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Notes

A New Gel as a Support for an Ionic Exchanger: A Copolymer of Butadiene–Acrylic Acid with Tannic Acid and HEMA Grafting

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I. Introduction

The formation of chelates and adducts from polymeric matrices has been used widely in the concentration and/or isolation of metallic ions.[1,2] New organic molecules with functional groups capable of attaching to metals are still an interesting research subject. It is known that tannic acid[3-5] with its active sites in the phenolic groups may be used as an ion-exchange compound.

The aim of this work was to incorporate tannic acid by covalent attachment to a co-oligomer butadiene–acrylic acid. The partially cross-linked product thus obtained was later copolymerized by HEMA grafting leading to a new product (gel).

II. Results and Discussion

1. **Synthesis.** Ligand covalent bonding to the supporting polymer was accomplished through ester formation between polymer I carboxyl groups derived from acid chloride and tannic acid phenolic hydroxyl. Esterification ranged from 40 to 50%. The presence of tannic acid as ligand turned the polymer into a yellowish gel, very swellable in organic solvents. Afterward, the gel was cross-linked by HEMA grafting through the double residual links; thus, an easily manageable, nonadhesive, nonresilient, hydrophilic, and hydrophobic product was attained.

2. **IR Spectroscopy.** New bands appearing in contrast with base polymer I are at 3440 (OH phenol) and 856 cm^{-1} (C–H outer aromatic rings). With regard to the R—CO—OR′ group, we found bands both at 1770 (C=O) and at 1185 cm^{-1} (asymmetric strain C—O—C), where R′ is aromatic, and at 1725 (vibration to C=O), 1350, and 1038 cm^{-1} (asymmetric and symmetric C—O—C), where R and R′ were aromatic as in tannic acid. Certain bands may be attached to or overlap those corresponding to C–OH phenol strain.

3. **Captation Properties. a. Aqueous Solutions.** Results from different experiments carried out in columns are listed in Table I. Experiments were carried out by using solutions of metallic ions at different concentrations.

These results showed that the gel is active in Cu^{2+} and Pb^{2+}.

In each case, the pH of effluents was lower than that measured in the feed solution, but the pH of effluents from acetate solutions was much higher than that from chlorides, as can be seen in Table I. Acetate had a buffering effect on the solutions which limited the lowering of pH in the effluent and allowed for removal of M^{2+} to proceed unhindered by dependence upon $M^{2+} - 2H^{+}$ balance.

From the nature of the materials that are effective in taking up heavy metal ions, it can be assumed that tannins are the active ion-exchange compounds and that active sites are found in phenolic groups of tannic ligands. We hypothesize that ion exchange is the main mechanism for metal removal.

Table I
Removal of Metal Ions from Aqueous Solution in Column Experiments

	concn, ppm (M^{2+})		pH		sorbed cation, mg/g of dried gel	desorbed, %
salts	initial	final	initial	final		
$Cu(AcO)_2$	135.0	88.0	5.82	4.89	1.02	100
$Cu(AcO)_2$	118.0	70.0	6.55	6.24	1.20	98
$CuCl_2$	114.4	107.9	3.80	3.01	0.14	73
$CuCl_2$	118.0	114.0	5.33	3.60	0.09	100
$CuCl_2$	100.8	73.3	6.66		0.62	100
$CuCl_2$	108.3	107.1	5.35	3.12	0.03	100
$CuCl_2$	139.5	16.0	10.70		8.79	92
$Pb(NO_3)_2$	91.0	39.5	5.78	3.46	1.66	90
$Pb(NO_3)_2$	269.0	201.0	5.80	3.22	2.01	83
$FeCl_3$	131.0	110.0	2.49	2.35	0.45	76

Table II
Fe^{3+} Ion Captation from $FeCl_3$ Benzene/THF Solutions

concn, ppm		sorption Fe^{3+}, mg/g of dried gel
initial	final	
137.0	56.5	2.17
241.0	57.0	4.96
67.5	4.4	1.70

Since pH decrease is not directly proportional to $[M^{2+}]$ uptake, another competitive mechanism cannot be ruled out.

b. Organic Solutions. Gel uptake is also effective in the sorption of Fe^{3+} from organic solutions. Table II shows results of experiments performed on column from $FeCl_3$ in benzene/THF solutions. As it may be noticed, captation properties are higher in this assay than those indicated in Table I. Such findings may hint at a higher metal uptake efficiency as in Fe^{3+} under hydrophobic conditions.

4. **Effects of pH.** Table I shows that efficiency in the sorption of Cu^{2+} and Pb^{2+} is a function of pH. Maximal absorption was noticed between pH 6.5 and 11.0. Values higher than pH 8.5 led the gel to dissolve under ester hydrolysis. At a pH lower than 5.5 the equilibrium with exchange ions yielded low values with no significance in the absorption of metals.

5. **HEMA Concentration Effect.** When grafted early, assays were performed in bulk, and unhomogeneous matrixes of a high attaching property were attained. Because of this difficulty, assays were made by using benzene and 2% P/P benzoyl peroxide.

In this instance homogeneous looking gels were obtained. Such products were ground, rinsed, and used for uptake assays in batch. Table III shows results obtained for the various matrices. We may infer that a 1:1 ratio was optimal for both trials since it yielded optimal properties and better uptake.

Besides, grafted matrixes were more efficient than those obtained by bulk grafting. At a 1:1 ratio, a higher HEMA

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Table III
Variation of Captation Properties with Different HEMA Concentrations in Batch Experiments from AcCu Solutions

type expt	ppm (M^{2+}) initial	ppm (M^{2+}) final	pH initial	pH final	ratio polymer II:HEMA	mg/g of M^{2+}
solution grafting	82.0	59.0	6.50	5.15	1:0.5	0.65
	82.0	44.0	6.50	5.60	1:1	1.25
	82.0	11.0	6.50	4.79	1:2	1.05
bulk grafting	55.0	31.4	6.50	5.08	1:0.5	0.67
	55.0	16.0	6.50	3.81	1:1	0.96
	55.0	50.0	6.50	4.97	1:2	0.10

Table IV
Swelling Index in Water and Benzene

polymer ratio and HEMA	swelling index in water	swelling index in benzene
1:0.5	1.20	2.40
1:1	1.35	2.20
1:2	1.39	1.97
1:0	0.85	6.90
0:1	1.62	1.80

concentration decreases captation properties since per unit gel active sites are lower.

6. Swelling Indexes. They were estimated to learn more about hydrophobic and hydrophilic behavior of the gel in two different polarity solvents; these results appear in Table IV, and as shown, gels of different cross-linkings display a mixed behavior.

Swelling index dropped with the increase of HEMA agregates on gels obtained from polymer II. This trend was reverted when water was used as solvent, although the rise was less significant.

Obviously, the gel is endowed with more hydrophobic than hydrophilic properties.

III. Experimental Section

1. Materials. Tannic acid was purchased from Mallinckrodt. It was dried in vacuo at 80 °C, 3 days before use. Thionyl chloride from Fluka was distilled prior to use. All solvents were previously distilled and dried.

2. BU/AA–Tannic Acid-*g*-HEMA Procedure. The gel was synthesized by means of a co-oligomer butadiene acrylic acid with 0.35–0.45 equiv of COOH/100 g (polymer I). Polymer I was attained by mass polymerization using 1,3-butadiene and acrylic acid as monomers and benzoyl peroxide as initiator.[6] The product was purified by fractional precipitation using benzene (solvent) and methanol (nonsolvent). Three main fractions F_1, F_2, and F_3 were isolated. The intermediate fraction, F_2, was used for the following reactions.

Carboxyl groups of polymer I were turned into acid chloride groups by using thionyl chloride in benzene with 0.5% DMF. For each carboxyl group 1.25 equiv of thionyl chloride was used. Solvents and volatile products were eliminated in vacuo. The residue was solubilized in benzene/DMF (1:1). Tannic acid in DMF was added to the agitated solution by dropping. The obtained product (polymer II) was precipitated with methanol, isolated by centrifugation, washed, and purified by several fractional precipitates. Determination of the carboxyl groups was carried out by titration using potassium hydroxide in a methanol solution (0.1 N) and thymol blue as indicator. The determination was made before and after esterification, thus approximating the percent conversion.

The final product was then copolymerized by grafting with HEMA, reacting 1 part of polymer II in 0.5, 1, and 2 parts of HEMA, respectively. Grafting was performed in benzene as 2% P/P benzoyl peroxide. The gel obtained was dried, charged into a column, and swelled in water or benzene/THF (3:1) repeatedly until no more soluble products were eluted.

3. Captation Experiments. Captation experiments were performed in batch and column. Batch captation experiments were made by stirring 0.5–1 g of dried gel swelled in water and placed with approximately 15 mL of solutions containing metal ions for 3 h.

Column captation experiments were performed in a glass column 15 mm wide by 40 mm long. Several columns were made weighing approximately 0.5–1.2 g of dry gel, and 25–30 mL of M^{2+} aliquots were run. Approximately 1 g of the dried gel was swelled in water or benzene/THF (3:1) and placed into a column, and metal ions were dissolved in water or benzene/THF in a known concentration; afterward, it was run through the column. The quantity of metal ions absorbed was calculated by difference between the initial and final concentrations of the solutions, by means of atomic absorption. Then, the batch and column experiments were completed, by washing until sorbed metal ions were completely eluted in 0.05 N citric acid and washed thoroughly in water or in organic solvents.

The captations of Cu^{2+} and Pb^{2+} were carried out in water, and Fe^{3+} captations were made from benzene/THF (3:1) solutions. *Swell Indexes*: Swell indexes were determined from

$$SI = G(s)/G(0)$$

where $G(s)$ is the swelled gel weight and $G(0)$ is the dried gel weight. The procedure was carried out according to modified ASTM Norm D 3616-77.

4. Analysis. Infrared spectra were recorded on KBr disks in a Nicolet 5-SXC FTIR spectrophotometer. Atomic absorption experiments were made on a polarized Zeeman atomic absorption Hitachi spectrophotometer in the Center for Research of Material and Metrology (CIMM) laboratories. pH assays were made with a calomel electrode in a Seindwold pH meter.

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Registry No. Cu, 7440-50-8; Pb, 7439-92-1; Fe, 7439-89-6.