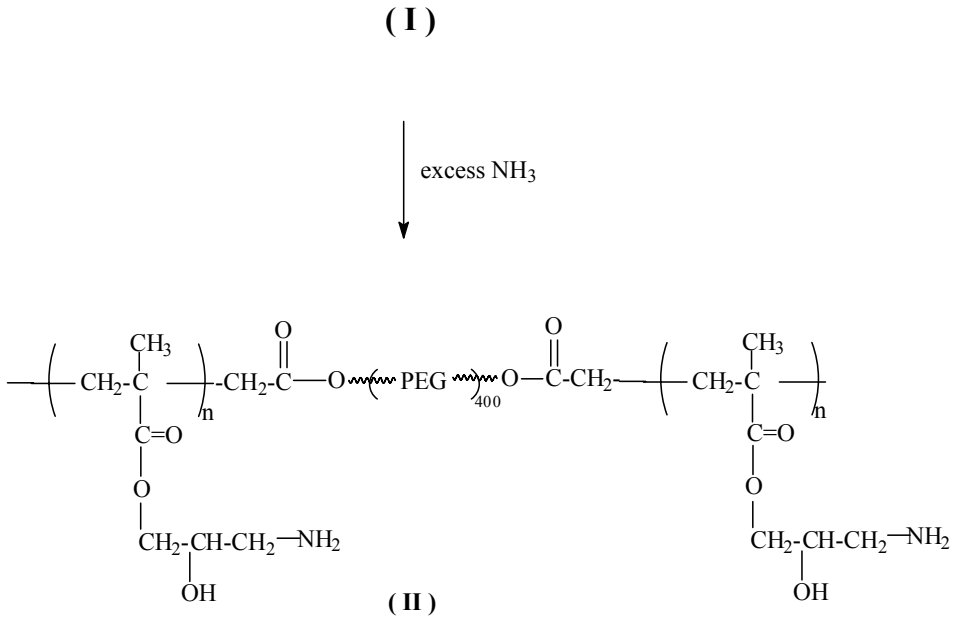


Figure 3. : Preparation of amine containing triblock copolymer (II)

The sulfamidation step (Figure 3.) was achieved by treating with excess of benzenesulfonyl chloride and the sulfonamide content was found to be about 2,8 mmol g^{-1}.

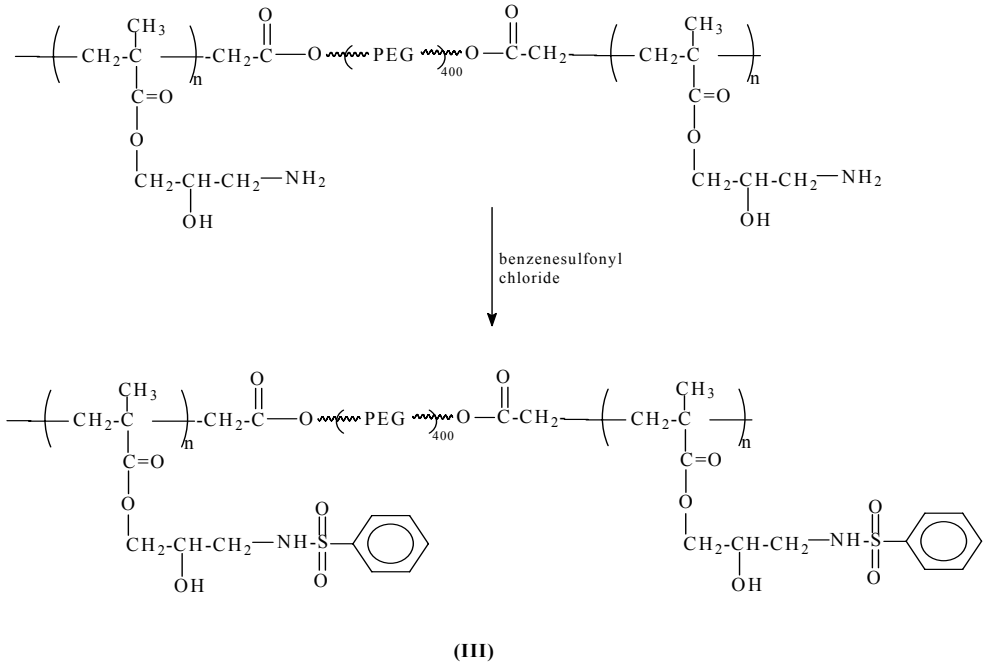


Figure 4. : Sulfamidation of primary amine containing block copolymer (III)

2. Mercury Uptake

The sulfonamide containing polymeric sorbent was an efficient sorbent to remove mercury.

On the basis of the basic reaction of the mercuric ions with sulfonamide groups, which yielded covalent mercury–sulfonamide linkages. The mercury binding of the polymeric sorbent can be depicted as shown in Figure 5.

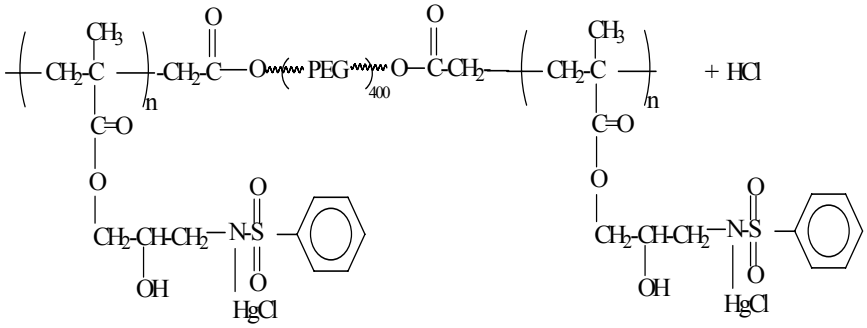


Figure 5. : Mercury binding of the polymeric sorbent.

The sorption capacity of the polymeric sorbent was analyzed by the determination of the excess mercury ions in the supernatant solutions. The mercury sorption capacity was found as 3.12 mmol g^{-1} (Table 1.).

To inspect mercury efficiency of the resin, metal extraction experiments were repeated with Cd(II), Mg(II),, and Fe(III) solutions. Each showed a small sorption capacities (0.35– 0.45 mmol/g) were found according to mercury sorption capacity (Table 1.).

Since, in ordinary conditions the sulfonamide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the sulfonamide nitrogen; the separation of mercury ions is expected to be highly selective.

Table 1 : Metal uptake characteristics of the sorbent

Metal ion	Initial concentration (M)	Sorbent capacity (mmol.g $^{-1}$)	Recovered metal (mmol.g-1)
Hg(II)	0.074	3.12	2.36
Hg(II)	0.05	3.10	
Hg(II)	0.025	3.00	
Cd(II)	0.150	0.35	-
Mg(II)	0.150	0	-
Fe(III)	0,071	0.45	-

3. Kinetics of the Mercury Sorption

To investigate the efficiency of the polymer presence of trace quantities, batch kinetic sorption experiments were performed with highly diluted $HgCl_2$ solutions (3,7 x 10^{-4} M). The concentration–time plots in Fig. 6 shows that within about 60 min of contact time, the Hg(II) concentration falls zero.

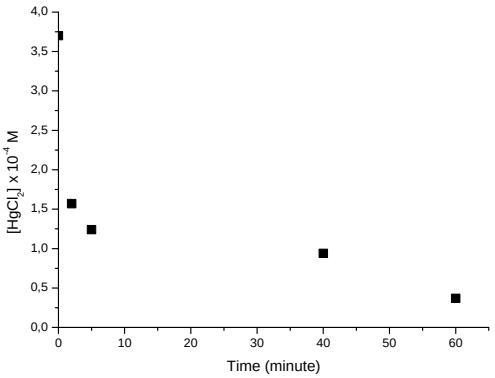


Figure 6. : Mercury sorption kinetics of the polymeric sorbent from diluted solution

The kinetics of the sorption obey second order kinetics (k = 6,19/M s with a correlation factor of 0.989) for the sorbent.

In the regeneration of mercury from loaded polymer, 5 M Nitric acid was used as an appropriate agent.. When loaded sample was interacted with nitric acid for 24 h, the amount of recovered mercury is around 2.36 mmol/g (Table 1), which is about 76 % of the capacity of fresh polymer.

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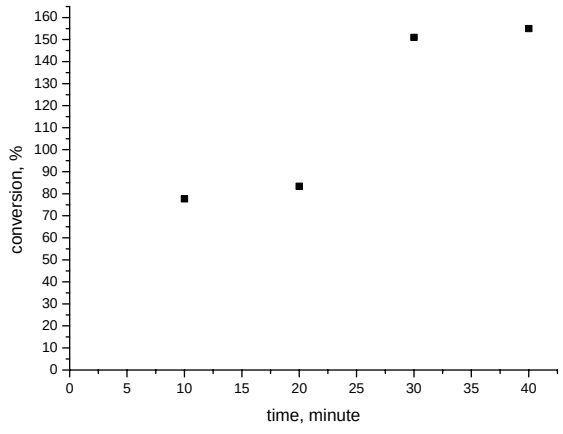
ÖZET

İnorganik maddelerin atık sulardan uzaklaştırılması organik maddelere nazaran daha zor bir prosestir. Çünkü organik maddeler aktif karbonla kolaylıkla yapıları bozulmadan giderilebilirler. Oysa ki inorganik maddelerin giderilmesi için bunlarla kimyasal oluşturabilecek ligant grupları taşıyan adsorbanlara ihtiyaç vardır.

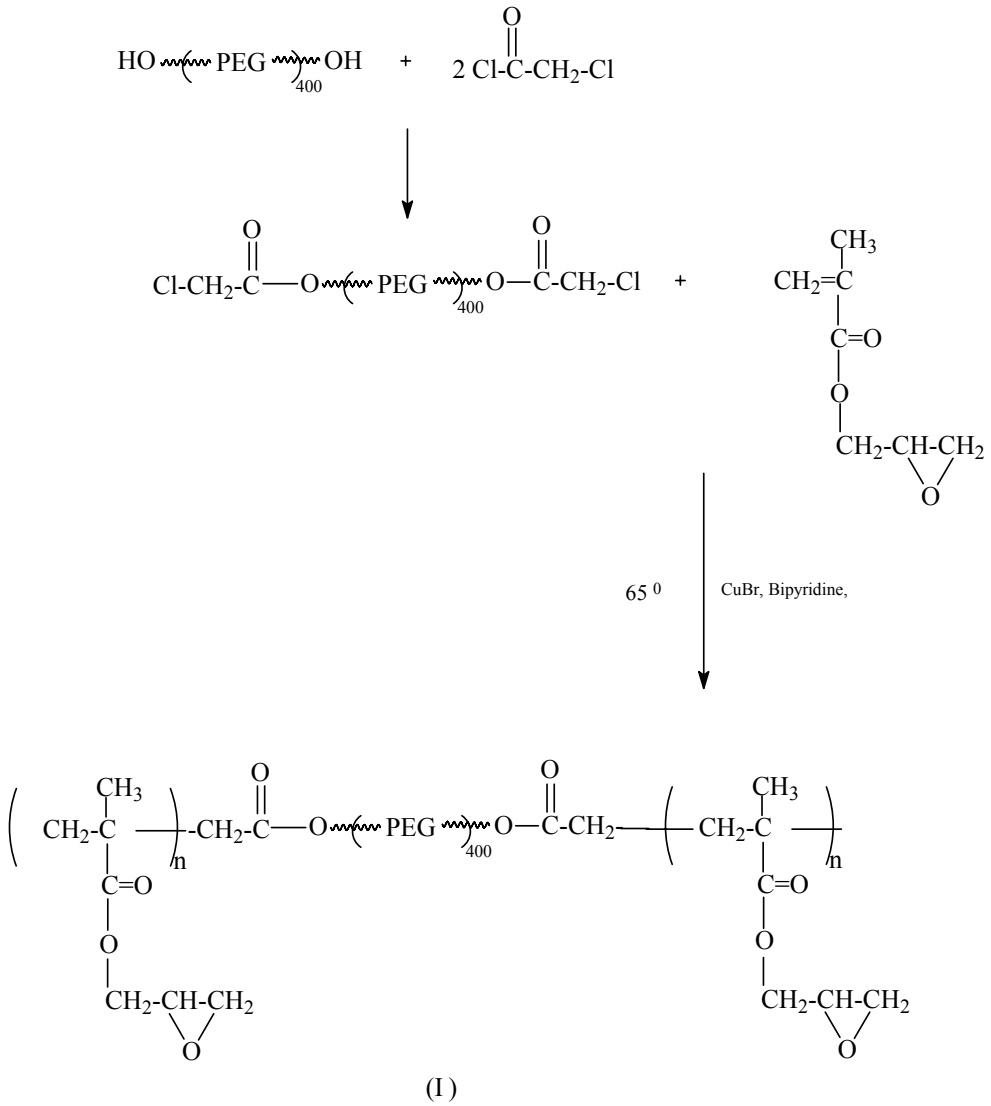
Civa elektrik boyaları, mantar ilaçları, kağıt, ilaç, klor-alkali vb. gibi endüstrilerde sıklıkla kullanılır. Yüksek oranda zehirli olmalarından dolayı bütün civa bileşiklerinin atık ve içme sularından giderilmesi özel bir önem teşkil etmektedir. Civanın seçici olarak giderilmesinde ligant bağlı polimerlerin kullanımı bir çok bilimsel makale ve derlemenin konusunu oluşturmaktadır.

Bu çalışmada ticari PEG-400 bir makrobaşlatıcı elde etmek amacıyla kloroasetil klorür ile modifiye edilmiştir.

Sentezlenen PEG esaslı makrobaşlatıcı varlığında glisidil metakrilatın atom transfer radikal polimerizasyonu (ATRP) gerçekleştirilmiştir (Şekil 2.). Blok kopolimerizasyonun dönüşüm-zaman grafiği Şekil 1'de verilmiştir.



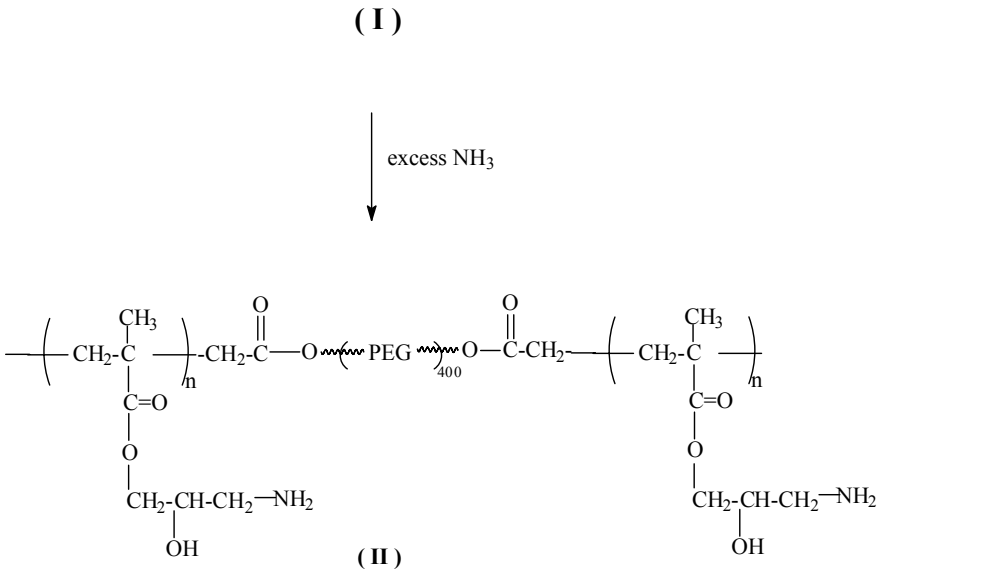
Şekil 1. : Glisidilmetakrilatın 65^0C 'deki blok kopolimerizasyonunda dönüşüm-zaman grafiği. [GMA]= 7,2 mol/lt; [PEG-Cl]= 0,17 mol/lt; [CuBr]= 1 mol/lt, [bpy]= 1 mol/lt



Şekil 2. : GMA'nın ATRP yöntemiyle blok kopolimerizasyonu

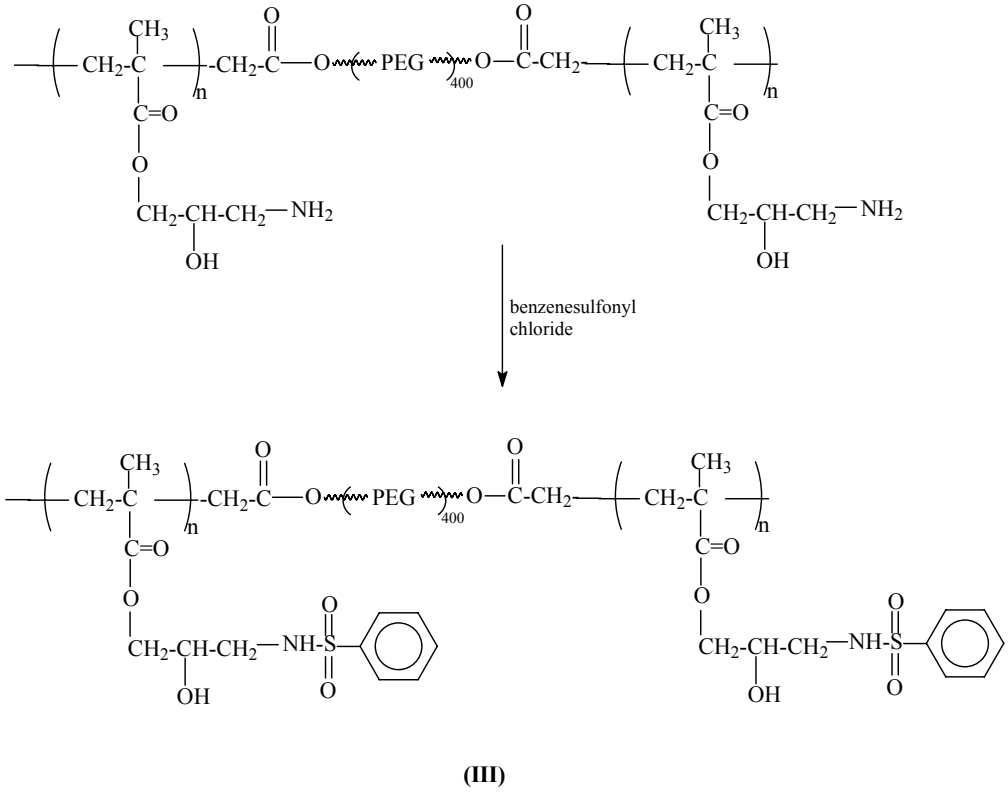
1. Blok kopolimerin Sülfonamit ile Modifikasyonu

PGMA-b-PEG-b-PGMA trikopolimerin aşırı miktarda amonyak ile reaksiyonu sonucu, 3.33 mmol.g^{-1} primer amin fonksiyonuna sahip kopolimer elde edilmiştir.



Şekil 3. : Primer amin içeren triblok kopolimer sentezi (II)

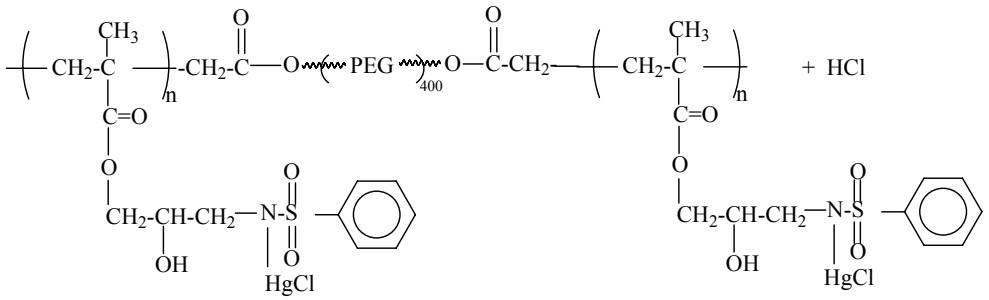
Sülfonamid oluşum basamağı, benzen sülfonil klorürün aşırısı ile amin fonksiyonuna sahip blok kopolimerin reaksiyonu ile gerçekleştirilmiştir (Şekil 3). Sülfonamid içeriği 2.8 mmol.g^{-1} olarak bulunmuştur.



Şekil 4. : Sülfonamid ile modifiye edilmiş polimerik sorbent

2. Civa Adsorpsiyonu

Sülfonamid içeren polimerik adsorbent civanın uzaklaştırılmasında etkili bir adsorbenttir. Civa iyonlarının sülfonamit gruplarıyla bazik ortamdaki reaksiyonu kovalent yapıda civa-sülfonamid bağları oluşturur. Polimerik sorbente civa bağlanması Şekil 3.'de gösterilmiştir.



Şekil 5. Polimerik Adsorbente Civa Bağlanması

Polimerik adsorbentin adsorpsiyon kapasitesi civayla etkileşme öncesi ve sonrasındaki çözeltilerdeki aşırı civa iyonlarının saptanmasıyla analiz edilmiştir. Civa adsorpsiyon kapasitesi 3.12 mmol g^{-1} olarak bulunmuştur (Tablo 1).

Polimerin civa tutma etkinliğini araştırmak için ,metal ekstraksiyon deneyleri Cd(II), Mg(II),, and Fe(III) çözeltileri ile de tekrar edilmiştir.Herbiri farklı adsorpsiyon kapasiteleri (0 – 1,45 mmol/g arasında değişen) göstermiştir (Tablo 1.) .

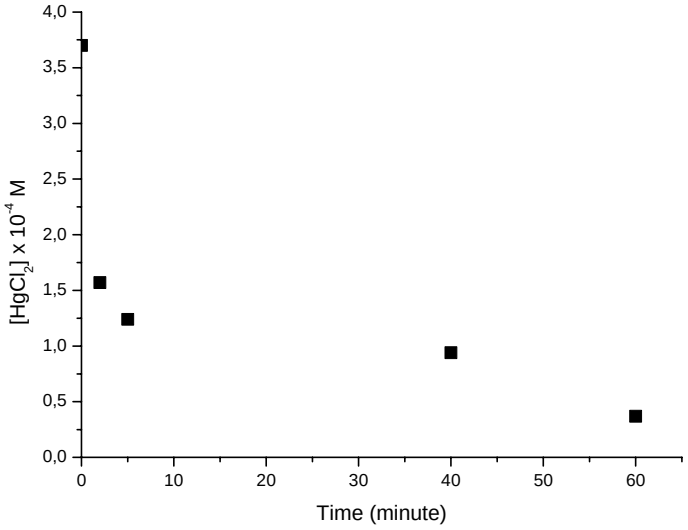
Normal şartlarda sulfonamit azotunun indirgenmiş elektron verici karakterinden dolayı sulfonamit grup diğer geçiş metalleriyle koordinasyon bağı oluşturmaz. Bundan dolayı civanın ayrılmasında yüksek seçicilik beklenir.

Tablo 1. : **Polimerik sorbentin civa adsorpsiyon karakteristiği**

Metal iyon	**Başlangıç Konsantrasyonu (M)**	**Sorbent Kapasitesi (mmol.g $^{-1}$)**	**Geri Kazanılan Metal (mmol.g-1)**
Hg(II)	0.074	3.12	2.36
Hg(II)	0.05	3.10	
Hg(II)	0.025	3.00	
Cd(II)	0.150	0.35	-
Mg(II)	0.150	0	-
Fe(III)	0,071	0.45	-

3. Civa Adsorpsiyon Kinetiği

Polimerin düşük miktarlardaki etkinliğinin bulunması için kesikli kinetik adsorsiyon deneyi oldukça seyreltik (3,7 x 10^{-4} M) $HgCl_2$ çözeltilerinde gerçekleştirilmiştir. Şekil 4.'deki konsantrasyon-zaman grafiği 60 dakikalık bir temas süresinde Hg (II) konsantrasyonunun sıfıra düştüğünü göstermektedir.



Şekil 6. : Civa'nın seyreltik çözeltilerden tutunma kinetiği
Polimer için adsorpsiyon kinetiği ikinci mertebe kinetiğine uyar
(k= 6,19/M s korelaston faktörü = 0,989)

Civa yüklü polimerin geri kazanımında 5 M nitrik asit kullanılmıştır. Yüklü polimer 24 saat süresince nitrik asitle etkileştirilmiş ve civa geri kazanım kapasitesi 2.36 olarak bulunmuştur.

1. INTRODUCTION

Waste waters containing heavy metals pollutants come from different industrial activities such as mining, power plants, plating facilities and electrical equipment manufacturing. All heavy metals are toxic and non-biodegradable and should be separated from waste waters.

Mercury is a highly toxic metal that is very poisonous for living organisms even in trace concentration (ppb).

Approximately two thirds of the Hg in natural environments is of anthropogenic origin .

Burning of fossil fuels, such as petroleum, natural gas and coal, is the most important contributor to the total environmental Hg budget, since they contain approximately 0.2 ppm of Hg (II). Mercury can be found in significant amounts in wastes from chloroalkali manufacturing plants, electrical and electronics manufacturing, and sulfide ore roasting operations.

Exposure to Hg can have toxic effects on reproduction, the central nervous system, liver, and kidneys, and cause sensory and psychological impairments.

Therefore, before the disposal of mercury containing industrial wastes their mercury content should be eliminated.

In the last decades, many different types of treatment techniques were applied to remove the heavy metals from waste waters. Some of them are chemical precipitation, filtration, neutralization, ion-exchange, and adsorption.

The synthesis of polymers with well-defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. Typically, living

polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination.

Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations. The development of controlled/living radical polymerization (CRP) methods such as atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer processes (RAFT), nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP) has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers.

In this study, PEG-400 was reacted with chloroacetyl chloride to obtain macroinitiator. Poly(glycidyl methacrylate) -*b*- poly(ethylene glycol)-*b*-poly(glycidyl methacrylate) triblock copolymer was prepared by using ATRP method. Epoxy groups on the block copolymer were functionalized via ring opening of epoxide group by using ammonia. Resulting primary amine containing sorbent was treated with excess of benzenesulfonyl chloride to obtain sulfonamide-based polymeric sorbent for removal mercury ions from water.

Obtained polymeric sorbent was used for removal of mercury from water. Also, experiments were carried out at different cations for investigating selectivity of the sorbent. Kinetic studies and regeneration studies were also studied in this thesis.

2. THEORITICAL PART

2.1 Atom Transfer Radical Polymerization

Addition of free radicals to alkenes is a fundamental reaction in organic and polymer synthesis. [1,2,3] This reaction in most cases is highly exothermic and rapid since one σ - bond is formed with the loss of one π-bond. The fast rate of radical addition as well as its tolerance to many functionalities, makes the radical addition reaction an attractive synthetic pathway. Therefore, it has been widely utilized for the synthesis of a variety of compounds ranging from complex natural products to commodity polymers.

Concurrently, the radical addition reaction possesses intrinsic side reactions, in particular, diffusion controlled radical-radical reactions through coupling or disproportionation. (Figure 2.3) Since these side reactions are extremely fast and unselective, they are difficult to control, and thus the radical addition reaction often becomes a non-exacting method to targeted products. This predicament is more pronounced in the polymerization process, where the addition reaction must be repeated many times, and the precise control of the reaction is even more important. Frequently, the polymers obtained from the radical process do not have well defined structures in terms of molecular weight, molecular weight distribution and functionalities. Therefore the precise control of radical polymerization has been one of the main challenges in polymer synthesis. [4]

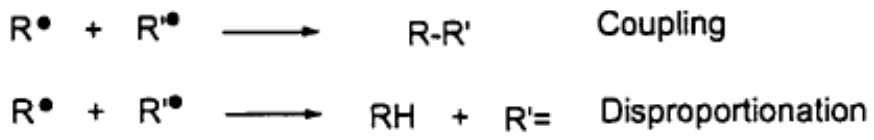


Figure 2.1 : Main Steps of ATRP

Fortunately, the side reactions between radicals can be minimized by decreasing the radical concentration ([R*]). While radical - radical reactions are second order in [R*], the addition of radical to alkene is first order in [R*]. A decrease in [R*] suppresses the radical-radical reaction effectively with a smaller reduction in addition rate. In organic synthesis, there have been several useful methods to maintain low radical concentrations, mostly based on chain reactions. . [1,2] (Figure 2.4) In the chain reactions, only a catalytic amount of radicals is required since the radical is regenerated in the reaction cycle.

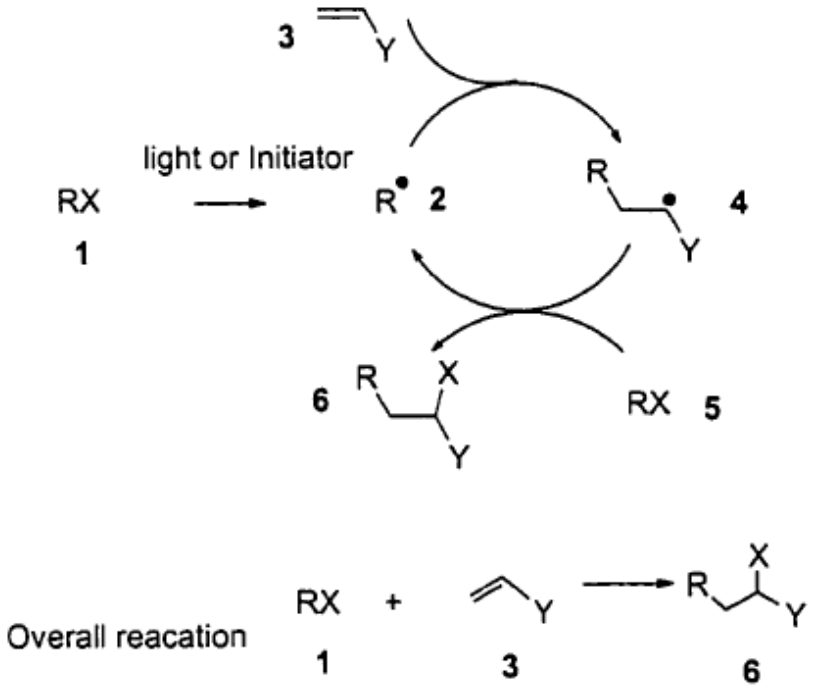


Figure 2.2 : An example of radical chain reactions- atom transfer radical addition

One such method is atom transfer radical addition (ATRA) or Kharasch reaction. [5,6,7,8] (Figure 2.4) In ATRA, the chain reaction is initiated by the formation of radicals 2 from non-radical species 1, promoted either by light, or thermally labile compounds such as AIBN or peroxide. The reaction cycle is composed of addition and transfer reactions. In the addition step, the produced radicals 2 attack alkenes 3 to form adducts 4. The addition should be a fast reaction, in which less reactive radicals 2 are converted to more reactive radicals 4. These reactive radical adducts 4 rapidly abstract atom (or group) X from substrates 5, to form targeted products 6 and to regenerate radicals 2 in the

transfer step. Continuous cycles of this chain reaction achieve the addition of I across the double bond of 3 to yield mono-addition products 6 while the radical concentration is kept low, which minimize the radical - radical reactions, termination (k_t). (Figure 2.2).

In ATRA, there is another important side reaction, which is the formation of oligomeric or polymeric species, namely, the propagation reaction. Before theradical adducts 4 converts to desired product 6 through atom transfer, radicals 4 can escape from the reaction cycle and add to one or more alkenes 3 to yield oligomers / polymers 7. (Figure 2.3) This side reaction becomes more significant for alkenes with a higher propagation rate constant, kp (i.e. radically homopolymerizable alkenes). The low radical concentration cannot effectively reduce the propagation rate which is also first order in [R*] as the addition reaction is. Instead, the propagation can be suppressed by the correct choice of the alkenes / RX or the increasing the ratio of RX to alkenes.

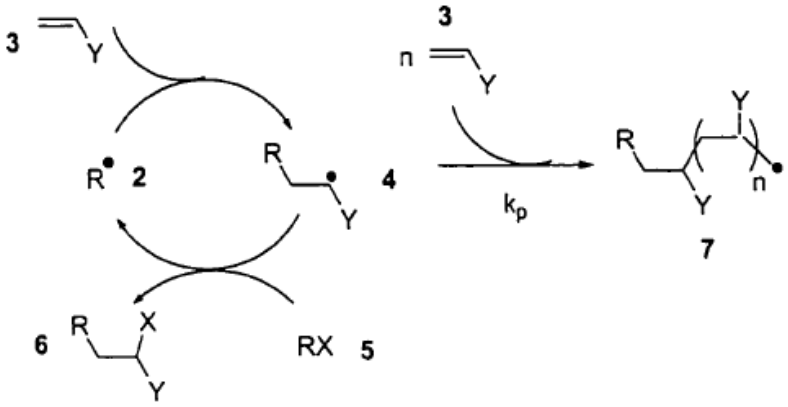


Figure 2.3 : Propagation reaction in ATRA

The use of a transition metal complex can be an alternative to expedite transfer relative to propagation. [9] Transition metal complexes 8 accelerate transfer of X to 4 without altering the rate of propagation so as to favor the formation of the mono addition product 6. (Figure 2.2) This process is referred to as deactivation, since unreactive products 6 are generated from reactive radicals 4. Transition metal complexes also abstract X from 1 to provide radicals 2 to the reaction cycle, in the activation step. The cycle does not need to be initiated by light or thermal initiator

since the activation reaction in the catalytic cycle generates its radicals. The whole reaction cycle in Figure 2.4 will be called transition metal catalyzed atom transfer radical addition (TMC ATRA) to distinguish it from non-metal mediated ATRA or Kharasch reaction.

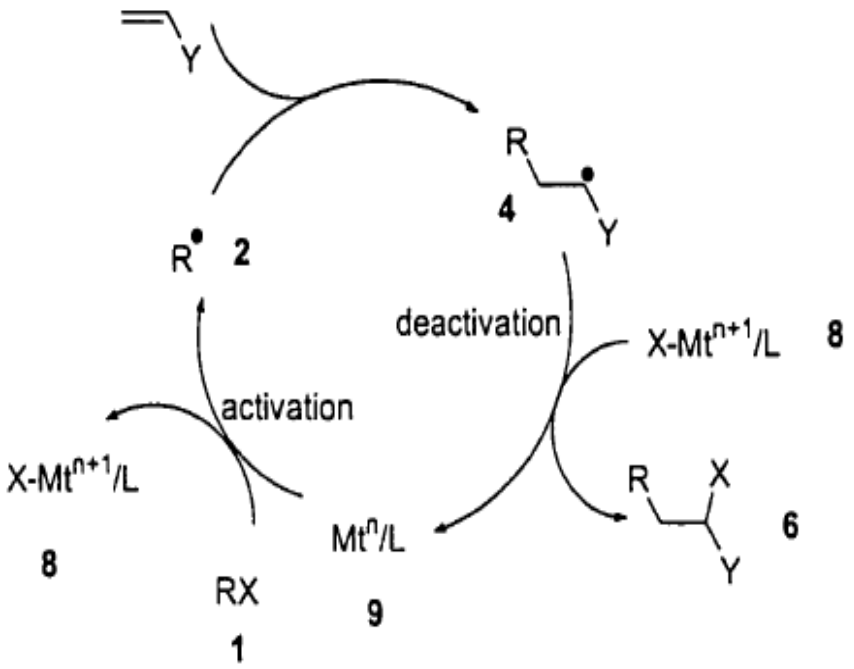


Figure 2.4 : Transition metal catalyzed atom transfer radical addition

The recent adaptation of TMC ATRA to polymerization processes resulted in a new living radical polymerization method, namely, atom transfer radical polymerization (ATRP).[10,11] Similar to TMC ATRA, ATRP employs transition metal complexes 9 to catalyze atom transfer between radicals 10 and alkyl halides 11 where 10 and 11 can be either monomeric or polymeric species. (Figure 2.5) The atom transfer from alkyl halides 11 to transition metal complexes 9, produces the corresponding alkyl radicals 10 and oxidized metal complexes 8 with the activation rate constant, $k_{act.}$ The reverse reaction yields 11 with reduction of 8, the deactivation rate constant, $k_{deact\bullet}$.

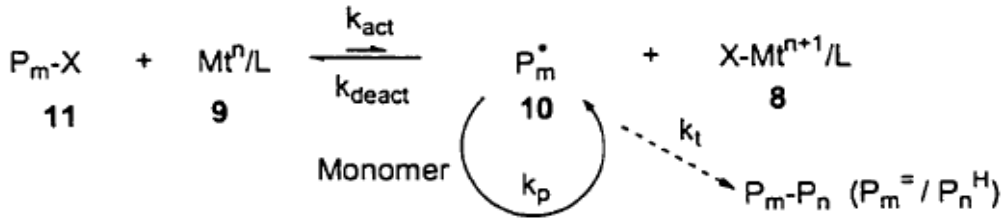


Figure 2.5 : Atom transfer radical polymerization

These activation and deactivation processes are reversible in ATRP, resulting in the reversible formation of radicals 10. The concentration of stationary radical 10 is low since the equilibrium between the activation and deactivation processes is shifted to left hand side, which reduces the termination reactions. The broken arrow in Figure 2.5 represents the small contribution by the termination reactions with k, The addition of monomer with the propagation rate constant, kp, proceeds in a controlled fashion for all chains through these reversible activation and deactivation cycles, and well-defined polymers with predetermined molecular weights and narrow molecular weight distributions can be produced.

It is important to note the concentration of 8 during the reaction (i.e. transition metal complex in higher oxidation state). In radical reactions, the radical - radical termination cannot entirely be eliminated, and their small contribution still exists even in the chain reactions of TMC ATRA / ATRP. This means that oxidized metal complexes 8 in Figure 2.4 and 2.5 are continuously generated throughout the reaction. At some point, the increased concentration of 8 further decreases the radical concentration and slows down the termination reactions and generation of 8. The role of this self-regulating system was first explained by Fischer [12] and later named as the "persistent radical effect (PRE). [13] The persistent radical refers to stable radicals which only react with transient radicals (e.g. 2 and 4 in Figure 2.4 and 10 in Figure 2.5) and do not react with other species including themselves. Now, it is believed that many of the transition metal catalyzed radical reactions are subject to the PRE and it is the persistent radical that may alter the kinetics of the process as well as the distribution of the products. Therefore, it would be useful to reinterpret some of the previous studies carried out and explained without considering the PRE.

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

2.1.1 Components of ATRP

In order to fully understand the ATRP technique, one must understand the roles of the various components. The ATRP system consists of monomer, initiator with a transferable halogen, and a catalyst system composed of a transition metal species and a suitable ligand. Solvent, reaction temperature, and additives are also important. As with any reaction, the conditions under which a particular reaction is to be performed must be optimized to achieve the desired results. Figure 2.6 shows that the relationship between Mw/Mn, Mn with conversion.

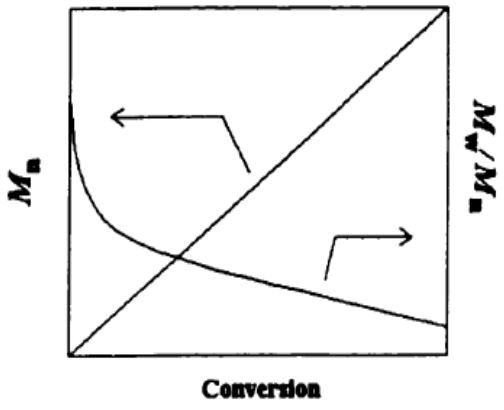


Figure 2.6 : Representation of Molecular Weights and Polydispersities with Conversion for a Living Radical Polymerization.

A wide variety of monomers have been successfully polymerized by ATRP. These include styrenes, [11,14] acrylates,[15,16] methacrylates,[17,18] vinylpyridine,[19] and acrylonitrile.[20] To be polymerizable via ATRP, the monomer must have stabilizing groups (e.g. phenyl or carbonyl) next to the carbon radical in order to

have a sufficiently large atom transfer equilibrium and the monomer must not have groups (e.g. acids) that interfere with the catalyst system. The radical polymerization rate is unique to each monomer so that the concentration of propagating radicals and the rate of deactivation need to be adjusted for each particular system in order to maintain control. The overall equilibrium of the reaction depends on the radical (monomer) and the dormant species as well as on the amount and reactivity of the transition metal catalyst added.

2.1.2 Initiators and Halogen Exchange

ATRP is typically initiated by an alkyl halide, which contains an activating substituent on the a-carbon, stabilizing the resulting radical. The initiation step proceeds by the same process as propagation, and the role of the initiator is to determine the number of growing polymer chains and to provide the head group of the polymer chain. If initiation is fast and transfer and termination reactions are negligible, the number of growing chains is constant and equal to initiator concentration. The theoretical molecular weight or degree of polymerization increases inversely with initial initiator concentration and is given by equation [21]:

$$M_n = \frac{\text{grams monomer}}{\text{moles initiator}}$$

Figure 2.7 : Formula of Theoritical Molecular Weight

To achieve control of molecular weight and narrow molecular weight distributions, the halide group must rapidly and selectively migrate between the growing chain and catalyst complex. Molecular weight control has been the most successful when the halogen is either chlorine or bromine. [22] Mixed halide initiation systems (i.e. R-X/Cu-Y (X,Y=C1 or Br) have also been investigated to obtain better control in ATRP of MMA. [23]

2.1.3 Solvents

ATRP has been successful in bulk, in solution, and in a heterogeneous system (for example, emulsion or suspension). A good solvent for ATRP will allow minimal chain transfer to solvent and solvent assisted side reactions. Polymerizations are typically carried out in organic non-polar media such as toluene or anisole although a wide range of solvents (e.g. diphenyl ether, ethylene carbonate, water, dimethylformamide, acetone, alcohols) have been effectively employed in various ATRP systems. Rate enhancement in polar media (e.g. using ethylene carbonate as solvent) has been observed and is attributed to a structural change in the copper complex.[24] Polar media also help to dissolve the catalyst.

2.1.4 Catalysts

The ideal ATRP catalyst should be highly selective for atom transfer and should not participate in other reactions. The catalyst determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. In order to be an efficient catalyst for ATRP, the metal must have at least two readily accessible oxidation states separated by one electron, have reasonable affinity toward a halogen, have an expandable coordination sphere upon oxidation to accommodate the halogen, and be strongly complexed to a ligand. To differentiate ATRP from redox-initiated polymerization, the oxidized transition state should rapidly deactivate the propagating polymer chains to form the dormant species, resulting in a controlled process. Although a variety of metals have been used such as

Fe (I), [25] Cu (II), [26-28] and Ni (II) [29,30] this work focuses on ATRP catalyzed by copper, which is superior to other metals in versatility and costs.

2.1.5 Ligands

The ligand serves to solubilize the catalyst in ATRP. Nitrogen ligands, which have been used in copper- and iron-mediated [31] .Multidentate ligands, are the ligands of choice and a variety have been developed. Some examples are shown in Figure 2.6. Derivatives of 2, 2'-bipyridine (bipy) are one example of ligands used in Cu-catalyzed ATRP.[32] The most common bipy ligand is the derivative with solubilizing nonyl groups in the 4, 4' position: 4, 4'-di(5-nonyl)-2, 2'- bipyridine. Haddleton et al.[33-35] reported use of π accepting, chelating imine-based ligands.

Other aliphatic multidentate amines such as N N, N. N'. N "-pentamethyldiethylene triamine (PMDETA) 1,1,4,7,10,10 hexamethyltriethylenetetramine (HMTETA), and tris[2 (dimethylamino)ethyl]amine (Me_6TREN)[36] have also been reported.

Electronic and steric effects of the ligands affect ligand behavior in ATRP [37,38] Catalytic activity is reduced when there is excessive steric bulk around the metal center or the ligand possesses strongly electron-withdrawing substituents. Activity also decreases with a decrease in coordinating sites and as the number of linking carbons increases. Although the catalyst/ligand species in ATRP may be a complex structure, the generally accepted complex is two bidentate ligands complexed to one copper bromide molecule.[39,40] order of decreasing activity for the various types of nitrogen ligands is as follows: R2N- > Pyridines > R-N= > Ph-N= > Ph-NR-. Aliphatic amine ligands cause faster polymerization rates due to their poorer n-accepting ability, which results in less stabilization of the copper (I) species. [36]Altering the a-donating and π- accepting properties of the ligand changes the redox potential for the copper oxidation and thereby increases the atom transfer equilibrium constant. [40].

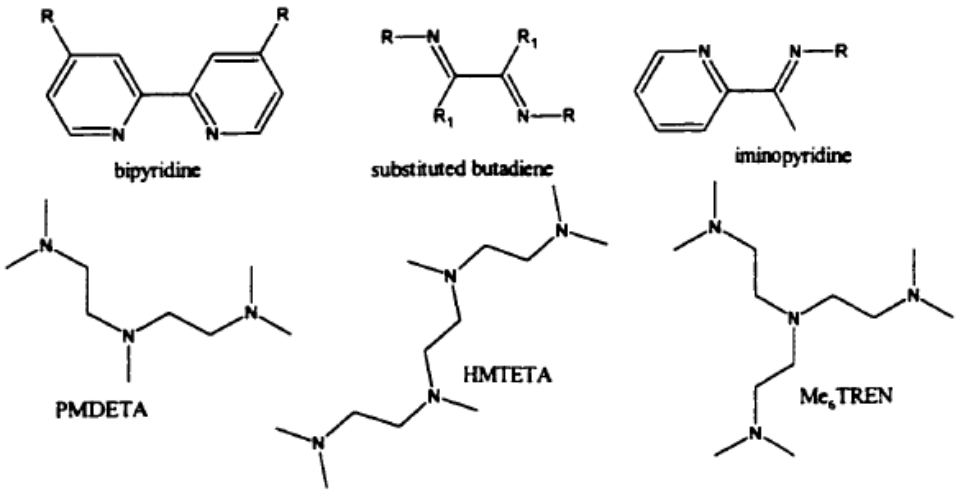


Figure 2.8 : Examples of ATRP Ligands

Proper choice of ligand for the particular ATRP system is very important. Both heterogeneous and homogeneous catalytic systems have been used. Early ATRP experiments comparing bipy ligands with and without solubilizing alkyl groups showed that the soluble catalyst systems resulted in lower polydispersities, similar initiator efficiencies, and slower overall polymerization rates as compared to the

heterogeneous bipy systems [41].The increased control is attributed to the better solubility of the copper (I) species which causes deactivation. Homogeneous systems also offer the advantage of allowing for detailed kinetic and mechanistic studies of the polymerization.[42,43]haupt and coworkers[44]have studied ATRP of styrene with various bipy and diimine ligands with CuBr catalyst and showed that ligand designs and steric constraints have an important effect on catalyst activity, which manifests itself either as incomplete initiation, slow deactivation, or a combination of both. Scheme 2.5 shows that some ATRP ligands.

2.1.6 Additives

Additives to ATRP reactions have been investigated as ways to affect the reaction rate and control in the polymerization. Significant rate enhancements were observed using zerovalent metal as an additive. For example, when a small amount of copper (0) (copper powder) is added to styrene and methacrylate polymerizations, polymerization rates increase.[45]Copper (0) is said to reduce "excess" copper (I) forming copper (I). Removal of small amounts of copper (II) enhanced the rate yet left a sufficient amount to maintain control of the polymerization. Addition of $CuBr_2$ has been used as a way to increase the rate of deactivation, in order to shift equilibrium to form the dormant species, which will in turn minimize side reactions and termination.

2.2 Functional Polymers

There is an ever increasing demand for polymers for specific end-use properties such as enhanced resistance to fire or environmental attack or, in some cases, enhanced degradability. Development of new polymeric materials to meet this challenge has involved the use of a multidisciplinary approach involving chemistry, physics, and engineering. Every decade since the middle of 20th century seems to have witnessed an additional dimension in the thrust of development research in polymer science: the 1950s saw serious advances in polymer chemistry, the 1960s in polymer physics, the 1970s in polymer engineering, and the 1980s in functional polymers.[47] We are currently witnessing the emergence of high performance polymeric materials such as alloys and blends and advanced composites (so-called polymer abc) being developed

through the application of polymer physics and engineering. In this discussion, we focus attention on functional polymers.

Functional polymers may be considered in broad terms as those polymers whose efficiency and characteristics are based on a functional group. A specific functional group is usually carefully designed and located at a proper place on the polymer chain. The functional groups may be dispersed along the polymer main chain (including chain ends) or attached to the main chain either directly or via spacer groups. The main objective of the introduction of special functional groups into the polymer backbone or side chains is to give the polymers special features. Functional groups are, therefore, typically chemical units that are chemically reactive, biologically active, electroactive, mesogenic (liquid crystals), photoactive, and, more commonly, ionic, polar, or optically active.[46] There are two general techniques used for the preparation of functional monomers:[47]

- Polymerization or copolymerization of functional monomers
- Chemical modification of preformed polymers

The use of functional monomers permits ready control of the content and sometimes the distribution of units along the polymer chain; this procedure gives more latitude concerning the physical properties of the final product. On the other hand, chemical modification of an existing polymer, when possible, enables the choice of molecular weight and the dispersity of the polymer. It also allows the synthesis of polymers inaccessible by direct route. [48]

Cross-linking, vulcanization, and grafting are some of the polymer reactions that take place on functional or reactive groups located in the polymer main chain. We have already discussed some of these reactions in the preceding sections. We now discuss other examples of modification of polymers based on reactive monomers, oligomers, or polymers.

2.2.1 Applications

Some existing markets targeted by materials prepared by CRP are :

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

Although this has been but a brief review of novel materials prepared using controlled radical polymerizations, one can easily see that, regardless of the type of controlled radical polymerization employed, these methodologies open the door to a wide range of novel polymers with unique properties. Indeed control over polymer sequence distributions continuously expanding and recently multi-block heteropolymer chains with up to 100 blocks in an ordered sequence and controllable block lengths have been reported [49]. Only time will tell, but undoubtedly the question is not if such materials will find commercial uses, but one of when and how.

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

To extend the usefulness of radical polymerization, various systems have been developed to allow for the 'control' of the polymerization such that termination and transfer processes can be avoided, or at least minimized. Towards this end, three systems have shown some ability to solve this problem; these are the nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and radical addition-fragmentation transfer (RAFT). All three have their benefits and deficiencies, but each may be particularly suited for certain applications, i.e., high molecular weight polymers vs. low molecular weight telechelic oligomers, etc. It has been demonstrated that polymers with novel compositions, architectures, and functionality can be readily prepared by using these methods. Although some terminal functionality of the chains is lost due to unavoidable termination reactions, these materials may provide unique properties that will be good enough, or significant enough, to be used in new applications.

2.3 Harms of Heavy Metal Ions

Metal ions are non-biodegradable in nature, and their intake at a certain level are toxic [50]. Environmental contamination with metal ions is of growing public concern because of health risks posed by human and animal exposure. The separation of metal ion, present as contaminants in water, is complicated because of the number of variables that must be considered, including the solution composition, salinity, pH, temperature, and the presence of organic substances. It is well known, for example, that heavy metal ions such as Pb(II) and Hg(II), which are toxic to most organisms, have found their way into the water system from different processes .[51]

Therefore, there is great interest in recovering metal ions for both environmental and economic reasons [52-53].

A serious problem encountered in the removal of the metal ions is that the target species are usually in low concentration and in complex mixtures. The innocuous ions, such as sodium and potassium, can saturate the extractants before they can effectively remove the toxic metal ions. Attempts to solve problems of removal of heavy metal ions have led to development and application of several techniques such as precipitation, adsorption, extraction and sorption or ion exchange [54-56].

With respect to the low concentrations and handling of large volumes of aqueous solution, extraction procedures are not economical, and precipitation procedures require the addition of relatively large amounts of chemicals, whereas applications of sorption or exchange on solids are preferable [57].

This makes the use of exchangers for selective separation of heavy metal ions very attractive. The ion exchange sorbents contain functional groups capable of complexing or ion exchanging with metal ions. Because interacting function group with the metal ions is covalently bound to an insoluble polymer, there is no loss of extractant into the aqueous phase. The chelating sorbents are ion-exchange-containing groups that are also able to complex metal ions.

The high metal ion selectivity of chelating exchangers is attributed not only to electrostatic forces but also to coordination bonds in metal chelating groups. The commercial sorbent Chelanine (Fluka), Bio-Rex-70, and Chelex 100 correspond to examples of ion-exchange sorbents that contain groups with a strong ability to bind heavy metal ions.

Their sorption mechanism is through chelation instead of simple ion exchange and, as a consequence, they should be much more selective than ion exchange sorbents. It

has been also claimed that their selectivity is at least qualitatively in agreement with the complexation constants of similar chelating monomers with metal ions in aqueous solution, although this is true only very roughly.

Such adsorbents have a larger specific surface and very small diameter, thus ensuring high kinetic parameters. As a result, adsorption and concentration procedures become more convenient and easier.

2.4 Complexation of polymeric ligand and metal ion

The analytical applications of chelating polymer depend on many factors. Normally a metal ion exists in water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration must be replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and and/or donor atom capable of

forming complexes with metal ions in solution and it is logical to classify chelating polymers on that basis.

This method of classification is not meant to imply that these systems are mutually exclusive. Indeed some polymers can belong to more than one class, depending on experimental conditions [58].

Among the many ligands [59] introduced 8-acryloyloxyquinoline is one of the recent origin. This kind of polymer-metal complexes are prepared by the chemical reaction of a polymer, containing ligands with metal ions. Generally, the reaction of a polymeric ligand with a metal ion or a stable metal complex, in which one coordination site remains vacant, results in different structures that can be grouped into pendant and inter/intra-molecular bridge polymer-metal complexes [60].

2.5 Inter/intra-molecular bridged polymer-metal complexes

When a polymer ligand is mixed directly with metal ion, which generally has four six coordinate bonding sites, the polymer-metal complex formed may be of the intra-polymer chelate type or inter polymer chelate type as shown in Figure 2.9 .

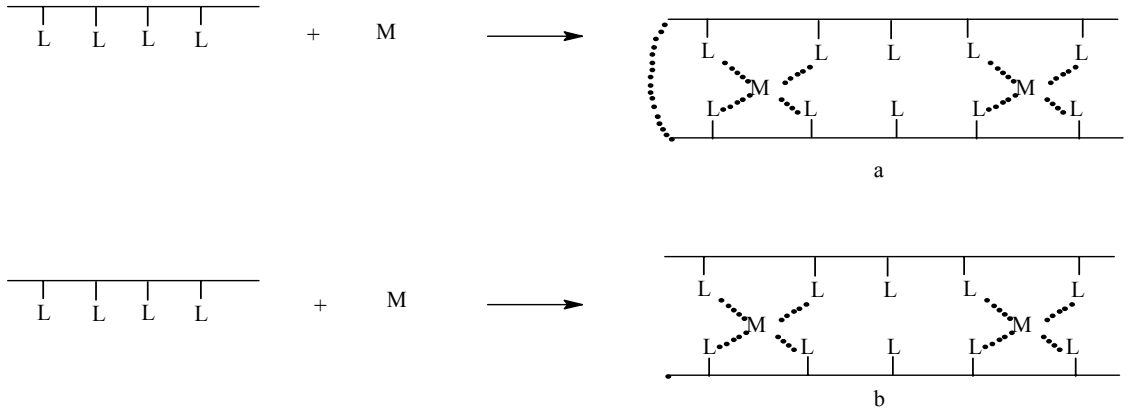


Figure 2.9 : Inter/intra molecular bridged polymer-metal complexes

The coordination structure in this type of polymer-metal complex is not clear and it is often difficult to distinguish between inter/intra-molecular binding.

Thus it is not easy to elucidate the polymer effect in studying the characteristics of the polymer-metal complexes. Intra-polymer metal complex is sometimes

soluble, while inter-polymer metal complex results precipitation of the linear polymer-metal complexes as exemplified by poly (acrylic acid)-Cu(II) complex [61].

2.6. Polyethyleneglycol (PEG)

Poly(ethylene glycol) (PEG), also known as poly(ethylene oxide) (PEO) or polyoxyethylene (POE), is the most commercially important type of polyether. PEG, PEO or POE refers to an oligomer or polymer of ethylene oxide. The three names are chemically synonymous, but historically PEG has tended to refer to oligomers and polymers with a molecular mass below 20,000 g/mol, PEO to polymers with a molecular mass above 20,000 g/mol, and POE to a polymer of any molecular mass. PEG and PEO are liquids or low-melting solids, depending on their molecular weights. PEGs are prepared by polymerization of ethylene oxide and are commercially available over a wide range of molecular weights from 300 g/mol to 10,000,000 g/mol. While PEG and PEO with different molecular weights find use in different applications and have different physical properties (e.g. viscosity) due to chain length effects, their chemical properties are nearly identical. Different forms of PEG are also available dependent on the initiator used for the polymerization process.

The size distribution can be characterized statistically by its weight average molecular weight (Mw) and its number average molecular weight (Mn), the ratio of which is called the polydispersity index (Mw/Mn). Mw and Mn can be measured by mass spectroscopy.

PEG is soluble in water, methanol, benzene, dichloromethane and is insoluble in diethyl ether and hexane. It is coupled to hydrophobic molecules to produce non-ionic surfactants.

2.6.1 Production

Poly (ethylene glycol) is produced by the interaction of ethylene oxide with water, ethylene glycol or ethylene glycol oligomers. The reaction is catalyzed by acidic or basic catalysts. Ethylene glycol and its oligomers are preferable as a starting material

instead of water, because it allows the creation of polymers with a low polydispersity (narrow molecular weight distribution). Polymer chain length depends on the ratio of reactants.

$$HOCH_2CH_2OH + n(CH_2CH_2O) \rightarrow HO(CH_2CH_2O)_{n+1}H$$

Figure 2.10 : Chemical Formula of PEG

Depending on the catalyst type, the mechanism of polymerization can be cationic or anionic. The anionic mechanism is preferable because it allows one to obtain PEG with a low polydispersity. Polymerization of ethylene oxide is an exothermic process. Overheating or contaminating ethylene oxide with catalysts such as alkalis or metal oxides can lead to runaway polymerization which can end with an explosion after few hours.

Polyethylene oxide or high-molecular polyethylene glycol is synthesized by suspension polymerization.It is necessary to hold the growing polymer chain in solution in the course of the polycondensation process. The reaction is catalyzed by magnesium-, aluminium- or calcium-organoelement compounds. To prevent coagulation of polymer chains from solution, chelating additives such as dimethylglyoxime are used.Alkali catalysts such as sodium hydroxide NaOH, potassium hydroxide KOH or sodium carbonate Na_2CO_3 are used to prepare low-molecular polyethylene glycol [62].

2.6.2. Uses of Polyethyleneglycol

Polyethylene glycol has a low toxicity and is used in a variety of products. This is a high volume chemical with production exceeding 1 million pounds annually in the U.S.

PEG is widely used in the below mentioned industries:

- Laboratory Chemicals
- Paper Coating
- Printed Circuit Board Manufacturing
- Textiles

- Wood

2.6.3. Clinical uses

Polyethylene glycol has a low toxicityan d is used in a variety of products. It is the basis of a number of laxatives (e.g. macrogol -containing products such as Movicol and polyethylene glycol 3350, or MiraLax or GlycoLax). It is the basis of many skin creams, as *cetomacrogol*, and sexual lubricants, frequently combined with glycerin. Whole bowel irrigation (polyethylene glycol with added electrolytes) is used for bowel preparation before surgery or colonoscopy and drug overdoses. It is sold under the brand names GoLYTELY, GlycoLax, Fortrans, TriLyte, and Colyte. When attached to various protein medications, polyethylene glycol allows a slowed clearance of the carried protein from the blood. This makes for a longer acting medicinal effect and reduces toxicity, and it allows longer dosing intervals.

2.6.4. Other uses

PEG is used in a number of toothpastes as a dispersant; it binds water and helps keep gum uniform throughout the toothpaste. It is also under investigation for use in body armor and tattoos to monitor diabetes. PEG is a popular precipitant for protein crystallization , X-ray diffraction of protein crystals can reveal the atomic structure of proteins.Polymer segments derived from PEG polyols impart flexibility to polyurethanes for applications such as elastomeric fibers (spandex) and foam cushions.Since PEG is a flexible, water-soluble polymer, it can be used to create very high osmotic pressures (tens of atmospheres). It also is unlikely to have specific interactions with biological chemicals. These properties make PEG one of the most useful molecules for applying osmotic pressure in biochemistry experiments, particularly when using the osmotic stress technique.PEG is also one of the main ingredients in Paintball fill since it's thick and flexible.PEG has also been used to preserve objects which have been salvaged fromunderwater, as was the case with the warship Vasa in Stockholm. It replaces water in wooden objects, which makes the wood dimensionally stable and prevents warping or shrinking of the wood.PEG is often seen (as an internal calibration compound) in mass spectrometry experiments, with a characteristic fragmentation pattern.In the field of microbiology, PEG precipitation is used to

concentrate viruses and PEG is also used to induce complete fusion (mixing of both inner and outerleaflets) in liposomes reconstituted *in vitro*.

PEG is also used in lubricant eye drops. PEG derivatives such as narrow range ethoxylates are used as surfactants. Dimethyl ethers of PEG are the key ingredient of Selexol, a solvent used by coal-burning, integrated gasification combined cycle (IGCC) power plants to remove carbon dioxide and hydrogen sulfide from the gas waste stream.PEG has been used as the hydrophilic block of amphiphilic block copolymers used to create some polymersomes.

Gene therapy vectors (such as viruses) can be PEG-coated to shield them from inactivation by the immune system and to de-target them from organs where they may build up and have a toxic effect. The size of the PEG polymer has been shown to be important, with large polymers achieving the best immune protection.

3. EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

PEG-400 (polyethylene glycol, Mw = 400), Glycidyl methacrylate (GMA) (Fluka), Bipyridine (Aldrich), CuBr (Aldrich), Diethylene amine, benzenesulfonyl chloride (Fluka), diphenylcarbazide (E-Merck), $HgCl_2$ (E-Merck) and all the other chemicals used were analytical grade commercial products.

3.1.2 Instruments

Perkin Elmer 25 UV Spektrometer for analytical measurements, and spectra of the sorbents and the sorbed chemicals were obtained using Perkin Elmer Spectrum One Fourier Transform Infrared Spectrum in between wavenumbers of 650-4000 cm^{-1}. The resolution was 4 and a total of 4 scans was collected for each spectrum.

3.2. Preparation of Poly(GMA)-*b*-Poly(PEG) –*b*-poly(GMA) Block Copolymer by ATRP Method

3.2.1. Preparation of PEG-400 Macroinitiators

Chloroacetyl chloride (44 mmol, 3.5 mL) in 10 mL of dry THF was added to dropwise to a stirring mixture of triethylamine, (43 mmol, 6mL) and PEG-400 (25 mmol , 10 g) in 40 ml of dry THF at 0°C. The reaction was continued under stirring for 18 h at room temperature. The solution was filtered, solvent was evaporated and the PEG macroinitiator was precipitated in cold diethyl ether. The macroinitiator was filtered and dried under vacuum.

3.2.2 The Synthesis of ABA Type Triblock Copolymers

In a typical bulk polymerization reaction, the glass tube was charged with 0.5 g (0.85 mmol) of PEG-400 macroinitiators , 0.717 g (7.2 mmol) of CuCl, and 2.1 ml (10 mmol) PMDETA. 5 mL (37.8 mmol) of GMA was then added and the system

was degassed under nitrogen atmosphere. The mixture was immersed in an oil bath at 65°C. The crude products were dissolved in N-Methyl Pyrrolidone and filtered through the alumina column and then poured into a large excess of hexane to precipitate the copolymers. The polymers were dried under vacuum.

3.3. Modification of Block Copolymer with Ammonia

5 g of (I) was put in 20 ml of Ammonia in a 100 ml of flask. The mixture was stirred for 24 h at room temperature. While stirring, it was heated at 90 ^{0}C in a termostated oil bath for 3 h. After chilling the mixture was poured into 250 ml of distilled water and washed with excess of water (1 L), 25 ml alcohol and dried overnight under vacuum for 24 h. The yield was 6.0 g.

3.3.1. Determination of Amine Content

For determination of the amine content, 0.2 g of the polymer sample was left in contact with 10 mL of 1 M HCl and the acid content of the solution was determined by titration with 0.11 M NaOH solution in the presence of phenolphthalein color indicator. A total amine content of the polymer was calculated as 3.33 mmol g^{-1} polymer.

3.4. Sulfonamidation of Amine Containing Copolymer (II) with Benzensulfonyl Chloride

5 g of the (II) was placed to THF (20 mL) and 10 mL of benzensulfonyl chloride was added drop wise to a stirred reaction mixture at 0 ^{0}C for 2 h and at room temperaturefor 24 h. The modified polymeric sorbent was filtered and washed with water and ethanol respectively. The polymeric sorbent was dried under vacuum at room temperature for 1 day. The yields were found 8.5 g (70 %).

3.4.1. Determination of Sulfonamide Content

For determination of the sulfonamide content, 0,1 g polymer sample was left in contact with 0,1 M 10 ml NaOH and the base content of the solution was determined by titration with 0,01 M HCl solution in the presence of phenolphthalein color indicator. A total sulfonamide content of the polymer was calculated as 2,8 mmol g^{-1} sorbent.

3.5. Swelling Kinetic of the Polymeric Sorbents

Dry polymer sample of (0.1506 g) was immersed in 100 ml of distilled water at room temperature until equilibrium swelling was reached. Then, the swollen gel sample was taken out and the excess of water was removed quickly with blotting paper and the sample was weighed. The percentage swelling was determined by calculating w/w_0, where w and w_0 are the weights of swollen and dry samples respectively. Swelling ratio was found as 364 %.

3.6. Mercury Sorption Experiments

The determination of the mercury sorption capacity of the polymer was performed by the interaction of polymer samples with aqueous $HgCl_2$ solutions as follows. The sorbent sample (0.2 g) was added an Hg (II) solution (20 mL, 0.074 M). No buffer was used in these experiments. The mixture was shaken for 24 h at room temperature and filtered. The residual mercury concentration of the final solution was assayed by the colorimetric analysis of a 1 mL filtrate, with diphenyl carbazide as the color reagent [63].

The desorbed amounts of mercury were calculated according to the residual mercury contents, as previously described. [63] The relevant data are listed in Table 4.1.

3.7. Sorption Tests for Foreign Ions

The sorption capacities of the sorbent toward foreign ions [Mg(II), Cd(II) and Fe(III)] were examined by the simple contact of the aqueous solutions of those ions with 0.15 mol / L initial concentrations for 24 h. Residual metal analyses for Mg(II) and Cd(II) were performed by complexometric ethylene diamine tetra acetic acid (EDTA) titrations, as described in the literature [64]. Fe (III) was analysed colorimetrically. The results are shown in Table 4.1.

3.8. Kinetics of Mercury Sorption

Batch kinetic experiments were performed with very dilute Hg solutions ($1x10^{-4}$ M).For this purpose, the polymeric sorbent (0.2 g) was wetted with distilled water (2 mL) and added to a solution of Hg (90 mL of $3,7x10^{-4}$ M $HgCl_2$). The mixture was

stirred magnetically and aliquots of the solutions (5 mL) were taken at appropriate time intervals for analysis of the residual Hg content by the described above. The collected analytical data were used to produce the concentration–time plot in Figure 3.1.

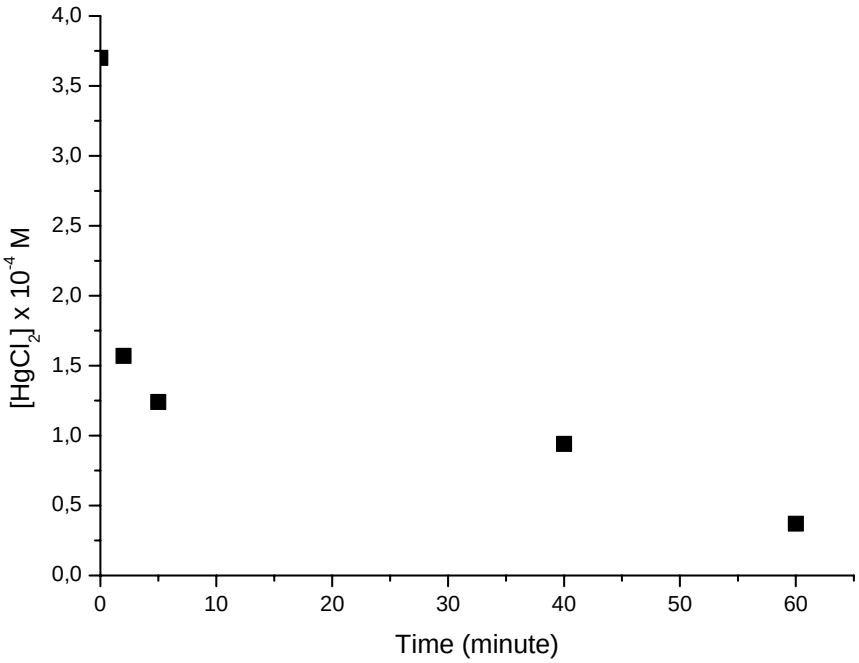


Figure 3.1 : Concentration – time plot of 0,2 g. Polymer sample with 90 ml of 3,7 M $HgCl_2$ solution

3.9 Regeneration of the Sorbent

0,1 gram of the mercury-loaded sample was placed into 10 mL of 5 M HNO_3 for 24 h at room temperature. The mixture was filtered and neutralizied with NaOH and 1 mL of the filtrate was used for colorimetric mercuric analysis. Desorption capacities of the sorbents were given in Table 1.

4. RESULTS AND DISCUSSION

In this study, in the first step of the synthesis of PGMA-*b*-PEG-*b*-PGMA triblock copolymer (I) (Scheme 4.1), a telechelic macroinitiator was prepared by reacting PEG-400 with chloroacetyl chloride. FT-IR spectra of the resulting telechelic macroinitator represent strong C–O stretching vibrations at 1732 cm^{-1}.

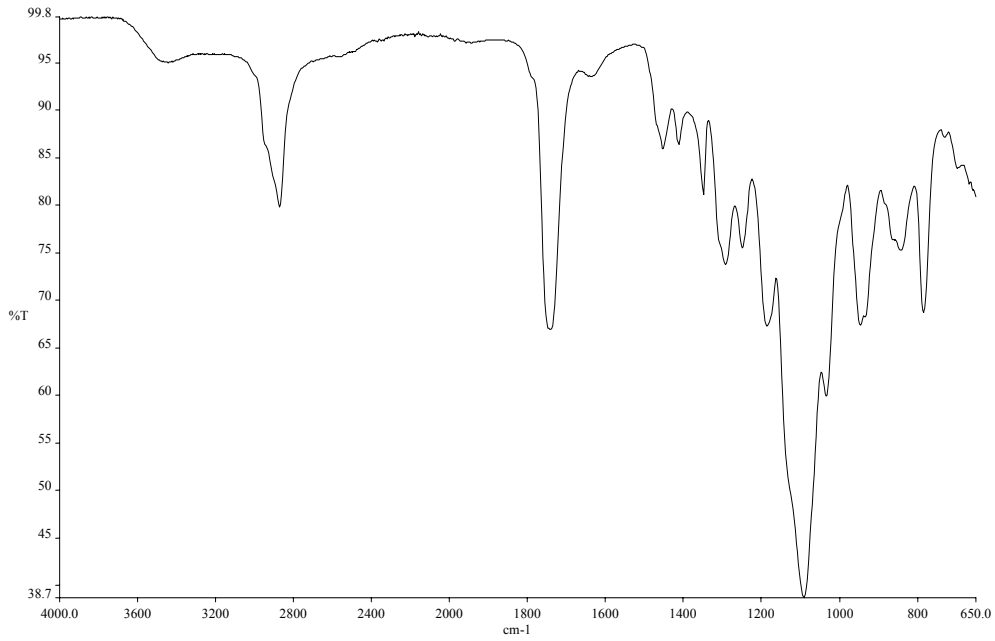


Figure 4.1 : FT-IR spectra of telechelic macroinitiator

Block copolymerization reaction of PGMA in the presence of PEG macroinitiator was carried out by atom transfer radical polymerization (ATRP) method . In the copolymerization reaction [CuBr]/[L] ratio was chosen as 1/3.

FT-IR spectra of the copolymer represents the strong C= O stretching vibrations of ester group at 1726 cm^{-1} and C-O stretching vibrations of epoxy group at 905 cm^{-1} , which indicate incorporation of the poly glycidyl methacrylate chains .

Copolymerization reaction was carried out at 65 ^{0}C for different time to obtain conversion-time plot given in Fig. 4.2.

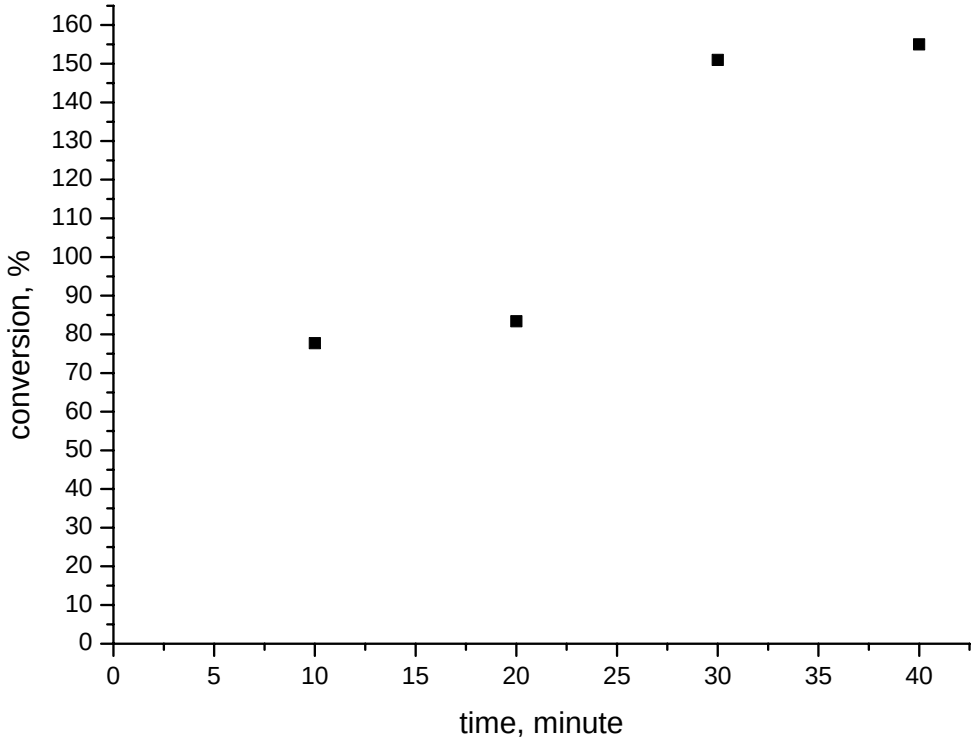
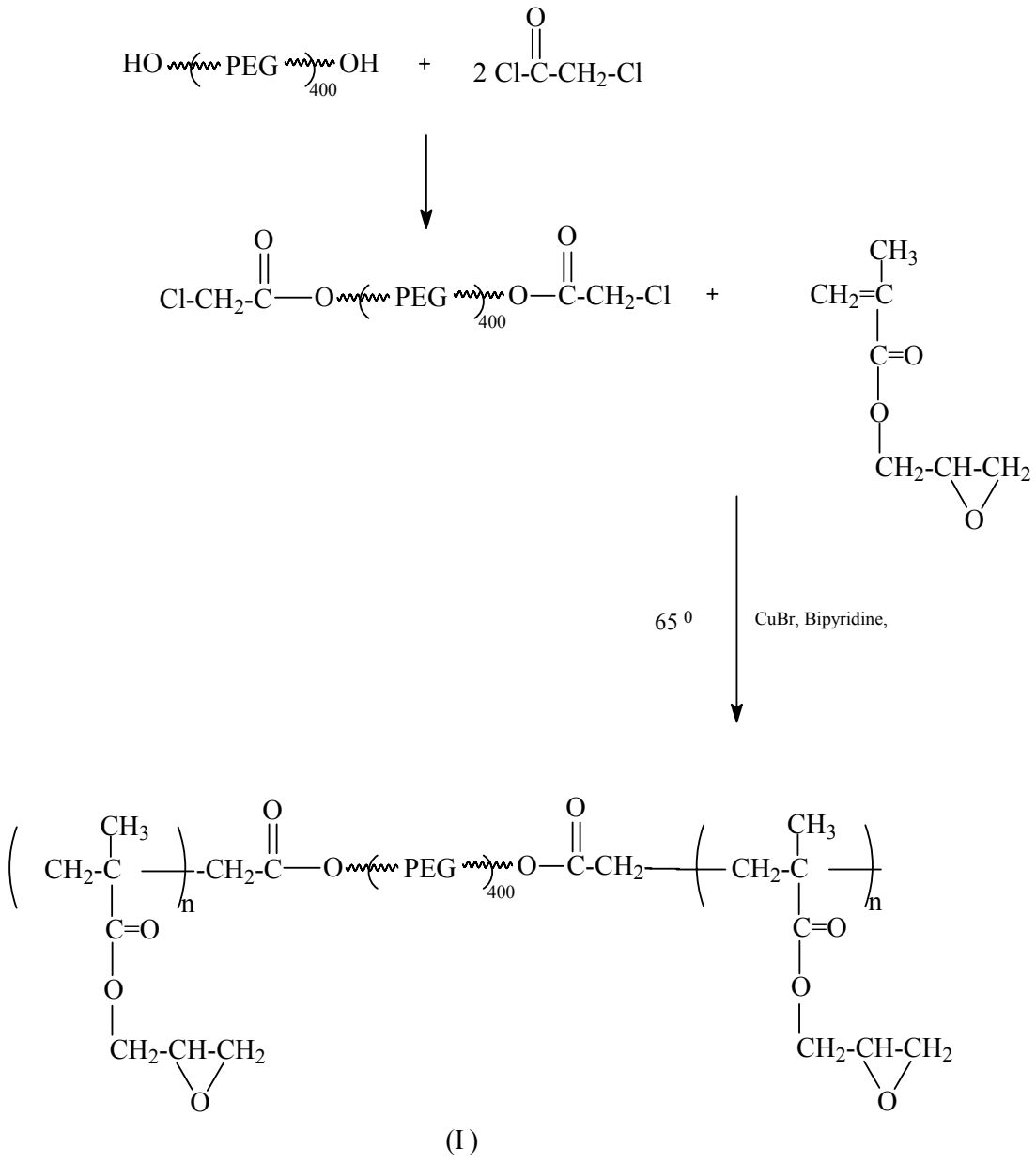


Figure 4.2 : Conversion of the block copolymerization of glycidyl methacrylate at 65 ^{0}C [GMA] = 7.2 mol/L; [PEG-Cl]= 0.17 mol/L; [CuBr]= 1 mol/L, [biprydyl]= 1 mol/L



(I)

Figure 4.3 : Preparation of triblock copolymer (I)

The block copolymer could not be dissolved in any solvent because of crosslinking during copolymerization.

4.1 Sulfonamidation of the Copolymer

Reaction with excess of ammonia was given a primary amine containing sorbent with 3,33 mmol g^{-1} amine functions (Scheme 4.2). The structure of the sorbent was characterized by IR spectroscopy (Fig. 4.3). Appearance of the strong stretching vibrations of N-H link at 3200. cm^{-1}, and the absence of stretching vibrations of the

C-O link of the epoxy group at 905 cm^{-1} proves the presence of amine groups in the polymeric sorbent.

(I)

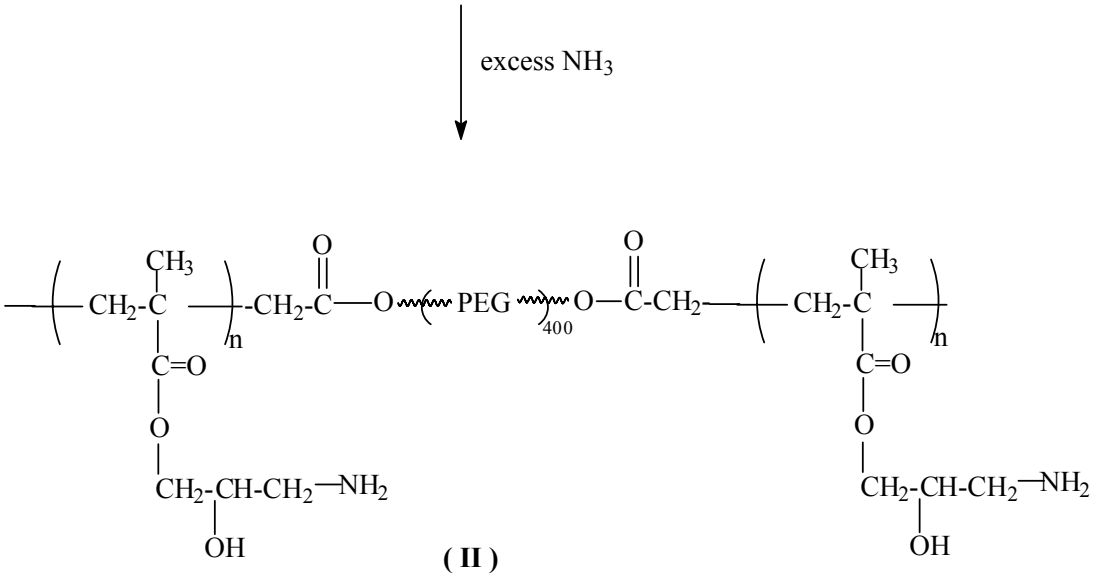


Figure 4.4 : Preparation of amine containing triblock copolymer (II)

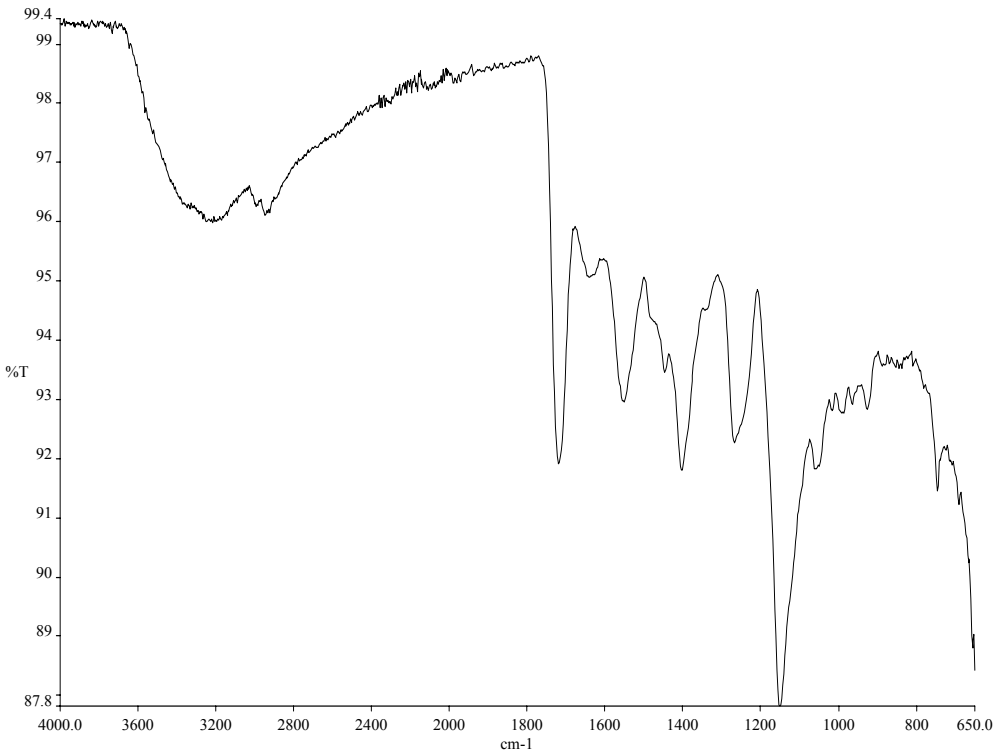
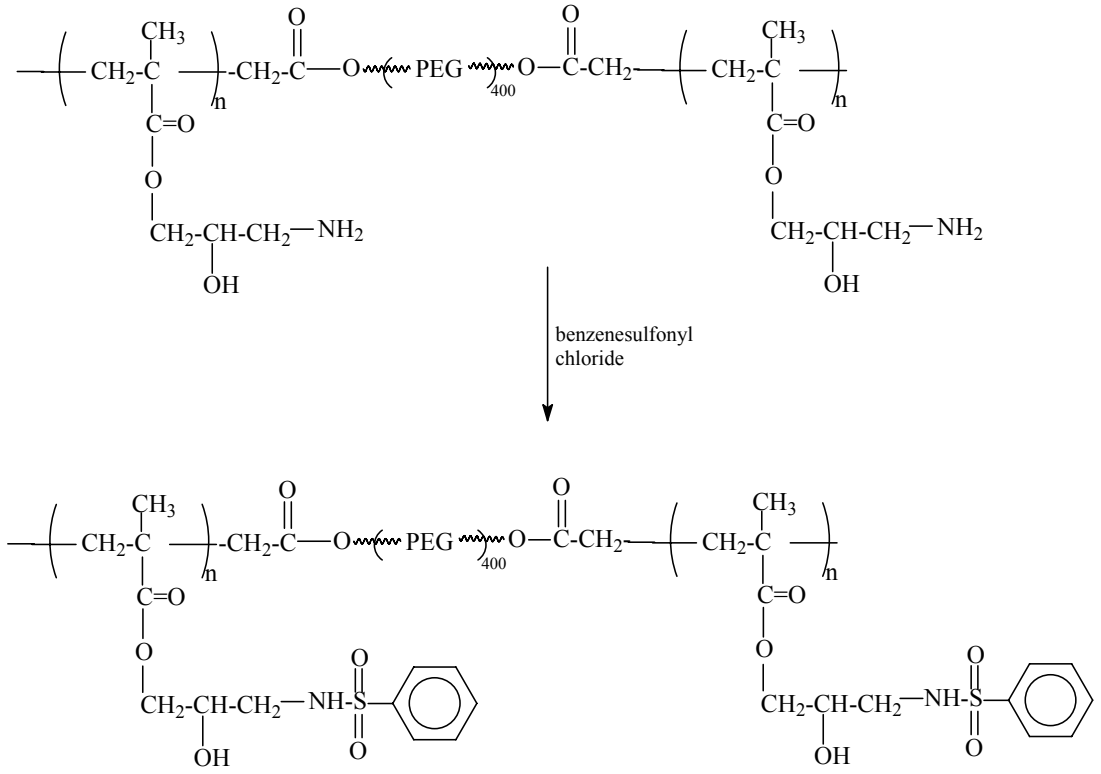


Figure 4.5 : FT-IR spectrum of primary amine containing sorbent

The sulfamidation step was achieved by treating primary amine containing sorbent with excess of benzenesulfonyl chloride and the sulfonamide content, determined according to the literature [65] was found to be about 2.8 mmol g^{-1} . This implies almost quantitative (84 %) conversion in this step.



(III)

Figure 4.6 : Preparation of sulfonamid- based copolymer (III)

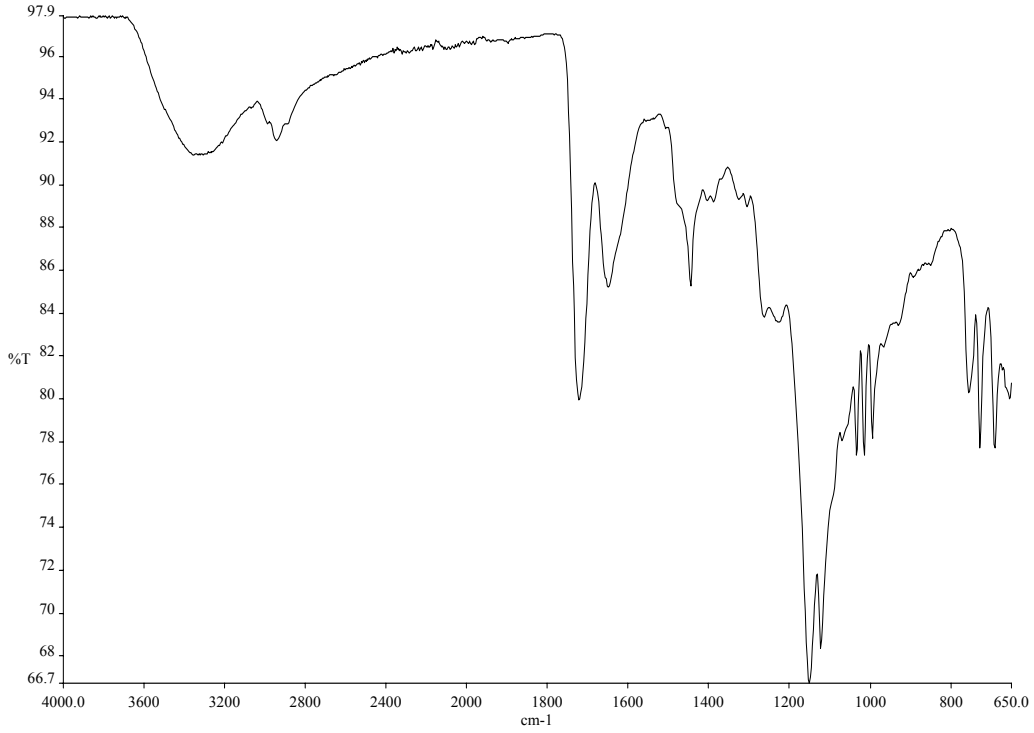


Figure 4.7: FT-IR spectrum of sulfonamid- based copolymer (III)

4.2 Swelling Characteristic of the Polymeric Sorbent

Swelling experiments were performed in distilled water at room temperature. The swelling experiments were carried out by placing a dry polymer sample into a Petri dish. The polymer was then immersed in distilled water and allowed to swell. The amount the hydrogel swelled was obtained by periodically removing the distilled water solution, pat-drying, and weighing the sample.

Swelling capability of the hydrogel was determined from Fig. 4.6 . According to the swelling ratio-time plots, the polymeric sorbent reached equilibrium within 2 hr. Swelling ratio was found to be 364%.

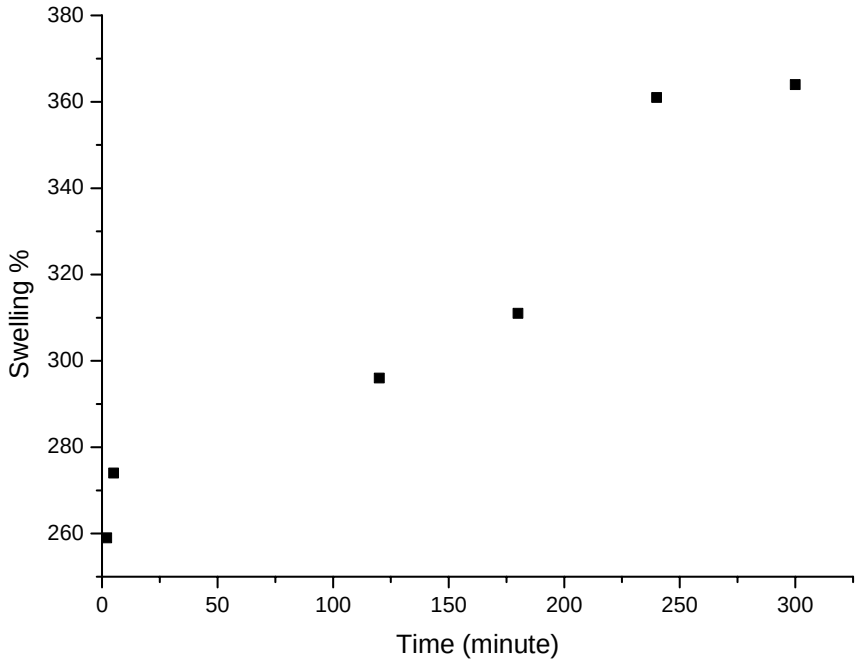


Figure .4.8 : Swelling ratio of the hydrogel in distilled water versus time.

4.3.Mercury Uptake

The sulfonamide containing polymeric sorbent was an efficient sorbent to remove mercury.

On the basis of the basic reaction of the mercuric ions with sulfonamide groups, which yielded covalent mercury–sulfonamide linkages ,the mercury binding of the polymer can be depicted as shown in Figure 4.7 .

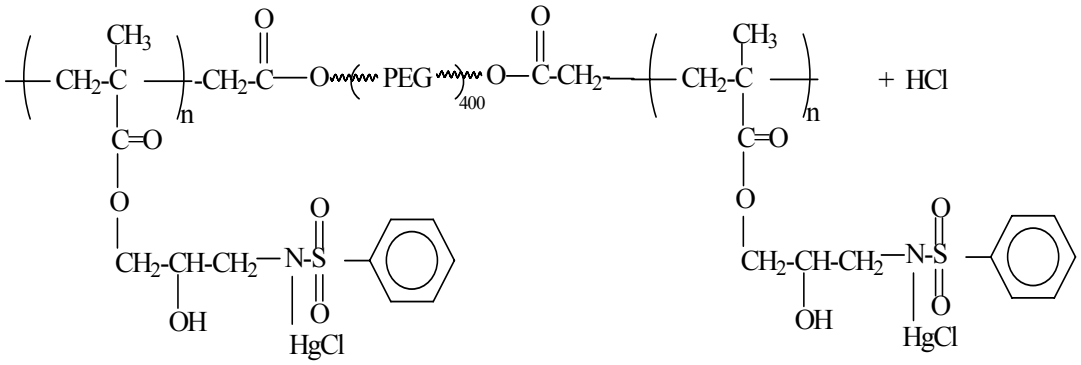


Figure 4.9 : The mercury uptake of the polymer

In the mercury uptake experiments, we deliberately used mercuric chloride because the Hg(II) ion has a reasonable affinity to chloride ions. In previous studies [66], we found mercury uptake to be somewhat higher when mercuric acetate is used. For this reason, in the present study, $HgCl_2$ was used to determine the capacity of the polymeric sorbent under extreme conditions.

The sorption capacity of the polymeric sorbent was analyzed by the determination of the excess mercury ions in the supernatant solutions. The mercury sorption capacity was found as 3.12 mmol g^{-1}(Table 4.1).

The pH of $HgCl_2$ solutions remained almost constant, in the 3.1–3.9 range, throughout the extraction process. We did not use buffer solutions in the experiments because their use is not practical in real application conditions.

To inspect mercury efficiency of the sorbent, metal extraction experiments were repeated with Cd(II), Mg(II),, and Fe(III) solutions. Each showed a small sorption capacities (0.35– 0.45 mmol/g) were found according to mercury sorption capacity (Table 4.1).

Since, in ordinary conditions the sulfonamide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the sulfonamide nitrogen; the separation of mercury ions is expected to be highly selective.

Table 4.1 : Metal uptake characteristics of the polymeric sorbent

Metal ion	**Initial concentration (M)**	**Sorbent capacity (mmol.g $^{-1}$)**	**Recovered metal (mmol.g-1)**
Hg(II)	0.074	3.12	2.36
Hg(II)	0.05	3.10	
Hg(II)	0.025	3.00	
Cd(II)	0.150	0,35	-
Mg(II)	0.150	0	-
Fe(III)	0,05	0.45	-

4.4 Kinetics of the Mercury Sorption

To investigate the efficiency of the sorbents in the presence of trace quantities, batch kinetic sorption experiments were performed with highly diluted $HgCl_2$ solutions ($3{,}7 \times 10^{-4}$ M). The concentration–time plots in Fig 2 shows that within about 60 min of contact time, the Hg(II) concentration falls zero.

The kinetics of the sorption obey second order kinetics (k = 6,19/M s with a correlation factor of 0.989) for the sorbent.

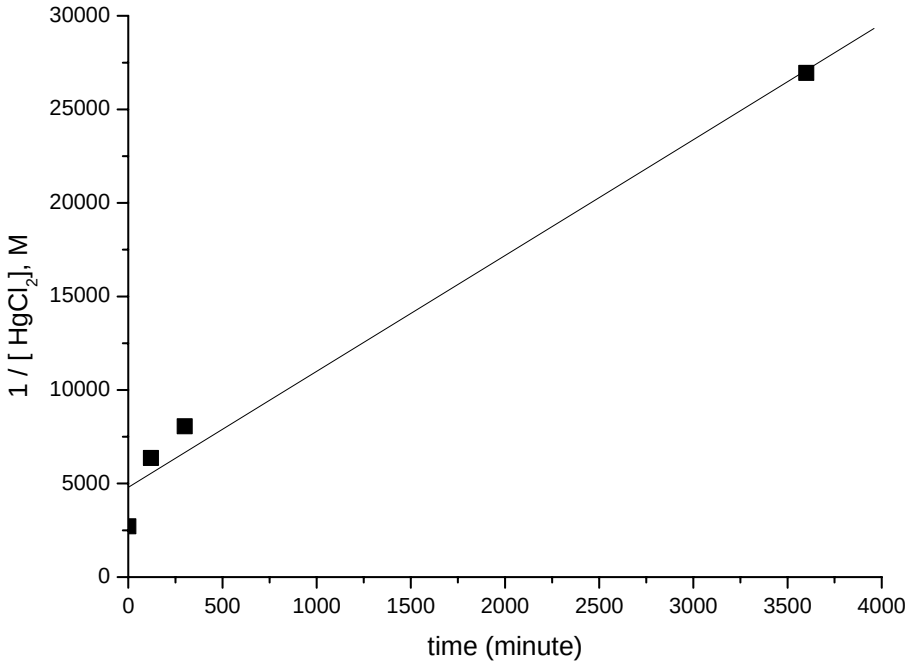


Figure 4.10 : Second order kinetic plot for sorption of mercury from 90 ml $HgCl_2$ solution while contacting with 0,2 g. of polymer sample.

4.5. Splitting of the Sorbed Mercury

In the regeneration of mercury from loaded polymer, 5 M Nitric acid was used as an appropriate agent. When loaded sample was interacted with nitric acid for 24 h, the amount of recovered mercury is around 2.36 mmol/g (Table 1), which is about 76% of the capacity of fresh polymer.

5. CONCLUSIONS

The Atom transfer radical copolymerization of glycidyl methacrylate was performed using poly(ethylene glycol)-based telechelic macroinitiator and CuBr/Bpy as a catalyst in bulk at 65 °C.

The obtained ABA type block copolymer was modified with ammonia to give primary amine functions. A new polymeric sorbent was prepared sulfonamidation of the amine containing sorbent.

This material was highly effective in removing mercury, and its format makes it of interest for technological use as a column-packing material. Under non-buffered conditions, the mercury uptake capacity was around 3.12 mmol/g. In addition, the conditions of regeneration of the sorbent are easy, which is important for industry.

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