# Branched and Linear Polyethyleneimine Supports for Resins with Retention Properties for Copper and Uranium. VII.

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## Synopsis

Weak and strong basic resins were synthesized by crosslinking with 1,7-dibromoheptane and 1,12-dibromododecane and subsequent *N*-methylation reaction of branched and linear polyethyleneimine. All the resins are insoluble in water. It was found that the *N*-methylated resins showed the highest retention ability for uranium. The resins do not retain significatively iron ($< 10\%$), and only two of them retain copper above 80% at optimum pH. Elution assays with sulphuric acid, sodium carbonate, and thermal stability were also carried out.

## INTRODUCTION

The application of commercial ion exchange resins to metal ion recovery from aqueous solution is a concept which has been extensively studied.[1,2] Polymers as metal ion complexing agents have also been important in solvent extraction chemistry.[3,4] Principles that are understood in this process are applied to solid–liquid extraction processes. The polymers may have the extractant ligands at the main or side chain or physically entangled. We now wish to report the use of polymer with an extractant ligand at the main chain. On the other hand, the polyethyleneimine is a functional polymer whose ability for metal complexation is well known.[5–10]

In this paper the synthesis of the water-insoluble resins by crosslinking reaction of the branched or linear polyethyleneimine with 1,7-dibromoheptane and 1,12-dibromododecane and posterior *N*-methylation with dimethylsulfate is reported. The retention properties for copper, iron, and uranium; elution assays; thermal stability were also studied.

## EXPERIMENTAL

**Materials.** All chemicals were used without further purification, except acetonitrile, dimethylsulfate, and 2-methyl-2-oxazoline, which were distilled before use. Branched polyethyleneimine (BPEI) is a commercial reagent (Aldrich Chem. Co.). Linear polyethyleneimine (LPEI) was obtained by cationic polymerization of 2-methyl-2-oxazoline; $\overline{M}_n = 2.095$ was determined by vapor pressure osmometry.[11]

**Crosslinking Reaction of Polyethyleneimine.** A mixture of 0.04 mol of crosslinker derivative, 60 mg Span 65 (emulsifier) and 120 mL petroleum ether was added to 15% PEI aqueous solution (0.012 mol) under stirring and heating at 95°C for 8 h. Then the resin was filtered, and the bromine was splitting off by washing with $1M$ NaOH. Subsequently, the resin was washed with enough water and then dried *in vacuo* at 30°C until constant weight. All the resins are insoluble in water.

*N*-**Methylation of Crosslinked Polyethyleneimine.** To a suspension of 0.1 eq/g of crosslinked polyethylene[3] in 50 mL $CH_3CN$, 0.24 mol of dimethylsulfate was added.[13] All the resins also are insoluble in water.

**pH Dependende for Copper, Iron, and Uranium.** The retention of copper, uranium, and iron was determined as follows: 0.1 g of the resin was shaken for 2 h in 50 mL of an aqueous solution containing 1 g/L copper (from $CuSO_4 \cdot 5H_2O$) or 1 g/L uranium (from uranylacetate); or 1 g/L iron (from $FeSO_4 \cdot 7H_2O$). The assays were performed in the pH range 0–2 for iron and 0–4 for copper and uranium. The amount of metal ion retained in the resin was analyzed in the filtrates by atomic absorption spectrometry for copper and iron and by spectroctrophotometry for uranium.[14]

**Determination of the Maximum Capacity of Load for Uranium.** A 250-mL beaker containing dry resin (1.0 g) and uranyl acetate aqueous solution (50 mL) (equivalent to 1.0 g uranium/L) was placed in a thermostatically controlled bath at 25°C. The mixture was shaken for 2 h at 200 cycles/s. The aqueous solution was separated by decanting and filtration and washed with water. This process was repeated three times using the same resin. Uranium was analyzed by the spectrophotometric method[14] and the uranium fixed in the resin is determined from the difference.

**Uranium Elution.** The resin loaded with uranium at pH 2.0 was contacted with sulfuric acid or sodium carbonate at different concentrations. The mixture was stirred for 1 h and then the resin was separated by filtration and the uranium was analyzed in the filtrates by spectrophotometry.[14]

**Measurements.** Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. Iron and copper were analyzed on a Perkin-Elmer 306 Atomic absorption spectrophotometer.

The thermal stability was examined by a Thermobalance Perkin-Elmer TGS-1. The heating rate was 10°/min in nitrogen atmosphere.

## RESULTS AND DISCUSSION

In the last few years we have been working with polyethyleneimine as support to obtain water-insoluble resins with retention properties for copper,

TABLE I
Crosslinker Derivatives and Names of the Resins

| | Name | |
|---|---|---|
| Crosslinker | Crosslinked resin | *N*-methylated resin |
| 1,7-Dibromoheptane | IM-5 (IML-5) | IM-5M (IML-5M) |
| 1,12-Dibromododecane | IM-7 (IML-7) | IM-7M (IML-7M) |

iron, and uranium.[15-19] In this paper, the branched and linear polyethyleneimine were crosslinked with 1,7-dibromoheptane and 1,12-dibromododecane and subsequently these resins were N-methylated in order to obtain all or the majority of the amine groups as ammonium salt (see Table I). Both reactions occur according to the following scheme:

$$\cdots -CH_2CH_2NH- \cdots + Br-R-Br \longrightarrow$$

$$\mathbf{1} \qquad\qquad \mathbf{2}$$

$$\cdots \left[-CH_2CH_2-\underset{\underset{R}{|}}{N}-\right]_{0.5,\,x} \cdots \left[-CH_2CH_2-\underset{\underset{\underset{Br}{|}}{R}}{N}-\right]_{y} \cdots \left[-CH_2CH_2-NH-\right]_{z} \cdots$$

$$\mathbf{3}$$

$$x + y + z = 100$$

$$\cdots -CH_2CH_2-\underset{\underset{R}{|}}{N}- \cdots + Me_2SO_4 \xrightarrow[CH_3CN]{} \cdots -CH_2CH_2-\overset{\overset{Me}{|}}{\underset{\underset{R}{|}}{N^+}}- \cdots \quad CH_3SO_4^-$$

$$\mathbf{4}$$

Scheme 1

Results of crosslinking and N-methylation reactions for BPEI and LPEI are given in Table II. The crosslinking and N-methylation percent was determined from elemental analyses according to the bromine content and the carbon/nitrogen (C/N) ratio.

The resin IML-5, which was obtained by crosslinking reaction of LPEI with 1,7-dibromoheptane, show the higher crosslinking percentage. This is probably

TABLE II
Results of Crosslinking and N-Methylation Reactions for Resins
Obtained from Branched and Linear Polyethyleneimine

| Resin | (C/N) ratio[a] | Crosslinking[b] (%) | N-alkylation[c] (%) | (C/N)$_M$ | $\Delta$(C/N)[a] | N/S ratio |
|---|---|---|---|---|---|---|
| IM-5 | 3.10 | 12.8 | 31.4 | — | — | — |
| IM-5M | — | — | — | 3.83 | 0.73 | 2.4 |
| IML-5 | 4.87 | 23.7 | 82.0 | — | — | — |
| IML-5M | — | — | — | 5.30 | 0.43 | 2.3 |
| IM-7 | 6.26 | 18.3 | 70.9 | — | — | — |
| IM-7M | — | — | — | 7.10 | 0.84 | 2.4 |
| IML-7 | 5.80 | 16.0 | 63.5 | — | — | — |
| IML-7M | — | — | — | 6.20 | 0.40 | 2.2 |

[a]$\Delta$(C/N) = (C/N)$_M$ − (C/N)$_C$.
[b]Percentage of bridged dihalogen derivatives per amine groups of BPEI = $X/2$ (if all amine groups of BPEI are crosslinked, crosslinking is 50%).
[c]Percentage of N-alkylated amine groups per amine groups of BPEI = $(x + y)$.

TABLE III
Adsorption Percent of Copper (II)

| Resin | pH | | | | |
|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 |
| IM-5 | 0.7 | 1.9 | 18.0 | 55.0 | 94.8 |
| IM-5M | 0.4 | 0.0 | 28.8 | 6.3 | 10.6 |
| IML-5 | 4.0 | 4.0 | 70.0 | 35.0 | 34.0 |
| IML-5M | 3.0 | 3.0 | 3.0 | 17.0 | 16.0 |
| IM-7 | 1.0 | 1.8 | 9.2 | 16.0 | 25.0 |
| IM-7M | 0.6 | 1.9 | 2.5 | 6.0 | 7.8 |
| IML-7 | 0.0 | 0.0 | 12.0 | 19.0 | 22.0 |
| IML-7M | 0.0 | 16.0 | 2.0 | 14.0 | 15.0 |

due to the shorter chain of crosslinked derivative than in the case of IML-7. The nitrogen/sulfur ratio as well as the $\Delta(C/N)$ show that the $N$-methylation reaction take place.

**Retention Capacity for Metal Ions (Batch Method).** The retention properties for all the resins were assayed by batch method, at different pH.

The resin IML-5 retain a 94.8% copper at pH 4.0 and the IML-5 resin has the optimum retention at pH 2.0 (70.0%). The other resins do not retain significatively this ion in the pH range assayed. The small retention capacity is due to the large distance between ligand centers of nitrogen decreasing the possibility of complex formation with Cu(II).[5] Moreover, all the crosslinked resins show a greater copper retention than $N$-methylated resins. It is due to the presence of the ammonium groups (see Table III). With respect to uranium retention, all the resins retain this ion in the pH range 0–3. To compare, we have also included the results obtained for Amberlite IRA-400, a commercial resin.

In general, the $N$-methylated resins retain more uranium than crosslinked resins. Besides the retention capacity for uranium is higher than for copper. This may be due to the presence of tertiary amine and ammonium group, which are assumed to favor the retention of $UO_2^{++}$. The resins IM-5, IM-5M, and IM-7M show a better retention behavior than IRA-400 (see Table IV).
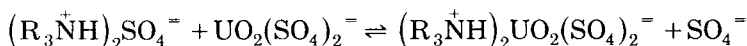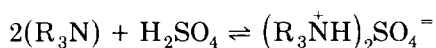
TABLE IV
Adsorption Percent of Uranium ($UO_2^{++}$)

| Resin | pH | | | |
|---|---|---|---|---|
| | 0 | 1 | 2 | 3 |
| IM-5 | 46.8 | 74.1 | 96.9 | 96.9 |
| IM-5M | 22.8 | 59.0 | 91.2 | 89.0 |
| IML-5 | 23.3 | 43.6 | 48.1 | 44.0 |
| IML-5M | 31.8 | 59.6 | 81.7 | 80.6 |
| IM-7 | 16.3 | 26.9 | 33.7 | 35.5 |
| IM-7M | 20.7 | 51.6 | 90.1 | 91.8 |
| IML-7 | 18.5 | 35.3 | 47.8 | 31.8 |
| IML-7M | 29.7 | 49.1 | 63.9 | 33.9 |
| IRA-400 | 14.2 | 31.9 | 70.9 | 28.5 |

TABLE V
Maximum Capacity of Adsorption for Uranium

| Resin | IM-5 | IM-5M | IML-5 | IML-5M | IM-7M | IML-7 | IML-7M | IRA-400 |
|-------|------|-------|-------|--------|-------|-------|--------|---------|
| Resin (meq/g) | 5.5 | 6.1 | 2.0 | 4.8 | 2.9 | 1.2 | 3.9 | 6.7 |

On the other hand, the maximum capacity of rentention for uranium was carried out at pH 2.0. After three contacts, the uranium was analyzed in the filtrates. The best resin IM-5M show a similar value to IRA-400 (see Table V). The uranium retention occurs probably in the way suggested for polymers with nitrogen atoms as ligands.[20] The weak or strong basic resins obtained by crosslinking and subsequent $N$-methylation, respectively, retain uranium by forming adducts in acid medium.

*Weak basic resin:*

$$2(R_3N) + H_2SO_4 \rightleftharpoons \left(R_3\overset{+}{N}H\right)_2SO_4^{=}$$

$$\left(R_3\overset{+}{N}H\right)_2SO_4^{=} + UO_2(SO_4)_2^{=} \rightleftharpoons \left(R_3\overset{+}{N}H\right)_2UO_2(SO_4)_2^{=} + SO_4^{=}$$

*Strong basic resin:*

$$\left(R_4\overset{+}{N}\right)_2SO_4^{=} + UO_2(SO_4)_2^{=} \rightleftharpoons \left(R_4\overset{+}{N}\right)_2UO_2(SO_4)_2^{=} + SO_4^{=}$$
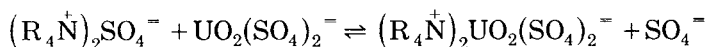
All the resins do not retain iron significatively ($< 10\%$).

**Elution Assays.** In order to recover the resin, sulfuric acid and sodium carbonate at different concentrations were added to the loaded resins (see Tables VI and VII).

The uranium from the resin IML-7 was eluted in 99.9% in 4.0$M$ H$_2$SO$_4$ and 1.0$M$ Na$_2$CO$_3$. Other resins that show a good elution behavior is IML-5. The uranium elution from the crosslinked resins is greater than $N$-methylated resins. In basic medium a more stable complex carbonate $[UO_2(CO_3)_3]^{-4}$ is probably formed.

**Thermal Stability.** The resins must show right-thermal stability. All the resins are stable up to 100°C. Besides the resins IML-5 and IML-7 do not lose

TABLE VI
Uranium Elution with Sulfuric Acid at Different Concentrations

| Resin | H$_2$SO$_4$ | | | |
|-------|------|------|------|------|
|  | 1.0$M$ | 2.0$M$ | 3.0$M$ | 4.0$M$ |
| IM-5 | 38.8 | 43.7 | 46.7 | 48.2 |
| IM-5M | 55.2 | 52.3 | 53.5 | 43.2 |
| IML-5 | 66.0 | 79.9 | 80.3 | 82.1 |
| IML-5M | 38.6 | 44.5 | 46.8 | 48.5 |
| IM-7M | 40.0 | 37.1 | 41.5 | 49.9 |
| IML-7 | 73.1 | 77.1 | 92.4 | 99.9 |
| IML-7M | 43.2 | 56.4 | 57.4 | 61.5 |
| IRA-400 | 73.0 | 86.7 | 91.2 | 93.7 |

TABLE VII
Uranium Elution with Sodium Carbonate at Different Concentrations

| Resin | Na$_2$CO$_3$ | | | |
|---|---|---|---|---|
| | 0.25$M$ | 0.50$M$ | 0.75$M$ | 1.0$M$ |
| IM-5 | 57.1 | 58.5 | 60.3 | 62.3 |
| IM-5M | 51.3 | 62.3 | 54.1 | 56.9 |
| IML-5 | 80.9 | 89.2 | 96.6 | 98.1 |
| IML-5M | 38.6 | 44.5 | 46.8 | 48.5 |
| IM-7M | 48.1 | 44.7 | 48.6 | 50.6 |
| IML-7 | 85.2 | 84.5 | 83.7 | 99.9 |
| IML-7M | 63.0 | 58.7 | 49.1 | 44.3 |
| IRA-400 | 47.0 | 53.5 | 56.3 | 72.3 |

TABLE VIII
Thermogravimetric Analyses of the Crosslinked and $N$-Methylated Resins

| Resin | Weight loss at various temperatures (%) | | | |
|---|---|---|---|---|
| | 100°C | 200°C | 300°C | 400°C |
| IM-5 | 0.0 | 5.4 | 12.1 | 93.0 |
| IM-5M | 0.0 | 2.1 | 55.8 | 65.3 |
| IML-5 | 0.0 | 0.0 | 7.3 | 99.9 |
| IML-5M | 0.0 | 5.7 | 30.5 | 90.6 |
| IM-7 | 0.0 | 6.0 | 18.1 | 89.7 |
| IM-7M | 0.0 | 1.2 | 39.8 | 62.2 |
| IML-7 | 0.0 | 0.0 | 8.3 | 99.9 |
| IML-7M | 0.0 | 1.6 | 53.4 | 79.9 |
| IRA-400 | 0.0 | 7.4 | 20.0 | 36.8 |

weight up to 200°C. Up to 200°C, all the resins show a similar or better thermal stability than IRA-400. Again, the crosslinked resins are more stable than $N$-methylated resins (see Table VIII).

## CONCLUSIONS

Polyethyleneimine is an excellent support to obtain water-insoluble resins by polymer-analogous reaction with 1,7-dibromoheptane and 1,12-dibromo-dodecane. Crosslinking and $N$-methylation reaction take place at different degrees according to the structure of the crosslinker derivatives and polyethyleneimine. All the resins do not significatively retain iron. They retained uranium in all the pH range assayed. Some of them show a similar behavior to Amberlite IRA 400 a commercial resin. According to the retention behavior it should be possible to separate uranium from copper and iron at pH 0 and 1 and at pH 2 for resins such as IML-5M, IM-7M, and IML-7M. It is possible to recover the loaded resins by uranium elution with sulfuric acid or sodium carbonate in particular for IML-7. All the resins are stable up to 100°C.

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