

# Selective Retention Properties to Silver(I) and Mercury(II) Ions of Poly(4-vinylpyridine) Methyl Iodide Studied by the Liquid-Phase Polymer-Based Retention Technique

B. L. RIVAS, E. D. PEREIRA

Department of Polymers, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

Received 4 February 2000; accepted 22 July 2000

**ABSTRACT:** The retention of various metal ions by water-soluble poly(4-vinylpyridine) methyl iodide in conjunction with ultrafiltration membrane was investigated. The method is based on the retention of inorganic ions by this polymer in a membrane filtration cell and subsequent separation of low-molecular weight species from the polymer metal ion complex formed. It is shown that the polychelator can bind silver(I) and mercury(II) ions in aqueous solution at pH 1. At higher pH, the water-soluble polymer can be applied to the separation and preconcentration of silver metal ions. Therefore, this polychelator is highly selective to Hg(II) at pH 1 with respect to metal ions such as Cd(II) and Zn(II). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2578–2582, 2001

**Key words:** poly(4-vinylpyridine) methyl iodide; metal ions; ultrafiltration membranes

## INTRODUCTION

The removal and separation of metal ions are a technological challenge with respect to industrial and environmental applications. Conventional methods include the use of water-insoluble polymers<sup>1–5</sup> that allow the quantitative and partially selective enrichment of ions. However, these heterogeneous methods require additional steps; for example, back extraction, elution, etc., and show less favorable kinetics, but the study of the metal ion complexing properties of water-soluble polymers has gained considerable importance because

of their potential applications in chemistry and technology. Many water-soluble polymer types have been synthesized by homo- and copolymerization as well as by polymer-analogous reactions.<sup>6–13</sup> These water-soluble polymers with the ability to chelate metal ions are named polychelators.

Membrane filtration processes are among the most promising technologies for enrichment of various species from solutions and for their separation. However, to date, membrane separation has seldom been used in analytical chemistry, particularly in inorganic analysis.

The possibility of preconcentration and separation of different species without separating agents is another advantage of some membrane technique. Membrane separation is most selective, if soluble reagents are added.

The liquid-phase polymer-based retention technique, which has been approved by IUPAC,<sup>14</sup> is used to test the chelating properties of poly-

---

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

Contract grant sponsor: FONDECYT; contract grant numbers: 8990011 and 2980051.

Contract grant sponsor: Dirección de Investigación, Universidad de Concepción; contract grant numbers: 98.24.17-1 and 98.24.16-6.

*Journal of Applied Polymer Science*, Vol. 80, 2578–2582 (2001)  
© 2001 John Wiley & Sons, Inc.

mers. This technique uses polychelatogens in combination with membrane filtration. Metal ions with high interaction rates with the polymer stay retained by the polymer whereas others are eluted through the ultrafiltration membrane. When solutions of mixtures of metal ions are put in contact with the polymer solution, a profile for the retention of the different metal ions by the polychelatogen during filtration can be obtained. This technique also allows the determination of the maximum capacities of polymers for a metal ion.<sup>6</sup>

The goal of this work was to obtain the water-soluble polymer, poly(4-vinyl pyridine) methyl iodide by radical polymerization of 4-vinylpyridine and subsequently the polymer-analogous reaction of poly(4-vinylpyridine) with methyl iodide and to study their metal ion-binding properties in conjunction with a membrane filtration. The investigated metal ions were: Ag(I), Cu(II), Co(II), Ni(II), Hg(II), Cd(II), and Zn(II). These were selected for their impact on the environment and also for the potential applications of their polymer complexes, i.e., as bactericides, semiconductors, etc.

## EXPERIMENTAL

### Reagents

4-Vinylpyridine (95%; Aldrich, Milwaukee, WI) was purified by distillation. 2,2'-azo-bis-isobutyronitrile was purified by recrystallization from methanol. Methyl iodide (99.5%; Fluka, Buchs, Switzerland) was used as received.

Metal ion solutions were prepared from the nitrate salts of Ag(I), Hg(II), Cu(II), Co(II), Ni(II), Cd(II), and Zn(II).

### Polychelatogen

In a polymerization flask, 0.19 mol (21.6 mL, 19.97 g) of 4-vinylpyridine and 0.95 mmol of 2,2'-azo-bis-isobutyronitrile (0.15 g) were reacted under nitrogen during 24 h at 70°C. The product was purified by ultrafiltration on a membrane with a cut-off of 3000 g mol<sup>-1</sup> and lyophilized. The polymerization yield was 92.1%. Subsequently, 15 g of poly(4-vinylpyridine) dissolved in 100 mL of tetrahydrofuran was heated during 24 h under stirring in the presence of 0.1425 mol (9.0 mL) of methyl iodide. The product was dissolved in water, purified by ultrafiltration membrane, and fractionated by ultrafiltration membrane with

different exclusion limits of molecular weight (3000, 10,000, 30,000, and 100,000 g mol<sup>-1</sup>). All the fractions were lyophilized. The yield was 16.8 g (48.3%). It is the ratio between the obtained weight of modified polymer and the weights of initial polymer and methyl iodide.

### Liquid-Phase Polymer-Based Retention Equipment

The unit used for retention studies consisted of a filtration cell with a magnetic stirrer, a membrane with an exclusion rating of 5000 g mol<sup>-1</sup> (Filtron), a reservoir, a selector, and a pressure source.<sup>14</sup>

### Procedure

Polychelatogen fraction, 0.2 mmol (21.1 mg), in the range of over 100,000 g mol<sup>-1</sup> was dissolved in bidistilled water and a solution containing a mixture of seven metal ions (0.005 mmol of each metal ion) was added to the cell solution. The solutions were brought to 20 mL of total volume and the pH was adjusted by adding 0.1M NaOH or 0.1M HNO<sub>3</sub>. The solutions were stored overnight. The pH of the cell and the reservoir solutions were adjusted by adding 0.1M NaOH or 0.1M HNO<sub>3</sub> at the same value. Filtration runs were performed under a total pressure of three bars using an ultrafiltration membrane with an exclusion rating of 5000 g mol<sup>-1</sup>. The total volume in the cell was kept constant. Fractions of 20 mL were collected by filtration and the metal ion concentrations analyzed.

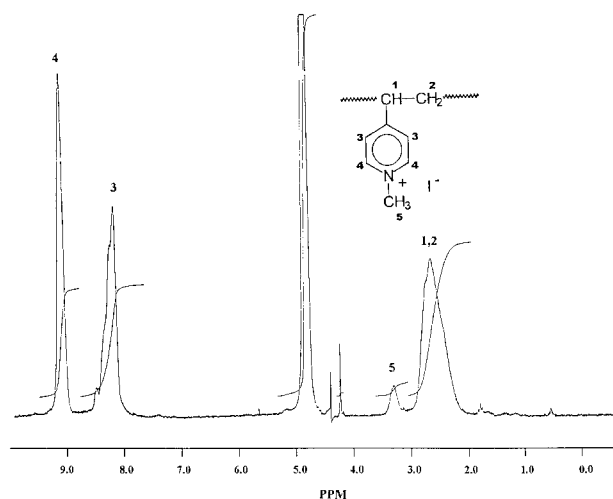
### Measurements

Metal ion concentrations were measured in the filtrate by atomic absorption spectrometry on a Perkin-Elmer 3100 spectrometer. The quantity of retained ion is then determined by the difference with the initial concentration. The pH was controlled by a pH meter (H. Jürgens and Co.).

The Fourier transform infrared and nuclear magnetic resonance (NMR) spectra of polychelatogen were recorded with a Magna Nicolet 550 and a multinucleus Bruker AC 250 Spectrometer, respectively. The thermal behavior under nitrogen was studied by thermogravimetric analysis using a TGA 625 from Polymer Laboratories. The heating rate was 10°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

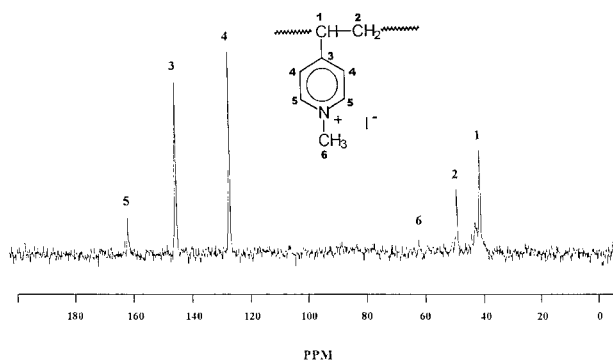
The ability of the pyridine groups to bind different metal ions is well known, but poly(4-vinylpyri-



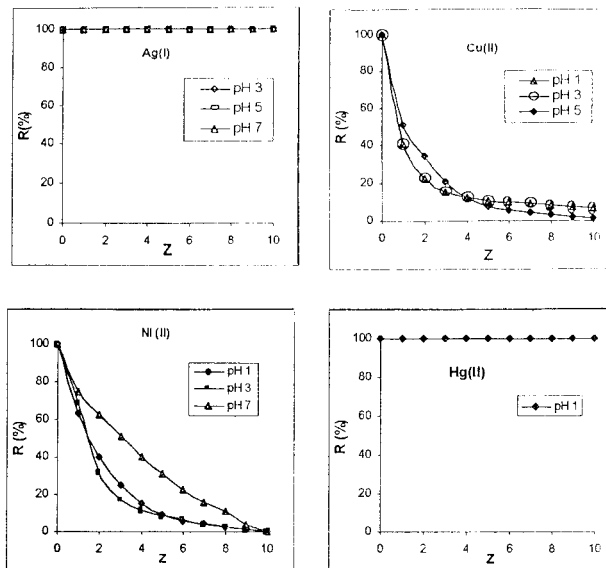
**Figure 1**  $^1\text{H-NMR}$  spectrum (200 MHz,  $70^\circ\text{C}$ , TMS,  $\text{D}_2\text{O}$ ) of poly(4-vinylpyridine) methyl iodide.

dine) usually is not soluble in water in a wide pH range. Therefore, our interest was to modify this structure by partial alkylation with methyl iodide to increase its water solubility, keeping the capability to bind metal ions and especially to increase the selectivity. Accordingly, the polychelator poly(4-vinylpyridine) methyl iodide was synthesized. The Fourier transform infrared spectrum shows the following most characteristic absorption bands (in  $\text{cm}^{-1}$ ): 3030 ( $\nu_{\text{ArC-H}}$ ), 2929 and 2861 ( $\nu_{\text{C-H}}$  of  $\text{C-CH}_2\text{-C}$  group), 1642 ( $\nu_{\text{C=N}}$ ).

The relationship between the alkylated and nonalkylated repeating units was determined by comparison of the signal absorption areas corresponding to the methyl and pyridine protons (see Fig. 1). It demonstrates that the alkylation degree was 8.8%. It is in agreement with the calculated value (8.87%) from the mass balance. The struc-



**Figure 2**  $^{13}\text{C-NMR}$  spectrum (200 MHz,  $70^\circ\text{C}$ , TMS,  $\text{D}_2\text{O}$ ) of poly(4-vinylpyridine) methyl iodide.



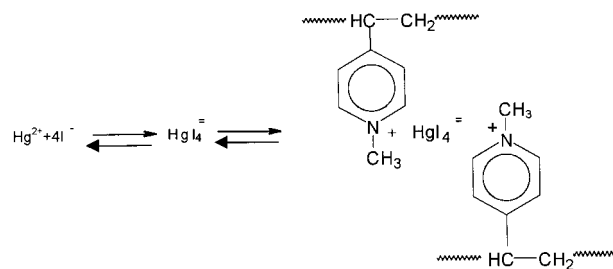
**Figure 3** Retention profiles of Ag(I), Cu(II), Ni(II), and Hg(II) from a mixture of seven cations using poly(4-vinylpyridine) methyl iodide. Absolute polychelator amount, 0.20 mmol; absolute metal ion amounts, 0.005 mmol.

ture was corroborated by  $^{13}\text{C-NMR}$  spectroscopy which shows the presence of the methyl carbon (see Fig. 2).

To study the retention properties of poly(4-vinylpyridine) methyl iodide, the effect of pH and filtration factor was carried out. A typical retention profile shows the metal ion retention ( $R\%$ ) versus filtration factor ( $Z$ ). The retention of metal ions in the cell solution by polymeric reagents can be calculated as follows:

$$R(\%) = C_r C_o^{-1} 100$$

where  $C_r$  is the metal ion concentration in the retentate (the cell solution after a filtrate volume of  $V_f$  has been passed) and  $C_o$  is the initial metal ion concentration in the cell.  $Z$  is defined as the



**Scheme 1**

**Table I Thermal Behavior of Poly(4-vinylpyridine) Methyl Iodide (P), and P Weighed with Different Contents of Ag(I)**

Sample	Ag (%)	Residual Weight (%)				
		<i>T</i> (°C)				
		100	200	300	400	500
P	0.0	92.5	90.5	65.9	5.56	2.87
P-Ag (1 mg)	4.5	93.1	90.5	69.3	15.8	12.3
P-Ag (2 mg)	8.7	93.8	90.7	76.2	25.7	19.4
P-Ag (3 mg)	12.5	94.9	93.3	79.7	37.6	28.9

ratio volume of the filtrate ( $V_f$ ) versus volume in the cell ( $V_o$ ). At  $Z$  values high enough a remaining residue of metal ions is frequently found that cannot be eluted by filtration at the same pH conditions. This remaining percentage is called "the retention capacity of a polychelator." Figure 3 shows the retention profiles for the different metal ions studied as a function of the pH.

In general, only Ag(I) and Hg(II) are retained at pH 1, which allows a selective separation of these metal ions from all the other metal ions. All of the other metal ions are almost completely eluted from  $Z = 5$ . This behavior is very similar in the whole pH range except for Ni(II) at pH 7 which is retained over 60% at  $Z = 2$  and then decreases to about 0% at  $Z = 10$ . Mercury ions were not studied at pH higher than 2 to avoid the metal salt precipitation.

The retention of Hg(II) is attributed to the adduct formation between the iodide anion and mercury ions, which according to the higher volume displaces the iodide forming the structure shown in Scheme 1. It is also important to establish that the measurements were made close to the detection limit for Hg(II). This means that the retention value for Hg(II) could vary from 90 to 100%.

The retention of silver(I) would occur through nonmethylated nitrogen atoms forming a complex similar to silver diamino complex. However, it is not possible to discard the possibility, especially at higher pH values, that the iodide forms a colloidal  $\text{AgI}_{(s)}$  and therefore is retained on the polymer surface and in the filtration cell.

Because of their possible use as thermoresistant and semiconductor materials, it is of interest to study the thermal behavior of the polychelator and metal ion polychelator. It is observed that up to 200°C, there is not an important effect of the Ag(I) on the thermal properties. All com-

pounds are very stable up to 200°C, with a weight loss lower than 10%. At higher temperatures, the thermal stability increases as the content of Ag(I) increases (see Table I).

## CONCLUSIONS

The water-soluble polychelator poly(4-vinylpyridine) methyl iodide with an 8.8% degree of alkylation was synthesized by polymer-analogous reaction of poly(4-vinyl pyridine) and methyl iodide. The metal ion interaction behavior of an aqueous solution of poly(4-vinylpyridine) methyl iodide with seven metal ions was investigated varying the pH and the filtration factor  $Z$ . At pH 1 the polychelator was completely selective to Ag(I) and Hg(II), retaining the totality of these two cations. At higher pH, only Ag(I) was compared with all the other metal ions, showing a high affinity of the polychelator for Ag(I) with respect to the other metal ions. Both behaviors allow separation of Hg(II) at pH 1 or 2 from other metal ions such as Cd(II), Zn(II). It is a great advantage from an environmental viewpoint. Besides that, the selectivity for Ag(I) at higher pH would allow selective separation of this metal ion, and use of the polymer-metal complex in other applications like bactericide.

E.D.P. thanks the CONICYT for the Ph.D. fellowship.

## REFERENCES

- Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W.; Horwitz, C. P.; Gatrone, R. C.; Charizia, R. *Macromolecules* 1996, 29, 1021.
- Bicak, N.; Koza, G.; Atay, T. *J Appl Polym Sci* 1996, 61, 799.

3. Trochimczuck, A. W. *Eur Polym J* 1999, 35, 1457.
4. Rivas, B. L.; Maturana, H. A.; Ocampo, X. *J Appl Polym Sci* 1995, 58, 2201.
5. Rivas, B. L.; Maturana, H. A.; Pereira, E. *Angew Makromol Chem* 1994, 220, 61.
6. Geckeler, K.; Lange, G.; Eberhardt, H.; Bayer, E. *Pure Appl Chem* 1980, 52, 1883.
7. Bayer, E.; Geckeler, K.; Weingärtner, K. *Makromol Chem* 1980, 181, 585.
8. Rivas, B. L.; Geckeler, K. E. *Adv Polym Sci* 1992, 102, 171.
9. Spivakov, B. Y.; Geckeler, K.; Bayer, E. *Nature* 1985, 315, 313.
10. Geckeler, K. E.; Shkinev, V. M.; Spivakov, B. Y. *Sep Purif Method* 1988, 17, 105.
11. Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. *J Polym Sci* 1997, 35, 2461.
12. Rivas, B. L.; Pereira, E. D. *Bol Soc Chil Quim* 2000, 45, 165.
13. Bayer, E.; Eberhardt, H.; Grathwohl, P. A.; Geckeler, K. E. *Israel J Chem* 1985, 26, 40.
14. Spivakov, B. Y.; Shkinev, V. M.; Geckeler, K. E. *Pure Appl Chem* 1994, 66, 631.