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Polymer – Metal Complexes

Linear Polyethyleneimine Supports for Resins with Retention Properties for Heavy Metals. Part 2

B.L. Rivas, H.A. Maturana, I.M. Perich, and U. Angne

Polímeros, Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción, Chile

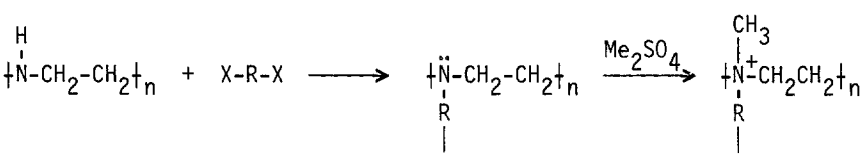
SUMMARY

A linear polyethyleneimine obtained by cationic polymerization of 2-methyl-2-oxazoline was crosslinked with 1,4-dibromo-2-butene (IML-1). This resin subsequently was N-alkylated with dimethylsulphate (IML-1M). With both resins were carried out analytical assays, such as: pH dependence for copper (II), uranium (VI), iron (II) and (III); maximum capacity of load for copper and uranium; elution assays. Moreover, the morphology by scanning electron microscopy and thermal stability were studied.

INTRODUCTION

Polymer-metal complexes are today of great interest (1-3). The formation of chelates and adducts by polymers has widely been used for concentration, separation and extraction of metal ions (4-5). One functional polymer is polyethyleneimine which is known to complex with heavy metals (6-9).

This paper reports the synthesis and crosslinking of polyethyleneimine (PEI) and its N-alkylation and the adsorption properties for copper (II), uranium (VI), iron (II) and (III).



PEI IML-1 IML-1M

x = Br; R = $-CH_2-CH=CH-CH_2-$

EXPERIMENTAL PART

Materials: All the chemicals used were chemically pure. They were used as such, except 2-methyl-2-oxazoline and dimethylsulphate which were distilled.

Synthesis of Polyethyleneimine: This polymer was obtained from 2-methyl-2-oxazoline according to the literature (10).

Crosslinking Reaction: Linear Polyethyleneimine was crosslinked with 1,4-dibromo-2-butene. The reaction was carried out in heterogeneous phase (11).

N-Alkylation Reaction. To 1.5 eq/g crosslinked polyethyleneimine suspended

in 60 ml CH_3CN, 0.36 mole dimethylsulphate were added. The mixture was stirred for 6 h to 95 °C. The resin was filtered and dried under vacuum.

Measurements: Copper and iron were determined on a Perkin Elmer 306 atomic absorption spectrometer. Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. The thermal stability was examined by a Thermobalance Perkin Elmer TGS-1. Morphology was studied by an Electron Scanning Microscope ETEC Autoscan U-1 Model.

pH dependence for copper (II), uranium (VI) and iron (II), (III). Ion solution 1.0 g/l was prepared at different pH's: 0 to 4 for copper and uranium and 0 to 2 for iron. These solutions were contacted with 0.5 g dry resin over 2h with constant stirring. The ions were analyzed in aqueous solution.

Determination of the maximum capacity of load for copper and uranium. It was carried out at pH 2.0. One g dry resin was contacted with 50 ml of a solution 1.0 g/l at 25 °C. After 1 h of stirring the aqueous solution was separated by decanting and washed several times. This process was repeated three times.

RESULTS AND DISCUSSION

The linear polyethyleneimine is obtained by ring opening polymerization of 2-methyl-2-oxazoline and followed by basic hydrolisis of poly(N-acetylethyleneimine). Molecular weight is 2, 100. This polymer was crosslinked in heterogeneous phase with 1,4-dibromo-2-butene. The resin obtained is completely insoluble (IML-1). Subsequently this resin was N-alkylated with dimethylsulphate (IML-1M). As the resins are insoluble, they were characterizated only by elemental analyses.

Adsorption properties for both resins were assayed under several conditions. The results are shown in Tables 1-4.

Table 1. Adsorption percent of copper (II)

Resin	Initial pH				
	0	1	2	3	4
IML-1	0.0	0.0	54.2	75.8	91.7
IML-1M	0.0	0.0	2.5	11.6	11.5

IML-1 at pH's 0.0 to 1.0 does not retain copper. From pH 2.0 up to pH 4.0 it adsorbs between 54.2% and 91.7% copper. On the other hand, IML-1M, over the pH range assayed, practically does not retain copper.

Table 2. Adsorption percent of uranium (VI)

Resin	Initial pH				
	0	1	2	3	4
IML-1	33.0	33.7	54.7	71.5	78.2
IML-1M	32.8	79.1	81.9	71.8	71.0

For IML-1 as the pH increases, the retention for uranium increases. The best retention for IML-1M is pH = 2.0 and for IML-1 pH = 4.0.

IML-1M shows a good adsorption behaviour: it practically does not retain copper (II) but retains significantly uranium (VI) (81.9% at pH=2).

Neither resins did retain iron (II) and (III).

In respect to the maximum load capacity, the best for uranium is IML-1M and for copper IML-1 (See Table 3).

Table 3. Maximum capacity of load for copper (II) and uranium (VI).

Resin	IML-1	IML-1M
meq Uranium per gr dry resin	1.42	5.51
meq Copper per gr dry resin	2.24	-[a]

a) not determined as resin IML-1M practically does not retain copper (II).

Elution assays were carried out in acid and basic medium. (See Table 4 and 5).

Table 4. Uranium elution with sodium carbonate and sulphuric acid.

Resin	Na_2CO_3		H_2SO_4	
	0.5M	1.0M	1.0M	3.0M
IML-1	19.5	21.4	18.3	17.1
IML-1M	60.7	56.1	63.0	65.7

Table 5. Copper elution with sodium carbonate and sulphuric acid.

Resin	Na_2CO_3		H_2SO_4	
	0.5M	1.0M	1.0M	3.0M
IML-1	13.8	13.8	62.9	63.3
IML-1M	8.5	9.4	57.4	52.5

Elution is affected by the medium. Copper is preferentially eluted in acidic medium and for uranium the elution medium is of secondary importance.

These results show that quaternized resins show great retention for uranium. This resin retains uranium by adduct formation. In contrast, resin IML-1 has the free electron pair of nitrogen to bind for copper.

Morphology

The morphology of unloaded resins IML-1 and IML-1M was examined. Electron microscopy shows that the surfaces are similar with holes and fissures. (See Figures 1 and 2). During adsorption the morphology does not seem to change.

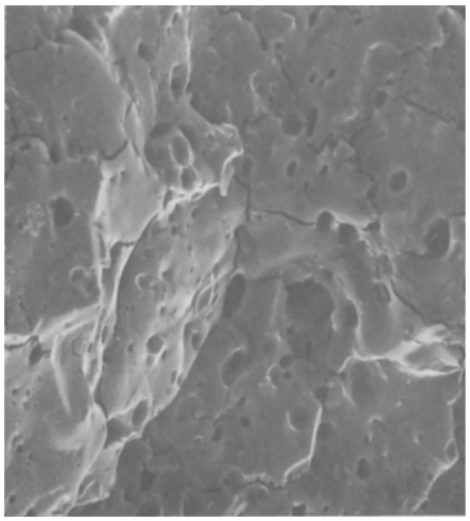


Figure 1. SEM micrograph of Resin IML-1 (400x). Unloded.

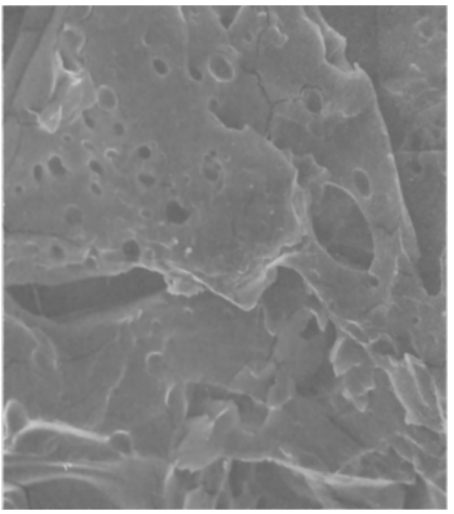


Figure 2. SEM micrograph of Resin IML-1M (400x). Unloaded.

Thermal stability.

Resin IML-1 is stable up to 140 °C. From this temperature until 300 °C, it looses 60% by weight. On the other hand, resin IML-1M shows a better thermal stability, does not loose weight until 200 °C and it looses 83% by weight up to 400 °C (See figure 3).

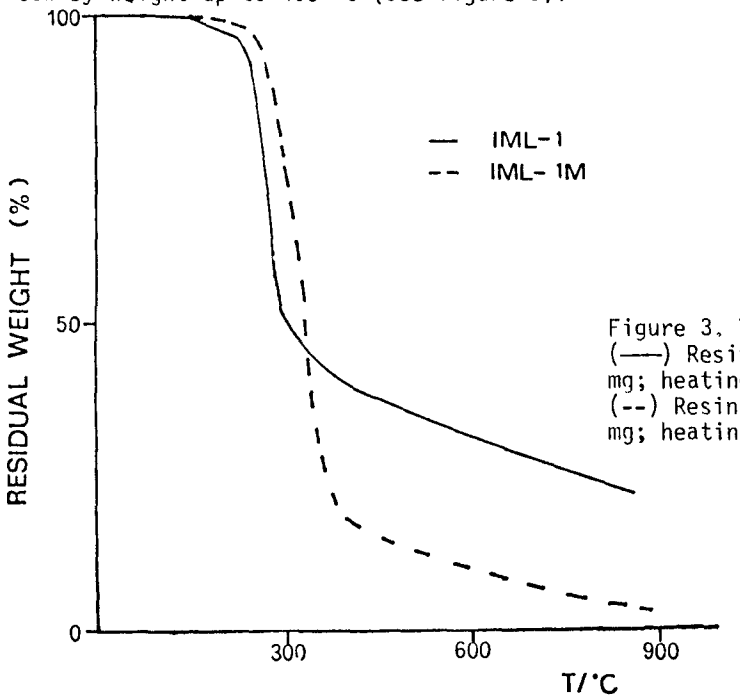


Figure 3. Thermal stability. (——) Resin IML-1. Mass 1.62 mg; heating rate: 10°/min. (--) Resin IML-1M. Mass 1.38 mg; heating rate: 10°/min.

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