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An alternative approach for grafting of acrylate esters from crosslinked polystyrene beads by ATRP and their modification for selective mercury extraction

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Abstract

Poly(methylmethacrylate) (PMMA) and Poly(ethyl acrylate) (PEA) have been grafted in high yields (i.e., 1000%) from 2-bromo, 2-methyl propionyl (BMP) groups on crosslinked poly(styrene beads), using copper-mediated atom transfer radical polymerization (ATRP) methodology. Graft reactions were first order with respect to the monomer concentrations in each case. Only minute amounts (2%) of free polymer formation have been observed. BMP groups have been anchored via acetoxy mercuration of the polystyrene beads. Aminolysis of the graft polyacrylate chains with ethanolamine yields corresponding hydroxyethyl acrylamides, which are capable of selective mercury binding from aqueous solutions. Aminolysed PMMA and PEA grafts show reasonable mercury uptakes (2.8 and 3.6 mmolg⁻¹, respectively) with high selectivity over potentially contaminating ions such as Zn(II), Cd(II), Pb(II) and Fe(III) ions. Sorbed mercuries can be eluted by repeatedly treating with hot acetic acid. Although both polymers are also efficient for removal of trace (71 ppm) quantities of mercuric ions, the regenerated aminolysis product derived from PEA graft sample represents somewhat activity loss (27%) in the mercury sorption. Fortunately, aminolysed PMMA graft samples do not loose their activity even after the third regeneration. The material presented here is regenerable and has the advantage of mobility of the graft chains in the selective mercury removal from aqueous mixtures.

Keywords: Mercury uptake; Mercury removal; Graft copolymer; Polymer beads; Surface graft

1. Introduction

Selective mercury uptake has been the subjected of many articles and reviews due to the high toxicity of mercury compounds [1]. Common ligating groups attached to crosslinked polymer beads are capable of chelating with many heavy metal ions. These are superior to ion exchangers when removal of trace quantities is in question. Most of the common ligating groups are also capable of binding mercury in high levels. Only few functional groups such as thiol [2], thioether [3],

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thioamide [4] and amide groups [5] show selectivity in mercury binding. Based on this key principle, many sulfur based polymer resins have been developed for selective mercury extraction from aqueous solutions [7]. Sulfur based ligands show also some affinities for Pb(II) and Cd(II) ions [6]. In other words, those ligands are not strictly selective for Hg(II) ions. Amide group, on the other hand, is unique for selective mercury binding because nitrogen atom in the amide group is a very weak electron donor and does not form coordinative linkages with transition metal ions but the amide nitrogen forms a covalent linkage with Hg(II) in ordinary conditions to give mono or diamido mercury compounds [7].

$$\begin{array}{cccc} O & O \\ R-C-NH_2 &+ HgX_2 & \longrightarrow & R-C-NH-HgX_{or} \\ O & O \\ R-C-NH-Hg-NH-C-R \end{array}$$

The corresponding reaction takes place even in aqueous solutions at room temperature. This behavior can be an advantage for selective mercury binding from mixtures.

In our previous studies, we have demonstrated that polymeric amides such as crosslinked polyacrylamides [8] and cellulose-g-polyacrylamides [9] were very efficient in selective extraction of mercuric ions, even in ppm levels. Hydrophyl-lyphophyl balance is crucial in mercury uptake from aqueous solutions. Mercury binding induces hydrophobicity to the polymer sorbent, thus about 60% of acrylamide units are involved in mercury binding. In other words, mercury binding takes place up to the level where the hydrophilic-hydrophobic balance is reached [9]. Although they are constituted with amide groups, nylon-66 and natural wool show almost no affinities in mercury sorption due to their hydrophobic nature. To impart permanent hydrophilicity, we have prepared crosslinked poly(4-vinyl pyridine) quaternized with 2-chloroacetamide. It was observed that this material binds mercury in monoamido form and almost all the amide groups are involved in the mercury uptake [10].

In continuing studies, we have investigated the use of polyacrylamide grafted on crosslinked spherical bead polymers for mercury extraction. We have proposed that the graft polyacrylamide chains attached to spherical beads might be very beneficial, due to mobility of the graft chains. This mobility provides quasi-homogeneous conditions in the reaction with mercuric ions. In other words, physical the advantages of spherical beads and mobility of the graft chains have been combined in such a structure. However, designing of such a structure by grafting from technique has disadvantage of free polymer formation as a side reaction when conventional radical initiation methods are employed. Fortunately, new emerging controlled radical polymerization techniques, such as copper-mediated atom transfer radical polymerization (ATRP) has been shown to be very useful to suppress side reactions yielding waste amounts of free polymer [11,12].

We have also studied grafting of polyacrylamide from polystyrene based beads by coppermediated ATRP. However, despite negligible amounts of free polymer formation, the chain growth in that case did not proceed in controlled fashion and the process was very slow [13].

In the present work, we have followed an alternative pathway to attain acrylamide surface grafts on the spherical beads. This pathway involves three steps: (i) incorporation of 2-methyl 2bromo propyl groups to crosslinked polystyrene beads; (ii) grafting of poly(methylmethacrylate) (PMMA) and poly(ethylacrylate) (PEA) from the surface by copper-mediated ATRP; (iii) aminolysis of the acrylate ester chains by ethanolamine. In the last part of the study, the mercury uptake ability of 2-hydroxylethyl acrylamide moieties in the resulting material has been investigated in various conditions.

2. Experimental

Styrene (E. Merck), methylmethacrylate (E. Merck) and ethylacrylate (E. Merck) were distilled prior to use. All the other chemicals were used without any further purification.

Colorimetric analyses were performed by Schimadzu 160 A UV-Vis spectrometer.

2.1. Crosslinked polystyrene-divinylbenzene beads

Crosslinked polystyrene–divinylbenzene (PS– DVB) beads were prepared by suspension polymerization using gum Arabic as stabilizer, according to the procedure described previously [14]. The beads were sieved and the 210–420 μ m size of fraction was used in further reactions.

2.2. Preparation of 1,1,4,7,10,10 hexacis-hexyl 1,4,7,10 tetraazadecane

1,1,4,7,10,10 Hexa*cis*-hexyl 1,4,7,10 tetraazadecane (H-TETA) was prepared by alkylation of triethylene tetramine (TETA) with 1-bromo hexane in ethanol as described before [15]. The resulting product with six hexyl groups on the nitrogen atoms was a viscous oil, which is miscible with many organic solvents.

2.3. Acetoxy mercuration of PS-DVB beads

Ten grams of 210-420 µm PS-DVB beads were added to 25 mL of dioxan in a 250 mL flask. Then, 21.6 g HgO and 20 mL acetic acid were added to the reaction mixture. The reaction content was refluxed for 24 h and the resulting mixture was poured into a large excess of water (500 mL). The polymer beads were collected and washed with excess of water and alcohol (40 mL). The crude product was used in the chlorine exchange reaction without drying. A rough estimation based on 248% of mass increase of the air dried bead product (the product was not dried in vacuum to avoid sublimation of the mercury) indicates that a maximum 72% of styrene units (in mol/mol) have been acetoxymercurated by assuming all the mercuration takes place by forming only acetoxymercury functions.

2.4. Chlorination with NaCl

The mercurated polymer resin was added to 100 mL saturated NaCl solution and shaken for 24 h at room temperature. Then the reaction mixture

was heated at 30 °C for 1 h and filtered. The polymer beads were washed with excess of water and alcohol (30 mL) and dried under open atmosphere at room temperature for 24 h to avoid sublimation of the mercury. The dry yield of the chloro mercurated product was 27.1 g.

2.5. Modification with 2-bromo 2-methyl propionyl bromide

Twenty grams of modified bead product was added to 40 mL of dioxan and shaken for 15 min in a continuous shaker. Then, 20 mL (161.8 mmol) 2-bromo 2-methyl propionyl bromide was added to the reaction mixture. Shaking was continued at room temperature for 24 h. The reaction content was poured into the water and the polymer beads were filtered off. Then they were washed twice with 40 mL alcohol to remove alcohol-soluble mercury bromide and filtered. The dried product weighed 9.0 g.

2.6. Determination of bromine content

0.2 g of brominated polymer was added to 10 mL of 5 M NaOH solution and refluxed for 2 h. The mixture was filtered and washed with 100 mL of distilled water. The filtrate and washings were combined and transferred into a volumetric flask and diluted to 250 mL with distilled water. The NaBr content of the solution was assayed by mercuric thiocyanate method [16]. This analysis gave 3.12 mmol bromine per gram of the polymer.

2.7. Grafting by ATRP method

The polymerizations were carried out in bulk polymerization conditions at 90 °C using ethylacrylate and methylmethacrylate monomers. To a 100 mL three-necked round bottom flask equipped with the reflux condenser and a nitrogen inlet, 40 mL ethylacrylate (0.367 mol), 2.5 g ($3.85 \ 10^{-3}$ mol) H-TETA and 0.56 g CuBr ($0.38 \ 10^{-3}$ mol) were added under nitrogen atmosphere. The flask was mounted in a silicon oil bath and the mixture was stirred until all the CuBr dissolved (10 min). Then reaction content was heated and kept constant at 90 °C while

stirring. The brominated bead polymer sample (1.938 g) was added to the mixture. The reaction was conducted for 60 h and the mixture was poured into acetone. The filtered resin was dried under vacuum at 50 °C for over night. Yield of the product was 7.865 g.

A similar procedure was adopted for the methylmethacrylate copolymers.

2.8. Removal of the copper contaminants

The crude product was greenish in color due to copper residues retained in the bead polymers. To remove the copper contaminants from the resin, the bead product was added to ethylenediamine tetraacetic acid sodium salt – Titriplex III (EDTA) solution (50 mL, 0.1 M) and the mixture was shaken for 24 h at room temperature. The resin was filtered and washed with excess of water. In this way, almost white polymer beads were obtained.

2.9. Kinetics of the graft reaction

The kinetics of the graft reactions were followed by a series of small-scale reactions (by using 0.2 g bead product with 9 mL of one of the acrylate monomers) for different reaction times, similar to



Fig. 1. Percentage mass increases in grafting of PMMA (\blacksquare) and PEA (\bullet) from 2-bromo 2-methyl propionyl groups on ST-DVB resin beads, as a function of time (at 90 °C using 0.2 g beads sample with 9 mL monomer).



Fig. 2. First order kinetics plots for grafting of MMA (\blacksquare) and EA (\bigcirc) monomers from the resin beads (conditions are the same as indicated in legend of Fig. 1).

the preparative reaction but in sealed tubes. The data collected were depicted in Figs. 1 and 2.

2.10. Aminolysis of the graft chains with monoethanolamine

2.690 g of graft copolymer and 30 mL of monoethanolamine were mixed and the mixture was heated to 100 °C and kept at this temperature for 15 h. The resulting product was washed with excess water and then alcohol. The vacuum dried (at 40 °C) sample weighed 2.74 g.

The same procedure was employed for the aminolysis of methylmethacrylate graft copolymers. Reaction time in this case was kept longer (36 h) due to stability of the methacrylate esters linkage.

2.11. Mercury sorption experiments

The mercury uptake capacity of the grafted resin was determined as follows: 0.5 g of the graft copolymer was wetted with 5 mL of distilled water for 24 h. Then 20 mL of 0.15 M Hg(III) solution (in pH 7 acetate buffer) was added and the mixture was shaken for 4 h at room temperature. Then the mixture was filtered and 5 mL of the supernatant solution was transferred to a volumetric flask and diluted to 500 mL with distilled water. The resid-



Fig. 3. Concentration-time plots of 100 mL Hg(II) solutions (with 3.53 10^{-4} M initial concentration) contacted with aminolysed PMMA (\blacksquare) and PEA (\bullet) graft samples (0.43 g of each).

ual Hg(II) concentration of the solution was assayed by modified colorimetric diphenyl carbazide method [17] (see Fig. 3).

2.12. Sorption tests for foreign ions

In order to examine the selectivity of the Hg uptake, the capacity measurements were also repeated using Cd(II), Zn(II), Pb(II) and Fe(III) ion solutions with 0.15 M initial concentrations. Analyses of the residual metal contents of supernatants were performed by complexometric titration method [18] using 0.1 M EDTA solution. The data obtained from those analyses were collected in Table 2.

2.13. Kinetics of Hg(II) sorption

In order to investigate the efficiency of the sorbent for low concentrations of Hg, batch kinetic experiments were performed with very dilute Hg(II) solution $(3.53.10^{-4} \text{ mol } \text{L}^{-1}, 71 \text{ ppm})$. For

this purpose, the polymer sample (0.43 g) was wetted with distilled water (5 mL) in a 250 mL flask for 24 h and 100 mL of Hg(II) solution was added to the flask. The mixture was stirred with a stirring bar and aliquots (10 mL) were taken at appropriate time intervals for analysis of the residual mercury as described above. The relevant data were pictured as shown in Fig. 2.

2.14. Regeneration of the resins

0.2 g of mercury-loaded sample was introduced to 10 mL glacial acetic acid at a constant temperature of 80 °C and stirred for 2 h. The mixture was filtered and 1 mL of the filtrate was used for colorimetric analysis. Amounts of the recovered mercury were collected in Table 2.

3. Results and discussion

Herein, we describe preparation and use of new mercury specific polymer sorbents in spherical bead form by copper-mediated ATRP. The preparative study consists of three main steps:

- (i) Modification of crosslinked polystyrene beads (210–420 μm) to incorporate α-keto isopropyl bromide groups as the initiating sites.
- (ii) Graft copolymerization of MMA and EA from the bromides on the spherical beads.
- (iii) Aminolysis of the graft chains by ethanolamine.

3.1. Modification of crosslinked PS-DVB beads

 α -Keto halides have been demonstrated to be efficient initiators in copper-mediated ATRP [19].



Scheme 1.

To incorporate bromo propionyl groups into crosslinked PS, we used an acetoxy mercuration method, as depicted in Scheme 1.

Mercuriation and the following reaction with the acyl bromide, in general, furnish a means of alternative method to common Fridel-Crafts acylation. In the acetoxy mercuration, diaryl mercury moieties may form, but this side reaction does not alter the yield of the next acylation reaction. Moreover, exchange of the acetate ions with chloride anions does not need to be quantitative. The advantage of this acylation method is that such a transformation cannot be achieved by the common Friedel-Crafts method due to possible side reaction through the alkyl bromide group. Reaction of chloro mercury groups with 2-bromo 2-methyl propionyl bromide (BMP) gives a product with 3.12 mmol bromine per gram of polymer beads. No trace mercurv was found in this product, which implies a quantitative reaction of the chloromercury functions. This result implies dense bromo 2-methyl propionyl functions on the beads.

3.2. Grafting

Grafting of PMMA and PEA have been performed from bromo propionyl groups on the crosslinked spherical beads to prepare flexible graft chains attached to the bead particles. This has been achieved simply by heating a few grams of bead samples in MMA or EA monomers containing CuBr complex of hexa*cis* (*N*-hexyl triethylene tetramine) at 90 °C. Extents of the graft reactions have been followed by mass increases of the bead particles. Since mass increase indicates the polymerized fraction of the monomers, this is directly related to the extent of the grafting reactions. The increase in mass (Fig. 1) showed that, grafting proceeds with reasonable rates. 1000% mass increase can be attained for MMA in 5 h. Grafting of EA is somewhat slower but the 200% mass increase can be attained for 6 h of reaction time in this case.

Linearity of $\ln(M_0/M)$ versus time plots (where M_0 is initial monomer concentration and M is monomer concentration at any time) indicates first order kinetics for both monomers. Corresponding rate constants are $k = 1.88 \times 10^{-5}$ and 5.42×10^{-7} s⁻¹ for the polymerization of MMA and EA, respectively (see Scheme 2).

3.3. The aminolysis

The graft materials were subjected to aminolysis by heating in 2-amino ethanol (ethanol amine) at constant temperature of 100 °C. In



Scheme 2.

Starting material	Aminolysis time	Aminolysis yield (%)	Nitrogen content (mmol g ⁻¹)	Water sorption (% w/w)	Mercury loading capacity $(mmol g^{-1})$	Sorbed Hg/amid (mol/mol)	
PS–DVB with PMMA grafts (900% graft)	36 h	74.6	6.1	790	2.8	0.46	
PS-DVB with PEA grafts (264% grafts)	15 h	96.0	6.3	201	3.6	0.56	

Table 1 Comparison of the aminolysed polyacrylate grafts on PS–DVB resin beads

this work, we did not study an optimization of the aminolysis reactions. The sample having 264% PEA graft gives a product with 6.3 mmol nitrogen per gram (from Kjeldahl analysis after heating for 16 h) (Table 1).

The nitrogen content of the aminolysed product can be correlated with molar percentage of the EA graft chains as follows (see Scheme 3).

Since the molecular weight of EA is 100 Da, number of repeating units (*n*) must be: $n = 2.64/100 = 2.64 \times 10^{-2}$ mol EA per gram of the initially crosslinked PS.

Since each aminolysis would yield 15 g of mass increase per mole, the amine content 6.3×10^{-3} mol g⁻¹ must be equal to x/(3.64 + 15x). This gives x = 0.0253 mmol g⁻¹. This amount accounts for 96% of the initial EA units per gram. In other words, the yield of the aminolysis is 96%.



Scheme 3.

Similar inspection for the samples with 900% MMA grafts indicates a 74.6% of aminolysis yield after 3 h of aminolysis. Apparently, slow aminolysis of MMA grafts is due to the well-known hydrolytic stability of the methacrylate ester linkage. The aminolysis must impart some hydrophilicity to the polymer.

The aminolysis products show appreciable water sorption (i.e., the product derived from PMMA grafts shows 790% water sorption). Whereas 201% water sorption was observed for the aminolysis product derived from PEA grafts. This result seems to be unusual. However, in the former case 900% grafting corresponds to 90 mmol repeating MMA units. The ratio of this amount to 3.12 mmol of initiator groups would be 90/3.12 = 29 repeating MMA units per initiation site. Therefore, 74.6% of aminolysis would give $29 \times 74.6 = 21.6$ hydroxy ethyl methacrylamide units per initiation site.

By similar analogy, we got 8 hydroxyethyl acrylamide units per initiation site for PEA graft sample. In other words, hydrophobicity of the core is dominant in the later case. Hence, water sorption ability would be lower (201%).

3.4. Selective mercury uptake by the aminolysis products

The mercury uptake ability of the aminolysis products were examined simply by soaking the polymer samples (0.2 g) into 20 mL of 0.15 M Hg(II) solutions (in acetate buffer, pH 7) for 24 h. Mercury loading capacities were assayed by analysis of residual mercury concentrations in the aqueous solution. Mercury loading capacities were found to be 2.8 and 3.6 mmol g^{-1} for the aminolysed MMA and EA grafts, respectively.

 Table 2

 Metal sorption capacities of the aminolysed graft resins

Hg(II) $2.80 (1.22)^a$ $3.57 (1.45)^a$ Cd(II) 0.08 0.09 Zn(II) 0.1 0.0 Pb(II) 0.09 0.07 E. (III) 0.0 0.0	Metal ion	Aminolysed PMMA $(mmol g^{-1})$	Aminolysed PEA $(mmol g^{-1})$
	Hg(II)	2.80 (1.22) ^a	3.57 (1.45) ^a
	Cd(II)	0.08	0.09
	Zn(II)	0.1	0.0
	Pb(II)	0.09	0.07
	Fe(III)	0.0	0.0

^a Desorption by acetic acid (in mmol per gram of the loaded polymer).

To examine mercury selectivity, the aminolysis products were separately interacted with the solutions of Zn(II), Cd(II), Pb(II) and Fe(III) ions (0.15 M initial concentrations). Experiments were repeated as in the case of the Hg(II) ion. The metal loading capacities were determined similarly by EDTA titrimetric analysis of the residual metal ion contents. These analyses clearly indicate that the sorbed amounts are about zero in each case (Table 2). Overall the results represent selectivity of the aminolysed polymers in the mercury uptake.

3.5. Kinetics of the mercury sorption

Kinetics of the mercury sorption from dilute Hg(II) solutions (3.53 10^{-4} M) is first order with respect to the mercury concentrations. Mercury uptake is reasonably fast for the case of aminolysed MMA graft sample ($k = 2.3 \times 10^{-3} \text{ s}^{-1}$). The rate constant of mercury sorption for the aminolysed PEA graft sample was calculated to be $k = 1.43 \times 10^{-3} \text{ s}^{-1}$.

3.6. Regeneration of the mercury loaded polymers

Since amide linkages are susceptible to hydrolysis, the use of mineral acids is not advisable. Acetic acid was found the most suitable regenerating acid to avoid hydrolysis, as described before. The loaded mercury was washed out by hot acetic acid in each case. The amounts of the recovered mercury were somewhat less in comparison to the sorbed amounts (Table 2). However, we think that there is no limitation because all of the mercury can be leached out from the sample by a next acetic acid treatment. The amount of mercury recovered from the aminolysed PMMA graft resin, in first contact with acetic acid is 1.22 mmol per gram of loaded polymer. If we assume all the sorbed mercury in monoamido mercury chloride form, 2.8 mmol of mercury should correspond to $2.8 \times 236 = 660$ mg of mass increase. 2.8 mmol of mercury loading would yield 2.8/1 + 0.660 = 1.69 mmol per gram of loaded polymer. So, 1.22 mmol mercury split in the first acetic acid treatment $1.22/1.69 \times 100 = 72\%$ of loaded mercury.

Similar analysis for the other graft polymer gives a 74.7% elution yield of the loaded mercury.

After removal of mercury, the polymer samples were regenerated. The regenerated resin sample obtained from MMA grafts represent almost the same loading capacities for Hg(II). But regenerated samples obtained from EA grafts showed lower capacities than those of the fresh samples. Repeated experiments gave the same results. The capacities were as low as 50% of the original capacities after the third regeneration. This might be ascribed to the catalytic effect of the Hg(II) ions leading to hydrolysis of the amide linkages. In this study, we did not investigate this phenomena any further. Whereas in the former case, methacrylamide groups are far more stable to the hydrolysis and regenerated samples represent the same capacities.

In conclusion, acetoxy mercuration of PS-DVB spherical beads and following acylation with 2bromo 2-methyl propionyl bromide is a fruitful method for incorporation of the α -keto isopropyl groups as initiator groups for ATRP. The initiation of ATRP of MMA and EA from those supported active alkyl bromide functions proceeds with reasonable rates with first order kinetics. High yields of grafting (200-1000%) can be attained in acceptable time intervals. Aminolysis of those graft polyacrylate ester chains with ethanolamine yields corresponding acrylamide moieties which are useful in the very selective removal of Hg(II) ions from aqueous solutions. The mercuric ions loaded can be eluted by hot acetic acid to give mercury - free sorbents. The sorbent obtained from PEA grafts losses about 27% its original activity in each regeneration with acetic acid. Regenerated sorbents derived from PMMA grafts show almost the same capacities in the mercury sorption.

As a result, this material is a very useful regenerable sorbent for the removal of Hg(II) ions from aqueous solutions. Its efficiency for trace quantities is an additional advantage and can be considered as a promising candidate for large-scale mercury removal processes.

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