116 | *Macromol. Symp.* **2006**, 245–246, 116–122 DOI: 10.1002/masy.200651315

Water-Soluble Polyelectrolytes with Metal Ion Removal Ability by Using the Liquid Phase Based Retention Technique

Bernabé L. Rivas, S. Amalia Pooley, Eduardo D. Pereira, Antonio Maureira*

Summary: Water-soluble polyelectrolytes containing carboxylic acid groups were investigated as polychelatogens, in view to study their metal ion binding properties, using the *liquid-phase polymer-based retention* technique under different experimental conditions. The divalent metal ions investigated were: Co^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. When the pH increased above 3, and especially at pH 5, metal ion retention capability increased as the majority of the functional groups are carboxylate, which can form more stable complexes with the metal ions. The retention capability also depended on the structure of the polyelectrolyte and the filtration factor, Z.

Keywords: metal-polymer complexes; radical polymerization; water-soluble polymers

Introduction

The increase world demand for most of the known metals, the decrease in the grade of the available ores, and strict environmental regulations make it interesting to find effective, efficient methods for processing waste solutions containing metal ions, even at very low concentrations. Liquid-liquid extraction, sorption, precipitation, and other methods based on two-phase distributions are generally used to separate inorganic species contained in dissolved matrices, industrial fluids or natural waters. Although many of these methods have been developed and successfully used, their application can cause problems. Some problems are related to heterogeneous reactions and interphase transfer. Heterogeneous two-phase system can be avoided by application of membrane process based separation methods, which are among the most promising techniques for enrichment of various species from solutions.[1,2] Ultrafiltration membrane separation depends on membrane pore size, solute-membrane interaction, and shape and size of the macromolecule. For maximum separation efficiency, there should be a 10-fold difference in the sizes of the species to be separated. In addition, because all ultrafiltration membranes have a certain pore size distribution, the molecular mass cut off (MMCO) of the membrane (defined as the molecular weight at which 90% of the macromolecular solute is rejected by the membrane) should be at least one-half that of the smallest macromolecule to be rejected.

Thus, a number of soluble and hydrophilic polymers have been prepared through addition polymerization and by functionalizing various polymers, and are found to be suitable for metal ion separation and enrichment in conjunction with membrane filtration. Membrane filtration easily allows the separation of metal ions bound to soluble polymers from non-bound metals. This method is known as the *liquid-phase polymer-based retention (LPR) technique*.[3–21]

Water-soluble polymers are commercially available or can be synthesized by different routes. Among the most important requirements for technological applications of these polymers are: high solubility in water; an easy, inexpensive synthesis

---

Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepcion, Chile
E-mail: brivas@udec.cl

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

route; an adequate molecular weight and molecular weight distribution; chemical stability; high affinity for one or more metal ions; and selectivity for the metal ion of interest. The most usual synthetic procedures are addition polymerization, especially radical polymerization, and functionalizing of polymer backbones through polymer-analogous reactions. The macromolecules can be homo- or copolymers, and may contain one or more coordinating and / or charged groups. These groups are placed at the backbone or at the side chain, directly or through a spacer group.

Polyelectrolytes may be distinguished from chelating polymers (polychelatogens). The former have charged groups, or easily ionizable groups in aqueous solution, while the latter bear functional groups with the ability to form coordination bonds. Carboxylic acids are one of the most investigated ligands present in the polychelatogens.

The aim of this paper is to investigate the retention properties of different polyelectrolytes containing carboxylic acid groups as pendant groups through the *liquid-phase polymer based retention* technique.

Experimental Part

Reagents

The monomers acrylic acid, AA, (Merck), methacrylic acid, MA, (Merck), 2-acrylamido glycolic acid, AGA, (Aldrich) were purified before the polymerization reaction. Poly (acrylic acid), P(AA), poly(methacrylic acid), P(MA), and poly(2-acrylamido glycolic acid), P(AGA), were synthesized by radical polymerization using ammonium persulfate, APS as initiator (1 mol-%) for 24 h. All the polymers were purified by passing them through an ultrafiltration membrane with a molar mass cut off (MMCO) of 3000 Daltons (Da). Then, the polymers were fractionated by membranes with different MMCO and the fraction >50000 Da of was used for LPR runs. $Co(NO_3)_2 \times 6\ H_2O$, 99%, p.a. Merck; $Cu(NO_3)_2 \times 3\ H_2O$, 99%, p.a. Merck; $Zn(NO_3)_2 \times 6\ H_2O$, extra pure, Merck; $Cd(NO_3)_2 \times 4\ H_2O$, 99%, p.a., were the metal salts studied. Sodium hydroxide (NaOH, Merck), nitric acid 70% (HNO_3, Caledon) were used to adjust the solution pH.

Procedure (Washing Method) of LPR Technique

The main features of an LPR system are a filtration cell with a magnetic stirrer containing a membrane filter with a known exclusion rating, a reservoir and a pressure source, *e.g.* a nitrogen bottle (see Figure 1). In ideal cases, this system may be considered a steady-state mixed flow reactor. Conventional stirred filtration cells or a specially designed tangential-flow cell equipped with a pump can be used. Essential parameters are the molar mass exclusion rate in a wide pH range (1–12), an appropriate permeate flow rate ($0.5–12\ mL \cdot min^{-1}$), retentate volume (2–50 mL) and gas pressure, where 300 kPa is a suitable pressure in most cases. The most usual molar mass cutoffs range between 1,000 and 300,000 Da. A nominal exclusion rate of 10,000 Da proved to be convenient for polymers having a molecular mass between 30 and 50 $kg \cdot mol^{-1}$.

20.0 mL of a solution containing $5.0 \cdot 10^{-3}$ meq/L of a water-soluble copolymer and $1.0 \cdot 10^{-4}$ M of metal ions are placed into the solution cell provided with an ultrafiltration membrane with a MMCO of 10000 Da (Millipore, Amicon).

The pH was adjusted with dilute HNO_3. A washing solution (water at pH = 3.0, 5.0, and 7.0, depending on the metal ion) was passed through under pressure (3.5 bar of N_2) from the reservoir through the cell solution. As the in- and out flux are rapidly equaled, the initial volume (20.0 mL) is kept constant during the experiment. Ten fractions of 20 mL were collected. Each fraction was collected in graduated tubes, and the corresponding metal ion concentration was determined.

Measurements

The pH was determined with a Jenco Electronics 1671 pH-meter. For the LPR

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

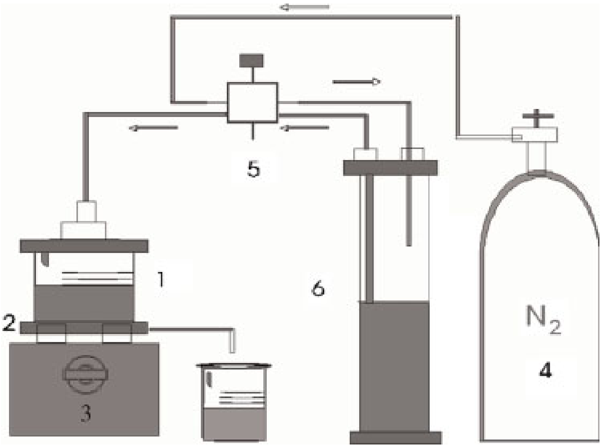


Figure 1.
Instrumental arrangement: (1) filtration cell with polymeric and metal ion solution; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with water.[3]

technique, a membrane filtration system was employed to test the coordinating properties of the polychelatogen. A Unicam Solaar M5 series Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate.

Results and Discussion

Different water-soluble polyelectrolytes containing the carboxylic acid/carboxyate groups as one the most important functional groups were synthesized by radical polymerization and studied as a polychelatogen using the LPR technique. The P(AA) and P(MA) contain only carboxylic groups, and P(AGA) corresponds to a weak polyelectrolyte containing three potential ligand groups as hydroxyl, amide, and carboxylic acid groups (see Table 1).

The metal ions were selected by their impact on the environment and human health, specially Cd^{2+} and Zn^{2+}, and they are also important for their potential applications as metal-polymer metal complexes, particularly those with Cu^{2+}.

In order to quantify the separation process, metal species retention versus the filtration factor is plotted. The binding and elution processes may be formulated as a chemical reaction, where reversible reaction in combination with an irreversible transfer of metal ions across the membrane is responsible for metal retention (see Scheme 1). Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration. The filtration factor (Z) is defined as the volume ratio of the filtrate (V_f) versus volume in the cell (Vo). The metal ion (M) remaining in the cell during filtration is equal to the sum of the metal ion bound to the polymer chain and the metal ion free in the solution.

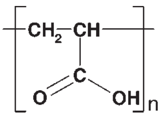
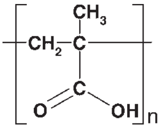
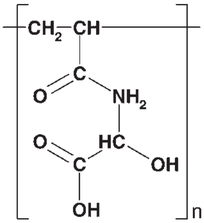
As an example, Figure 2 presents the effect of the pH on the retention profile of P(AGA). As the pH increases, retention increases. It is very important that metal ion retention is highest at pH 7.

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase.

The features of coordination between polymers and metal ions may be described by the usual coordination theories, but some special aspects may be considered. When intra-chain complexes are predomi-

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

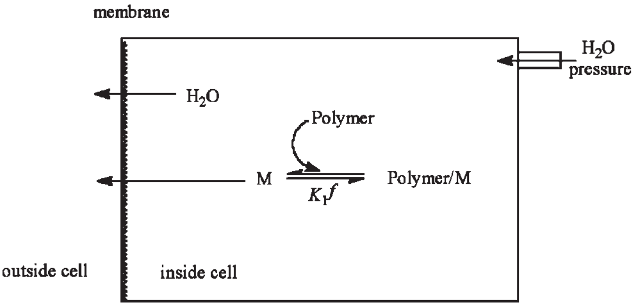
Table 1.
Structure of the polychelatogens, pKa, and metal ions investigated.

Polymer	Structure	Investigated cations	pKa
Poly(acrylic acid) P(AA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	4.80
Poly(methacrylic acid) P(MA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	4.85
Poly(2-acrylamido glycolic acid) P(AGA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	4.37

nant, the existence of a polymer domain with near constant ligand concentration is normally recognized since the distances between them keep them within a narrow range for a given polymer chain. As a result, the chelating reaction appears as a one-step reaction. For relative low ligand amounts in the solution, completely complexed metal ions may coexist with free, uncomplexed ones. The reactivity of the complexes is sometimes strongly affected by the polymer ligand that exists outside the coordination sphere and surrounds the metal complex by means of special chemical environment and steric effects.

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase.

The interactions between polyelectrolytes and metal ions are very dependent on the ionic strength, and low interaction rates are found when the ionic strength is high. Consequently, at pH 1, where the concentration of the monovalent H^+ ions is high, low interaction rates are always found. The interaction rates increase rapidly with increasing pH, and high retention values



Scheme 1.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

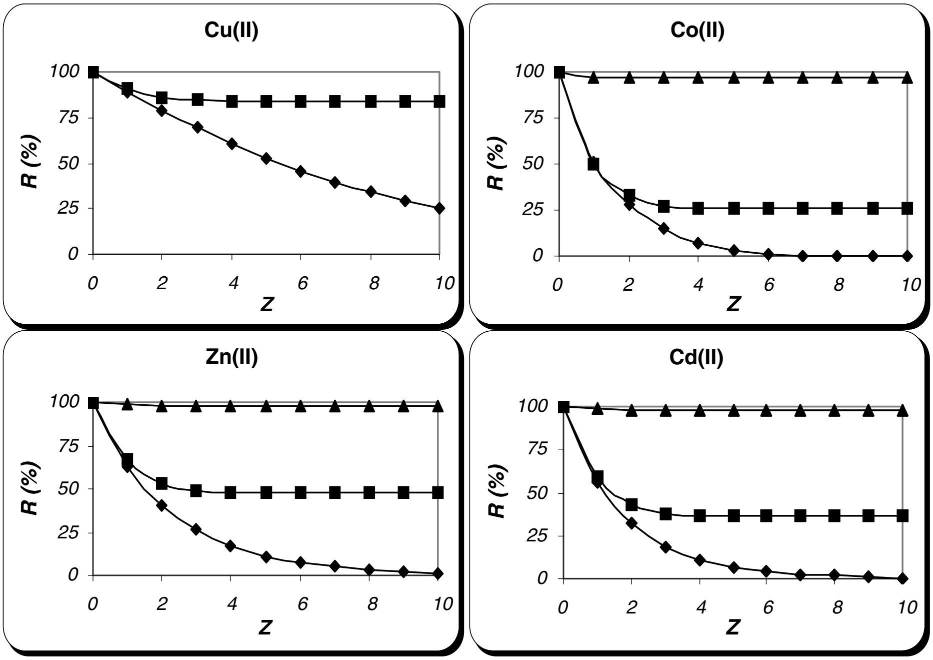


Figure 2.
Retention profile of P(AGA) at pH 3, 5, and 7.

are found for divalent and trivalent metal ions at pH above 3.

In contrast, when interactions occur by formation of coordinating bonds, the nature of the metal ions and the effect of the pH may induce differences in the retention profiles of like-charged metal ions and selectivity is often informed. Polymers containing carboxylic groups, such as PAA or PMA, behave as weak polyelectrolytes and present high retention values at pH above 3. They also have chelating properties, and it is found that interactions with Cu^{2+} are normally more intense than with other divalent metal ions.

The effect of the pH may be regarded in several ways. For strong polyelectrolytes, very low pH values are associated to a high ionic strength, and in consequence, competition of H^+ with divalent metal ions to condense on the polymer surface is established. Thus, in ultrafiltration experiments performed at pH near 1, elution of divalent metal ions takes place from the polymer domain; while at pH 3 significant binding is found as can be seen in Figure 2. Weak polyelectrolytes, such as polycarboxylic acids, present high retention ability at pH above pH 4.5 where most carboxylic units are deprotonated. The pKa for the three polymers ranged from 4.4 and 4.8. Therefore, the metal ion retention increased at pH 5 and pH 7.

The filtration factor Z is also a qualitative measurement of the strength between the ligand group and the metal ions. Thus, when these interactions are weak, it is only necessary to pass it through pure twice-distilled water to break this interaction. However, if these interactions are strong, they will be maintained and it is necessary to employ another method to recover the polychelatogen (see Figures 3 and 4).

Figure 5 shows the suggested polymer-ligand-metal ion interactions that involve the carboxylate groups. This explication means that this mechanism should be occurring at $pH > 4.5$, where the majority of the ligand groups are found as carboxylate groups.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

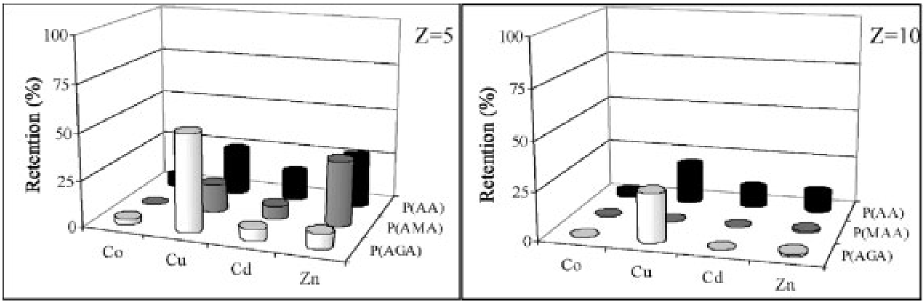


Figure 3.
Retention properties of the polychelatogens P(AA), P(MAA) and P(AGA). at pH 3 and Z = 5, and pH 3 at Z = 10.

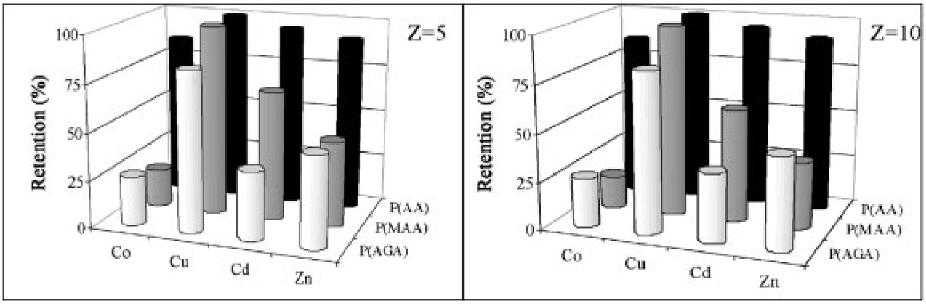


Figure 4.
Retention properties of the polychelatogens P(AA), P(MAA) and P(AGA). at pH 5 and Z = 5, and pH 5 at Z = 10.

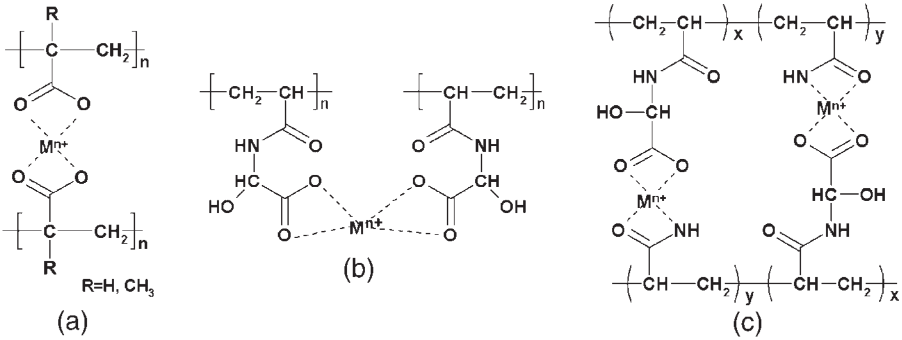


Figure 5.
Suggested polymer-ligand-metal ion interactions for a) P(AA) R=H and P(MA) R=CH_3, b) and c) for P(AGA).

Conclusions

pH has a strong effect on the metal ion retention ability. The three polychelatogens investigated P(AA), P(MA), and P(AGA) presented the highest retention properties for Cu^{2+} forming the most stable complexes. There was not observed an important effect of the structure of the these polychelatogens on the metal ion retention capability, but P(AGA) showed a stronger interaction with Cu^{2+}. With respect to the metal ions, predominant species may be present as a function of the pH. Since hydroxy-complex precipitation is a phenomenon that should be avoided in

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

LPR studies, Cu^{2+} ions cannot be studied at relatively high concentrations at a above pH 5.

Acknowledgements: The authors thank to FONDECYT (Grant No 1030669) for financial support. AM thanks CONICYT for the PhD Scholarship.

[1] S. Ahamadi, B. Batchelor, S. S. Koseoglu.The diafiltration method for the study of the binding of macromolecules to heavy metal ions. *J. Membrane Sci.* **1994**, *89*, 257–265.

[2] T. Tomida, T. Inoue, K. Tsuchiya, S. Masuda.Concentration and / or removal of metal ions using a water-soluble chelating polymer and microporous hollow fiber membrane. *Ind. Eng. Chem. Res.* **1994**, *33*, 904–906.

[3] K. Geckeler, G. Lange, H. Eberhardt, E. Bayer.Preparation and application of water-soluble polymer-metal complexes. *Pure Appl. Chem.* **1980**, *52*, 1883–1905.

[4] B. Ya. Spivakov, K. Geckeler, E. Bayer.Liquid-phase polymer based retention technique: the separation of metals by ultrafiltration on polychelatogens. *Nature* **1985**, *315*, 313–315.

[5] E. Bayer, B. Ya. Spivakov, K. Geckeler.Poly(ethyleneimine) as complexing agent for separation of metal ions using membrane filtration. *Polym. Bull.* **1985**, *13*, 307–311.

[6] B. L. Rivas, K. E. Geckeler.Synthesis and metal complexation of poly(ethylenimine) and derivatives. *Adv. Polym. Sci.* **1992**, *102*, 171–188.

[7] B. L. Rivas, I. Moreno-Villoslada.Binding of Cd^{++} and Na^{+} ions by poly(sodium 4-styrene sulfonate) analyzed by ultrafiltration and its relation with the counterion condensation theory. *J. Phys. Chem. B* **1998**, *102*, 6994–6999.

[8] B. L. Rivas, I. Moreno-Villoslada.Evaluation of the counterion condensation theory from the metal ion distributions obtained by ultrafiltration of a system poly(sodium 4-styrene sulfonate)/Cd^{2+}/Na^{+}. *J. Phys. Chem. B* **1998**, *102*, 11024–11028.

[9] G. Asman, O. Sanli.Ultrafiltration of Fe(III) solution in the presence of poly(vinyl alcohol) using modified poly(methylmethacrylate-co-methacrylic acid) membranes. *J. Appl. Polym. Sci.* **1997**, *64*, 1115–1121.

[10] B. L. Rivas, I. Moreno-Villoslada. Poly[acrylamide-*co*-1-(2-hydroxyethyl) aziridine]: An efficient water-soluble polymer for selective separation of metal ions. *J. Appl. Polym. Sci.* **1998**, *69*, 817–824.

[11] B. L. Rivas, I. Moreno-Villoslada.Chelation properties of polymer complexes of poly(acrylic acid) with poly(acrylamide), and poly(acrylic acid) with poly(N,N-dimethylacrylamide). *Macromol. Chem. Phys.* **1998**, *199*, 1153–11601.

[12] I. Moreno-Villoslada, B. L. Rivas.Metal Ion Enrichment of a Water-Soluble Chelating Polymer studied by Ultrafiltration. *J. Membrane Sci.* **2002**, *208*, 69–73.

[13] I. Moreno-Villoslada, B. L. Rivas.Competition of divalent metal ions with monovalent metal ions on the adsorption on water-soluble polymers. *J. Phys. Chem. B* **2002**, *106*, 9708–9711.

[14] B. L. Rivas, E. D. Pereira, I. Moreno-Villoslada. Water-Soluble polymer-metal ion interaction. *Prog. Polym. Sci.* **2003**, *28*, 173–208.

[15] B. L. Rivas, S. Villegas.Water-insoluble polymers with ability to remove metal ions. *J. Appl. Polym. Sci.* **2004**, *91*, 3679–3685.

[16] B. L. Rivas, L. N. Schiappacasse, E. Pereira, I. Moreno-Villoslada.Polyelectrolyte-metal ion interaction by liquid-phase polymer-based retention (LPR) technique. *Polymer* **2004**, *45*, 1771–1775.

[17] I. Moreno-Villoslada, F. Gonzalez, M. Jofré, P. Chandía, S. Hess, B. L. Rivas.Complexation behavior of Cu^{2+} in the presence of imino diacetic acid and poly(ethyleneimine). *Macromol. Chem. Phys.* **2005**, *206*, 1541–1548.

[18] B. L. Rivas, A. Maureira, K. E. Geckeler.Novel water-soluble acryloylmorpholine copolymers: Synthesis, characterization, and metal ion binding properties. *J. Appl. Polym. Sci.* **2006**, *101*, 180–185.

[19] I. Moreno-Villoslada, V. Miranda, M. Jofré, P. Chandía, F. González, J. L. Bulnes, M. Cortés, S. Hess, B. L. Rivas.Simultaneous interactions between a low molecular-weight species and two high molecular-weight species studied by diafiltration. *J. Membrane Sci.* **2006**, *272*, 137–142.

[20] B. L. Rivas, E. Pereira, P. Robles, R. Cid.Removal of metal ions from aqueous solution through liquid phase polymer based retention technique. *Macromol. Symposia* **2006**, *235*, 152–160.

[21] I. Moreno-Villoslada, M. Jofré, V. Miranda, R. Gonzalez, T. Sotelo, F. González, S. Hess, B. L. Rivas.pH Dependence of the Interaction between Rhodamine B and the Water-Soluble Poly(sodium 4-styrenesulfonate). *J. Phys. Chem. Part B* **2006**, *110*, 11809–11812.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim