Macromol. Chem. Phys. **199,** 2731–2735 (1998)

Crosslinked poly(styrenesulfonamide) with iminoacetic acid chelating groups for hard-water treatment

Niyazi Biçak, Bahire Filiz Şenkal, Tuğrul Yarbaş*

Istanbul Technical University, Department of Chemistry, Maslak 80626 Istanbul/Turkey

(Received: January 21, 1998; revised: June 4, 1998)

SUMMARY: Chlorosulfonated polystyrene-DVB (10%) copolymer (in beads form, 720–840 μm) has been modified with triethylenetetramine (TETA) to give the corresponding polymeric sulfonamide. By treating with the potassium salt of chloroacetic acid in water, amino groups of the polymer have been carboxymethylated almost quantitatively. The resulting material with iminoacetic acid pendant groups has very efficient chelating ability for Ca(II) and Mg(II) ions in ppm levels. The chelating polymer can be regenerated ten times by acid leaching without losing its original reactivity. It is suitable for removal of calcium and magnesium ions to supply soft water.

Introduction

Removal of calcium and magnesium from water is of great interest to supply soft water for steam generators and domestic applications. Although many improvements have been carried out on ion exchangers and chelating resins, hard water treatment is still a confronting subject, especially for large water quantities.

For Ca(II) and Mg(II) ion uptakes, ion-exchange polymers having carboxyl ligating groups seem to be somewhat superior to sulfonated polystyrenes. Among many organic complexing agents, probably ethylenediaminetetraacetic acid (EDTA) is one of the most efficient chelating agents for metal ions. There have been numerous reports on its use in complexometric titrations of various metal ions[1)]. EDTA can be used over a wide pH range, and it has reasonable stability against acid and base hydrolyses. Since it is a hexadentate ligand, its Ca(II) and Mg(II) complexes have relatively high stability constants ($\log K = 10.6$ for Ca(II) and 8.7 for Mg(II)). On complexation it coordinates with metal ions by forming five-membered chelate rings which are stable thermodynamically. Because of this fact, some insoluble metal salts (e.g., $CaCO_3$) become soluble in EDTA solutions. Although its lower and higher analogues have similar chelating abilities, EDTA has attracted most attention as complexing agent.

For this reason, polymers bearing EDTA-like structures have found interest for metal uptakes in the last two decades. Of several polymers, poly(glycidyl methacrylate)[2)] and chloromethylated polystyrene[3)] have received special attention as iminoacetic acid-carrying polymers. Also polyacrylamide with iminodiacetic acid pendant groups has been presented as chelating polymer, although it tends to hydrolyse in mineral acid solutions during regeneration[4)].

Hexamethylenediamine has been incorporated into chloromethylated polystyrene resin and carboxymethylated to obtain chelating polymers with high binding capacities[5)]. Recently Fritz et al. have described the use of this type of chelating resins in packed columns for large scale water processing to remove Ca(II) and Mg(II) ions[6)].

The present paper deals with preparation of crosslinked poly(styrenesulfonamide) with diethylenetriaminetetraacetate chelating groups. Its efficiency in removal of trace quantities of Ca(II) and Mg(II) ions from aqueous solutions has been studied.

Although the material is also quite reactive towards various heavy metal ions, this study has been confined to hard water treatments. pH dependence of metal binding and its regenerability conditions have also been investigated.

Experimental part

Materials and methods

Chloroacetic acid was purified by recrystallization from chloroform before use. All the other chemicals were analytical grade chemical products. They were used as supplied. Chemical transformations on the crosslinked polymers were followed by classical titration methods. All the metal analyses were performed by classical complexometric titrations using EDTA or its salts, as described in text books[7)].

Crosslinked polystyrene-DVB (10%) beads were prepared by suspension polymerization as described before[8)]. After drying, the product was sieved and the 720–840 μm fraction was used for further reactions.

Chlorosulfonation of the polystyrene-DVB (10%) beads was performed with chlorosulfonic acid as reported before[8)]. The degree of chlorosulfonation was determined by boiling the product with a 10% NaOH solution for 4 h. The chlorine content of the NaOH solution was determined by the mercuric thiocyanate method[9)]. The chlorine content was found to be $3.24\ \mathrm{mmol \cdot g^{-1}}$.

1022-1352/98/1212–2731$17.50+.50/0

Sulfamidation of the above polymer with triethylenetetramine (TETA) was carried out by treating with excess of triethylenetetramine as described elsewhere[8)].

Determination of the amine content of the sulfamidation product

For determination of the amine content, 0.2 g of polymer sample was left in contact with 10 mL of 5% NH_3 solution for 3 h. It was filtered and washed with excess of water. Then it was transferred into 10 mL 2 M HCl solution and left overnight. After filtration 5 mL of the filtrate was taken and diluted to 25 mL, and its acid content was determined by titration with 0.4 M NaOH solution in the presence phenolphthalein color indicator. A total amine group content of 7.10 $mmol \cdot g^{-1}$ (sum of both primary and secondary amine functionalities) was determined from the difference between HCl contents in original and final solutions.

Elemental analysis was also considered for the determination of nitrogen. However, this measurement failed as a result of incomplete burning of the samples. The Kjeldahl method was considered as an alternative method for the determination of the nitrogen content. For this 0.2 g of polymer sample was added to 10 mL of H_2SO_4 (65.0%) solution and boiled for 4 h. This enables both hydrolysis of the sulfonamide linkages and extraction of amines from the polymer. After chilling, the mixture was filtered and washed with cold water. The filtrate together with washings was diluted to 50 mL and subjected to Kjeldahl analysis as usual. The analysis gave 9.44 $mmol \cdot g^{-1}$ of total nitrogen. By assuming ideally one-fourth of the total nitrogen is being used for sulfamide linkages, the free amine content of the polymer must be $9.44 \times 3/4 = 7.08\ mmol \cdot g^{-1}$, which is in good agreement with the one obtained by the titration method.

Carboxymethylation of the amine groups of the polymer

For this purpose, first the potassium salt of monochloroacetic acid was prepared. 23.6 g (0.25 mol) monochloroacetic acid was dissolved in 35 mL of water. While stirring at 0 °C, to this solution the solution of 17.25 g (0.25 mol) K_2CO_3 in 40 mL water was added dropwise. The resulting solution was directly reacted with 10 g of the polymer sample, i. e., the amount of choroacetic acid was about 1.5 times in excess of the total amine content. The mixture was stirred at room temperature for 24 h. The reaction content was filtered and washed several times with water and 30 mL of ethanol. The weight of the dried product was 15.1 g. Based on the weight increment the transformation yield was roughly estimated as 98.3%.

Determination of the carboxyl content of the modified polymer

For this purpose 0.2 g of the polymer sample was treated with 10 mL of 2 M NaOH solution for 4 h. Then it was filtered, and 5 mL of the filtrate was titrated with 0.1 M HCl solution. The carboxyl content was calculated as 6.04 $mmol \cdot g^{-1}$. Comparison of the amino and carboxyl contents reveals that 98% of the free amino groups of the polymer have been carboxymethylated.

Determination of metal chelating capacities of the polymer

Metal loading experiments were performed with 0.2 M aqueous solutions of Ca(II), Mg(II), Ni(II), Co(II), Cu(II), Fe(III), Zn(II) and Cd(II). Thus, 2.4 g of the carboxymethylated polymer was treated with 30 mL of 4 M NaOH solution for 3 h. By this way all the carboxyl groups were neutralized to attain maximal loading capacities. After filtration it was washed with water and dried under vacuo at room temperature for 24 h. The sample was divided into parts of 0.2 g, and each part was treated with 10 mL of the metal ion solution for 3 h. 1 mL aliquots of the filtered solutions were used for the metal ion determinations. The unreacted metal contents of the aliquots were assayed by complexometric titrations using 0.01 M EDTA solutions. From the differences of the metal contents of the initial and final solutions, the metal chelating capacities were calculated, cf. Tab. 1.

Binding kinetics of Ca(II) and Mg(II) ions

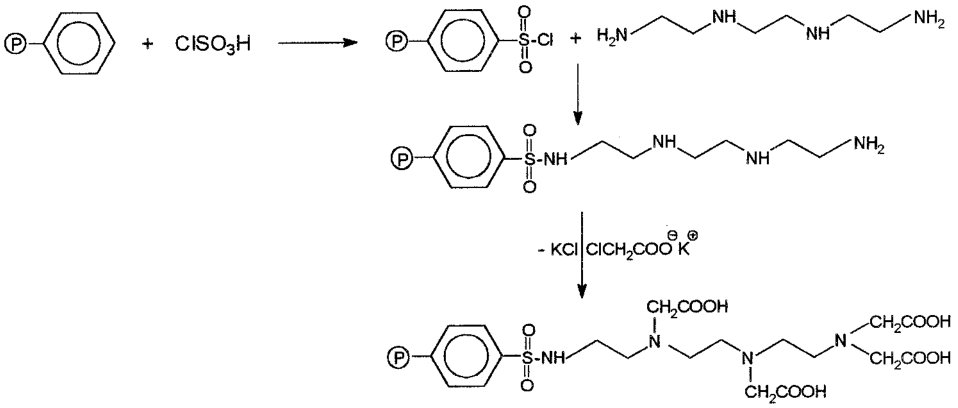
Kinetics of Ca(II) and Mg(II) ions sorption were performed by simple batch experiments at different pH's which were adjusted by NH_4Cl/NH_3 (for pH = 8.2, 6.3) or $Na(CH_3COO)_2/CH_3COOH$ (for pH = 4). Experiments were conducted by interacting 0.225 g of polymer samples with 50 mL of $9.4 \cdot 10^{-4}$ M Ca(II) and $7.7 \cdot 10^{-4}$ M Mg(II) solutions at different pH's. While stirring, 2.5 mL of samples were taken from the mixtures and transferred into 50 mL flasks through filter paper. The filtrate together with washing was titrated with 0.01 M EDTA solution (Titriplex III) in the presence of Erichrome black T, as described in the literature[7)]. Variations of the concentrations of Ca(II) and Mg(II) ion solutions are shown in Fig. 1 and Fig. 2.

Regeneration of the loaded samples

In order to follow regenerability of the metal-loaded polymer, extracted Ca(II) and Mg(II) ions were stripped off by interaction of the loaded polymer samples with 10 mL of 4 M HCl solutions for 3 h, and the polymer was filtered. The amounts of metal ions in 5 mL of the filtrate were determined as described above. For comparison the extracted and stripped amounts (per gram of dry polymer) are listed in Tab. 1.

One of the filtered polymer samples was washed with water and transferred into about 20 mL of 2 M NaOH solution. By this way amino groups are converted into acid-free amino groups and carboxyl groups are transformed into their sodium salts. The above procedure, metal extraction (Ca(II)) and acid-base treatment, was repeated 9 times more without measuring Ca(II) concentrations at the intermediate steps. This was done to test the recycling frequency of the polymer used. In order to examine any probable change in the chelating ability, the polymer sample was subjected to Ca(II) sorption in the same conditions. In that case the amount of extracted Ca(II) ion was determined to be 1.53 $mmol \cdot g^{-1}$.

Scheme 1:



Results and discussion

In order to remove trace quantities of Ca(II) and Mg(II) ions from water, we have developed a chelating resinous polymer with iminoacetic acid pendant groups by the reaction steps outlined in Scheme 1. The reaction of the chlorosulfonated polystyrene beads with an excess of triethylenetetramine proceeds quantitatively. Due to the greater nucleophilicity of primary amines, the sulfamidation is expected to occur preferably through primary amino groups rather than the secondary ones. But inevitably the sulfamidation may also take place via secondary amines. Also, linking through two amine functions of the same TETA molecule is another less probable sulfamidation. So the formula of the sulfamidation product shown in the Scheme 1 is substantially simplified.

Chemistries of these reaction steps are well known in organic chemistry. For long term uses, in the metal chelating polymers the backbone of the polymer must preferably be as inert as possible, beside the strong chelating ability of the ligating groups. This requirement is being fulfilled in our case because the sulfonamide group is highly stable towards acid and base hydrolysis. It has been reported that, for a complete hydrolysis of sulfamide groups, the sulfonamide compound should be boiled in 60% H_2SO_4 solution for 3 h$^{10)}$. Moreover, incorporation of sulfonyl groups in phenyl ring provides additional inertness to the phenyl ring due to the electron-withdrawing character of the sulfone group. This point is especially important for recycling and long term uses of polymer supports.

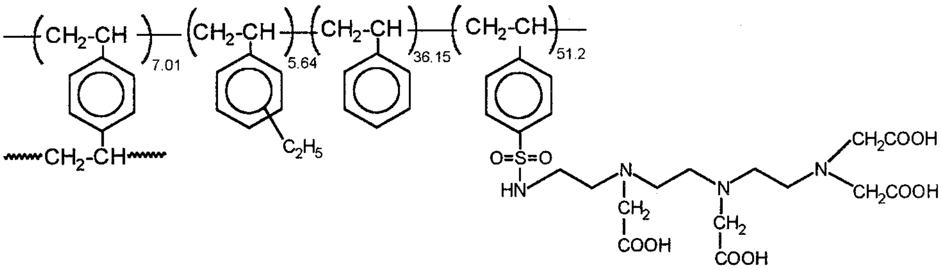
In the carboxymethylation of the amino groups of the polymer, we have obtained almost quantitative conversion yields. Calculation based on weight increment gives 98.3% transformation. By carboxyl group determination we found 98%. These results are in good agreement, and the minor difference is within experimental error limits. Here, substitution on the sulfonamide nitrogen is rather improbable because, generally, sulfamide groups have pK_a's between 8–10. Hence their deprotonation or salt formation can only be achieved by concentrated alkaline solutions.

The high conversion yield obtained seems to be contradictory in view of those reported by Morcellet et al.$^{11)}$ But, most probably, the low conversion yields in that report arose from the use of chloroacetic acid instead of its potassium salt for modification of the vinylamine copolymer.

Taking into consideration the high conversion yields, the carboxymethylation can be assumed to be quantitative, and the full structure of the resulting modified polymer can be written as displayed in Scheme 2. Amine and carboxyl group determinations reveal that the second and third steps of the reaction proceed almost quantitatively.

In the last step, carboxymethylation of the polymer carrying TETA functions can be followed by FT-IR spec-

Scheme 2:



tra. After carboxymethylation, the broad N—H stretching vibration of amino groups of the TETA at 3300 cm^{-1} becomes wider, which is typical for amino acids. Moreover, carboxyl group vibrations of the carboxyl functions appear as a sharp band at 1660 cm^{-1}.

Chelating with Ca(II) and Mg(II) ions

Having seven ligating groups, the polymer is expected to represent an efficient chelating ability for Ca(II) and Mg(II) ions, as in the case of EDTA. Fortunately, this assumption has been established by both kinetics and loading experiments. From Fig. 1 and Fig. 2 it is clearly seen that Ca(II) and Mg(II) extractions are reasonably fast even for very diluted metal ion solutions, and their kinetics obey a second order relation with k_{Ca} = 9.2 L · mol^{-1} · s^{-1} (per g of resin), k_{Mg} = 6.54 L · mol^{-1} · s^{-1} (per g of resin). Also, metal chelations are pH dependent, and obviously in acidic media complexion becomes slower. It is interesting to note that, during complexation of the polymer, the pH of the non-buffered metal ion solutions decreases to the pH = 1.9 level. Fig. 3 is a representative example of pH variation for Ca(II) complexation. This implies that metal chelation proceeds by deprotonation of the carboxyl groups of the polymer, as might be expected.

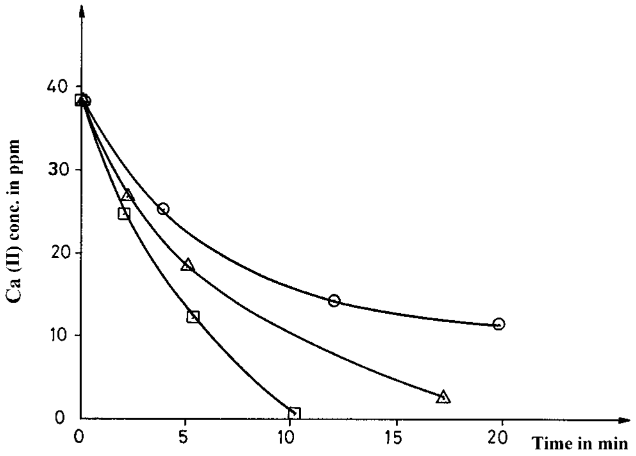


Fig. 1. Concentration – time plots of 50 mL Ca(II) solution (38 ppm) interacting with 0.225 g polymer at different pH's (○: pH 4, △: pH 6.0, □: pH 8.2)

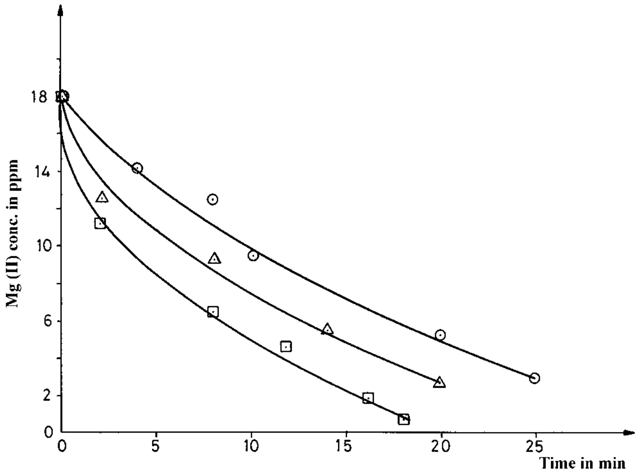


Fig. 2. Concentration – time plots of 50 mL Mg(II) solution (38 ppm) interacting with 0.225 g polymer at different pH's (○: pH 4, △: pH 6.0, □: pH 8.2)

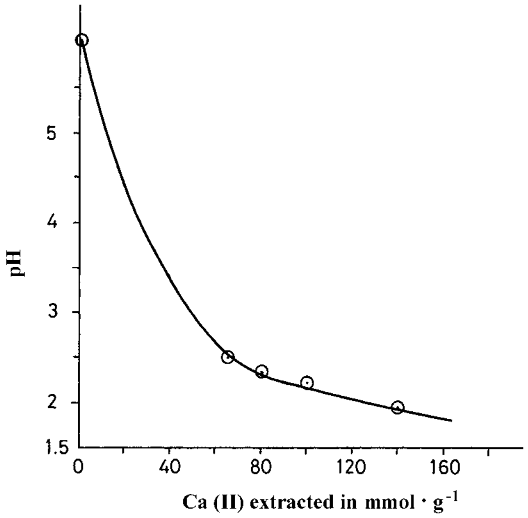


Fig. 3. Variation of pH during extraction of Ca(II) ions with 0.225 g polymer from 50 mL solution (with 38 ppm initial Ca(II) concentration)

Tab. 1. Metal chelating characteristics of the polymer

Metal ion	Capacity of the polymer in mmol · g^{-1}	Color of the metal-loaded polymer[a]	Stripped metal ion[b] in mmol · g^{-1}
Ca(II)	1.53	colorless	1.53
Mg(II)	1.54	colorless	1.53
Fe(III)	1.42	light brown	–
Ni(II)	1.53	green	–
Co(II)	1.57	purple	–
Zn(II)	1.61	colorless	–
Cd(II)	1.47	colorless	–

[a] The polymer itself is light yellow in color.

[b] Metal desorptions were determined only for Ca(II) and Mg(II) ions. The results given are based on dry polymer.

The loading data given in Tab. 1 indicate that the chelating capacities of the polymer for different metal ions are about 1.5 mmol · g^{-1}. This corresponds to one metal ion per seven ligating groups, which means that each pendant unit in Scheme 2 is occupied by one metal ion.

Regeneration of the loaded polymer samples by 1 M HCl is not complete in one step. Only 86% of Ca(II) ions are decomplexed in the first contact with acid solutions for 30 min. However, it has been observed that, if the acid treatments are repeated three times, the polymer samples could be completely freed from the metal ions. Or else, using 4 M HCl solutions, Ca(II) ions can be totally decomplexed in one step.

In order to find any potential difference in the reactivities of the used and original polymer, the chelating polymer was loaded with Ca(II) and decomplexed with 4 M acid solutions, then recovered by treating with diluted NaOH. This procedure was repeated ten times, and the Ca(II) binding capacity was determined again. This inspection implies that, after ten times of recycling, the calcium uptake capacity of the polymer becomes 1.53 mmol · g^{-1}, which is the same as that of the original polymer.

In conclusion, this study reveals that the polymer presented has a strong chelating ability like its monomeric analogue EDTA. The chelatation with Ca(II) and Mg(II) ions is reasonably fast and suitable for water treatment. The chelated polymer is completely regenerable, and it can be recycled at least ten times without losing its original reactivity. Since the starting chemicals are available commercially with acceptable costs, the chelating polymer presented may be of interest for large-scale water treatment to remove Ca(II) and Mg(II) ions.

Acknowledgement: This article is dedicated to the 225th anniversary of the Istanbul Technical University.

1) A. Ringbom, "*Complexation in Analytical Chemistry*", Interscience Publ., New York 1969

2) F. Svec, *Acta Polym.* **31**, 68 (1980)

3) C. Lecat-Tillier, F. Lafuma, C. Quivoron, *Eur. Polym. J.* **16**, 437 (1980)

4) M. Yamada, M. Tagagi, K. Ueno, *J. Coord. Chem.* **10**, 257 (1980)

5) E. Blasius, I. Bock, *J. Chromatogr.* **14**, 244 (1964)

6) J. S. Fritz, R. C. Freeze, M. J. Thornton, D. T. Gjerde, *J. Chromatogr.* A **739**, 57 (1996)

7) J. Basset, R. C. Denney, G. H. Jeffery, J. Mendham, "*Vogel's Textbook of Quantitative Inorganic Analysis*", 4th ed., Longman group Ltd., London 1978, p. 319–334

8) N. Biçak, B. F. Şenkal, *J. Polym. Sci., Part A: Polym. Chem.* **35**, 2857 (1997)

9) Ref. 7, p. 754–755

10) H. R. Synder, R. E. Heckert, *J. Am. Chem. Soc.* **71**, 2006 (1952)

11) H. Tbal, M. Delporte, J. Morcellet, M. Morcellet, *Eur. Polym. J.* **28**, 671 (1992)