**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Preparation of the Sulfonamide Containing Block Copolymer as Polymeric Sorbent for Removal of Mercury from Aqueous Solutions

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**To cite this Article** Gursel, Yesim , Yavuz, Erdem , Gokay, Gulsah and Senkal, Bahire Filiz(2010) 'Preparation of the Sulfonamide Containing Block Copolymer as Polymeric Sorbent for Removal of Mercury from Aqueous Solutions', Separation Science and Technology, 45: 16, 2406 — 2412

**To link to this Article: DOI:** 10.1080/01496395.2010.490543

**URL:** http://dx.doi.org/10.1080/01496395.2010.490543

*Separation Science and Technology*, 45: 2406–2412, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.490543

# Preparation of the Sulfonamide Containing Block Copolymer as Polymeric Sorbent for Removal of Mercury from Aqueous Solutions

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**A new sulfonamide containing polymeric sorbent for the removal of mercury ions from waste waters was prepared starting from poly(glycidyl methacrylate)-*b*-poly(ethylene glycol)-*b*-poly(glycidyl methacrylate) (PGMA-*b*-PEG-*b*-PGMA) triblock copolymer prepared by using the ATRP method. Epoxy groups on the block copolymer were functionalized with amino groups. Ammonia-functionalized PGMA-*b*-PEG-*b*-PGMA was treated with excess of benzenesulfonyl chloride to obtain a sulfonamide-based polymeric sorbent. The sulfonamide containing the polymeric sorbent with a 3.5 $\text{mmol}\cdot\text{g}^{-1}$ total nitrogen content is able to selectively sorb mercury from aqueous solutions. The mercury sorption capacity of the resin is around 3.12 $\text{mmol g}^{-1}$ under non-buffered conditions. Experiments performed in identical conditions with several metal ions revealed that Cd(II), Pb(II), Zn(II), Fe(III), and Fe(II) also were extractable in quantities (0–0.45 mmol/g). The sorbed mercury can be eluted by repeated treatment with 4 M $HNO_3$ without hydrolysis of the sulfonamide groups.**

**Keywords** block copolymer; metal complexes; PEG; polymeric sorbent; sulfonamide

## INTRODUCTION

The synthesis of materials with well-defined compositions, architectures, and functionalities has attracted growing scientific interest in recent years. A number of strategies have been sought by polymer researchers in need of preparing new materials displaying improved physical and chemical properties.

Such improved properties might be achieved by combining a number of physical and chemical properties of the homopolymers in the block copolymer structure.

One way to prepare block copolymers is by using main chain macroinitiators. In this method, reactive sites are produced at the chain ends, which serve as initiating moieties in the polymerization of a second monomer.

Controlled/living radical polymerization (CRP) methods such as atom transfer radical polymerization ATRP, where the polymerizations proceed in the absence of irreversible chain transfer and chain termination, allows for the facile preparation of di-, tri-, or multi-block copolymers as well as star polymers using bi- or multi-functional initiators carrying the active halogen atoms.

The macroinitiators prepared by various other routes such as ring-opening, anionic, cationic, and conventional radical processes can also be used in the chain extensions through ATRP to get diblock or triblock copolymers. For this purpose, a modification reaction from one or both ends of the precursor polymer is usually necessary to incorporate the desired halogen functionality to the chain.

The radical polymerization behaviors of GMA have been intensively investigated because of the high reactivity of its double bond under radical polymerization (1–3). At the same time the presence of reactive epoxy groups offers an opportunity for modifying the resulting polymers. Mercury is one of the heavy metals which represents a serious environmental problem. Mercury is a highly toxic metal that is very poisonous for living organisms even in trace concentration (ppb). It is widely used or disposed off from different industries such as electrical, paints, fungicides, chlor-alkali, paper and pulp, pharmaceuticals, etc. (4).

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.

A number of techniques have been suggested for the removal of mercury from aqueous solution. These include reduction, precipitation, coagulation, ion exchange, reverse osmosis, adsorption, etc. (5–7).

Removal of trace mercury cannot be achieved by conventional ion exchangers. Removal ofmercury and other toxic metals require more efficient sorbents.

Specially designed chelating polymers show excellent metal-uptake capabilities and thesehave been discussed in

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Received 6 January 2010; accepted 29 April 2010.

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many articles and reviews (8,9). Thio and amide groups have been used in the design of polymeric sorbents for binding mercury ion selectively. The well-known reactivity of thiol (10–14) and thioether (15) compounds toward mercuric ions is the main principle of selective mercury uptake for laboratory or industrial levels of applications. In fact, mercury–thiol interaction is not specific because thiol and thioether functions react also with other metal ions (16).

In our previous studies we have demonstrated that amide groups provide better selectivity inmercury binding (17). The mercury–amide linkage is covalent (18) and the reaction takesplace even in aqueous solutions at room temperature.

In this study, commercial PEG-400 was modified with chloroacetyl chloride to obtain the macroinitiator. The atom transfer radical copolymerization of glycidyl methacrylate was performed using a poly (ethylene glycol)-based macroinitiator and CuBr/Bpy as a catalyst in bulk at 65°C.

The reaction of the resultant ABA type block copolymer with excess of ammonia was given a primary amine containing resin. After, the reaction of the resin with excess of benzenesulfonyl chloride, sulfonamid-based polymeric sorbent was obtained the mercury sorption capacity of the polymeric sorbent was found as $3.20\,\mathrm{mmol \cdot g^{-1}}$ and this value is reasonably high according to the sorbents described in the literature.

Amido-mercury compounds are hydrophobic in nature. For this reason, during mercury sorption by crosslinked polyacrylamide, hydrophobicity increases as the mercury binding proceeds and a hydrophilic–lyophilic balance is reached when about 60% of the amide groups are utilized. Beyond this point the hydrophobicity does not allow binding of additional mercury. Therefore. the mercury sorption capacity of sulfonamide containing resin described in the literature was found as $0.83–1.64\,\mathrm{mmol \cdot g^{-1}}$(19).

Also, water insoluble polyamides such as natural wool and Nylon-6 show only negligible mercury sorptions (0.24 and $0.09\,\mathrm{mmol\,g^{-1}}$, respectively) (20).

In the literature, crosslinked polyacrylamide has been shown as an extremely powerful sorbent for mercury uptake (21) sorbing as high as 1.5 g Hg(II) per gram of polymer.

In the previous studies, the mercury binding capacities of the polymeric sorbents were found as $1.60\,\mathrm{mmol\,g^{-1}}$ for ureasulfonamide containing polymeric sorbent (22), $2.20\,\mathrm{mmol\,g^{-1}}$ for glycidyl methacrylate–based resin crosslinked beads with acetamide functions (23) and $0.70–0.85\,\mathrm{g^{-1}Hg\,g^{-1}}$ for polythioamides (24). Mercury sorption characteristics and regeneration conditions of the resulting polymericsorbent was studied. Affinity of the polymer for some other metal ions such as Cd(II), Pb(II), Fe(III), and Zn(II) was also investigated.

# EXPERIMENTAL

## Materials

PEG-400 (polyethylene glycol, Mw = 400), Glycidyl methacrylate (GMA) (Fluka), N,N,N′,N′,N″-Pentamethyldiethylenetriamine (PMDETA) (Aldrich), CuBr (Aldrich), diethylamine, benzenesulfonyl chloride (Fluka), diphenylcarbazide (E-Merck), $HgCl_2$ (E-Merck), disodium hydrogen phosphate-potassium dihydrogen phosphate buffer (E-Merck), and all the other chemicals used were analytical grade commercial products.

## Preparation of PEG-400 Macroinitiators

Chloroacetyl chloride (44 mmol, 3.5 mL) in 10 mL of dry THF was added dropwise to a stirring mixture of triethylamine, (43 mmol, 6 mL) 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, the solvent was evaporated, and the PEG macroinitiator was precipitated in cold diethyl ether. The macroinitiator was filtered and dried under vacuum.

### *The Synthesis of PolyGMA–PEG–PolyGMA Triblock Copolymers by ATRP Method*

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.

### *Determination of Epoxy Content*

The epoxy content of the block copolymer was determined by a pyridine-HCl method described previously (25). Titration of the filtrated pyridine-HCl solution with NaOH (0.052 M) yielded an epoxy content of 5 mmol/g.

## 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 hat room temperature. While stirring, it was heated at 90°C in a thermostated oil bath for 3 h. After chilling the mixture was poured into 250 ml of distilled water and washed with excess of water and alcohol. Modified polymer was dried overnight under vacuum for 24 h. The yield was 6.0 g.

### *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 0.10 M NaOH solution in the presence of a phenol–phatalein color indicator. A total amine content of the polymer was calculated as 4.1 mmol $g^{-1}$ resin.

## Sulfonamidation of Amine Containing Copolymer (II) with Benzenesulfonyl Chloride

5 g of the (II) was placed to THF (20 mL) and 10 mL of Benzenesulfonyl chloride was added dropwise to a stirred reaction mixture at 0°C for 2 h and at room temperature for 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. Yield: 6.3 g. The sulfonamid content of the sorbent was determined according to the literature (26) and was found as 3.5 mmol $g^{-1}$ resin.

## Swelling of the Polymeric Sorbent

A dry polymer sample of (0.1506 g) was immersed in 100 ml of distilled water at room temperature until equilibrium swelling was reached. The percentage swelling was determined by calculating $w/w_0$, where w and $w_0$ are the weights of the swollen and the dry samples respectively. The swelling ratio was found as 364% for 24 h.

## 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. To the resin 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 (27). Similar experiments were repeated under the same conditions with different initial mercury concentrations (0.025, 0.05, and 0.1 M). The sorbed amounts were calculated according to the residual mercury contents, as previously described. The relevant data are listed in Table 1.

### *Sorption Tests for Foreign Ions*

The sorption capacities of the resin 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 (28). The results are shown in Table 1.

### *Mercury Sorption in the Presence of Fe(III) Ion*

The mercury loading experiment was repeated in the presence of Fe(III) according to the previous study (17). A binary mixture of $HgCl_2$ and $FeCl_3 \cdot 6H_2O$ was prepared so that the final concentration of each component was 0.074 M. 10 mL of this solution was interacted with 0.20 g of the resin sample for 24 h at room temperature. The mixture was filtered and 1 mL of the filtrate was treated with 5 mL of 0.3 M KSCN and 5 mL of a dithizone solution (2 g in 50 mL of $CCl_4$). An analysis of the mercury in the extract phase was performed by monitoring of the absorbance of the mercury–dithizone complex at 496 nm as described in the literature (29). This analysis gave 3.0 mmol of Hg(II)/g of polymer.

TABLE 1
Metal uptake characteristics of the resin

| Metal ion | Initial concentration, M | Resin capacity $(mmol \cdot g^{-1})$ | Recovered metal $(mmol \cdot g^{-1})$ |
|---|---|---|---|
| Hg(II) | 0.074 | 3.12 | 2.36 |
| Hg(II) | 0.050 | 3.10 | – |
| Hg(II) | 0.025 | 3.00 | – |
| Cd(II) | 0.150 | 0.35 | – |
| Mg(II) | 0.150 | 0 | – |
| Fe(III) | 0.050 | 0.45 | – |
| Zn (II) | 0.074 | 0.05 | – |

### *Mercury Sorption in the Presence of Zn(II)*

The same experiments described previously were repeated with a Hg(II)–Zn(II) binary mixture (17). Determination of unreacted Hg(II) and Zn(II) in the solution were performed by the EDTA titration method with potassium iodide as a masking agent for the mercury, according to ageneral procedure given in the literature (30). This analysis gave 0.05 and 3.1 mmol $g^{-1}$ Zn(II) and Hg(II) sorptions, respectively.

### *Kinetics of Mercury Sorption*

Batch kinetic experiments were performed with very dilute Hg solutions ($3.7 \times 10^{-4}$ 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 $3{,}7 \times 10^{-4}$ 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 experiment described above. The same experiment was repeated at different pH values adjusted using buffered solution (pH 7.0). The collected analytical data were used to produce the concentration–time plot in Fig. 3.

### *Regeneration of the Resin*

A half-gram of the mercury-loaded sample was introduced to 10 mL of glacial acetic acid at a constant temperature of 80°C, and the mixture was stirred for 1 h.

Desorption experiments were repeated with 4 M $HNO_3$ for 24 h at room temperature. The mixture was filtered, and 1 mL of the filtrate was used for colorimetric mercuric analysis. Desorption capacities of the resins were given in Table 1.

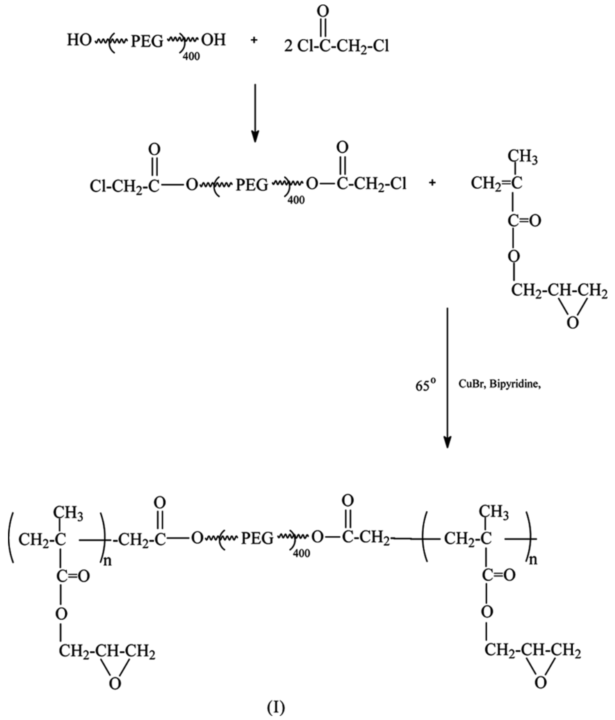
## RESULTS AND DISCUSSION

In this study, PEG-400 was reacted with chloroacetyl chloride to obtain the macroinitiator. Block copolymerization reaction of Poly (glycidyl methacrylate) with PEG containing initiator was carried out by atom transfer radical polymerization (ATRP) method (Scheme 1). In the copolymerization [CuBr]/[L] ratio was chosen as 1/3. The copolymerization reaction was carried out at 65°C for different times to obtain a conversion-time plot given in Fig. 1.

The epoxy content of the resin was determined as 5 mmol $g^{-1}$, by the pyridine–HCl method.

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 the incorporation of the poly glycidyl methacrylate chains (Fig. 2a). The block copolymer is not dissolved in any solvent because of partial crosslinking during copolymerization.

Reaction with excess of ammonia was given a primary amine containing sorbent with 4.1 mmol $g^{-1}$ amine functions (Scheme 2). The structure of the sorbent was characterized by IR spectroscopy (Fig. 2b). 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)

SCH. 1. Preparation of block copolymer (I).

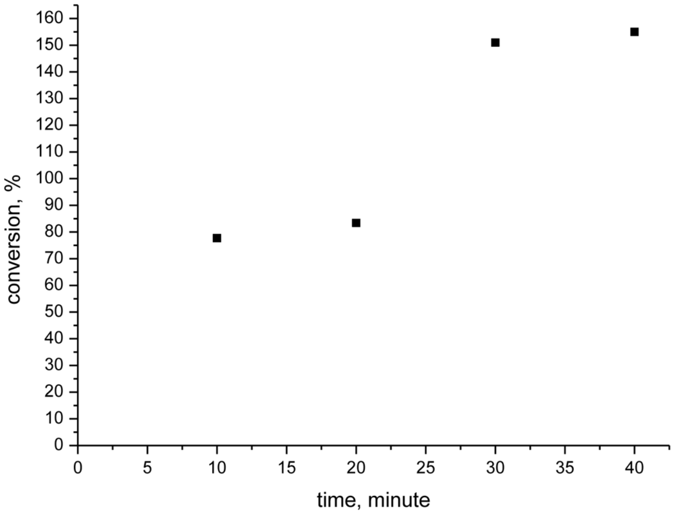


FIG. 1. Conversion of the block copolymerization of glycidyl methacrylate at 65°C [GMA] = 7.2 mol/L; [PEG-Cl] = 0.17 mol/L; [CuBr] = 1 mol/L [biprydyl] = 1 mol/L.

### Sulfonamidation of the Copolymer

The sulfamidation step (Scheme 2) was achieved by treating with excess of benzenesulfonyl chloride and the sulfonamide content was found to be about 3.5 mmol $g^{-1}$.

The spectroscopic characterization of the polymeric sorbent was achieved by FT-IR spectrophotometer. In Fig. 2c, S=O the stretching vibration of the sulfonamide group at 1122 $cm^{-1}$ and aromatic out-of-plane bending vibrations at 900–690 $cm^{-1}$ proves the presence of sulfonamide groups in the polymeric sorbent.

### 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 sorbent swelled was obtained by periodically removing the distilled water solution, pat-drying, and weighing the sample. The swelling ratio was found to be 364%.

### 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, this yielded covalent mercury–sulfonamide

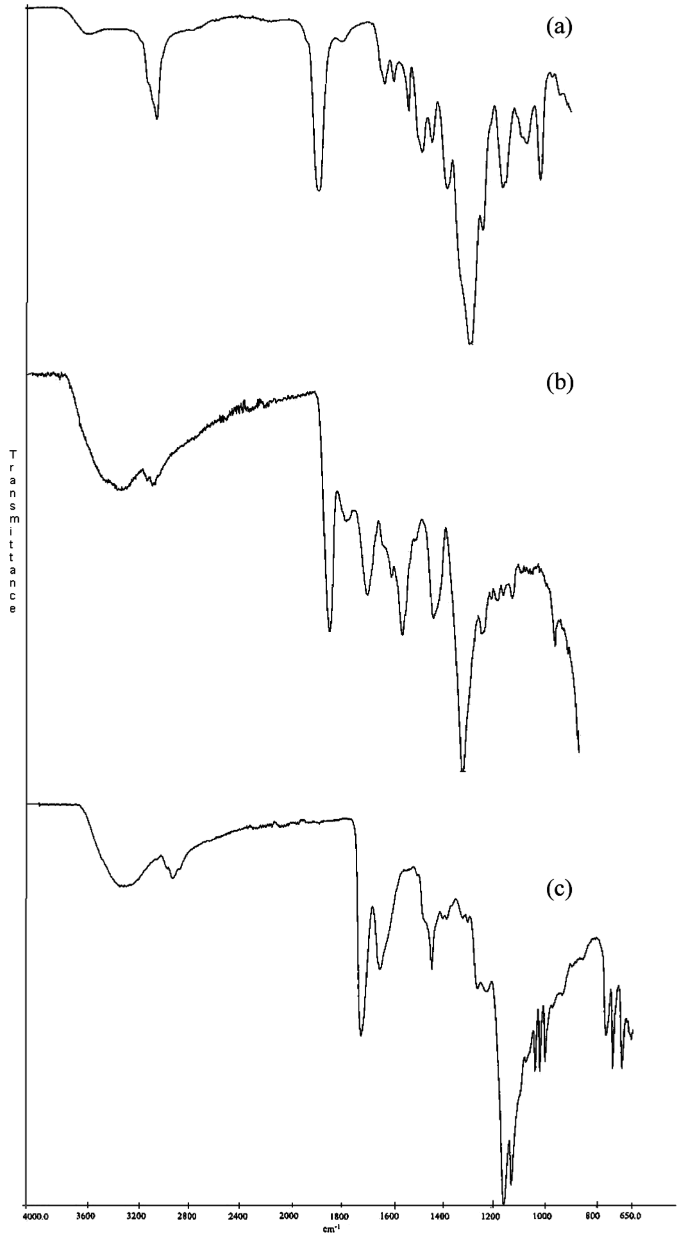
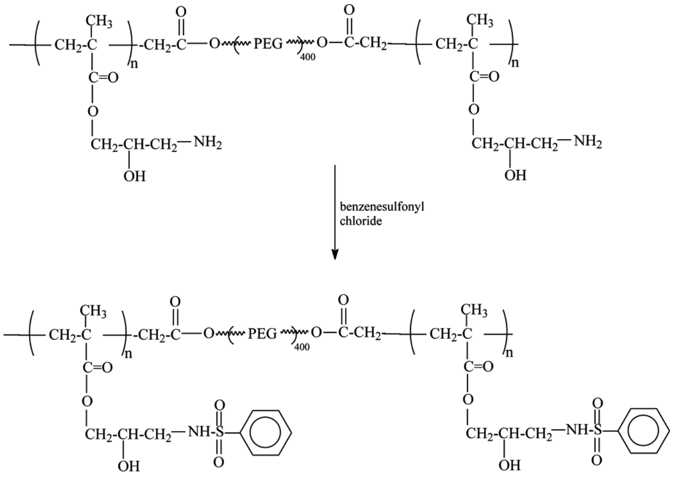


FIG. 2. FT-IR spectra of the polymeric sorbents (a) PGMA-PEG-PGMA copolymer (b) aminated copolymer (c) sulfonamide containing polymeric sorbent.

linkages (31). The mercury binding of the polymer can bedepicted as shown in Scheme 3.

In the mercury uptake experiments, we deliberately used mercuric chloride because the Hg(II) ion has a reasonable affinity to chloride ions. In a previous study (31), 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 1). Extracted amounts of mercury from Hg(II)–Fe(III) and Hg(II)–Zn(II) binary mixtures are almost the same as those observed in the absence of Fe(III) and Zn(II) ions.



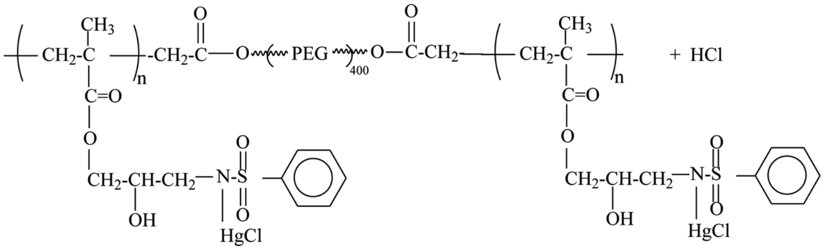
SCH. 2. Preparation of sulfonamide based copolymer.

The pH of $HgCl_2$ solutions remained almost constant, in the 3.1–3.9 range, throughout theextraction process. We did not use buffer solutions in the experiments because their use is notpractical in real application conditions. To inspect mercury efficiency of the resin, metal extraction experiments were repeated with Cd(II), Mg(II), and Fe(III) solutions. Each showed that small sorption capacities (0.00–0.45 mmol/g) were found according to the mercury sorption capacity (Table 1). Since, in ordinary conditions the sulfonamide group is not capable of forming coordinativebonds with other transition metal ions, as a result of the reduced electron-donating character of the sulfonamide nitrogens, the separation of mercury ions is expected to be highly selective.

## Kinetics of the Mercury Sorption

To investigate the efficiency of the resins in the presence of trace quantities, batch kineticsorption experiments were performed with diluted $HgCl_2$ solutions ($3.7 \times 10^{-4}$ M). The concentration–time plots in Fig. 3 show that within about 60 min of contact time, the Hg(II) concentration (without buffer solution) falls to zero.

When a mercuric ion solution is contacted with the polymeric sorbent without the buffer solution the pH goes from 6.4 to 4.4 depending on the concentration and amount of the sorbent. This confirms that the mercury binding process proceeds simultaneously with deprotonation of the sulfonamide groups. This material is quite efficient for the removal of Hg(II) with all the mercury at 374 ppm



SCH. 3. Mercury binding of sulfonamide containing polymeric sorbent.

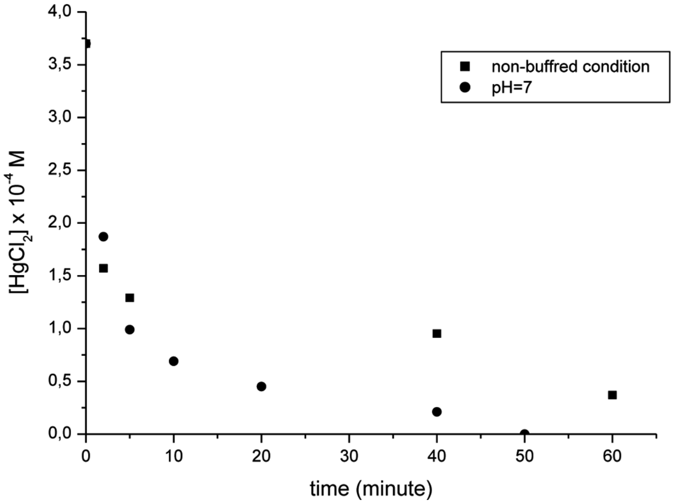


FIG. 3. Concentration-time plot of 0,2 g. Polymer sample with 90 ml of $3{,}7 \times 10^{-4}$ M $HgCl_2$. Solution in buffer and non-buffer conditions.

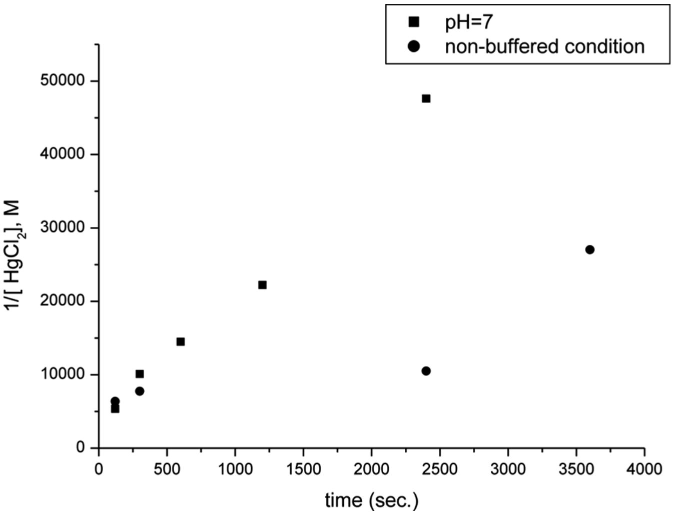


FIG. 4. Second order kinetic plot for sorption of mercury from 90 ml $HgCl_2$ solution while contacting with 0.2 g of polymer sample in buffer and non-buffer conditions.

concentration being completely removed in about 50 min at pH 7.

The kinetics of the sorption obey second-order kinetics (k = 6.19/M s with a correlation factor of 0.989 at non-buffered condition and k = 18.00 M s with a correlation factor of 0.995 at pH 7, respectively) for the resin (Fig. 4).

## Splitting of the Sorbed Mercury

In the regeneration of mercury from the loaded polymer, 4 M nitric acid was used as an appropriate agent. When the loaded sample was interacted with nitric acid for 24 h, the amount of the recovered mercury was around 2.36 mmol/g (Table 1), which is about 75.6% of the capacity of the fresh polymer. When the mercury-loading experiment was repeated five times with the regenerated polymer, the observed loading capacity was 2.1 mmol.

## CONCLUSIONS

ABA triblock copolymer poly(glycidyl methacrylate)-*block*-poly(ethylene glycol)-*block*-poly(glycidyl methacrylate) was synthesized via atom transfer radical polymerization by using a PEG-Cl macroinitiator prepared from commercially available PEG-400.

The obtained copolymer was modified with ammonia to give primary amine functions. A new polymeric sorbent was prepared by the sulfonamidation of the amine groups in the copolymer. This material was highly effective in removing mercury and the mercury uptake capacity was around 3.12 mmol/g under non-buffered conditions. In addition, the conditions of regeneration of the resin are easy, which is important for industry.

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