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UPTAKE OF GOLD FROM HYDROCHLORIC ACID SOLUTIONS BY POLYMERIC RESINS BEARING VARIOUS PHOSPHORUS CONTAINING LIGANDS

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ABSTRACT

Polymeric resins with phosphonate esters, phosphinate esters, and phosphine oxide ligands are synthesized via Arbusov reaction, characterized and used in the removal of Au(III) from hydrochloric acid solutions. It is found that phosphonate ethyl and butyl esters are able to adsorb as much as 100–120 mg Au/g of the resin. Affinity of these two resins towards gold, measured as the logarithm of distribution coefficient, is very high: 4.0–5.1 for the $1 \times 10^{-4}\,M$ Au(III) in 0.1–6.0 M hydrochloric acid solutions. Other metal chlorocomplexes, typical for the processing of the electronic parts scrap, such as Fe(III) and Ag(I), are removed to a lesser extent and, what is most important is that these resins do not absorb Cu(II) chlorocomplexes. This allows for the use of the synthesized resins in the selective removal of Au(III) from concentrated copper solution.

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Some of the studied resins are sulfonated in order to increase their swelling in aqueous solutions and to achieve greater accessibility of the phosphorous containing groups. All sulfonated resins displayed better swelling in aqueous solutions but the affinity and capacity of resins towards tetrachloroaurate at equilibrium Au(III) concentration of 20 mg/L was decreased. This effect is ascribed to an increasing distance between phosphonate groups and more difficult formation of their complexes with tetrachloroaurate.

Key Words: Phosphonate resins; Tetrachloroaurate; Coordination

INTRODUCTION

The majority of gold is obtained using alkaline cyanide leaching but other processes utilizing thiosulphate,[1,2,3] acidified thiourea,[4] and hydrochloric acid solutions have been studied as well. Solvent extraction is the most important method of gold recovery from secondary sources. The solvent extraction of gold from hydrochloric acid solutions is recently gaining more attention because of the considerable interest in developing safer alternative to cyanide leaching, and hence, increasing amount of this metal is reclaimed from secondary and waste material, for example electronic scrap.[5] Gold plated electronic parts are being stripped of this metal with acid and the resulting solution contains high amount of copper (ca. 600 mg/L), whereas gold is usually present at the concentration of ca. 20 mg/L.

Many extractants used in the removal of Au(III) from various HCl solutions are solvating ones. Examples include Cyanex-923[6] and Cyanex-471.[7] These phosphorus containing compounds are capable of solvating $AuCl_4^-$ from acidic solutions using hard phosphoryl oxygen from their P=O and P=S bonds. In Ref. [8], a group of solvating extractants, containing two phosphonate groups in one molecule of the compound, has been used in the removal of $AuCl_4^-$ from hydrochloric acid solutions. It has been found that the extractant selectivity depended on the distance between phosphonate groups. Newly obtained extractant, namely tetrabutyl 1,3-xylylenediphosphonate was proved to be superior to tetrabutylalkylene diphosphonates in respect to gold removal.[8]

This type of extractant, i.e., diphosphonate, has been already anchored onto insoluble polymeric matrices. Examples include resin obtained by the polymerization of tetraalkyl vinylidenediphosphonate with the suitable crosslinker followed by hydrolysis of an ester functionality[9] and the immobilization of tetraalkyl methylenediphosphonate[10] on the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer. In addition, other difunctional extractants containing phosphonate and carboxylate groups, such as carboxymethylphosphonate[11] and triethyl phosphonopropionate[12] have been immobilized on the VBC/DVB. Some of the functionalized resins, listed above, were applied in the removal of tetrachloroaurate from simulated hydrochloric acid solutions.[14] It has been found that both diphosphonates and carboxymethylphosphonates immobilized on the VBC/DVB copolymers were extremely efficient in the separation of tetrachloroaurate from copper, silver, and iron chlorocomplexes. However, synthesis of these functionalized resins requires costly chemicals and proceeds with one side reaction, which causes additional chemical crosslinking of the resins, thus lowering the accessibility of the ligands and slowing down diffusion within the polymeric network.[14] In view of these results, it seems interesting to investigate whether monodentate phosphorus containing ligands immobilized on VBC/DVB matrix can be used for $AuCl_4^-$.

The aim of this work was to evaluate the use of polymeric resins in which phosphonate and other phosphorus containing ligands (phosphinate, phosphine oxide) are deposited randomly within polymeric networks in the removal of gold from hydrochloric acid solution. Such resins are easily obtainable from VBC/DVB polymers via Arbusov reaction. Factors concerning type of ligand and the presence of hydrophilic sulfonic groups were taken into account during the selectivity and kinetic experiments.

EXPERIMENTAL

The expanded gel type copolymers of VBC and technical DVB, which consists of 65.8% m- and p-DVB and 34.2% ethylstyrenes are prepared by suspension polymerization method with 0.5 wt.% of benzoyl peroxide as initiator. Polymerization mixture consists of 100 g of monomers, 96.96 g of which is VBC and 3.04 g is DVB, so the nominal crosslinking degree is 2 wt.%, and 100 g of toluene. Presence of toluene causes better solvation of growing polymeric chains and the resultant beads have expanded gel structure. Detailed procedure of obtaining polymer is presented in Ref. [12]. After polymerization beads have been washed with hot water (to free them from stabilizer and salt), water at room temperature, and acetone (to remove most of the organic impurities such as initiator, unreacted monomers, solvents). They are then dried, preswollen in toluene, and extracted with this solvent in Soxhlet extractor for 12 hr. Beads were subsequently modified in the Arbusov reaction. The following phosphorylation compounds were obtained from Aldrich Co. (Aldrich GmbH, Germany), and used as received: triethyl phosphite, tributyl phosphite, triphenyl phosphite, diethyl phenylphosphonite, and ethyl diphenylphosphinite. Typical procedure consists of heating 5 g of VBC/DVB polymer with a three-fold molar excess of phosphorus compound (in respect to chloromethyl groups in VBC/DVB copolymer) for 15 hr at 150–160°C. After such time, beads were removed by filtration and washed with dioxane, dioxane/water mixture, acetone, and finally with plenty of distilled water.

The following procedure is used to introduce hydrophilic sulfonic acid groups into polymer structure: 5 g of dry VBC/DVB polymer bearing phosphorus containing ligand is placed in a 100 mL round bottom flask and allowed to swell in 25 mL of dichloroethane for 2 hr. After that, 15 mL of chlorosulfonic acid solution in dichloroethane (1:2 v/v) is added and the entire mixture is mixed for 2 hr at room temperature. Next, 40 mL of dioxane is added and the beads are transferred to the separatory funnel. Beads are then washed with the remaining portion of dioxane, dioxane/water (1:1), water, and finally 1 *M* NaOH solution and left in 2 *M* NaOH overnight. The entire procedure is ended with resin washing using water, 1 *M* HCl, and again water.

The phosphorus capacity is measured by digesting ca. 20 mg of resin in 20 mL of perchloric acid followed by reaction with amidol and ammonium molybdate.

The acid capacity (content of $-SO_3H$ groups) is determined by contacting ca. 1 g of swollen polymer with 100 mL of 0.1 *M* NaOH for 24 hr and titrating a 25 mL aliquot of base with 0.1 *M* HCl in the presence of phenolphthalein.

Water content in the polymer is measured by centrifugation method in which ca. 1 g of swollen polymer is placed in a short column having a sintered glass bottom, centrifuged for 5 min at 3000 rpm and expressed as $W = (m_w - m_d)m_d$, where m_w is the weight of swollen polymer after centrifugation, and m_d is the weight of dry polymer. Drying conditions are 20 hr at 110°C.

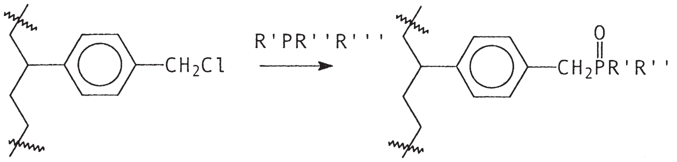
The performance of the resins in gold (III), iron (III), silver (I), and copper (II) removal from hydrochloric acid solutions is measured by contacting the amount of resin equivalent to 0.05 mmol of ligand with 20 mL of $1 \times 10^{-4}\,M$ metal solution. Solutions are formulated with various amounts of HCl and the equilibrium metal concentration is measured using AAS technique (Perkin-Elmer AAnalyst 100) with wavelength set at 242.8, 248.3, 328.1, and 324.8 nm, respectively. Sorption isotherms are taken by contacting the amount of resin equivalent to 0.05 mmol of ligand with 20 mL of solution with various concentrations of gold (III) in 3 *M* HCl and plotting sorption as a function of equilibrium concentration.

The distribution coefficient was calculated as the ratio of the amount of metal taken by 1 g (in respect to dry polymer) of resin and amount of the metal left at equilibrium in 1 mL of feed solution.

RESULTS AND DISCUSSION

The resins studied in this work have been obtained via Arbusov reaction between VBC/DVB copolymer and suitable phosphorylating agents. The above method of chemical modification was already applied to the modification of crosslinked polymers,[14] however, at that time only trialkyl phosphites were used which resulted in resins with phosphonate functionalities. This time, substituted phosphonite and phosphinite are also employed, what allowed for the synthesis of resins with phosphinic acid ester and phosphine oxide groups. Scheme of the resins synthesis is presented in Fig. 1 and their basic characteristics in Table 1. The yield of modification can be calculated from phosphorus content in the resultant resins. It is very high, within 90–100%, indicating completeness of the reactions. Resins 1, 4, and 5 contain phosphonate groups differing only in the type of ester (ethyl, butyl, phenyl). These resins modification proceeds to almost the same extent and differences in the phosphorus content are solely due to the various weight gain during introduction of the phosphonate functionalities. Percentage of solid of all these resins is high, indicating their hydrophobicity. It is clearly seen that Resin 4 (with butyl ester) is the most hydrophobic one with water regain equal to only 0.08 g of water per 1 g of polymeric material. Resins 2 and 3 contain ethyl ester of substituted phosphinic acid and phosphine oxide groups, respectively. For them, also, water regain is low, reflecting the lack of ionizable groups and presence of hydrophobic, phenyl substituents.

All of these resins have phosphoryl oxygen in the structure of their ligands, and the oxygen atoms can be used for coordinating purposes. In this respect, resins with phosphonate, phosphinate, and phosphine oxide functionalities, studied in this article, are quite similar to previously studied diphosphonates.[13] One very important difference between previously studied[13] diphosphonate resins and the resins investigated here is that now groups with single P=O bond are placed randomly within polymeric network and in diphosphonates P=O bonds were arranged in pairs separated by one methylene group, i.e., they were in geminal position.



Resin	R'	R''	R'''	Type
1	EtO	EtO	EtO	Phosphonate
2	Ph	EtO	EtO	Phosphinate
3	Ph	Ph	EtO	Phosphine oxide
4	BuO	BuO	BuO	Phosphonate
5	PhO	PhO	PhO	Phosphonate

Figure 1. Scheme of the resins synthesis.

Table 1. Basic Characteristics of the Obtained Coordinating Resins

Resin Number	Ligand	P (mmol/g)	S (mmol/g)	Acid Capacity (mmmol/g)	Percentage of Solid (%)	Water Regain (g/g)
1	$CH_2P(O)(OEt)_2$	3.52	—	—	73.38	0.36
1S	$CH_2P(O)(OEt)_2$ SO_3H	3.40	1.46	1.03	38.71	1.58
2	$CH_2P(O)Ph(OEt)$	2.88	—	—	72.08	0.39
3	$CH_2P(O)(Ph)_2$	2.83	—	—	83.57	0.20
3S	$CH_2P(O)(Ph)_2$ SO_3H	2.58	0.79	1.01	40.87	1.45
4	$CH_2P(O)(OBu)_2$	2.77	—	—	92.18	0.08
4S	$CH_2P(O)(OBu)_2SO_3H$	2.82	1.31	1.85	64.49	0.54
5	$CH_2P(O)(OPh)_2$	2.50	—	—	57.83	0.73

The extractive ability of resins 1–5 towards gold from acidic solutions has been studied by measuring Au distribution coefficient between resin and solutions. The results are shown in Fig. 2, where it can be seen that both resins 1 and 4 (ethyl phosphonate and butyl phosphonate) display extremely high affinity towards tetrachloroaurate. For them, distribution coefficients are very high and in 1–2 *M* hydrochloric acid solutions are reaching values close to 100,000. This value is comparable to the results obtained previously for the diphosphonate type resins.[13] Other resins studied in this work, with phenyl phosphonate, phosphinate, and phosphine oxide ligand do not perform well as gold distribution coefficients are within the range 10–100. Silver chlorocomplexes are removed by resins to a very limited extent. Iron chlorocomplexes are coordinated by resins 1 and 4, however, at HCl concentration higher than 2 *M*. The most importantly, resins do not coordinate copper chlorocomplexes at the studied pH range (see Fig. 2). This feature makes possible use of resins 1 and 4 in the selective removal of gold from hydrochloric acid solutions containing large amounts of copper chlorocomplexes.

For the resins with the highest affinity towards tetrachloroaurate (resins 1 and 4), sorption isotherms have been obtained and plotted in Fig. 3. It can be seen that at high tetrachloroaurate concentration at equilibrium sorption can be as high as 110–120 mg of Au(III) per 1 g of resin. At equilibrium concentration of 20 mg Au(III)/L, typical for processing of the electronic scrap, sorption is lesser: for resin 1 reaches ca. 90 mg Au(III)/g, and for resin 4 ca. 68 mg Au(III)/g. If 1:1 complex formation between phosphonate and $AuCl_4^-$ can be assumed, as it was observed for low molecular weight phosphate,[8] then only a fraction of the resins' phosphoryl oxygen is used to form complexes. In the case of resin 1, it is ca. 13% [90 mg of Au(III) sorbed at equilibrium concentration of 20 mg Au(III)/L is equal to 0.46 mmol of this metal; total number of phosphoryl groups in resin 1

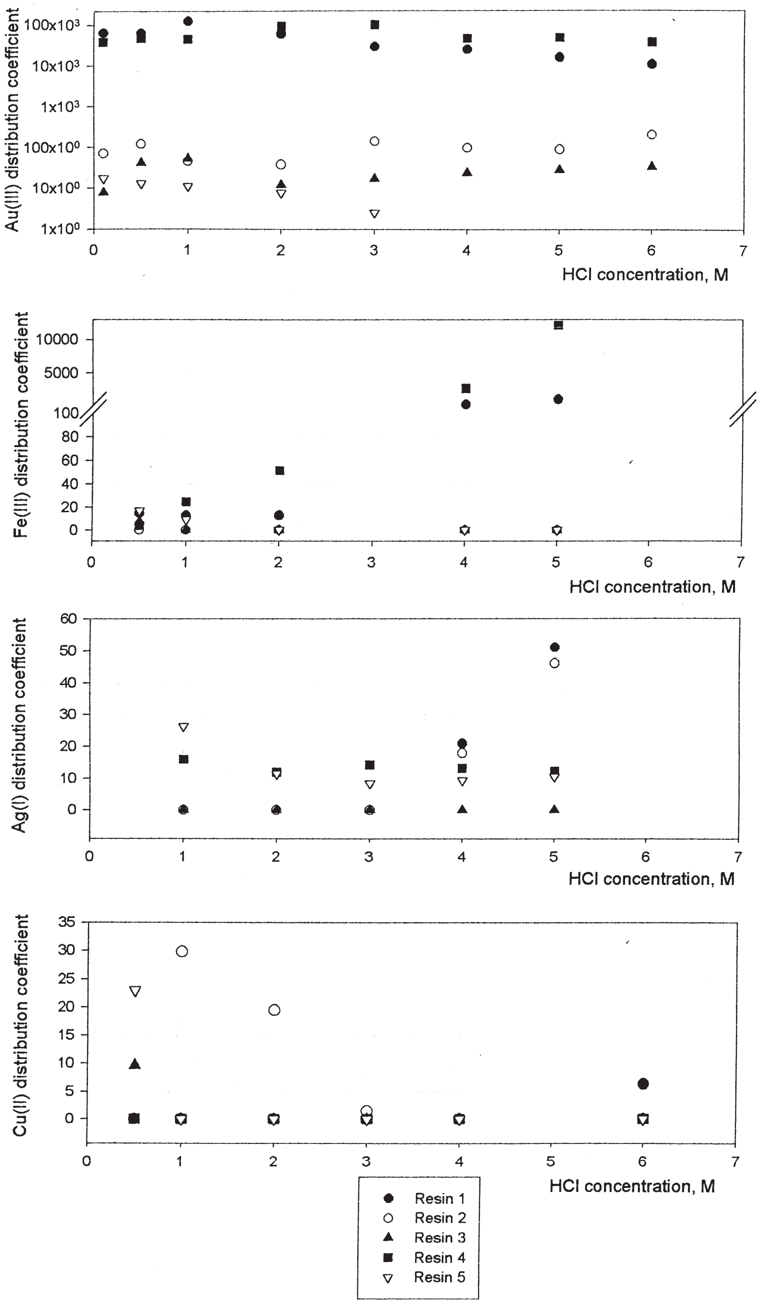


Figure 2. Au(III), Fe(III), Ag(I), and Cu(II) distribution coefficients as the function of HCl concentration.

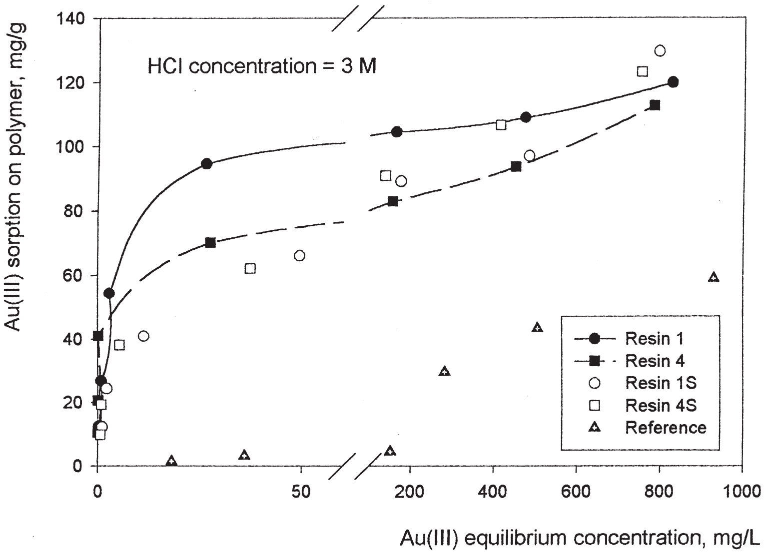


Figure 3. Au(III) sorption isotherms for resins 1, 1S, 4, and 4S.

is 3.52 mmol/g]. The same result is obtained in the case of resin 4. In most cases inefficient participation of crosslinked polymers' functional groups in the formation of complexes with ions is poor accessibility of these groups. This is either due to the presence of the crosslinks and hence low mobility of the polymeric chains or to the hydrophobicity of polymers. The former limitation is inevitable since nominal crosslinking level must be kept sufficiently high in order to maintain mechanical stability of the resins. Hydrophilicity/hydrophobicity balance of the resins can be adjusted to some extent by introduction of suitable groups. These groups should be polar and highly hydrated as for example sulfonic ones. Introduction of sulfonic groups into the structure of ion-exchangers and observed increase of metal ion uptake by such resins were reported previously.[14] The same method of resins hydrophilization has been employed in the present work. The resins containing, in addition to phosphorus functionality, also sulfonic groups are denoted by "S" and their basic characteristics are presented in Table 1. As can be seen, the most significant effect is observed increase of water regain. Upon introduction of sulfonic groups, the water uptake increases fourfold for resin 1S as compared to the resin before sulfonation, i.e., resin 1. An even stronger effect is observed for resin 4S where water uptake increases ca. seven times.

The distribution coefficients of gold for resins 1S and 4S are 11,146 and 16,291, respectively. For the resins before introduction of the sulfonic groups, i.e., for resins 1 and 4, the respective values are 31,169 and 105,800. Gold uptake by the reference resin containing only sulfonic groups and no groups with P=O bonds gave distribution coefficient 78. This value is negligible compared to distribution coefficient obtained in the case of resins 1S and 4S. It is clearly seen that introduction of sulfonic groups and observed increase of water uptake results in significant drop of the affinity of resins towards tetrachloroaurate anions. Sorption isotherms of gold on resins 1S and 4S can be seen in Fig. 3. It can be noted that at low equilibrium concentration the sorption of gold on both 1S and 4S resins is lesser than on resins 1 and 4. This difference is more visible when resins 1 and 1S are compared. At the tetrachloroaurate equilibrium concentration of 19.7 mg/L, typical for processing of the electronic scrap, resin 1S is able to sorb ca. 45 mg Au/g. Resin 1, under the same conditions, is able to sorb ca. 90 mg Au/g. Thus, the fraction of phosphoryl oxygen involved in coordination is in the case of resin 1S equal to ca. 6.7%, which is markedly less than the 13% observed for resin 1. Only at high equilibrium concentrations such as 700–800 mg of Au(III)/L sorption of gold on the resins containing phosphonate and phosphonate/sulfonic groups is almost the same.

It seems that the most probable explanation of decreased affinity of the sulfonated resins bearing phosphonate ligands towards tetrachloroaurate is better swelling of the now better hydrated polymeric network. This swelling increases the distance between polymeric chains and hence the distance between phosphonate groups what makes more difficult the interaction of two phosphoryl groups with one tetrachloroaurate anion. The above indicates that assumption of the formation of 1:1 complex between phosphonate and tetrachloroaurate does not hold. Formation of 2:1 complexes seems more likely as it explains the adverse effect of better swelling on the gold uptake by resins with phosphonate and sulfonic functional groups.

REFERENCES

1. Langhans, J.W.; Lei, K.P.V.; Carnahan, T.G. Copper Catalyzed Thiosulfate Leaching of Low Grade Gold Ores. Hydrometallurgy **1992**, *29*, 191–203.
2. Abbruzzese, C.; Fornari, P.; Massida, R.; Veglio, F.; Ubaldini, S. Thiosulphate Leaching for Gold Hydrometallurgy. Hydrometallurgy **1995**, *39*, 265–276.
3. Zhao, J.; Wu, Z.; Chen, J. Extraction of Gold from Thiosulfate Solutions Using Amine Mixed with Neutral Donor Reagents. Hydrometallurgy **1998**, *48*, 133–144.
4. Songling, Y.; Jimin, Y.; Zhonquan, Y. 19-23 Alkyliminodimethylenephosphonic Acid, a New Extractant for Gold from Acidic Thiourea Solutions. Hydrometallurgy **1993**, *32*, 181–188.

5. Pareau, D.; Stambouli, M.; Durand, G. Selective Recovery of Gold from Electronic Waste Products by Solvent Extraction and Liquid Membranes Extraction. Proceedings of ISEC '96, Melbourne, Australia, 1996; Vol. 1, 653–658.
6. Martinez, S.; Sastre, A.; Miralles, N.; Alguacil, F.J. Gold (III) Extraction Equilibrium in the System Cyanex 923-HCl-Au(III). Hydrometallurgy **1996**, *40*, 77–88.
7. Salvado, V.; Hidalgo, M.; Masana, A.; Munoz, M.; Valiente, M.; Muhammed, M. Extraction of Gold (III) from Hydrochloric Acid Solutions by Triisobutylphosphine Sulfide in Toluene. Solvent Extr. Ion Exch. **1990**, *8*, 491–502.
8. Chowdhury, D.A.; Kamata, S. Neutral Bifunctional Phosphonates as Reagents for Solvent Extraction of Au(III): Selective Recovery of Gold from Hydrochloric Acid Solution Using Tetrabutyl 1,3 Xylylenediphosphonate. Solvent Extr. Ion Exch. **1997**, *15*, 231–248.
9. Alexandratos, S.D.; Trochimczuk, A.W.; Crick, D.W.; Horwitz, E.P.; Gatrone, R.C.; Chiarizia, R. Synthesis and Ion Complexing Properties of a Novel Polymer Supported Reagent with Diphosphonate Ligands. Macromolecules **1996**, *29*, 1021–1026.
10. Alexandratos, S.D.; Trochimczuk, A.W.; Horwitz, E.P.; Gatrone, R.C. Synthesis and Characterization of Bifunctional Ion Exchange Resin with Polystyrene Immobilized Diphosphonic Acid Ligands. J. Appl. Polym. Sci. **1996**, *61*, 273–278.
11. Natesan, S.; Alexandratos, S.D. Polymer Supported Reagents with Enhanced Metal Ion Affinities: Mechanistic Studies. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **1998**, *39* (2), 784–785.
12. Trochimczuk, A.W. Novel Ion Exchange/Coordination Resins with Carboxyethylphosphonate Ligands. Eur. Polym. J. **1998**, *34*, 1047–1051.
13. Trochimczuk, A.W. Selective Recovery of Gold from Acidic Solutions Using Resins with Methylenediphosphonate and Carboxymethylphosphonate Ligands. Solvent Extr. Ion Exch. **2001**, *19*, 301–313.
14. Trochimczuk, A.W.; Alexandratos, S.D. Synthesis of Bifunctional Ion-Exchange Resins Through the Arbusov Reaction: Effect on Selectivity and Kinetics. J. Appl. Polym. Sci. **1994**, *52*, 1273–1277.

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