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Atom transfer radical graft polymerization of acrylamide from *N*-chlorosulfonamidated polystyrene resin, and use of the resin in selective mercury removal

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Abstract

Polyacrylamide was grafted from *N*-chlorosulfonamide groups onto crosslinked polystyrene beads using copper-mediated atom transfer radical polymerization (ATRP) methodology. A beaded polymer with a polyacrylamide surface shell was prepared in four steps, starting from styrene–divinylbenzene (10%) copolymer beads of 210–420 μ m particle size: chlorosulfonation; sulfamidation with propylamine; *N*-chlorination with aqueous hypochloride; and grafting using a concentrated aqueous acrylamide solution with a CuBr–tetramethylethylenediamine complex (1:2). The resulting polymer resin with 84 wt% grafted polyacrylamide has been demonstrated to be an efficient mercury-specific sorbent, able to remove Hg(II) from solutions at ppm levels. No interference arises from common metal ions such as Cd(II), Fe(III), Zn(II), and Pb(II). The sorbed mercury can be eluted by repeated treatment with hot acetic acid without hydrolysis of the amide groups. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Linear polymers grafted onto crosslinked polymer resin particles offer numerous potential applications due to the combination of resin insolubility and the flexibility of the graft polymer side-chains as the functional group carrier. The flexible side-chains can provide pseudo-homogeneous reaction conditions and better accessibility of the functional groups involved. While the post-crosslinking of one block of a diblock copolymer can yield a core– shell copolymer architecture [1,2], using this approach it is difficult to obtain polymers in a well-defined spherical bead form. Likewise, introducing linear polymer chains onto the matrix of crosslinked beads by the 'grafting from' technique using common radical initiation

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procedures without also generating considerable amounts of wasteful non-grafted homopolymer as by-product, is also very difficult. However, the emerging 'controlled chain growth' techniques such as atom transfer radical polymerization (ATRP) [3,4] have been demonstrated to be applicable to grafting from chloroalkylated solid surfaces such as silica, silicone [5–8] and polybutadiene microgels [9].

In a previous study we demonstrated that *N*-chlorosulfonamides can also be used as the initiator in the copper-mediated ATRP of styrene and acrylate monomers [10]. In the present work, this chemistry has been exploited in the preparation of crosslinked polystyrene sulfonamide beads bearing a polyacrylamide surface shell. *N*-Chlorosulfonamide groups have been incorporated by a four-step chemical modification of crosslinked polystyrene beads, and then these groups used as the initiator site for the ATRP of acrylamide.

The resulting grafted resin material has been shown to be an efficient mercury-specific sorbent, because the amide group has a unique reactivity towards mercuric ions, leading to the formation of amido-mercury compounds under ambient conditions. Since the electron-donating character of the amide nitrogen atom is greatly reduced by the adjacent electron-withdrawing carbonyl group, the ability of the amide groups to coordinate with other transition metal ions is extremely low. The chemistry of the mercuryamide interaction therefore makes the amide group unique for selective mercury removal. We have utilized this strategy in earlier work and demonstrated that crosslinked polyacrylamide and cellulose-g-polyacrylamide [11] are very useful sorbents for the selective removal of mercuric ions from aqueous solutions. Although polymer-supported thiol [12], thioether [13] and pyridinium [14] groups have also been reported to have good selectivity for Hg(II) over some metal ions, these materials are not particularly selective in competition with some key metal ions such as Pb(II) and Cd(II). In this respect, amide groups seems to be superior to the other functions for mercury binding.

In the present work we chose to graft polyacrylamide onto a polystyrene resin in order to produce a sorbent with a robust macroscopic form potentially suitable for technological application on a large scale. We now report on the synthesis, characterization and exploitation of this resin.

2. Experimental

Inhibitor-free styrene monomer (E. Merck) was obtained by redistillation. All other chemicals were analytical grade: divinylbenzene (Fluka) (50% mixture of *meta* and *para* isomers in ethyl vinyl benzene), diphenyl carbazide (E. Merck), and acrylamide (E. Merck). Colorimetric analyses were performed using a Schimadzu 160 A UV-vis spectrometer.

2.1. Crosslinked styrene-divinyl benzene beads

These were prepared by the suspension polymerization of a styrene (54 ml, 0.48 mol) and DVB (55% grade, 10 ml, 0.038 mol) mixture in toluene (60 ml), using gum-arabic as stabilizer, according to the procedure described previously [15]. The beads were sieved and the 210–420 μ m size fraction was used in further reactions.

2.2. Chlorosulfonation of the bead polymer

The bead polymer was chlorosulfonated using chlorsulfonic acid as described previously [16]. The chlorosulfonation reaction was monitored by analysis of the liberation of chloride ions. For this purpose, a polymer (0.2 g) sample was added to 10% NaOH (20 ml) and boiled for 4 h. After filtration and neutralization with HNO₃ (5 M), the chloride content of the solution was assayed by the mercuric thiocyanate method [17]. This gave a final chlorosulfonation degree of 4.0 mmol g⁻¹.

2.3. Sulfamidation of the beads

The chlorosulfonated polymer (10 g) was added portion wise to a stirred solution of

propyl amine (12 ml, 0.145 mol) in 2-methyl pyrrolidone (15 ml) at 0 °C. Stirring was continued at room temperature for 10 h. The reaction mixture was poured into water (500 ml), the polymer collected and washed with excess water and alcohol (20 ml) and dried under vacuum at 50 °C for 6 h. The yield of dry polymer was 11 g.

2.4. Chlorination with aqueous hypochloride

The resin polymer with sulfonamide groups (10 g) was added to commercial bleach liquor (50 ml, 26% active chlorine) and left to stand in a refrigerator for 3 days. The resin was recovered by suction filtration and washed with excess water (500 ml), alcohol (30 ml) and ether (30 ml). To avoid decomposition, yielding free chlorine, the product was dried open to the atmosphere at room temperature for 24 h, and then stored in a refrigerator. The yield was 11.2 g.

2.5. Determination of chlorine content

The chlorine content of the resin was determined by a modified iodometric method [18] as follows: the polymer sample (0.25 g) and CCl_4 (10 ml) were placed in a tightly closed bottle and KI (0.5 g) in distilled water (15 ml) and acetic acid (5 ml) was added to the bottle. The mixture was stirred magnetically in the closed bottle for 24 h. The iodine liberated was titrated with 0.1 M $Na_2S_2O_3$ solution, and indicated the loading of *N*-chlorosulfonamide groups to be 3.3 mmol g⁻¹.

2.6. Grafting by the ATRP method

To a 100 ml two-necked flask, acrylamide (7.5 g,105.6 mmol) in distilled water (15 ml), CuBr (1.1 g, 7.64 mmol) and tetramethylethylenediamine (TMED) (1.8 ml, 15.28 mmol) were added under nitrogen flow. Then the N-chlorosulfonated polymer (2.5 g) was added to the mixture and the flask agitated on a continuous shaker for 114 h at room temperature. The reaction contents were poured into water (250 ml), the resin filtered off and washed with excess water. The yield of crude product was 4.7 g.

2.7. Removal of the copper contaminant

The crude product was greenish in colour due to residues of copper retained in the polymer beads. To remove these, the resin was added to Titriplex III (disodium salt-ethylenediaminetetraacetic acid, EDTA) solution (40 ml of 0.1 M) and the mixture was shaken for 16 h at room temperature. The resin was filtered off and washed with excess distilled water until the electrical conductivity of the washings fell to 6 μ S. Off-white polymer beads were obtained. The vacuum-dried sample (at 50 °C) weighed 4.6 g.

2.8. Monitoring of the grafting reaction

The progress of the grafting reaction was monitored by carrying out a series of small-scale reactions (0.2 g) for different times similarly to the preparative reaction, but in sealed tubes.

2.9. Measurements of pore volume and surface area

Dry state surface area and pore volume data were obtained from N_2 sorption isotherms and application of the BET theory. The instrument used was a micromeritics ASAP 2010 and the supplied software was used to manipulate the experimental data.

These measurements indicated that both polymers have very small pore volumes and surface areas. The starting polymer with *N*-chloro-sulfonamide functions has a total dry state surface area of $0.89 \text{ m}^2 \text{ g}^{-1}$ and $6.3 \cdot 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ pore volume. The graft polymer exhibits a dry state surface area of $1.15 \text{ m}^2 \text{ g}^{-1}$ and $8.15 \cdot 10^{-4} \text{ cm}^3 \text{ g}^{-1}$ pore volume.

2.10. Hg uptake experiments

The Hg sorption capacity of the grafted beads was determined as follows. To the grafted polymer resin (0.2 g) in water (5 ml) was added Hg(II) solution (20 ml of 0.1 M). The mixture was left for a given period of time and then filtered. A sample (1 ml) of the supernatant solution was transferred to a volumetric flask and diluted to 10 ml with alcohol. The residual Hg content of the solution was assayed using a colorimetric method as described in the literature [19]. Analysis of the supernatant in contact with the resin for 24 h indicated a Hg(II) concentration of 0.031 M in the final solution, which corresponds to a mercury loading capacity of 6.9 mmol g⁻¹.

In order to examine the selectivity of Hg binding, sorption capacity measurements were also performed using Cd(II), Pb(II), Zn(II) and Fe(III) ion solutions (0.15 M initial concentrations). Analyses of the residual metal contents of supernatant solutions were performed by a complexometric titration method using EDTA solution (0.01 M). The data collected are summarised in Table 1.

2.11. Kinetics of Hg sorption

In order to investigate the efficiency of the sorbent for trace quantities of Hg, batch kinetic experiments were performed with very dilute Hg solutions (211.7 ppm). For this purpose the polymer resin sample (0.5 g) was wetted with

 Table 1

 Metal uptake characteristics of the polyacrylamide grafted beads

Metal ion	Initial conc. (M)	Resin capacity (mmol g^{-1}) ^a	Recovered metal $(\text{mmol } \text{g}^{-1})^{\text{b}}$
Hg(II)	0.05	4.35	1.2
Hg(II)	0.10	6.90	2.1
Cd(II)	0.15	0.01	_
Pb(II)	0.15	0.0	_
Zn(II)	0.15	0.01	_
Fe(III)	0.15	0.0	_

^a Per gram of non-loaded resin, in 24 h contact time.

^b Per gram of Hg loaded resin; stripping using hot acetic acid.

distilled water (5 ml) and added to a solution of Hg (100 ml of 0.3 g $HgCl_2$ in 1 l water). The mixture was stirred magnetically and aliquots of the solution (10 ml) were taken at appropriate time intervals for analysis of the residual Hg content by the method described above. Fig. 2 below shows the data obtained.

3. Results and discussion

Crosslinked polystyrene-graft-polyacrylamide was prepared successfully by grafting 'from' *N*-chlorosulfonamidated styrene-divinylbenzene resin (210–420 μ m), the latter being obtained via the following stepwise modifications (Scheme 1)

Chloride analysis of the product in the first step (4 mmol g^{-1}) reveals the chlorosulfonation of the phenyl rings to be ~70%. The second step is performed with essentially quantitative conversion of chlorosulfonyl groups when excess propylamine is used. N-chlorination of the sulfamide nitrogen is achieved readily using excess commercial bleach, yielding a resin with a chlorine content of 3.3 mmol g^{-1} , corresponding to ~98% conversion of the sulfon-amide groups in the third step.

3.1. Grafting of acrylamide by ATRP

The grafting is achieved simply by interaction of the crosslinked beads functionalised with *N*-



Scheme 1. Synthetic scheme for introducing *N*-chlorosulfonamide groups into PS–DVB resin.

chlorosulfonamide groups with a concentrated aqueous solution (33%) of acrylamide in the presence of CuBr and TMED. The use of TMED as ligand in ATRP has already been described in the literature [20]. The polymerization proceeds at room temperature.

As suggested in our previous report [10] the initiation appears to take place via radical formation in a redox reaction of *N*-chloro-sulfonamide groups with CuBr, as shown in Scheme 2. During the grafting reaction a progressive increase in the mass of the resin is observed (Fig. 1), but this does not conform to simple first-order kinetics. This unusual behavior is in accordance with a previous report involving the ATRP of acrylamide in water with haloalkyl initiators [21,22].

The significant deviation from typical ATRP behaviour may arise because the reverse



Scheme 2. Proposed mechanism for ATRP grafting of polyacrylamide onto functional PS-DVB resin.



Fig. 1. Plot of wt% grafting of polyacrylamide onto polystyrene resin beads as a function of time (see text for details).

halogen transfer step might be very slow. The sharp rise in grafting seen after 40 h can be ascribed to the increase in the overall hydrophilicity of the beads, which makes penetration of the aqueous acrylamide phase into the resin much easier. Conversely, it can be deduced that the initial liphophilicity of the resin is responsible for the very slow grafting of monomer onto the beads in the early stages of the reaction.

Due to the very small pore volume $(6.32 \cdot 10^{-3} \text{ cm}^3 \text{ g}^{-1})$ of the starting polymer the chain growth in ATRP is expected to occur mostly from the outer surface of the bead polymer. The small pore volume after grafting $(8.15 \cdot 10^{-4} \text{ cm}^3 \text{ g}^{-1})$ and the small increase in surface area from 0.89 to 1.15 m² g⁻¹ is confirmatory evidence to support this assumption.

Perhaps, more importantly, however, no homopolymer formation is observed even after 114 h of reaction. This seems to be the most significant aspect of this grafting method and one which cannot be achieved using conventional non-living radical procedures.

The resulting grafted resin is greenish in colour, due to residues of the Cu complex. In fact, coloured Cu contaminants in polymer products is a common problem in ATRP. These can be removed completely, however, by treating with EDTA solution, yielding, in the present case, a white resin. The increase in mass found for the resin indicates grafting of ~ 83 wt% for the sample obtained after 114 h reaction. Kjeldahl nitrogen analysis indicates 8.4 mmol of amide nitrogen, including sulfonamide nitrogens. This corresponds to a polyacrylamide graft of ~ 84 wt%, and a loading of acrylamide residues of ~ 6.4 mmol per gram of grafted resin. If it is assumed that all the N-chloro groups are involved in the initiation process, 84 wt% of grafting would correspond to about 2.0 repeating units per initiation site. This is very low and suggests that, in practice, there is inefficient use of these sites.

In terms of a usable material, 84 wt% grafting of polyacrylamide is very adequate and yields a particulate resin with no tendency to become sticky on contact with an aqueous phase.

Due to the high hydrolytic stability of the sulfonamide linkage, the polyacrylamide chains seem to be robustly attached to the resin, so much so that cleavage of these for molecular weight analysis proved difficult to achieve.

3.2. Hg uptake

The resulting bead polymer with polyacrylamide grafts is expected to have the characteristics of typical core-shell polymers. In principle, the carbonamide functions on the flexible polyacrylamide graft chains should offer the opportunity for rapid interaction with aqueous Hg(II) solutions to form mercuryamide linkages (Scheme 3), as in the case for low molecular weight amide compounds.

Binding can occur, in principle, either by formation of monoamido– or diamido–Hg structures, which provide a means of capturing Hg^{2+} from aqueous solution. Since the amide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen, the separation of Hg^{2+} can be highly selective. Since the hydrogen atom on the amide nitrogen is not replaceable by simple ion-exchange, salts with either alkaline or alkaline earth metal ions cannot be formed.



Scheme 3. Formation of monoamido and diamido Hg structures on grafted polyacrylamide chains.

Aqueous solutions of $HgCl_2$ were used in the Hg sorption experiments. The sorption capacity of the grafted beads was assessed by analysis of the excess Hg^{2+} in the supernatant solutions.

In these experiments the solutions were not buffered because this is the most likely situation under practical conditions. Also, the buffer components might be competitive with the binding of Hg^{2+} . The overall Hg^{2+} uptake capacity from 0.10 M HgCl₂ solution is high, ~ 6.9 mmol g^{-1} . Indeed, this seems to be higher than the theoretical capacity. However, since not all the initiation sites are involved in grafting, residual sulfonamide groups, formed by spontaneous decomposition of unreacted chlorosulfonamide groups, might produce an additional contribution to the Hg²⁺ sorption capacity. If, for example, an initiation efficiency of 0.2 is assumed, the total amide content after grafting might be around 8.3 mmol g^{-1} . Since the sulfonamide function might also become involved in Hg uptake the upper limit of the capacity could be ~8.3 mmol g^{-1} . Interestingly, when the initial concentration of HgCl₂ is reduced to 0.05 M the resin sorption capacity falls to about half of that found using 0.1 M HgCl₂. This concentration dependence of the sorption capacity suggests that, at low initial concentrations, the sorption proceeds with preferential formation of diamido-Hg structures. This might be due to kinetic factors, i.e. when Hg accumulation on the graft chains is slow (because of the low concentration), formation of the diamido Hg linkages becomes favored. However, at higher Hg feed levels, the accumulation of Hg is faster, and before a suitable site can be captured within a diamido linkage it is consumed by a second incoming Hg^{2+} .

To probe the degree of selectivity of the Hg²⁺ sorption properties, the sorption behavior of other potentially contaminating ions was investigated. In particular, 0.15 M single metal ion solutions of Cd(II), Zn(II), Pb(II) and Fe(III) were examined. Very small capacities (~0.01 mmol g⁻¹) were observed for Zn(II) and Cd(II) ions and, indeed, even these are

close to the experimental error limits (Table 1). Pb(II) and Fe(III) ions showed no tendency to be absorbed at all. Therefore, overall, the results clearly indicate that Hg sorption is extremely selective, at least in the presence of the foreign ions studied. This is in complete accordance with our previous observations [23].

Batch kinetic sorption experiments from highly dilute (211.7 ppm) Hg(II) solutions indicate relatively fast binding of Hg (Fig. 2). The uptake obeys second-order kinetics (k =14.4 M⁻¹ s⁻¹ with a correlation factor of 0.987) as in the case of many metal complexations involving solid surfaces.

Despite the high efficiency and selectivity of Hg binding by the grafted resin, regeneration of the latter and stripping of the bound Hg by simple acid treatment is almost impossible with mineral acids because of the hydrolysability of the amide groups. This can be avoided, however, by stripping with hot acetic acid, which readily removes the Hg without inducing amide hydrolysis (Table 1). Although the data in Table 1 appear to show that the level of Hg stripped is much less than that initially loaded, in fact the two sets of data are quoted per gram of nonloaded resin for the uptake data and per gram of loaded resin for the recovery data. Since the density of Hg is very high, these two bases for comparison are very different, and when the



Fig. 2. Plot of solution concentration of Hg(II) (ppm) in contact with polyacrylamide grafted polystyrene resin as a function of time (see text for details).

recovery data are adjusted per gram of nonloaded resin the data are in effect very comparable, and stripping is quite efficient.

To date, no data are available on the re-use of stripped resin, however since our cellulose-gpolyacrylamide material [11] showed no loss of capacity over 10 sorption–desorption cycles, we have no reason to doubt that the present grafted polystyrene resin-based species will be any less stable, indeed we feel the stability is likely to be higher.

4. Conclusion

Graft polymerization of acrylamide from polystyrene resin-supported *N*-chlorosulfonamide groups using an ATRP methodology occurs efficiently and without homopolymer formation. Although the process differs kinetically from solution ATRP systems it can be performed at room temperature and gives reasonable degrees of grafting. The resulting graft polymer resin is highly effective and selective for Hg sorption and the resin format makes the material of interest as a column packing material for technological use.

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