

Selective Binding of Mercury Ions by Poly(4-vinylpyridine) Hydrochloride Resin

B. L. RIVAS, H. A. MATURANA, M. LUNA

Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 160-C, Concepción, Chile

Received 3 November 1998; accepted 20 March 1999

ABSTRACT: The binding ability of poly(4-vinylpyridine) hydrochloride resin for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), Cr(III), and U(VI) was investigated. All these ions, except Hg(II), could be not removed from aqueous solutions under the same conditions. The selective sorption of Hg(II) from mixtures of ions was observed. The elution of Hg(II) bound to the resin was also investigated using various concentrations of nitric acid and perchloric acid. Due to rapid complexation, a high mercury ion-binding capacity, high selectivity, and ease of regenerability, the resin can be useful for the removal and recovery of mercury ions from aqueous solutions. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1557–1562, 1999

Key words: poly(4-vinyl pyridine) hydrochloride; ion-exchange resin; mercury ions; selectivity

INTRODUCTION

The design of host molecules for metal ions is a relevant subject in the field of molecular recognition.^{1,2} The selective removal and recovery of metal ions has a potentially vast range of applications in conservation of the environment and use of resources. In this regard, the chelate-forming polymeric ligands have been extensively studied and many reviews are available in the field.^{3–10} These resins have been used for the pre-concentration and separation of trace elements from sea waters and their analytical use in conjunction with atomic absorption spectroscopy has been well established.

For practical applications, strong and selective binding of the target metal ion, rapid complexation of the metal ion, as well as the recovery of the resin are required. Moreover, minimal loss of the metal-ion-binding capability after many cy-

cles of applications is needed. The chemical nature of the functional groups containing atoms able to form donor–acceptor bonds representing the basis of the polymer–metal complexes is very different and, generally, complicated. The primary, secondary, and tertiary amine groups are probably the simplest. The complex-formation ability of the pyridine structural moiety of linear poly(4-vinylpyridine) and derivatives with transitional-metal ions as Fe(III), Ni(II), Co(II), and Pd(IV) is well known.^{11,12} In general, the sorption selectivity of chelating resins has been reported to be dependent mainly on the chelate-forming properties of functional groups chemically bonded on the supports such as macroporous copolymers, chitosan, and cellulose at appropriate pH values. The selectivity in the metal-ion uptake of the polymers can be well explained by Pearson's principle,¹³ that is, soft acids prefer to bind soft bases and hard acids prefer to bind hard bases. Thus, ligand groups containing pendant sulfur which are considered soft bases will bind efficiently Hg(II) and Cd(II) ions classified as soft acid in respect to the harder Ni(II) and Zn(II) ions. The metal-complexed polymers show the following features: (a) the polymeric ligand is markedly

Correspondence to: B. L. Rivas.
Contract grant sponsor: Dirección de Investigación, Universidad de Concepción.

Journal of Applied Polymer Science, Vol. 74, 1557–1562 (1999)
© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/061557-06

contracted because of an intrapolymer chelation causing a very compact form of the complexed polymer, and (b) the formation constants of a complexed polymer are much larger than those of a complexed monomer analog, which is caused by the enhancement of successive formation constants due to the polymer effect. Therefore, during the last few years, we have made many efforts to achieve efficient and selective resins.^{14–18} One of the most serious challenges is to develop resins to bind contaminant heavy metal ions. In that context, the term heavy metals refers to those that are used or discharged by industrial enterprises or used by humans in various ways. These elements are Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Pb, and Zn. Depending on their concentrations, all are hazardous to plants or animal life, but the elements that are toxic at low concentrations or quantities are Cd, Cu, Hg, Mn, Mo, Pb, and Zn. On the other hand, Cd, Cr, Hg, Ni, and Pb are not essential for animal or plants or animals in any quantity and biological effects are limited to toxicoses. Accordingly, this article describes the metal ion-sorption behavior for Hg(II), Cd(II), Zn(II), Cu(II), Cr(III), and U(VI) of crosslinked poly(4-vinylpyridine) hydrochloride at different pH and competitive conditions.

EXPERIMENTAL

Materials

Poly(4-vinylpyridine) hydrochloride (Pyr) · HCl crosslinked with 2% divinylbenzene, 100–200 mesh, 6.5 mmol Cl/g resin was purchased from Aldrich (Milwaukee, WI) and dried under a vacuum before to use. Reagent-grade Zn(NO₃)₂·x4H₂O, Pb(NO₃)₂, (CH₃COO)₂UO₂·x2H₂O, CuSO₄·x5H₂O, Cd(NO₃)₂·x4H₂O, Cr(NO₃)₃·x9H₂O, and HgCl₂ were purchased from Merck (Stuttgart, Germany).

Batch Equilibrium

A weighed amount of (Pyr) · HCl was added to the metal-ion solution to the desired pH and the mixture was shaken for 2 h at 25°C. The mixture was filtered off and the amount of the metal ion remaining in the filtrate was determined by atomic absorption spectrometry, except uranium(VI) which was determined by colorimetry.¹⁹ The amount of the metal ion sorbed on (Pyr) · HCl was calculated from the difference between amounts of the metal ion in the filtrate and in the starting

solution. In determining the pH dependence on the sorption of metal ions and the effect of different ions on the sorption of Hg(II), a weighed amount of (Pyr) · HCl was added to a metal-ion solution or a mixed solution and the mixture was adjusted to the required pH by addition of dilute HNO₃ or NaOH.

Sorption Isotherm of Hg(II) Ion

(Pyr) · HCl, 0.1 g, was equilibrated with 10 mL of the Hg(II) solution in the concentration range 7–40 mg/L. The mixture was allowed to equilibrate with occasional shaking for 2 days and then filtered off. The amount of Hg(II) remaining in the filtrate was determined.

Desorption of Metal Ions

The Hg(II)-complexes (Pyr) · HCl resin (100 mg) was added to an aqueous solution of HNO₃ (1–4M) and HClO₄ (0.1–4M) and stirred for 1 h, and then the resin was filtered and washed with water. Hg(II) was determined in the filtrates by atomic absorption spectrometry.

Measurements

Infrared spectra were obtained on an FTIR 550 Magna Nicolet spectrophotometer. The determination of metal ions was performed with a Perkin–Elmer 3100 atomic absorption spectrometer. Uranium(VI) was determined by colorimetry¹⁹ using a Cadas 100 spectrophotometer. Thermal stabilities under N₂ of the resins were evaluated by thermogravimetric analysis with a Polymer Laboratories STA-625 thermogravimetric analyzer. The carbon dioxide adsorption isotherm at 273 K was determined in a Micromeritics Model Gemini 2370 apparatus. Surface-area evaluation was done using the BET equation.

RESULTS AND DISCUSSION

The selective sorption and desorption of metal ions with polyvinylpyridine resins, which includes the sorption of metal ions on crosslinked poly(4-vinylpyridine) resins prepared with a metal ion as template, is well known.^{20–22} The commercial (Pyr) · HCl matrix is resin crosslinked by divinylbenzene. Hence, the matrix does not dissolve in aqueous media due to its three-dimensional network structure, but the chains do expand. In this case, the transport of metal ions into the polymer network is diffusion-controlled. In

Table I Retention of a Series of Metal Ions for the Crosslinked (Pyr) · HCl at Different pH

Metal Ion	pH			
	1	2	3	5
Cd(II)	1.2	3.5	4.6	14.0
Pb(II)	0.6	0.8	1.0	3.2
Zn(II)	10.3	14.0	21.0	—
Hg(II)	80.0	100.0	—	—
Cu(II)	1.2	5.5	3.2	4.6
Cr(III)	0.5	0.9	1.4	2.8
U(VI)	3.1	4.2	8.1	10.5

[Pyr · HCl] = 7×10^{-4} and [metal ion] = 1.5×10^{-3} .

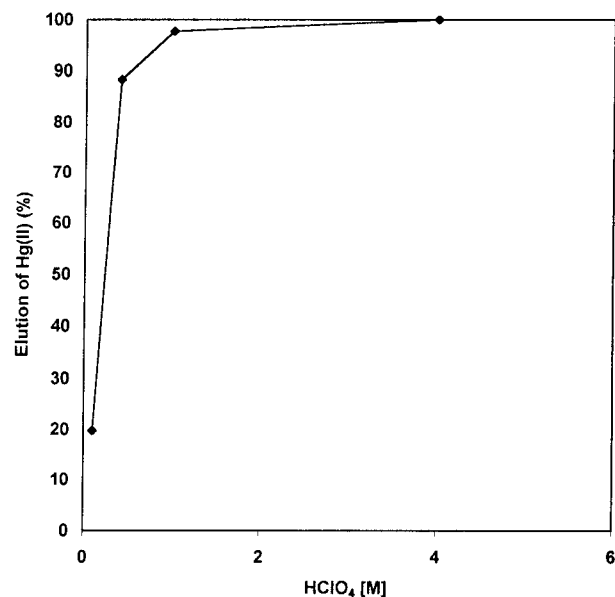
the complexation of polymeric ligands with metal ions, the polymer matrix contracts or expands by intrachain or interchain complexation, respectively, with metal ions through the pyridine groups.

The surface area evaluated from the CO₂ adsorption data at 273 K and calculated from the BET equation was 26.7 m²/g. The correlation factor was 0.99.

The sorption characteristics of the sorbent toward seven metal ions [i.e., Cd(II), Pb(II), Zn(II), Hg(II), Cu(II), Cr(III), and U(VI)] were investigated in an aqueous solution over pH range 1–5 using a batch equilibrium procedure. The sorption affinity of the sorbent as a function of the pH is summarized in Table I. In general, the amount of the metal-ion uptake by the sorbent is lower than 20%, except for the mercury ions. The resin adsorbed 80 and 100% of Hg(II) at pH 1 and 2, respectively, indicating that the resin is highly efficient and selective to remove Hg(II) ions from an aqueous solution. Accordingly, the next studies were carried considering Hg(II) at the optimum pH 2.0.

One hundred percent of the sorption capacity of the sorbent for Hg(II) ions was achieved within the first 15 min. The high availability of the ligand groups to interact fast with Hg(II) ions in a heterogeneous medium was demonstrated. Mercury ions were completely sorbed by the resin in all concentration ranges studied, 7–40 mg/L, and the temperature range of 20–35°C.

The nitrogen atoms in the pyridine groups were probably protonated at low pH, particularly at pH range 1–2, forming —NH⁺A[−] groups, where A[−] is an anion, chloride in this case. In these protonated groups, the nitrogen atom did not have a free-electron pair capable of forming

**Figure 1** Recovery of the resin by HClO₄ at different concentrations.

coordination bonds with the metal ions. Therefore, it could be possible suggest that an ion-exchange process is involved in the retention of Hg(II) ions. In this case, it would exchange the chloride anion by the anion [Hg(Cl)₄]^{2−} and/or [Hg(NO₃)₄]^{2−}.²³

To explore the applications of the sorbent, it is relevant to obtain knowledge on the sorption capacity of the resin toward Hg(II) ions. A maximum amount of metal ion can be removed from the solution when the chelating sites of the resin are saturated [100%, 0.44 meq Hg(II)/g].

To be useful in the ion-recycling process, the metal ion adsorbed by the resin should be easily released under appropriate conditions. Perchloric

Table II Adsorption Selectivity of the Resin for Hg(II) Ions from Binary Mixtures at pH 2.0

Metal	Initial Amount (meq/g)	Adsorbed Amount (meq/g)		Selectivity ^a
		Metal 1	Metal 2	
Hg(II)	Cd(II) (0.305)	0.302	0.014	95.6
Hg(II)	Zn(II) (0.309)	0.302	0.003	99.0
Hg(II)	Pb(II) (0.312)	0.302	0.000	100.0

Initial amount of Hg(II): 0.302 meq/g.

^a Defined by adsorption percent of metal 1, Hg(II), in total adsorbed metal ions (metal 1 + metal 2).

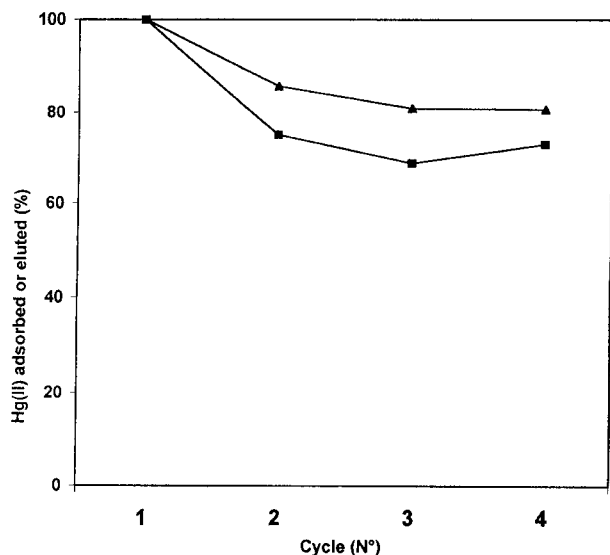


Figure 2 (■-) Sorption-(▲-) desorption cycles of the retention of Hg(II) ions on the resin at pH 2 for 1 h and the elution of the Hg(II) ions by 4M HClO₄ after 1 h.

acid (0.1–4M), in contrast to hydrochloric acid (1–4M), emerged as the most effective one for the recovery of Hg(II) ions from the resin (see Fig. 1). In fact, there is a strong effect of the [HClO₄], increasing the recovery of Hg(II) as [HClO₄] increases. At 4M, the recovery was complete by a treatment for 1 h. Moreover, the sorbent was able to withstand the strong acidic conditions, and its metal-ion-binding ability was retained after repeated acid treatment. Hence, to obtain the reusability of (Pyr) · HCl, the sorption–desorption cycle was repeated four times using the same sorbent. An initial amount of Hg(II) ions of 2 g/L was employed to load the resin. In each cycle, adsorption was performed at pH 2.0 for 1 h, and desorption was performed at pH 2.0 for 1 h using 4M HClO₄. Figure 2 shows the results of these studies. As seen here, the resorption ability of the

Table III Adsorption and Elution Selectivity of the Resin for Hg(II) from Quaternary Mixtures at pH 2.0

	Metal 1 Hg(II)	Metal 2 Cd(II)	Metal 3 Zn(II)	Metal 4 Pb(II)
Initial amount (meq/g)	0.302	0.305	0.309	0.312
Adsorbed amount (meq/g)	0.302	0.023	0.000	0.056
Eluted amount (meq/g)	0.302	0.000	0.000	0.000

Initial amount of Hg(II): 0.302 meq/g.

resin decreases around 25–30% during repeated sorption–desorption cycling.

For comparison, competitive sorption of Hg(II) from different binary mixtures and one quaternary mixture containing Hg(II), Cd(II), Zn(II), and Pb(II) ions (approximately 0.300 meq in each) by the commercial resin (Pyr) · HCl at pH 2.0 for 1 h was conducted. Results from the competitive metal-ion-sorption experiments are summarized in Tables II and III. Hg(II) is bound preferentially (over 95%) versus all the other metal ions studied. Moreover, over 98% of the Hg(II) adsorbed was eluted from binary and quaternary mixtures using 4M HClO₄ (see Tables III and IV).

Figure 3 shows the FTIR spectra of the resin alone and saturated with Hg²⁺ at pH 2.0. Comparing trace (a) with (b), it can be seen that, in general, the presence of the mercury ions produces a shift of the C–N absorption signals and, particularly, a narrowing of the stretching signal of N–H placed at 3415 cm⁻¹, confirming the interaction of the mercury ion with the pyridine hydrochloride group.

To determine the effect of the Hg(II) ions adsorbed on the resin on the thermal stability, ther-

Table IV Elution Behavior of Hg(II) from Binary Mixtures by 4M HClO₄ for 1 h at 20°C

Adsorbed Amount (meq/g)		Eluted Amount (meq/g)		
Metal 1	Metal 2	Metal 1	Metal 2	Elution ^a
Hg(II) (0.302)	Cd(II) (0.305)	0.292	0.006	98
Hg(II) (0.302)	Zn(II) (0.309)	0.286	0.002	99
Hg(II) (0.302)	Pb(II) (0.312)	0.292	0.000	100

^a Defined as elution percent of metal 1, Hg(II), from quaternary mixtures in total eluted metal ions (M₁ + M₂).

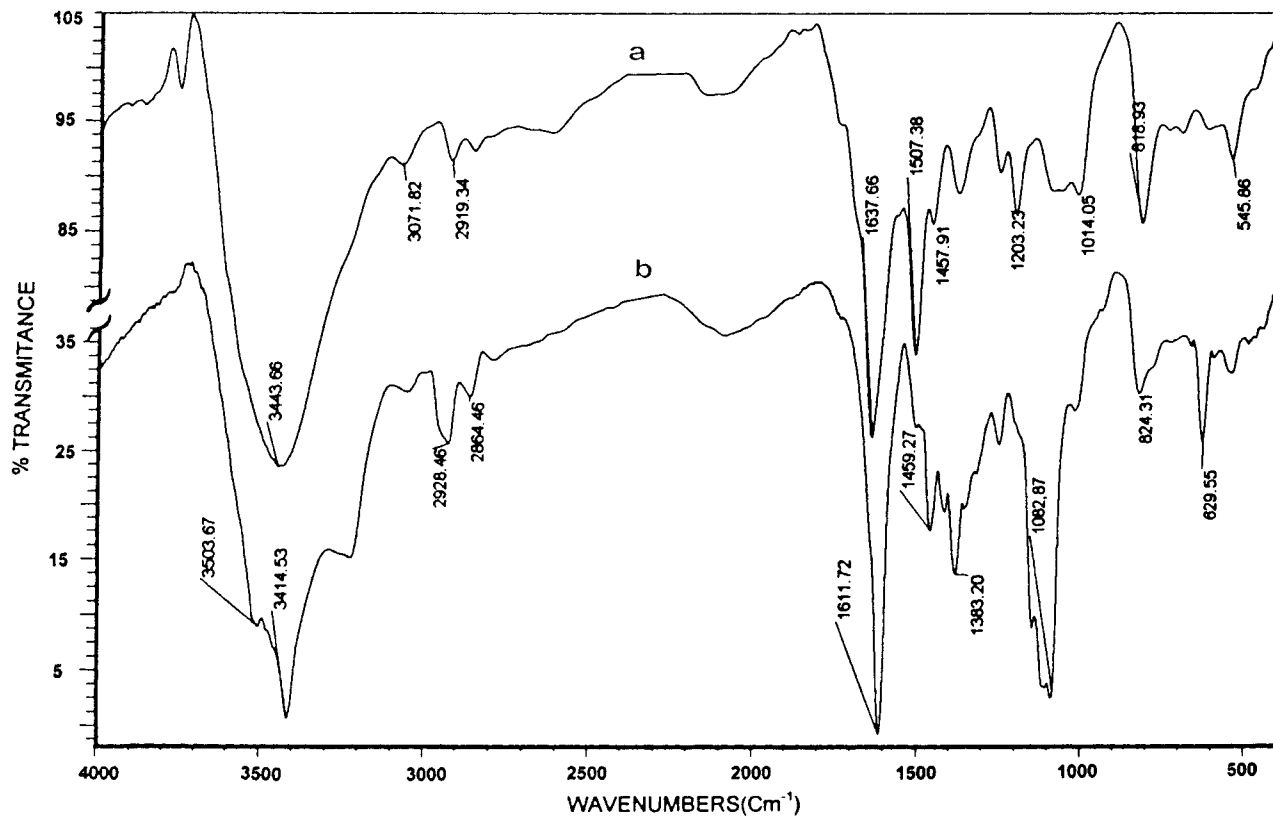


Figure 3 FTIR spectra of the (a) unloaded resin and (b) Hg(II)-loaded resin at maximum capacity.

mogravimetric analyses were carried out. The resin was saturated with Hg(II) at pH 2.0. Up to 300°C, the weight loss is almost the same. There-

fore, the thermal stability of the loaded resin is higher, close to 25% at 500°C, due to the presence of Hg(II) ions (see Fig. 4).

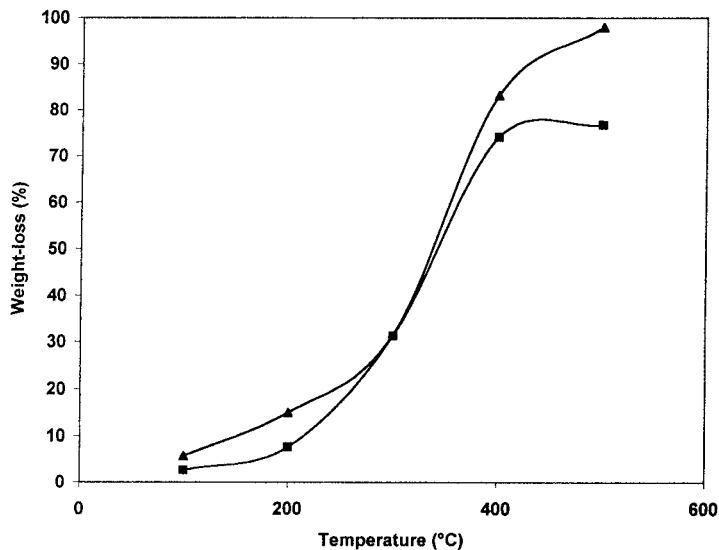


Figure 4 Thermal behavior of the (▲) unloaded resin and (■) Hg(II)-loaded resin at maximum capacity.

CONCLUSIONS

The vinylpyridine hydrochloride moiety showed a high ability and selectivity to remove Hg(II) from an aqueous solution in respect to Cd(II), Zn(II), Pb(II), Co(II), Cr(III), and U(VI), particularly at pH 2.0. This behavior was kept in binary and quaternary mixtures. The retention occurs by an ion-exchange process of the chloride anion by $[\text{HgCl}_4]^{2-}$ and/or $[\text{Hg}(\text{NO}_3)_4]^{2-}$. The recovery of Hg(II) from the loaded resin by 4M HClO_4 was over 90% under non- and competitive conditions. Therefore, it is possible to suggest their usefulness for the removal and recovery of mercury ions from aqueous solutions. The sorption capacity decreased around 25% after four sorption–desorption cycles using 4M HClO_4 as the stripping medium.

The authors thank the Dirección de Investigación, Universidad de Concepción, for financial support.

REFERENCES

- Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem Rev* 1991, 91, 1721.
- Lindoy, L. F. In *Cation Binding by Macrocycles*; Inoue, Y.; Gokel, G. W., Eds.; Marcel Dekker: New York, 1990; p 599.
- Kartipuly, C.; Katragadda, S.; Chow, A.; Gesser, H. D. *Talanta* 1990, 37, 491.
- Schmuckler, G. *Talanta* 1965, 12, 281.
- Warshawsky, A. *Crit Rep Appl Chem* 1987, 19, 166.
- Gupta, S. N.; Neckers, D. C. *J Polym Sci Polym Chem Ed* 1982, 20, 1609.
- Rivas, B. L.; Geckeler, K. E. *Adv Polym Sci* 1992, 102, 171.
- Rivas, B. L. In *Polymeric Materials Encyclopedia*. Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 6, p 4137.
- Sahni, S. K.; Reedijk, J. *Coord Chem Rev* 1984, 59, 1.
- Zagorodni, A. A.; Muinaviev, D. N.; Muhammed, M. *Sep Sci Technol* 1997, 32, 413.
- Bekturov, E. A.; Kudaibergenov, S. E.; Konapynova, G. S.; Saltybaeva, S. S.; Skushnikova, A. I.; Pavlova, A. L.; Dommic, E. S. *Polym J* 1991, 23, 339.
- Roda, J.; Hrabak, F. *Makromol Chem* 1976, 177, 1.
- Pearson, R. G. *J Am Chem Soc* 1963, 93, 3533.
- Rivas, B. L.; Maturana, H. A.; Pereira, E. *Angew Makromol Chem* 1994, 220, 61.
- Rivas, B. L.; Maturana, H. A.; Villegas, S. *Polym Bull* 1997, 39, 445.
- Rivas, B. L.; Maturana, H. A.; Molina, M. J.; Gómez-Antón, M. R.; Piérola, I. F. *J Appl Polym Sci* 1998, 67, 1109.
- Rivas, B. L.; Maturana, H. A.; Villegas, S.; Pereira, E. *Polym Bull* 1998, 40, 721.
- Rivas, B. L.; Maturana, H. A.; Hauser, P. *J Appl Polym Sci* 1999, 73, 369.
- Pérez, J.; Bustamante, F. *Analyst* 1971, 96, 407.
- Sugii, A.; Ogawa, N.; Inuma, Y.; Yamamura, H. *Talanta* 1981, 28, 551.
- Nishide, H.; Tsuchida, E. *Makromol Chem* 1976, 177, 2295.
- Nishide, H.; Deguchi, J.; Tsuchida, E. *Bol Chem Soc Jpn* 1976, 49, 3498.
- Bullock, J. I.; Tuck, D. G. *J Chem Soc* 1967, 1877.