

# Poly(ethylene-*alt*-maleic acid) as Complexing Reagent to Separate Metal Ions Using Membrane Filtration

Bernabé L. Rivas, S. Amalia Pooley, Eduardo Pereira, Erika Montoya, Rocío Cid

Faculty of Chemistry, University of Concepción, Concepción, Chile

Received 9 August 2005; accepted 2 November 2005

DOI 10.1002/app.23794

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Commercial, water-soluble poly(ethylene-*alt*-maleic anhydride), P(E-*alt*-MAN), was quantitatively hydrolyzed by 0.2M NaOH to yield poly(ethylene-*alt*-maleic acid), P(E-*alt*-MAc). The polymer structure is confirmed by FT-IR spectroscopy. As the pH increases, metal ion affinity increases because the majority of the functional groups are present as carboxylate anions, which can form more stable complexes at a higher pH. By increasing the filtration factor,

Z, metal ion affinity does not significantly decrease, which means that the ligand–metal interaction is strong and cannot be destroyed by washing with water at the filtration cell's pH. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2057–2061, 2006

**Key words:** water-soluble polymers; membranes; metal-polymer complexes

## INTRODUCTION

Polymer interactions with metal ions are a subject of interest because of their potential analytical and technological applications in fields like environmental science, wastewater treatment, metallurgy industry, etc., as well as their implications in biological systems. The main uses and applications for insoluble polymeric matrix are related to metal recovery from dilute solutions.<sup>1–6</sup> There are different natural and synthetic products that present ion-exchange properties. Organic resins are the most commonly used ion exchangers, providing high chemical and mechanical stability, high ion-exchange capacity and ion-exchange rates, and the possibility to select the fixed ligand groups and the crosslinking degree.

Water-soluble polymer-metal ion interactions take place in a homogeneous medium. To face the problem of separating metal ions bound and not bound to the polymer, among the most promising techniques used are separation methods based in the membrane process.<sup>7–35</sup> Membrane filtration easily allows this separation by means of the *liquid-phase polymer-based retention (LPR) technique*.<sup>9,10,16</sup> Applications of water-soluble polymers (WSP) to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Ultrafiltration is found as the most suitable technique for LPR studies.<sup>7–35</sup> For use in homogeneous metal ion recovery, appropriate WSP should present high water solubility,

an easy and inexpensive synthesis 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.

Water-soluble chelating polymers containing chelating groups are called *polychelators*. The features of coordination between polymers and metal ions may be described by the usual coordination theories, but some special aspects should be considered. When intrachain complexes are predominant, the existence of a polymer domain with near constant concentration of ligands is normally recognized since the distances between them keep them within a narrow range for a given polymer chain.<sup>25</sup> Consequently, 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. Sometimes, the reactivity of the complexes is strongly affected by the polymer ligand that exists outside the coordination sphere and surrounds the metal complex through special chemical environmental and steric effects.

The interactions between polymers and metal ions are very dependent on ionic strength, and low interaction rates are found when ionic strength is high.<sup>32,33</sup> Consequently, at pH 1.0, where the concentration of the monovalent H<sup>+</sup> ions is high, low interaction rates are always found. The interaction rates increase rapidly with pH increases, and high retention values are found for divalent and trivalent metal ions at pHs above 3.0. In contrast, when interactions occur through the formation of coordinating bonds, the nature of the metal ions and the pH effect may induce differences in the retention pro-

Correspondence to: B. L. Rivas (brivas@udec.cl).

files of like-charged metal ions and selectivity is often influenced.<sup>12,16,17,20,23,24,26,27,31,35</sup>

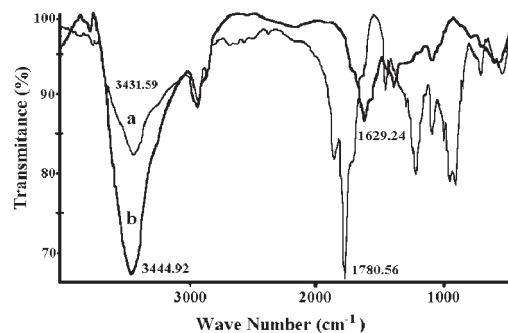
The polyelectrolyte pattern has been found in homopolymers containing sulfonate groups like poly(styrene sulfonate) (PSS) or poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAPS). Polymers containing carboxylic groups, such as poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMA), behave as weak polyelectrolytes and present high retention values at pHs above 3. They also have chelating properties, and it is found that interactions with Cu(II) are normally more intense than with other divalent metal ions. This polychelator pattern is found in polychelators like poly(*N*-methyl-*N'*-methacryloyl piperazine) (PAMP), poly[*N*-hydroxyethyl]ethyleneimine] (PHEI), and poly(ethyleneimine) (PEI). When copolymers that contain both chelating and charged groups are concerned, their relative comonomer composition influences their behavior. The retention behavior for the copolymer P(AMP-APS) containing sulfonate groups and amino groups in a 1:1 composition was compared with the behavior of the corresponding two homopolymers PAPS and PAMP.<sup>28</sup> The experiments were performed so that 0.01M of the sulfonate groups were present in the cell solution containing PAPS or P(AMP-APS), and 0.01M of piperazine pendant groups were present when using PAMP or P(AMP-APS). The results for the Co(II) retention when the initial solution has been eluted with a volume of water of 10 times the volume of the solution inside the ultrafiltration cell [ $R_2(10)$ ] indicate that the copolymer loses its ability to bind the metal ion, a fact that can be explained postulating an interaction of the sulfonate groups with the amino groups by charge-transfer or hydrogen-bonded forces that should block both functional groups. Concerning the evolution of the  $R_2(10)$  values with the pH, it can be seen that PAPS shows a typical polyelectrolyte behavior, while PAMP shows a pattern corresponding to a chelating polymer.

The aim of this article is to investigate the metal ion properties of a water-soluble copolymer containing only one moiety with functional groups (such as carboxylic/carboxylate groups) and a monomer unit (like ethylene) to improve the mechanical properties of the polymer without decreasing the metal ion retention properties.

## EXPERIMENTAL

### Reagents

Poly(ethylene-*alt* maleic anhydride), P(*E-alt*-MAn), was obtained from Aldrich Co. (Milwaukee, WI). All metal salt are analytically pure from Merck (Stuttgart, Germany). Ni(NO<sub>3</sub>)<sub>2</sub> × 6 H<sub>2</sub>O, 99%, Co(NO<sub>3</sub>)<sub>2</sub> × 6 H<sub>2</sub>O, 99%, Mg(NO<sub>3</sub>)<sub>2</sub> × 6 H<sub>2</sub>O, 99%, Cd(NO<sub>3</sub>)<sub>2</sub> × 4 H<sub>2</sub>O, 99%, Ca(NO<sub>3</sub>)<sub>2</sub> × 4 H<sub>2</sub>O, 99%, Cu(NO<sub>3</sub>)<sub>2</sub> × 3 H<sub>2</sub>O, 99%,



**Figure 1** FT-IR spectra for (a) P(*E-alt*-MAn) and (b) P(*E-alt*-MAc), KBr, at room temperature.

Zn(NO<sub>3</sub>)<sub>2</sub> × 6 H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Cr(NO<sub>3</sub>)<sub>3</sub> × 4 H<sub>2</sub>O, 99%, nitric acid, 65%, were all obtained from Merck, and sodium hydroxide, 97%, from Aldrich was used to adjust the pH.

The solutions were prepared with twice-distilled water whose conductivity was lower than that 1 μS cm<sup>-1</sup>.

### Hydrolysis of poly(ethylene-*alt*-maleic anhydride)

P(*E-alt*-MAn) (16.0000 g) was dissolved in 200.0 mL of 2M NaOH and stirred for 24 h. The product is water soluble and corresponds to poly(ethylene-*co*-maleic acid) P(*E-alt*-MAc). The FT-IR spectrum of P(*E-alt*-MAc) shows two special characteristics, a broadening and higher intensity of the absorption signal at 3444 cm<sup>-1</sup> (O—H, from carboxylic acid) and the complete disappearance of the signal at 1780 cm<sup>-1</sup> (C=O, anhydride) with the presence of the signal at 1629 cm<sup>-1</sup> corresponding to the carboxylic acid (C=O) (see Fig. 1). On the basis of this information, the hydrolysis is quantitative.

The polymer is fractionated and characterized. The GPC-determined molecular weight is 240,000 g mol<sup>-1</sup>.

### Procedure (washing method)

With 20.0 mL of a solution containing 5.0 × 10<sup>-3</sup> eq/L of a water-soluble copolymer, 0.010 or 0.10M of NaNO<sub>3</sub> and 1.0 × 10<sup>-4</sup>M of metal ions are placed into the solution cell provided with an ultrafiltration membrane with a membrane's molecular mass cut off (MMCO) of 10,000 Da (Millipore, Amicon).

The pH was adjusted to 5.0 with dilute HNO<sub>3</sub>. The washing solution (0.010M or 0.10M of NaNO<sub>3</sub> in water at pH = 3.0, 5.0, and 7.0, depending on the metal ion) was passed under pressure (3 bar of N<sub>2</sub>) from the reservoir into the cell solution. All the experiments were performed at constant ionic strength (see Table I). As the in- and out-flux are rapidly equaled, the initial volume (20.0 mL) is maintained constant during the experiment. Ten fractions of 20 mL were collected.

TABLE I  
General Conditions for the Washing Method

Metal ion	Metal ion concentration (ppm)	Amount of metal ion (mmol)	pH
Cd <sup>2+</sup>	28.0	0.005	3, 5, 7
Ca <sup>2+</sup>	10.0	0.005	3, 5, 7
Co <sup>2+</sup>	14.5	0.005	3, 5, 7
Cu <sup>2+</sup>	16.0	0.005	3, 5
Cr <sup>3+</sup>	13.0	0.005	3
Mg <sup>2+</sup>	6.0	0.005	3, 5, 7
Ni <sup>2+</sup>	14.5	0.005	3, 5, 7
Pb <sup>2+</sup>	52.0	0.005	3, 5
Zn <sup>2+</sup>	16.5	0.005	3, 5, 7

Volume, final concentration, and pH and volume of metal ion aqueous solution (1000 ppm). Cell volume: 20 mL, pressure: 3.5 bar, eluent: water at different pHs.

Each fraction was collected in graduated tubes, and the corresponding metal ion concentration was determined.

### Measurements

The molecular weight of the polychelator was determined by gel permeation chromatography (GPC), using a Perkin-Elmer series 200 with a differential refractive index (DRI) detector and PL-aqua gel-OH columns. The water and polystyrene were the solvent and standard, respectively. The FT-IR spectra are recorded on a Magna Nicolet 550 spectrophotometer.

The pH is determined with a Jenco Electronics 1671 pH-meter. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelator. A Unicam Solaar M5 series Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate.

## RESULTS AND DISCUSSION

To study the metal ion retention properties of the polychelator poly(ethylene-*alt*-maleic acid), the LPR technique by the washing procedure is used.

This is a batch-like method where a liquid sample containing the polymer and the metal ions to be separated is placed in the ultrafiltration cell at a given pH and ionic strength. This is then washed with a water solution contained in the reservoir that should reproduce the same pH and ionic strength values. Conditions should be produced in which the ions of interest are retained and other species are removed.

The binding and elution processes may be formulated as a chemical reaction, where a reversible interaction reaction of the metal ion with the polymer in combination with an irreversible transfer of metal ions across the membrane is responsible for metal reten-

tion. Irreversible binding of metal ions to the polymer may also be found. The influence of the membrane in metal retention inside the ultrafiltration cell is low and may be negligible in most cases.

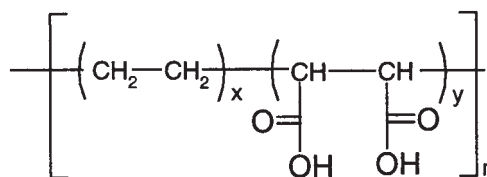
The retention profiles for the following metal ions: Co(II), Ni(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), Cr(III), and Cu(II) were studied using the LPR technique at pH 3, 5, and 7, while changing the filtration factor *Z* from 0 to 10.

To obtain the retention profiles, a P(*E-*alt**-MAc): metal ion 40 : 1.0 relationship is used and corresponds to 0.2 : 0.005 mmol. This ratio should ensure an excess of ligand groups with respect to the metal ion. At the investigated pH, the metal ions are present basically in free form, avoiding the presence of species such as M(OH)<sup>n+</sup> and M(OH)<sub>*n*</sub>.

The metal ion retention ability of the water-soluble polymer depends strongly on the pH (see Fig. 2). As the pH increases, the metal ion retention increases. This behavior is because at higher pH, the majority of carboxylic acid groups are nonprotonated. Therefore, the carboxylate is more available to bind metal ions and especially at pH > 5, which is above to the pK<sub>a</sub> value for an acrylic acid.

P(*E-*alt**-MAc) shows a high affinity for all the metal ions. At low pH, by increasing the filtration factor (*Z*), metal ion affinity decreases. This result means that the ligand-metal interaction is very weak, and that it is possible to destroy it by washing it with water at the filtration cell's pH. This is because the carboxylic groups of malonic ligands are protonated, and the complexing reaction between the ligands and metal ions is in competition with the protonation reaction. But at a higher pH, such as pH 5.0 and pH 7.0 that are above the pK<sub>a</sub> of malonic groups, the protonation reaction is negligible and the carboxylic groups are deprotonated, yielding a high ligand capacity for complex metal ions. Therefore, there is no important decrease in the retention as *Z* increases, indicating that the carboxylate-metal ion complexes are strong.

As *Z* is a qualitative measurement of the strength between the metal ion and the ligand group, the metal ion retention capacity was studied at pH 7.0 and *Z* = 10. (see Fig. 3). The higher retention values are achieved for transition metal ions like Ni(II) (0.005 mol), Co(II) (0.005 mol), Cd(II) (0.005 mol), and Zn(II) (0.005 mol), while Ca(II) (0.0033 mol) and Mg(II) (0.0043 mol) are less retained. This difference is related

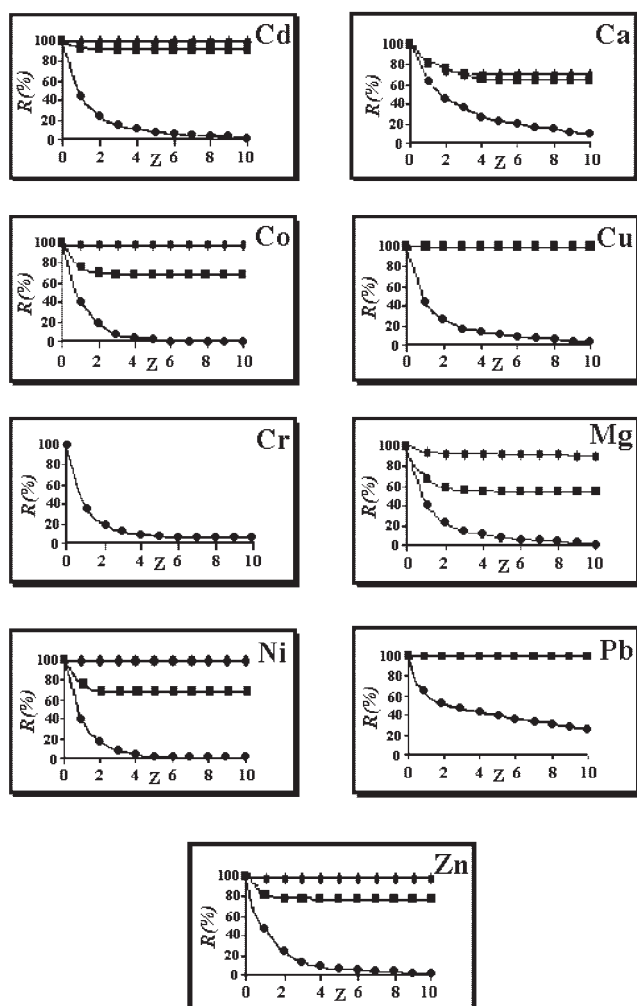


Scheme 1 Poly(ethylene-*alt*-maleic acid)

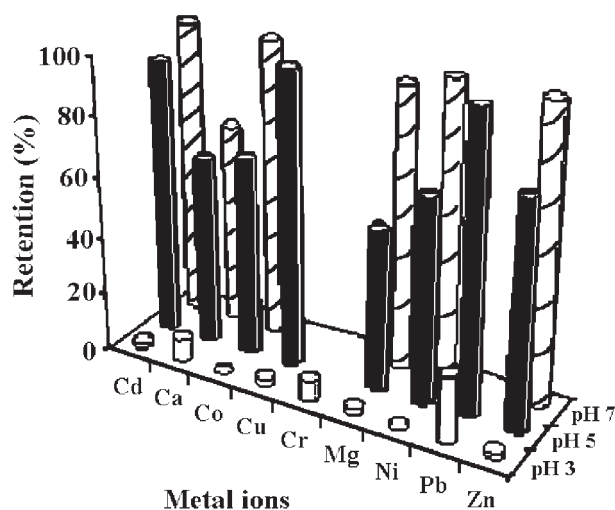
to the empty orbitals in transition metal ions and the electronic cloud deformation capacity.

The coordination features between polymers and metal ions can be described by the usual coordination theories, but some special aspects should be considered. When intrachain complexes are predominant, the existence of a polymer domain with a near constant ligand concentration is normally recognized since the distances between them keep them in a narrow range for a given polymer chain. This characteristic feature is responsible for the appearance of the chelating reaction as an 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 environmental and steric effects.

Depending on the pH value, ionized carboxylic acid may form complexes with  $D_{2h}$  or  $D_{4h}$  (dimer) sym-



**Figure 2** Retention profiles of P(E-alt-MAC). Polymer fraction: 100,000 Da at pH (●) 3.0, (■) 5.0, and (◆) 7.0.



**Figure 3** Metal ion retention properties of P(E-alt-MAC) at different pH and filtration factor  $Z = 10$ . Polymer fraction: 100,000 Da.

metry. At high pH values, the polymer chain has a drawn shape because of the electrostatic repulsion of charged carboxylate groups, where metal ions are then binding with either one or two neighboring groups. At pHs close to 4.5, the macromolecular coil contract and the metal ions are able to coordinate two to four carboxylic groups.

The necessary time to achieve 100% retention depends on the membrane's MMCO, the polymer's molecular weight, and pH. The time was not determined for these measurements, but for a membrane with a MMCO of 10,000 Da, in general the time is approximately 1 h (after  $Z = 10$ ). The polymer can be regenerated by protolysis and electrolysis of the polymer-metal ion complexes.

## CONCLUSIONS

The water-soluble polyelectrolyte poly(ethylene-alt-maleic acid) presented a high affinity for the following metal ions: Co(II), Ni(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), and Cu(II), but not for the trivalent cation, Cr(III). At low pH, by increasing the filtration factor,  $Z$ , metal ion affinity is very poor, indicating a very weak ligand-metal interaction and one that can be destroyed by washing with water at the filtration cell's pH. At these pHs, the metal cation must compete with the protons. But at a higher pH, such as pH 5.0 and pH 7.0, the ability to bind metal ions increased significantly and there is no important decrease in the retention as  $Z$  increases, which means that the carboxylate-metal ion complexes are very strong. At these pHs, the metal ions are able to coordinate two to four carboxylic groups. The polymer-metal ion interaction may be intramolecular or intermolecular or both.

**References**

1. Ni, C.; Yi, Ch.; Feng, Z. *J Appl Polym Sci* 2001, 82, 3127.
2. Marinsky, J. A.; Anspach, W. M. *J Phys Chem* 1975, 79, 439.
3. Rivas, B. L. In *Polymeric Materials Encyclopedia. Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Florida, 1996; Vol. 6, pp 4137–4145.
4. Molina, M. J.; Gómez-Antón, M. R.; Rivas, B. L.; Maturana, H. M.; Piérola, I. F. *J Appl Polym Sci* 2001, 79, 1467.
5. Dominguez, L.; Benak, K. R.; Economy, J. *Polym Adv Technol* 2001, 12, 197.
6. Warshawsky, A.; Marques, G.; Kahana, N.; Kampel, V.; Bourdelande, J. L.; Valiente, M. *Macromol Chem Phys* 2001, 202, 2659.
7. Ahamadi, S.; Batchelor, B.; Koseoglu, S. S. *J Membr Sci* 1994, 89, 257.
8. Tomida, T.; Inoue, T.; Tsuchiya, K.; Masuda, S. *Ind Eng Chem Res* 1994, 33, 904.
9. Geckeler, K.; Lange, G.; Eberhardt, H.; Bayer, E. *Pure Appl Chem* 1980, 52, 1883.
10. Spivakov, B. Ya.; Geckeler, K.; Bayer, E. *Nature* 1985, 315, 313.
11. Bayer, E.; Eberhardt, H.; Geckeler, K. *Angew Makromol Chem* 1981, 97, 217.
12. Rivas, B. L.; Pereira, E. D.; Gallegos, P.; Geckeler, K. E. *Polym Adv Technol* 2002, 13, 1000.
13. Geckeler, K. E.; Rivas, B. L.; Zhou, R. *Angew Makromol Chem* 1991, 193, 195.
14. Geckeler, K. E.; Rivas, B. L.; Zhou, R. *Angew Makromol Chem* 1992, 197, 107.
15. Rivas, B. L.; Geckeler, K. E. *Adv Polym Sci* 1992, 102, 171.
16. Spivakov, B. Ya.; Shkinev, V. M.; Geckeler, K. E. *Pure Appl Chem* 1994, 66, 632.
17. Geckeler, K. E.; Zhou, R.; Fink, A.; Rivas, B. L. *J Appl Polym Sci* 1996, 60, 2191.
18. Spivakov, B. Ya.; Shkinev, V. M.; Golovanov, V. I.; Bayer, E.; Geckeler, K. E. *Macromol Theory Simul* 1996, 5, 357.
19. Asman, G.; Sanli, O. *J Appl Polym Sci* 1997, 64, 1115.
20. Rivas, B. L.; Moreno-Villoslada, I. *Macromol Chem Phys* 1998, 199, 1153.
21. Rivas, B. L.; Moreno-Villoslada, I. *J Phys Chem B* 1998, 102, 6994.
22. Rivas, B. L.; Moreno-Villoslada, I. *J Phys Chem B* 1998, 102, 11024.
23. Rivas, B. L.; Pooley, S. A.; Luna, M. *Macromol Rapid Commun* 2000, 21, 905.
24. Rivas, B. L.; Moreno-Villoslada, I. *J Membr Sci* 2000, 178, 165.
25. Rivas, B. L.; Moreno-Villoslada, I. *Chem Lett* 2000, 166.
26. Rivas, B. L.; Pooley, S. A.; Luna, M. *Macromol Rapid Commun* 2001, 22, 418.
27. Rivas, B. L.; Moreno-Villoslada, I.; Elvira, C.; San Román, J. *J Membr Sci* 2001, 192, 187.
28. Rivas, B. L.; Moreno-Villoslada, I. *J Membr Sci* 2001, 187, 271.
29. Uludag, Y.; Özbelgçe, H. O.; Yilmaz, L. *J Membr Sci* 1997, 129, 93.
30. Vonk, P.; Noordman, R.; Schippers, D.; Tilstra, B.; Wesselingh, H. *J Membr Sci* 1997, 130, 249.
31. Rivas, B. L.; Pooley, S. A.; Luna, M. *J Appl Polym Sci* 2002, 83, 2556.
32. Moreno-Villoslada, I.; Rivas, B. L. *J Phys Chem B* 2002, 106, 9708.
33. Moreno-Villoslada, I.; Rivas, B. L. *J Membr Sci* 2002, 208, 69.
34. Moreno-Villoslada, I.; Miranda, V.; Jofré, M.; Chandía, P.; González, F.; Bulnes, J. L.; Cortés, M.; Hess, S.; Rivas, B. L. *J Membr Sci* 2006, 272, 137.
35. Rivas, B. L.; Pereira, E. D.; Moreno-Villoslada, I. *Prog Polym Sci* 2003, 28, 173.