

Poly (styrene sulfonamides) with EDTA-Like Chelating Groups for Removal of Transition Metal Ions

NIYAZI BIÇAK, BAHIRE FILİZ SENKAL, DEMET MELEKASLAN

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

Received 29 May 1999; accepted 10 September 1999

ABSTRACT: Chlorosulfonated styrene–divinyl benzene (10%) resin beads (420–590 μm), when treated with an excess of triethylene tetramine (TETA), give a corresponding polymeric sulfonamide with three amine functions. The free amine functions of the resin were carboxymethylated almost quantitatively by reacting with 20% excess of potassium chloroacetate in aqueous solution. The resulting resin with iminoacetic acid functions showed rapid chelating abilities for transition metal ions such as Zn (II), Cd (II), Cu (II), Ni (II), Co (II), and Fe (III) ions. At the neutral pHs the chelating resin was able to reduce the metal ion concentrations lower than 1 ppm in about 15 min of the contacting time. Interestingly, when the resin was used in sodium form, metal binding capacities were higher than the theoretical capacity ($1.66 \text{ mmol} \cdot \text{g}^{-1}$), due to simultaneous precipitation of the transition metal hydroxides on bead particles. The resin samples loaded with metal ions can be regenerated more than 10 times by simple acid–base treatments, without activity loss. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2749–2755, 2000

Key words: functional polymers; chelating polymer; ion-exchange; polystyrene sulfonamides; polymer with triethylene triamine tetra acetic acid functions

INTRODUCTION

Most of the transition metal ions are four or five coordinating in complexation with many ligands. Principally, with tetra- or hexa-dentate ligands these metal ions give highly stable complexes, especially when five- or six-membered chelates form. This principle can be extended to polymeric ligands. Multidentate ligands attached to polymers are expected to have better complexing abilities in comparison to the other polymer ligands. In fact, in many polymers or ion exchangers, common ligating groups such as $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{SH}$, $-\text{NH}_2$, or $-\text{PO}(\text{OH})_2$ groups are far apart from each other, and sterically, these cannot form stable chelates around the metal ions. In these polymers metal binding generally occurs through one or two bonds.

In studies, dealing with polymer metal complexes or removal of metal ions, this phenomena seems to be overlooked. In the literature, a relatively small number of polymers carry multidentate ligands that surround metal ions completely.

Presumably, polyethylene imines,¹ their dithiocarbamates,² carboxymethyl,³ or phosphomethyl⁴ derivatives are the most common examples of polydentate ligands forming four chelate rings around the metal ions.

Some of these type polymers have found commercial applications. For instance, crosslinked polystyrene beads carrying aminomethylphosphonic acid groups^{5,6} (i.e., Duolite ES 467) and iminodiacetic acid groups⁷ (i.e., Chelex 100) have been demonstrated to be efficient in the removal of trace quantities of metal ions. Due to chelating effects, these are superior to the common ion exchange resins.

One interesting aspect of the all amine ligating polymers is that these polymers form cationic

Correspondence to: N. Biçak.

Journal of Applied Polymer Science, Vol. 77, 2749–2755 (2000)
© 2000 John Wiley & Sons, Inc.

complexes, so-called other sphere complexes, with metal ions counter anions of the metal cations, and the overall process of complexation is sorption of the metal ions together with their counter anions.⁸

Also, some polyamines derived from epichlorohydrin and ethylenediamine condensates⁹ are important examples of polymer ligands yielding stable metal complexes. Polymers with pendant oligoethyleneimine functions are less common in the literature for chelating with metal ions. The most striking examples of these polymers are chloromethylated polystyrenes modified with ethylenediamine (EDA), diethylene triamine (DETA), or triethylene tetramine (TETA) functions. These polymers have extremely powerful chelating abilities for various metals and now these are being exploited commercially.¹⁰

In our previous study, chlorosulfonated styrene-DVB (10%) resin beads were interacted with an excess of ethylenediamine to give the corresponding sulfamide derivative. Upon treating with a 20% excess of potassium chloroacetate, the amine functions on the polymer were carboxymethylated almost quantitatively. We observed that the resulting chelating polymer is an extremely powerful sorbent for Ca (II) and Mg (II) ions.¹¹

Having an EDTA-like structure, the crosslinked polymer is expected to also show strong complexation for transition metal ions.

In the present study, metal sorption ability of the resin has been investigated for various transition metal ions such as Zn (II), Cd (II), Cu (II), Ni (II), Co (II), Fe (III). In their study, its efficiency for trace quantities (i.e., 50–70 ppm) of metal ions has been studied. PH-dependent metal uptakes and regeneration conditions have also been studied.

EXPERIMENTAL

Crosslinked polystyrene-(10% DVB) resin in bead form (420–590 μm) was prepared by the suspension polymerization method as described before.¹² Chlorosulfonation of the polystyrene resin beads was performed using chlorosulfonic acid as reported elsewhere.¹² The degree of the chlorosulfonation was indirectly determined by chlorine analysis of the product. This was performed by boiling a 0.4-g polymer sample with a 10-mL NaOH solution (10%). Chlorine analysis of the NaOH solution by the mercuric thiocyanate

method¹³ indicates a $3.84 \text{ mmol} \cdot \text{g}^{-1}$ chlorosulfonate group.

Sulfamidation with TETA

Chlorosulfonated resin was treated with an excess of triethylene tetramine (TETA), and an excess of TETA was removed by filtration as described before.¹⁴

Determination of the Amine Content

Elementary microanalysis of the resin with TETA function was considered as the most direct way of estimating amine functions. However, elementary analysis gave no satisfactory results due to incomplete burning of the samples during the experiments. For the nitrogen analysis the following two alternative procedures were used. (1) Kjeldahl nitrogen analysis: the resin sample (0.5 g) was boiled in 10 mL H_2SO_4 (65%) for 8 h. About two-thirds of the acid was removed by heating under fume cupboard. The residue was subjected to Kjeldahl ammonia analysis as usual, and nitrogen content was found to be $10.7 \text{ mmol} \cdot \text{g}^{-1}$. (2) Acid titration method: in this method 1 g of the resin sample was contacted with 5 mL of 3 M HCl solution for 6 h, and filtered. One milligram of the filtrate was titrated with 0.1 M NaOH solution in the presence of a phenol-phthalein color indicator. NaOH (13.8 mL) consumption corresponds to $1.38 \cdot 5 = 6.9 \text{ mmol}$ unreacted acid. This indicates a $5.3\text{--}6.9 = 8.1 \text{ mmol}$ amine per gram of the resin. Because each TETA substitution contains three amine functions, the substitution degree is $8.1/3 = 2.70 \text{ mmol} \cdot \text{g}^{-1}$, whereas from the Kjeldahl nitrogen analysis, TETA content was found to be $10.7/4 = 2.675 \text{ mmol} \cdot \text{g}^{-1}$. The average $(2.70 + 2.675)/2 \approx 2.69 \text{ mmol} \cdot \text{g}^{-1}$.

Modification by Chloroacetic Acid

Amine groups of the polymer were carboxymethylated using the potassium salt of chloroacetic acid as described elsewhere.¹¹

Determination of the Carboxyl Content

A weighed amount (0.2 g) of the polymer sample was soaked into 10 mL of 2 M NaOH solution at room temperature for 4 h. The mixture was filtered and unreacted NaOH content was determined by titration of a 5 mL filtrate with 0.1 M HCl solution. The carboxyl content found was $6.65 \text{ mmol} \cdot \text{g}^{-1}$.

Table I Metal Sorption-Desorption Characteristics of the Resin

Metal Ion ^a	Capacity of Sodium Form (mmol · g ⁻¹) ^b (± 0.04)	Desorbed Metal Ion (mmol · g ⁻¹) ^c (± 0.04)	Capacity of Hydrogen Form (mmol · g ⁻¹)
Ni (II)	2.18	1.42	1.63
Co (II)	2.42	1.50	1.61
Cu (II)	2.24	1.92	1.68
Zn (II)	2.65	1.40	1.41
Cd (II)	2.69	2.11	1.37
Fe (III)	2.64	1.53	1.43
Ca (II)	1.67	1.64	1.66
Mg (II)	1.66	1.66	1.64

^a Sample 20 mL of metal ion solution with 0.1 M initial concentration, interacted with 1 g dry resin.

^b The capacities quoted are mean-average values of three measurements.

^c Desorbed amounts after first treatment with 3 M HCl solutions. The results are mean average values of two independent measurements.

In comparison to the amine content, conversion yield of the carboxymethylation is about 99.8%.

Determination of the Metal Sorption Capacities of the Resin

Metal sorption capacities of the polymer were performed using 0.1 M metal ion solutions. Metal solutions used were $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, CaCl_2 , $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

To attain maximum capacities, first, all the carboxyl groups of the polymer were neutralized with NaOH solution. Thus, 15 g of polymer sample was left in 100 mL of 4 M NaOH solution for 3 h. After filtration, it was washed several times with distilled water, and dried under vacuum at room temperature for 24 h. For the metal sorptions, 0.5 g parts of the sample were interacted with 20 mL of 0.1 M metal ion solutions for 3 h, under continuous stirring. Aliquots (1 mL) of the filtrates were used to assay the unreacted metal contents. Metal ions were determined by complexometric titration using 0.01 M EDTA (Titriplex III) solutions in the presence of suitable color reagents.¹⁵ Based on the differences of the initial and final metal contents, capacities were calculated (Table I).

pH-Dependent Metal Sorptions

To examine the effect of the pH, the metal sorption experiments were repeated in buffered solutions.

In these experiments, metal salts were dissolved in buffer solutions at pH 3.4, pH 4.0, and pH 6.0 (sodium acetate/acetic acid).

Similar experiments were repeated as described above. Based on the results, capacity-pH plots are pictured in Figure 1.

Metal Binding Kinetics of the Resin

Metal sorption kinetics were performed by simple batch experiments using highly diluted ($8\text{--}9.5 \cdot 10^{-4}$ M) metal ion solutions. At this concentration metal contents were in the 50–70 ppm level,

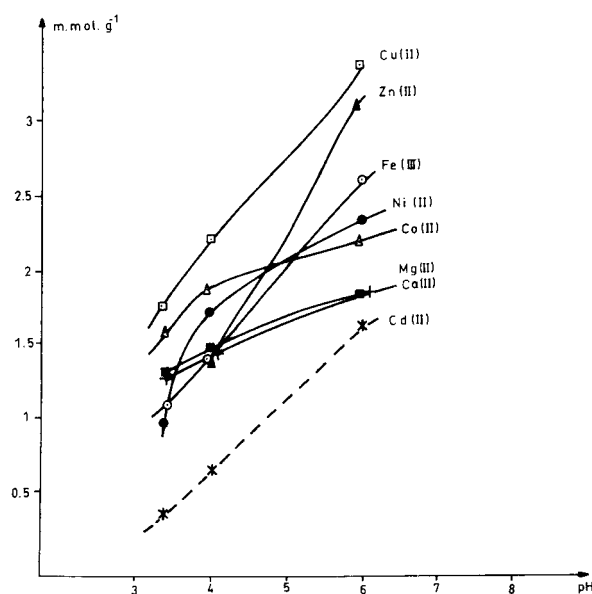


Figure 1 Loading-pH plots of the resin (from 0.1 M buffered metal solutions).

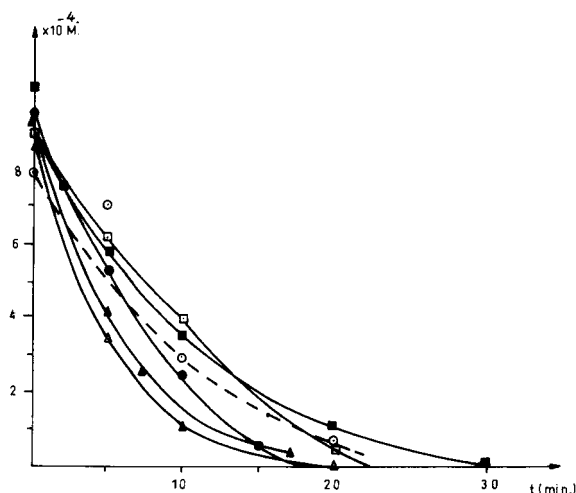


Figure 2 Concentration–time plots of the metal ion solutions (80 mL) with about 9.10^{-4} M initial concentrations, interacted with 0.1 g of resin samples in sodium form. Δ : Ni (II), $\circ$: Cu (II), $\bullet$: Co (II), $\blacktriangle$: Cd (II), $\blacksquare$: Zn (II), $\square$: Fe (III).

which is common for the spring water sources. For this purpose, 0.5-g polymer samples in sodium form were interacted with 50 mL of the metal ion solutions. While stirring continuously, 2.5 mL of the samples were taken out by a pipette at appropriate time intervals. These were transferred into 50-mL volumetric flasks through filter papers. Metal contents of the samples were determined by AAS. Based on these results, concentration–time plots were obtained as depicted in Figure 2.

Regeneration of the Metal-Loaded Samples

To regenerate used polymer samples, each (0.4 g) was placed in 10 mL of 4 M HCl solution and stirred for 3 h. The mixtures were filtered and metal chlorides leached were analyzed by AAS. For comparison of the extracted and stripped metal ion contents (per gram of dry polymers), see Table I.

The Recycling of the Used Polymer Samples

The resins loaded with Ca (II) and Mg (II) ions became metal free after acid leaching. However, in the case of other metal ions, the resins were still colored after acid treatments.

Also, metal analysis of the resulting acid solutions by AAS, indicated a 53–92% of metal ion releasing from the polymers.

To be sure of the metal removal, the resin samples were treated at least five times successively with 1 M HCl solutions, and finally washed with 0.1 M NaOH solutions (20 mL per g) with water. In this way the resin samples became metal-free and reusable.

RESULTS AND DISCUSSION

Polystyrene–divinyl benzene (10%) macroporous resins with EDTA-like chelating groups were prepared according to the following sequences of reactions (Scheme 1). The reaction steps involve (i) chlorosulfonation of polystyrene–DVB (10%) resin beads (420–590 μm), (ii) sulfamidation with excess of triethylene tetramine (TETA), (iii) quantitative carboxymethylation of the amino groups by ClCH_2COOK .

Based on the chlorine analysis,² nitrogen analysis³ by the Kjeldahl method, and acid-base titration,⁴ the full structure of the resulting chelating polymer can be depicted as shown in Scheme 2. This structure implies 1.66 mmol of the ligating group per gram of the resin.

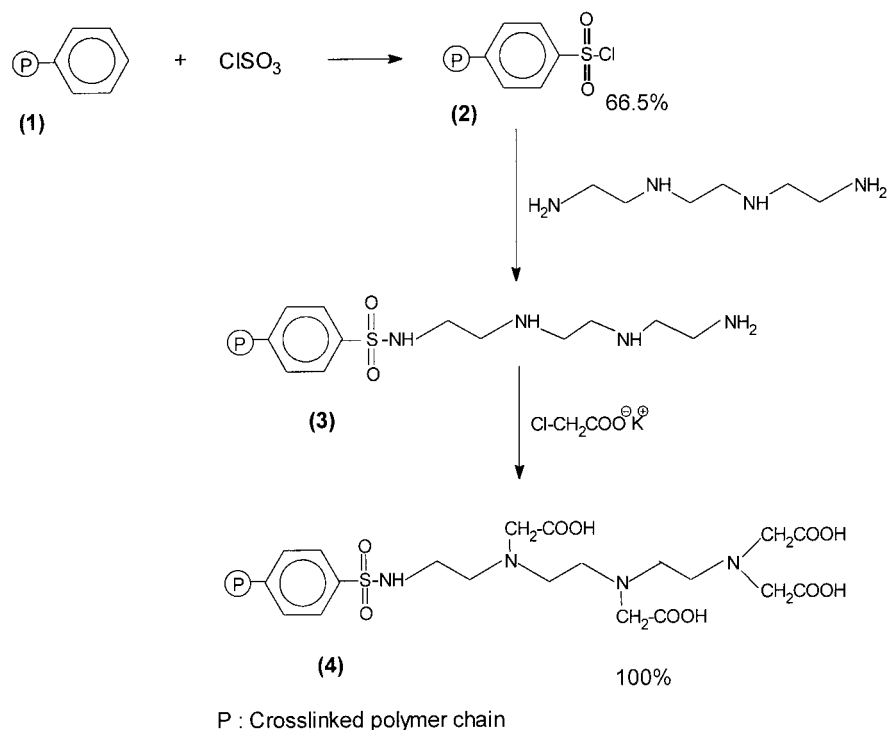
In the sulfamidation step an excess amount of TETA was used to suppress the side reaction in which two sulfonyl groups can bind with a single TETA molecule. Additionally, due to relatively high crosslinking density (10%) and 66.5% of the sulfonyl group content, the probability of the side reaction yielding additional crosslinking is expected to be greatly reduced. Here, a second question concerns any probable sulfamidation via secondary amino groups. Although reactivity of the primary amine functions in TETA is greater than those of the secondary amino functions, sulfamidation through the secondary amines is also possible to some extent. So the structure pictured in Scheme 1 is only representative, and following carboxymethylated, forms of both binding modes are expected to have almost equal chelating abilities.

The only hydrolyzable bond appearing in the structure is the sulfamide linkage. However, sulfamide bonds are known to be highly resistant to acid–base hydrolyses. For a complete hydrolysis of sulfamides, they need boiling in 60% H_2SO_4 for 3 h.¹⁶

For this reason the chelating resin must be stable enough towards relatively concentrated acid or base solutions.

Metal Sorption Characteristic of the Resin

To investigate metal sorption characteristics of the resin metal, complexations were performed in



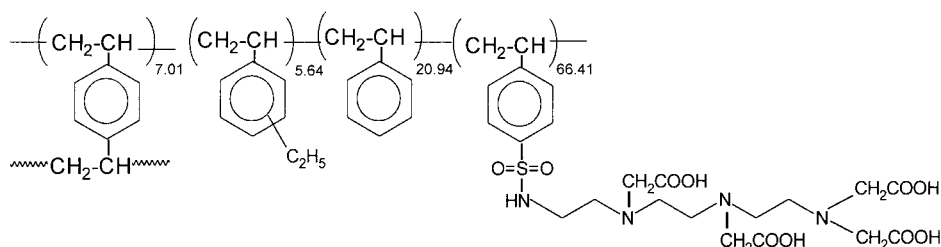
Scheme 1

the following manner: (a) direct interaction of the resin with a pure metal ion solution without buffer solutions; (b) pH-dependent metal sorptions from buffer solutions; or (c) kinetics of metal sorption from diluted solutions.

From the application view point, the use of buffer solution is not practical. Therefore, we deliberately have not used buffer solutions in the first series of experiments. In these experiments the sodium form of the resin was used to attain high metal uptakes. For this purpose, 20 mL of 0.1 *M* metal ion solutions were simply mixed with 0.5 g of the polymer sample, and unreacted metal ions remaining in the solutions were analyzed. From the difference in the initial and final concentrations, the capacities were calculated. The results are given in Table I.

However, under the conditions we studied, with the exception of Ca (II) and Mg (II) ions, the chelating capacities found were about 1.5 or two times in excess of the theoretical capacities. Apparently these results represent large contradictions with the expected capacities. An alternative possibility is that complexation of the diethylene triamino tetraacetic acid group with more than one metal ion seems not to be realistic because, in the complexation of its low molecular weight analogue, the EDTA metal/ligand ratio is 1/1.

Presumably the most plausible reason for the excess metal ion sorption is simultaneous precipitation of metal hydroxides during complexations in the microdomains of the solid phase. Lower pH limits for precipitation of transition metal hydroxides are in the pH 7–9 range.



Scheme 2

To prove this assumption, the sample loaded with Co (II) was sieved through a filter with a 210- μm mesh size. The resin sample was repeatedly washed with an excess of water to remove the cobalt hydroxide stuck to the resin beads.

After acidification of the filtrate (200 mL), it was analyzed, and the total Co (II) content of the filtrate was found (0.32 mmol), which corresponds to $1.78 \text{ mmol} \cdot \text{g}^{-1}$ of the Co (II) loading capacity. Of course, this amount is still higher than the theoretical capacity ($1.66 \text{ mmol} \cdot \text{g}^{-1}$), because, practically, removal of all the hydroxide precipitate from the small pores inside the bead particles is not possible. As a result, hydroxide formation is responsible for the apparent high metal uptakes, when the sodium form of the resin was used.

In another series of experiments the hydrogen form of the resin was used. In that case, the capacities (cf Table I) of the resin were close to or somewhat lower than the theoretical capacity.

pH-Dependent Metal Sorptions

Similar anomalies are observed in the pH-dependent absorption curves (Fig. 1). At a pH of 6, all the metal sorptions are higher than the theoretically expected value. There appears to be some selectivity between copper and cadmium sorptions. Although some other selectivities are observed in Figure 1, we have not studied selectivities any further. From Figure 1 it can be deduced that the affinity of the resin is somewhat less for Cd (II) ions.

Metal Sorption Kinetics

Although metal sorption kinetics depend on many external factors such as stirring rate, temperature, and concentration to obtain comparable results, batch kinetic experiments were carried out in aqueous solutions containing trace quantities of metal ions without buffer.

These experiments provide testing of the efficiency of the resin for trace quantities. This information is beneficial to understand applicability of the resin for removal of trace amounts of metal ions from waste or drinking waters.

Figure 2 shows that the resin works well with trace metal concentrations, and metal sorptions are reasonably fast for the metal ions studied. Binding of Fe(III) ions is faster, whereas complexation with Cd(II) ions is somewhat slower. Overall results imply that, in about 15 min contact time, metal concentration levels drop to an

average of 0–2 ppm levels. These amounts are satisfactory for most purposes.

The Regeneration

To investigate regenerability of the polymer, the loaded resin samples were treated with 1 M HCl solutions, and metal contents of the solutions were analyzed. These experiments show that except for the Ca (II) and Mg (II) ions, all the other metal ions are released from resin at 60–90% levels with a first treatment by the acid solutions. After the acid leaching process, the resin samples were still colored, especially in the case of the Fe (III) ions.

The samples with the Fe(III) and Zn (II) ions become metal free only after leaching five times of with the acid solutions. Obviously, this is because of complex salt formation of ammonium groups with FeCl_4^- anionic groups. Because the anionic complex formation tendencies of Ni (II) and Co (II) ions are low, these can be eluted at relatively high percentages. In this work, no systematic study was considered dealing with optimum conditions of metal ion decomplexations from the resin samples.

Nevertheless, we have observed that the resin sample with Fe (III) ions can be completely metal free only after five acid treatments. After removal of metal ions, when the resin samples are treated simply with 0.1 M NaOH solution, they become regenerated and ready for the next cycles.

To test recyclability and any probable activity loss of the resin, the resin sample loaded with Ca(II) ions was decomplexed and loaded in turn 10 times without measuring loading capacities at the intermediate steps. After 10 times of regeneration, the capacity was surprisingly the same ($1.66 \text{ mmol} \cdot \text{g}^{-1}$) as in the initial step. This result indicates that the resin can be recycled more than 10 times.

In conclusion, the resin with EDTA-like chelating groups shows rapid chelation with the metal ions [Ca (II), Mg (II), Co (II), Ni (II), Fe (III), Zn (II), Cd (II)] and is quite reactive towards trace quantities. In the sodium form, the metal-uptake capacity of the resin is greater than the theoretical capacity, presumably due to metal hydroxide precipitations on bead particles.

Although, for recovery of strongly chelated metals one needs successive acid treatments, the resin samples can be regenerated more than 10 times without activity lost. Of course, hydrolytic stability of sulfamide linkages involved is an additional advantage of the chelating resin.

Presumably the only drawback of the regenerated resin samples is their mechanical disintegration in the latter steps. Roughly one-third of the beads becomes smaller after 10 times of recycling.

Because the chelating resin is derived from commercially available chemicals with acceptable costs, it may be of interest for large-scale water treatments, including drinking water.

REFERENCES

1. Rivas, B. L.; Maturana, H. A.; Perich, I. M.; Angne, U. *Polym Bull* 1986, 15, 121.
2. Barnes, J. H.; Esslemont, G. F. *Makromol Chem* 1976, 177, 307.
3. Blasius, E.; Bock, I. *J Chromatogr* 1964, 14, 244.
4. Kobayashi, S.; Tokunoh, M.; Saegusa, T.; Mashio, F. *Macromolecules* 1985, 18, 2257.
5. Leinonen, H.; Lehto, J.; Makela, A. *React Funct Polym* 1994, 23, 221.
6. Popat, K. M.; Anand, P. S.; Dasare, B. D. *React Funct Polym* 1994, 23, 23.
7. Sherman, J. H.; Danielson, N. D.; Taylor, R. T.; Marsh, J. R.; Esterline, D. T. *Environ Technol* 1993, 14, 1097.
8. Biçak, N.; Atay, T.; Koza, G. *J Appl Polym Sci* 1996, 61, 799.
9. Biçak, N.; Atay, T.; Koza, G. *J Appl Polym Sci* 1998, 68, 103.
10. Saegusa, T.; Kobayashi, S.; Yamada, A. *Macromolecules* 1975, 8, 390.
11. Biçak, N.; Senkal, B. F.; Yarbass, T. *Macromol Chem Phys* 1998, 199, 2731.
12. Biçak, N.; Senkal, B. F. *React Funct Polym* 1996, 29, 123.
13. Basset, J.; Denney, R. C.; Jeffery, G. H.; Mendham, J., Eds.; *Vogel's Textbook of Quantitative Inorganic Analysis*; Longmann Group Ltd.: New York, 1978, p. 754, 4th ed.
14. Biçak, N.; Senkal, B. F. *J Polym Sci Part A* 1997, 35, 2857.
15. Basset, J.; Denney, R. C.; Jeffery, G. H.; Mendham, J., Eds.; *Vogel's Textbook of Quantitative Inorganic Analysis*; Longmann Group Ltd.: New York, 1978, p. 319, 4th ed.
16. Synder, H. R.; Heckert, R. E. *J Am Chem Soc* 1952, 74, 2006.