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Design and Development of Polymer-Based Separations: Dual Mechanism Bifunctional Polymers as a New Category of Metal Ion Complexing Agents with Enhanced Ionic Recognition

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DESIGN AND DEVELOPMENT OF POLYMER-BASED SEPARATIONS: DUAL MECHANISM BIFUNCTIONAL POLYMERS AS A NEW CATEGORY OF METAL ION COMPLEXING AGENTS WITH ENHANCED IONIC RECOGNITION

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ABSTRACT

A new series of ionic polymers has been synthesized with unique applications to separations science, in general, and metal ion separations, in particular. The unifying concept underlying these polymers is that specificity in molecular or ionic separations is most readily brought about by multifunctional substrates which can participate in multipoint interactions. The **dual mechanism bifunctional polymers** form a new category of synthetic multifunctional substrates with enhanced molecular/ionic recognition. These polymers are synthesized with two groups on a given support network each of which operates by a different mechanism. One mechanism is relatively aspecific and its primary purpose is to allow the solution species access to the highly specific recognition mechanism. The principal application has been to selective metal ion separations from aqueous solutions. The dual mechanism bifunctional polymers (DMBP's) are divided into three classes. In each case, ion exchange is the access mechanism while the recognition mechanism defines the class of resins. The Class I DMBP's are the ion exchange/redox resins: they superimpose a redox component on top of the ion exchange reaction and so allow for the recovery of pure metal from a solution of its ions. The Class II DMBP's are the ion exchange/coordination resins: they superimpose a purely coordinative component on top of the ion exchange reaction and so allow for tight binding of targeted ions onto the polymer support according to the principles of hard-soft acid-base theory. The Class III DMBP's are the ion exchange/precipitation resins: they superimpose a precipitation reaction on top of the ion exchange reaction and so allow for the recovery of insoluble metal salts from multi-ion solutions. Bifunctional group cooperativity is most clearly quantified with the Class III resins. The resin characteristics which allow for the observation of polymer - supported synergistic extraction and a concomitant enhanced ionic recognition are detailed.

INTRODUCTION

The selective separation of molecular or ionic species from aqueous solutions is of critical importance to many processes, including those dealing with metal ion separations,[1] optical isomer separations,[2] and bioseparations.[3] Polymer-supported reagents form ideal substrates for such separations due to their ease of operation in both analytical and preparative modes under continuous recovery conditions.[4] This ease of operation can be coupled with very high degrees of selectivity once the most exoergic electrostatic interactions which the targeted species can form with any given substrate are identified. An understanding of these interactions is required for any theory with predictive capability of enhanced molecular recognition between substrate and target species. Such a theory would permit a rapid determination of the optimum support-ligand arrangement needed for any given separation.

The synthesis of polymer-supported reagents with a systematic variation in ligand structure and concomitant mechanism of action in molecular/ionic separations forms the basis of our research. The principal application to date of these polymeric reagents has been in metal ion separations. Formulating an overall theory for the observed ligand-to-metal interactions using the principles of hard-soft acid-base theory is a continuing objective. Understanding metal ion separations with the polymers to be described below will then allow for the efficient design of biomolecular separations with the emphasis on protein separations.

The synthesis of specific polymer-supported metal ion extractants has received a good deal of attention.[5] A wide variety of polymeric extractants have been prepared. Supported hydroxyoximes have been found to display high Cu(II) affinities,[6] and various polymers have been prepared via the Fries Rearrangement.[7] Copper-selective resins have also been prepared by utilizing the picolylamine structure.[8] Polystyrene-supported dithiocarbamate derivatives[9,10] have a high affinity for silver ions. Sulfur-containing resins, in general, have been found to be more selective toward the noble and heavy metals than resins with nitrogen or oxygen-based ligands,[11] especially as applied to mercury, silver and gold complexation.[12] Resins have been synthesized having the simple thiol ligand,[13] the more complex isothiouronium ligand,[14] and the thioglycolate ligand.[15] The extraction of uranium with organophilic amides was the basis for the synthesis of a polystyrene-supported amide via the reaction of polystyrene with N,N,-dibutyl-4-chlorobutylamide which was uranium-selective.[16] Arsonic acid resins have been synthesized by Parrish,[13] Hirsch,[17] and Fritz[18] and found to be more selective towards thorium, uranium, and the rare earths than the transition metals. Uranium recovery from sources such as sea water has been the target of polyethyleneimine resin production.[19] Given that acetylacetone is such a good chelating agent, comparable polystyrene-supported resins have been synthesized and found to act as effective chelating agents.[20] Other resins which have been synthesized as chelating agents include the N-(2'-pyridyl)hydrazone resin,[21] the poly(oxime)s,[22] and the polymeric histidine resin.[23] As suggested by the resins given as examples above, highly specialized polymeric extractants can have a number of drawbacks including a lack of versatility due to a narrow range of optimum operating conditions and a difficult preparative procedure, both of which hinder large scale applicability. Additionally, polymers with non-ionic substituents are less hydrophilic than those with ionic ligands which tends to decrease metal ion accessibility and hence yields low apparent capacities. Nonetheless, such resins are important because they underscore the features of ligand-to-metal specificity.

Perhaps the easiest and least expensive modification to the polystyrene network involves its reaction with sulfuric acid to give the strongly acidic sulfonic acid cation exchange resin.[24] This resin can be used in metal recovery processes: for example, it has proven to be effective in the treatment of waste streams from rayon manufacturing plants containing 100 ppm zinc.[25] The most serious drawback is that it is not selective enough in which cations it absorbs given that its range of reaction free energy values with a wide variety of metal ions is within a few kilocalories per mole.[26] As a result, its use is precluded in the recovery of uranium from low grade ores due to the fact that it exchanges with the iron, aluminum, and other metals also present.[27] Similar conclusions have been made in the attempt to recover cationic gold[28] and in other cases where the metal of interest is present in low concentrations relative to other metal ions in the solution.[29] Selective recovery can be effected for those metals which form anionic complexes, such as the uranyl disulfate dianion and the dicyano aurium monoanion, through the use of the dimethyl or trimethylammonium anion exchange resins,[27] but this avenue is clearly of limited applicability. The commercially available weakly acidic carboxylic resins display an enhanced selectivity, especially for multivalent over univalent ions,[30,31] but their high proton affinity requires that the ion exchange be carried out over a pH range restricted toward the higher end relative to the sulfonic resins.[32]

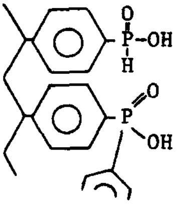
The ideal polymer-supported complexing agents must be selective for targeted metal ions under a wide range of experimental conditions. They must also be readily prepared and display a high capacity for metal ions in both low and high pH solutions. Ionic ligands are important in order to enhance the support's hydrophilicity and, hence, accessibility by dissolved ionic species. Given the advantages and disadvantages of the sulfonic acid and carboxylic acid resins noted above,it soon becomes clear that phosphorus-based resins could occupy a unique position as selective extractants. Phosphorus-based liquid extractants have been utilized extensively in solvent extraction chemistry.[33] The phosphorus acid ligand is less acidic than the sulfonic acid and thus a more selective ion exchanger in low pH solutions.[34] This gives it an important advantage over the carboxylic acid ligand which, while selective, displays almost no ion exchange capacity in low pH solutions due to its weakly acidic nature.[35] Polymer-supported extractants with phosphorus acid ligands could thus display an important degree of selectivity for different metal ions in acidic solutions. Indeed, the ion exchange properties of the phosphonic acid ligand covalently bonded onto polystyrene,[36] polyvinyl alcohol,[37] poly(2-hydroxyethyl methacrylate),[38] polyethylene,[39] and phenol-formaldehyde resins[40] have been studied. Such studies point to the potential that polymer-supported phosphorus acid ligands, in general, have in metal ion separations.

Ion exchange is an important reaction of metal ions but it is not the only reaction that they are capable of undergoing. Other reactions can be more specific and lead to a more readily recoverable form of the metal (vide infra). Our aim is to induce a high degree of selectivity into ion exchange resins by incorporating particular metal-specific reactions into particular polymers. That reactive polymers can be prepared for a variety of purposes has been described by Janauer[41] and by Helfferich.[42] We have introduced a category of resins termed **dual mechanism bifunctional polymers** (DMBP's) for the selective complexation and recovery of metal ions. These are polymeric reagents with two different functional groups on the support network and so capable of interacting with metal ions via two different mechanisms which are labeled the **access mechanism** and the **recognition mechanism.** The access mechanism is relatively aspecific: it serves mainly to bring ionic species into the polymer network and maintain ionic mobility within the network. The recognition mechanism is responsible for specificity: it is activated once a metal ion with a specific property comes in close enough proximity through the access mechanism and the corresponding recognition reaction allows the polymer network to act as a sink for the targeted ion leading to its isolation and recovery. Ion exchange is the access mechanism for the reasons stated earlier: an ion exchange ligand enhances ionic accessibility and mobility within the polymer network. The recognition mechanism then occurs simultaneous with or subsequent to the ion exchange reaction.

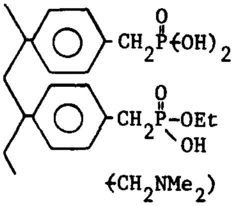
The first class of resins within the DMBP category utilizes reduction as the recognition mechanism which is therefore superimposed on the ion exchange process. These ion exchange/redox resins allow for the recovery of pure metal from a solution of its ions. The second class of resins superimposes a coordinative component as the recognition mechanism on top of the ion exchange reaction. These ion exchange/coordination resins can then lead to polymer-supported synergistic extraction in which both groups operating together complex more metal from solution than either one could alone. Lastly, the third class of resins superimposes a precipitation reaction as the recognition mechanism on top of the ion exchange reaction. These ion exchange/

precipitation resins can then allow for the recovery of insoluble metal salts from multi-ion solutions and high levels of recovery could also arise from a synergistic interaction between the ligands.

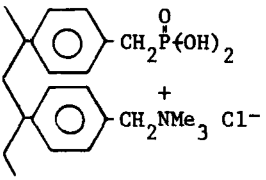
The three classes of DMBP's are summarized below with representative examples. All have a polystyrene support structure due to polystyrene's chemical versatility and stability. The phosphorus acids are the ion exchange ligands because of their inherently greater selectivity than the sulfonic ligand with significant exchangeability in high acid solutions. It was also expected that in solutions too acidic for ion exchange, the phosphorus acid ligands would still be active by coordination through the phosphoryl oxygen which is known to be an excellent Lewis base, in contrast to the poorly coordinating sulfonyl oxygen (v.i.).



Class I



Class II



Class III

Each class of resins will be detailed in the following sections, but their overall characteristics can be noted at this point. The Class I ion exchange/redox resins consist of primary and secondary phosphinic acid groups; ion exchange occurs through the acidic -OH moiety while redox occurs through the non-acidic P-H bond. The Class II ion exchange/coordination resins consist of phosphonic acid groups for ion exchange and either phosphorus ester or tertiary amine groups for neutral coordination. The phosphonic acid ligand is also used for ion exchange in the Class III ion exchange/precipitation resins along with quaternary amine groups which are responsible for the precipitation component through the associated anion. In each case, the bifunctional nature of the DMBP's leads to the specific recovery of different metal ions through the redox, coordination, or precipitation recognition mechanisms.

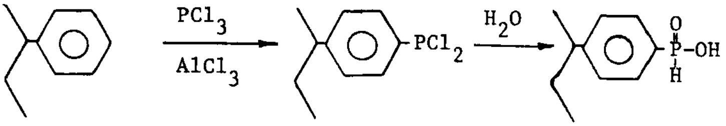
It should be emphasized that whereas the following discussion will deal with metal ion separations, the bifunctional polymers are currently being extended to biomolecular separations. Just as bifunctionality will be seen to be important for enhanced ionic specificity, multifunctional interactions are critical to enhanced molecular recognition. This, of course, is central to the precise molecular recognitions possible in enzymatic reactions and with affinity chromatography.[43] The preparation of multifunctional polymers with a primary application to enhanced protein recognition via multi-point attachments is currently underway in our laboratory.

CLASS I DMBP's: ION EXCHANGE/REDOX RESINS

The monosubstituted monobasic primary phosphinic acid ligand, R-PH(O)OH, is the simplest phosphorus acid ligand which could be covalently bonded onto a polymer support network. The ability of the acidic hydrogen to ion exchange can be studied with neither the superimposed electronic effect of an additional -OH group on the phosphorus nor the superimposed steric effect of an alkyl group on that same phosphorus. The phosphoryl hydrogen which would be proximate to each acid site would be relatively neutral both electronically and sterically to the ion exchange reaction. The P-H bond, however, is critical to the ligand's overall reactivity through its ability to reduce metal ions. Phosphinic (or phosphonous) acid, H_3PO_2, is an inorganic reductant with an oxidation potential of +0.50 V.[44] Covalent bonding of the primary phosphinic acid ligand onto polystyrene beads can thus be expected to produce a hydrophilic resin which will ion exchange with metal ions in solution and then reduce those with a reduction potential greater than some minimum value (v.i.). The resin would act as a sink for those metal ions which are reduced to the free metal form and lead to a high observed selectivity for them.

Synthesis

The synthesis of the phosphorus-based ion exchange /redox resins is summarized in equation (1). Electrophilic aromatic substitution by the PCl_3 on the phenyl rings of the 2% divinylbenzene (DVB) crosslinked polystyrene gel beads is catalyzed by $AlCl_3$. The reaction goes to completion upon refluxing at 73°C for 4 hours. Subsequent hydrolysis of the chlorophosphine intermediate leads to the isolation of the phosphinic acid resin.[45,46] The final resin is actually a mix of both primary and secondary phosphinic acid groups. The latter ligands arise from a limited amount of disproportionation by the intermediate dichlorophosphine groups to give diaryl monochlorophosphine groups and PCl_3; hydrolysis then yields the diaryl (secondary) phosphinic acid groups which can be detected by ion exchange but have no redox capacity. Characterization of a typical 2% DVB gel resin shows a phosphorus



(1)

capacity of 4.9 mequiv/g and an almost identical ion exchange capacity via sodium hydroxide titration. The primary acid capacity is determined via an iodine oxidation analysis (back-titration with sodium thiosulfate) and typically shows a value of 2.5 +/- 0.5 mequiv/g. This leads us to conclude that the phosphinic acid resin is fully substituted with phosphorus ligands, all of which display ion exchange sites and half of which display redox capacity. The purely ion exchange phosphonic acid resin was prepared from the phosphinic resin by peroxide oxidation. The sulfonic acid resin was also prepared for a subsequent comparative metal ion study with the phosphinic resin in order to isolate the influence of the redox reaction on the metal ion extraction results.

Metal ion studies

The ability of the redox reaction to dominate metal ion extractions can be illustrated by Figure 1.[47] The plot of percent metal ion loaded onto the resin from solution at equilibrium as a function of the initial ratio (R_i) of mequiv M^{+n}/mequiv resin acid sites shows significant affinity for zinc on the part of both the phosphinic and phosphonic resins. The affinity for Hg(II) by the phosphonic resin is greater still but, most importantly, the highest level of affinity for Hg(II) is shown by the phosphinic resin. Since the R_i value accounts only for the ion exchange reaction, the 136% loading observed at an R_i of 1.50 indicates the intervention of the redox mechanism. This is further confirmed by the results summarized in Figure 2 for both the phosphinic and sulfonic acid resins. Contacting a constant volume (5 mL) of aqueous mercuric nitrate solution of varying concentration (0.1 mequiv Hg(II) for an R_i of 0.1, 0.3 mequiv Hg(II) for

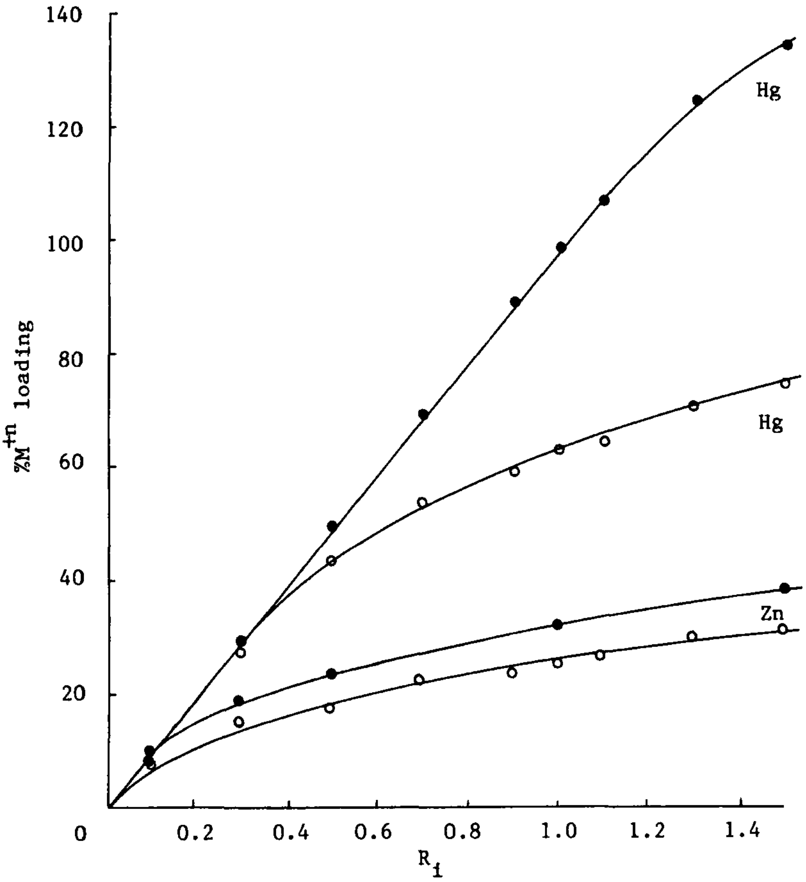


FIGURE 1
$\%M^{+n}$ loading as a function of R_i (no Na^+ in solution). (● Phosphinic, ○ Phosphonic) Reprinted with permission from S.D. Alexandratos and D.L. Wilson, Macromolecules, 19, 280 (1986). Copyright 1986 by the American Chemical Society.

an R_i of 0.3, etc.) with a constant concentration (1 mequiv) of resin acid sites, shows the loading capacity series of resins as phosphinic >> sulfonic >phosphonic. The redox mechanism thus allows for a higher level of mercury absorption from solution than even the highly

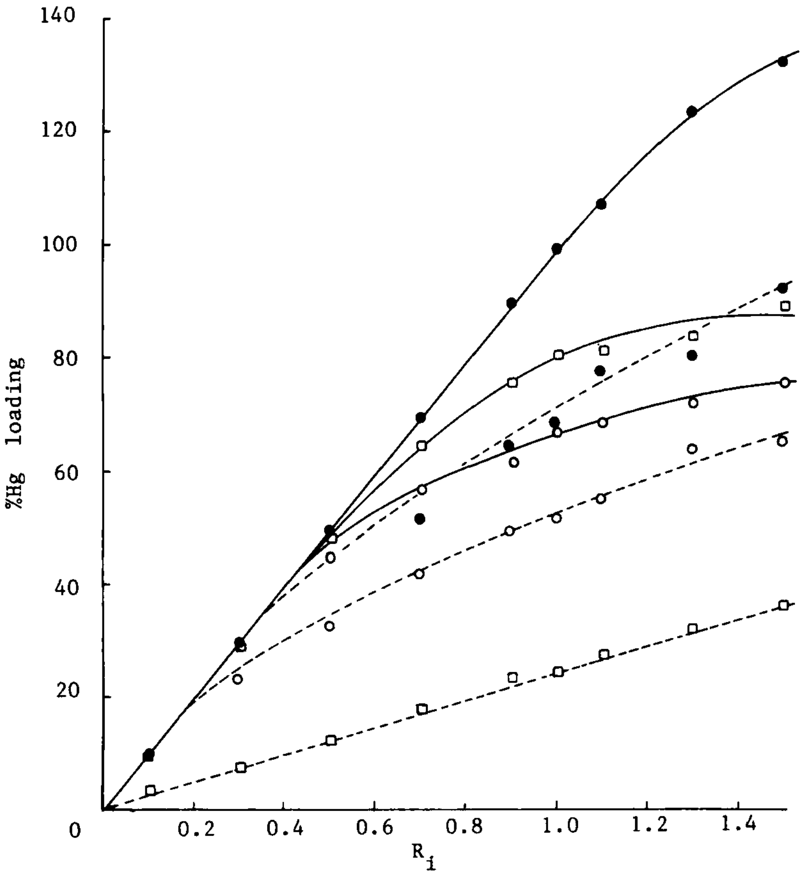
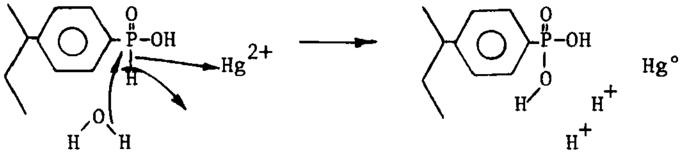


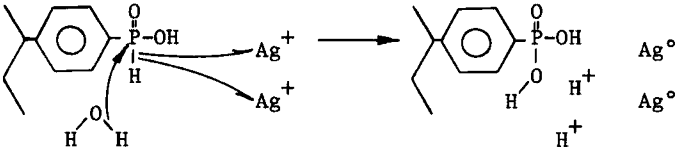
FIGURE 2
%Hg loading vs. R_i with (---) and without (——) Na^+. (● Phosphinic, ○ Phosphonic, ◻ Sulfonic) Reprinted with permission from S.D. Alexandratos and D.L. Wilson, Macromolecules, 19, 280 (1986). Copyright 1986 by the American Chemical Society.

acidic sulfonic resin can attain. Extractions which maintain a constant 4N nitrate background through the addition of varying levels of sodium nitrate yield a resin loading series of phosphinic > phosphonic > sulfonic. The redox mechanism continues its selective reactivity for Hg(II) under conditions where the pure ion exchange mechanism, as typified by the sulfonic resin, loses its selectivity due to the exchange with sodium ions. That the phosphonic resin loads to a significantly higher level than the sulfonic resin in the presence of sodium ions is evidence for the inherently greater selectivity of phosphorus over sulfur acids, as will be further confirmed later (v.i.). The redox reaction with the phosphinic resin which is responsible for its Hg(II) selectivity is postulated to occur via equation (2). Qualitative evidence for the redox reaction is the presence of metallic mercury which collects on the bottom of the vial containing the macroporous resin. Quantitative evidence is provided by regenerating the resin acid sites after mercury contact with 8N nitric acid and then repeating the sodium hydroxide titrimetric analysis: the new acid capacity is greater than the original capacity by the amount of mercury absorbed.



(2)

The phosphinic acid resin has also been found to reduce silver ions via equation (3) to the free metal form.[47] A complete R_i study which quantified both the amount of silver absorbed from solution and the new resin acid capacity after subsequent regeneration of the acid sites, led to the conclusion that, at equili-



(3)

brium, the phosphinic resin reduces all of the metal which it has absorbed to the maximum permitted by its primary acid capacity, after which point the ion exchange mechanism is utilized.

Mercury and silver ions have similar reduction potentials to the free metal (0.85 V and 0.80 V, respectively). An attempt was made to define the minimum metal ion reduction potential required by the phosphinic resin below which recovery of the free metal would be obviated. Thus, along with Hg(II) [E^o= 0.85V], Cu(II) [E^o= 0.34V], Sn(II) [E^o= -0.14V] and Zn(II) [E^o= -0.76V] were contacted with the phosphinic resin as a measure of the degree to which the redox reaction was favored for the different metal ion reduction potentials. While the reduction potential is clearly a variable of the thermodynamics, not the kinetics of a reaction, successful correlations between the two are not unprecedented[49] allowing for at least tentative conclusions. In this case, Hg(II) shows the most favorable kinetics (2 hours to 100% oxidation) and highest E^o; Sn(II) and Zn(II) show no resin oxidation at all and have the lowest E^o's; and Cu(II) shows a slow rate of oxidation (240 hours to 80% oxidation) and also has the intermediate E^o value. That metal ion reduction is definitely occurring, albeit at a slow rate, is evidenced by the disappearance of the blue aqueous copper nitrate color and formation of a fine metallic layer of copper on the bottom of the vial. It is thus probable that the minimum metal ion reduction potential below which the redox reaction does not occur is somewhere between 0.0 and 0.3 V with a rapid reaction rate at room temperature requiring a value greater than 0.5 V. Along these lines, it is important to note that the phosphinic resin is completely stable to prolonged contact with water, 4N sodium nitrate, and 4N nitric acid under ambient conditions.

Important selectivity advantages for the phosphinic resin over the sulfonic resin are evident from a distribution coefficient study involving the recovery of lanthanides and actinides from aqueous solutions.[50] The distribution coefficient is defined as the concentration ratio of metal ion in the organic (i.e., resin) phase to metal ion in the aqueous phase. Equation (4) represents the extraction process at equilibrium.

$$M^{+n} + nA^{-} + \overline{R\text{-}H} \rightleftharpoons \overline{R_n\text{-}M} + nH^{+} + nA^{-} \qquad (4)$$

M^{+n} = metal ion in aqueous solution
A^{-} = associated anion in aqueous solution
$\overline{R\text{-}H}$ = resin phase in the acid form
$\overline{R_n\text{-}M}$= resin phase in the metal-exchanged form

The standard equilibrium constant is then given in equation (5) which is rewritten as equation (6) in terms of the distribution coefficient. The logarithmic

$$K = ([\overline{R_nM}][H^{+}]^{n}) / ([M^{+n}][\overline{RH}]) \qquad (5)$$

$$D = [H^{+}]^{-n} K [\overline{RH}]^{n} \qquad (6)$$

$$\log D = n\,pH + (n \log [\overline{RH}] + \log K) \qquad (7)$$

form of the equation is its most useful form as it emphasizes the dependence of the extraction on the pH of the aqueous solution (equation (7)). Measuring log D as a function of solution pH with trace levels of solution ions (i.e., $<10^{-4}$ N) so as to keep the rightmost term constant, may be expected to yield a straight line with slope n, the number of protons exchanged for each metal ion transferred into the resin phase. For a pure ion exchange reaction, the slope is also the valence of the metal ion; it can be less than the valence, though, due to the formation of intermediate salt complexes. Note that a purely coordinative mechanism gives a slope of zero since no protons are exchanged into the solution and the extraction is pH-independent.

The extraction of europium and various actinides was studied at radiotracer levels from acidic solutions of varying strength (4N, 2N, 1N, and 0.2N HNO_3).[50] In order to verify that any observations were not simply artifacts of the changing ionic strength, experiments were also run at a constant ionic strength by adding enough $NaNO_3$ to each of the above acid solutions to yield a constant 4N nitrate background for all four solutions. The performance of the phosphinic resin was compared to that of the sulfonic resin. The comparison here is more of two purely ion exchange resins since the reduction potentials of the lanthanide and actinide ions are much too low for them to be affected by the phosphinic resin's redox reaction.

The results with europium, given in Figure 3, are quite representative. In solutions of varying acid strength, the sulfonic resin ion exchanges with the europium; the log D/pH correlation yields a slope of 3, as expected for exchange with the trivalent Eu(III) and can be taken as evidence that Eu(III) is probably the only ionic species present in solution. Under the same conditions, the phosphinic resin yields a slope of 1.75 suggesting that the neutral salt complex is also being extracted in a proportion with the trivalent Eu(III) so as to give the observed slope. Clearly, then, coordination of the neutral salt to the phosphinic resin through the phosphoryl oxygen is an important additional mechanism in metal ion extractions. That this conclusion is practically independent of the solution ionic strength is seen by the fact that the correlation

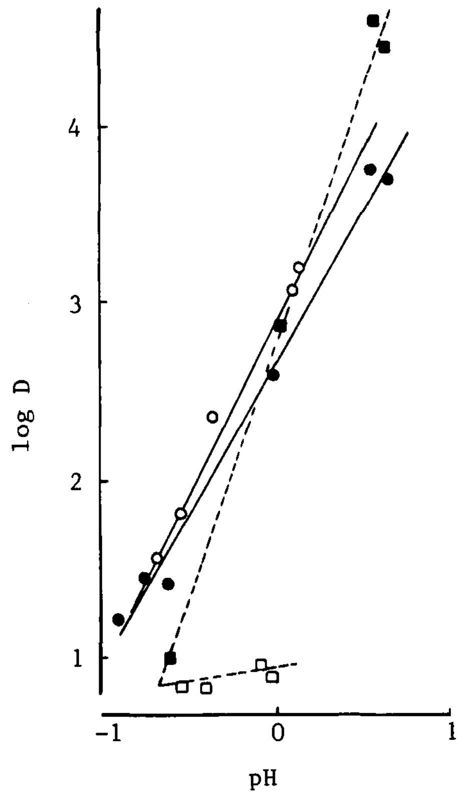


FIGURE 3
Log D vs. pH for Eu(III) extraction (● Phosphinic, without Na$^+$ in solution; ○ Phosphinic, with Na$^+$ in solution; ■ Sulfonic, without Na$^+$ in solution; □ Sulfonic, with Na$^+$ in solution) Reprinted with permission from S.D. Alexandratos, D.R. Quillen and W.J. McDowell, Sep. Sci. Tech., 22, 983 (1987). Copyright 1987 by Marcel Dekker.

at constant 4N nitrate background yields similar log D values and a slope of 1.90. The selective nature of the phosphinic resin is emphasized by the results obtained with the sulfonic resin under constant nitrate conditions: sodium exchange with the sulfonic resin depresses the distribution coefficients by up to three orders of magnitude while there is practically no effect on the phosphinic resin. Similar conclusions can be drawn from studies with americium, uranium and thorium.[50]

The strongly coordinating ability of the phosphoryl oxygen is thus seen to be essential to the selectivity displayed by the phosphinic acid ligand, especially in low pH aqueous solutions where its ion exchange ability might be expected to be diminished. The importance of an additional coordinative capability on the part of polymer-supported extractants was then investigated in detail in the second class of DMBP's.

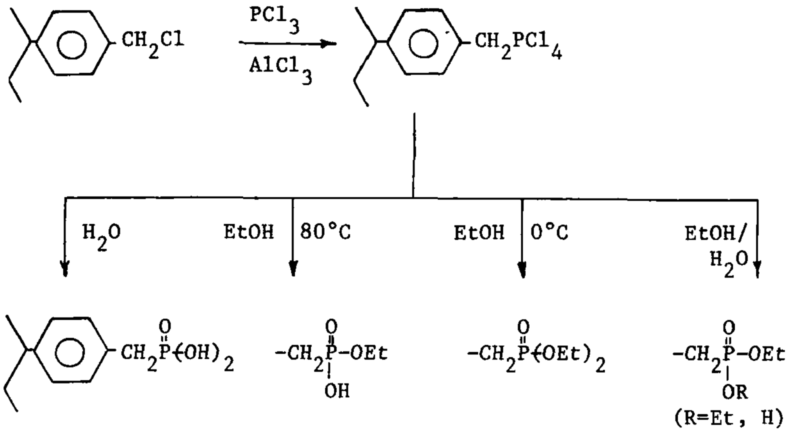
CLASS II DMBP's: ION EXCHANGE/COORDINATION RESINS

The importance of organic-soluble coordinating extractants in metal ion recovery processes is well established.[52] Particularly widespread have been compounds with a phosphoryl oxygen as the coordinating site. Both tributylphosphate[53] and trioctylphosphine oxide[54] have been used in the recovery of metals as diverse as the actinides and the first row transition series. Extensive studies with the phosphorus-based compounds and with amines such as quinoline[55] show them able to extract metal ions from water by forming inner sphere and outer sphere complexes thus replacing waters of hydration. This also leads to the observation of synergistic extraction in which a coordinating extractant along with a liquid ion exchange extractant can, together, remove greater amounts of metal from water than either one could alone due to the formation of mixed complexes.[56] The mixed complexes are formed by replacing most of the waters of hydration with the coordinating extractant or else having it directly ligate to the central metal ion; in both cases, a more organophilic complex is formed which distributes to a greater extent into the organic phase.[57]

Purely coordinating polymeric extractants have been prepared. In addition to those noted in the Introduction, polymeric dipyridylamines have been found to show a selectivity for iron (III) over chromium (III),[58] polymeric macrocycles can show selectivity for Group IA ions,[59] and polymeric phosphine oxides can be used in the recovery of uranium from seawater.[60] A significant problem with polymeric coordinating extractants can be a low apparent metal ion capacity due to their limited hydrophilicity and, hence, accessibility. In some cases, this problem can be overcome through the synthesis of a support network with a high level of macroporosity. For example, a thiol resin with a gel support structure showed no mercury loading capacity but showed significant capacity with a macroporous network.[61] An alternative, and more general, solution is to synthesize bifunctional polymers with ion exchange ligands for enhanced ionic accessibility and coordinating ligands for enhanced selectivity. Such polymers form our second class of DMBP's, the ion exchange/coordination resins.

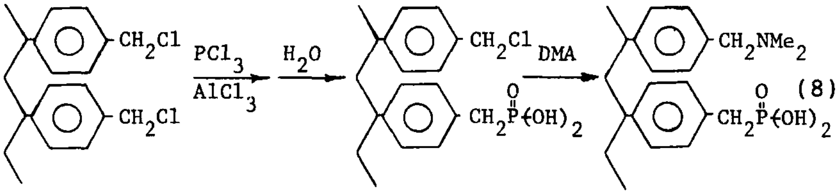
Synthesis

The ion exchange ligand in the Class II resins is the phosphonic acid group; the coordinating ligand is either a phosphorus ester or an amine.[62] Synthesis of the phosphorus acid/ester resins is summarized in the scheme below. The initial point for each resin is the poly(vinylbenzyl chloride) support with 2% DVB cross-linking prepared via suspension polymerization. The primary advantage to this route is that it allows for the preparation of any of the resins indicated by



simply adjusting the conditions of the solvolysis reaction on the intermediate. Hydrolysis of the intermediate leads directly to the pure phosphonic acid resin. Ethanolysis leads either to the pure phosphonate monoester resin or diester resin depending upon the reaction temperature (80°C and 0°C, respectively). Bifunctional diester/monoester resins having differing concentrations of the two ligands can be prepared by adding various amounts of water to the ethanol quench solution. An excess of water over ethanol leads to a bifunctional resin with monoester/diacid ligands. All resins except the diester resin show a total phosphorus capacity of approximately 3.5 mequiv/g indicating that the polymer is 70% - 80% functionalized. The diester resin is functionalized only to approximately 50% capacity (1.88 mequiv P /g): the $-CH_2PCl_4$ intermediate must be prepared at this lower functionalization level in order to ensure a mild ethanolysis reaction which seems to be critical to maintaining the integrity of the diester moiety.

Synthesis of the diacid/amine Class II resin is given by equation (8). A low temperature (40°C) phosphorylation reaction yields an intermediate resin with 50% functionalization to the diacid. Subsequent reaction with dimethylamine leads to the diacid/amine bifunctional resin with an approximately equal mix of the two groups.



(8)

Comparative study of Class I and Class II resins: Transition metal ion recovery

The utility of the phosphinic resin, especially over the commercially available sulfonic resin, was indicated by the extraction studies with mercury, silver, europium, and the actinides. In order to fully define a given resin's ability to interact with different metal ions under a variety of conditions, a metal ion affinity series is being established with six transition metal ions having a wide range of hard/soft character. The affinity series is currently being established under highly acidic conditions (4N HNO_3 to 0.2N HNO_3) at a constant 4N nitrate background through the addition of appropriate levels of sodium nitrate.[63] A study is underway to determine whether affinity reversals occur in less acidic (pH 2-4) conditions.

The results to date are summarized in Table I. The logD values for six metals (iron(III), mercury(II), silver, manganese, cobalt(II) and zinc) with seven resins from a single representative solution (1N HNO_3/ 3N $NaNO_3$) are presented. Clearly, any detailed explanation must await completion of all log D/pH plots, but some important points are already evident. The sulfonic resin is completely non-selective for the

TABLE I

METAL ION AFFINITY SERIES FOR THE DMBP RESINS
LOG D FROM 1N HNO_3/3N $NaNO_3$ BACKGROUND SOLUTION
0.0001N INITIAL METAL ION CONCENTRATION

	Resin						
M^{+n}	SO_3H	PHOOH	$PO(OH)_2$	NMe_2	$acid/NR_2$	Ester	Diester
Fe^{+3}	0.76	4.15	3.66	(0%)	3.63	3.67	0.44
Hg^{+2}	0.78	3.70	1.54	1.53	1.40	3.09	0.99
Ag^{+}	0.83	1.06	1.36	0.63	0.72	2.16	2.09
Mn^{+2}	0.64	0.67	-0.01	-0.60	0.00	0.11	-0.07
Co^{+2}	0.38	0.23	-0.14	-0.24	0.03	-0.03	-0.28
Zn^{+2}	0.48	0.20	-0.23	-0.41	-0.25	-0.26	-0.24

different ions, loading to log D levels less than 1, probably because it is exchanging with the excess sodium ions also present. The DMBP's are more selective. All except the diester resin show a very high affinity for Fe(III), then Hg(II) and Ag(I) under these conditions. The diester resin shows an opposite trend with Ag > Hg > Fe. The phosphinic resin shows the highest affinity for Hg(II) relative to the remaining resins and this is almost surely due to intervention by the resin's redox reaction. The silver ion affinity is much less than mercury's, in spite of the fact that silver is also reduced by the phosphinic resin at much higher concentrations. It is likely that silver is not reduced, or reduced at a much slower rate, under these highly dilute conditions due to the stoichiometric requirements of the redox reaction: two silver ions must be in close proximity to each other and in close proximity to a P-H bond in order for the two-electron transfer to occur, and this has a low probability in dilute solution conditions. That the redox component is critical to the very high mercury loading observed with the phosphinic resin is further indicated by the results obtained with the structurally similar phosphonic resin. The biggest effect upon going from the phosphinic to the phosphonic ligand is the precipitous drop in the log D value for mercury making it almost indistinguishable from silver. The mercury/silver separability can then be enhanced by placing amine groups near the diacid groups to yield the diacid/amine bifunctional resin or by monoesterifying the diacid groups to yield the phosphonate monoester resin. In both cases, the Fe > Hg > Ag trend is maintained. The trend reverses to Ag > Hg > Fe upon fully esterifying to the diester resin; this, along with the phosphinic resin results and the high Fe capacity displayed by the other phosphorus resins, are the most important observations to date.

The observations noted above and the full log D/pH plots for the complete set of resins, as well as for various liquid extractants being studied as controls, are being utilized to form a comprehensive theory of ionic recognition in polymeric ligand to metal interactions. Based on the present results, it seems as if ionic recognition can be controlled by two mechanisms which superimpose themselves on the inherent coordinative attraction defined by the principles of hard-soft acid-base theory.[64] Ionic recognition is thus subject to **reaction control** or **steric control** of the coordinative interaction. At this point, the phosphonic acid and monoester resin results indicate that the inherent coordinative interaction with the polymeric phosphoryl ligand tends to a preference for Hg(II) over Ag(I) ions (the separation factor (SF, which is the ratio of the distribution coefficients) for Hg/Ag with the phosphonic resin is 1.5 and with the monoester resin is 8.5).

The phosphinic resin, on the other hand, vastly prefers Hg over Ag (SF 437.) due to reaction control of the extraction process (which leads to consumption of Hg(II) into mercury metal). The diester resin shows an affinity reversal (SF(Hg/Ag) 0.08) due to steric control of the extraction process which leads to a preference for the less bulky $Ag^+NO_3^-$ ion pair.

Continuing studies focus on the principle of reaction control vs. steric control of ionic recognition in polymer-supported complexes and its implications for the design of specific metal ion complexing polymers.

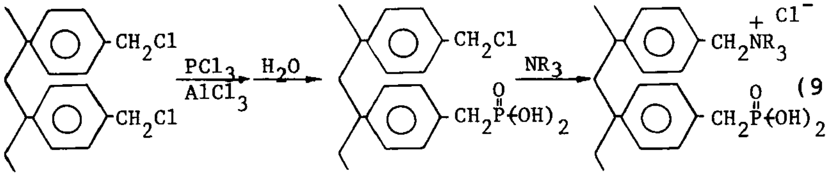
CLASS III DMBP's: ION EXCHANGE/PRECIPITATION RESINS

Metal ion recovery through reduction to the free metal is not a reasonable option if the ion has a low reduction potential, as does, say, barium. Recovery with a coordinating agent requires the availability of a specific coordinator which may or may not be readily synthesized. In many cases, removal of metal ions from aqueous solutions by the formation of insoluble salts is quite easily accomplished. Precipitation thus forms a third option in metal ion recovery processes. Electroplating facilities, for one, remove metal ions from the wastewater by precipitation of the hydroxide salts.[65] While this yields water of much higher purity, a continuing problem is recovery of the metals from the resulting sludge. Monofunctional ion exchange resins which introduce the precipitating ion into the aqueous solution containing the species targeted for removal have also been used.[66] For example, a sulfonic acid cation exchange resin in the barium form removes sulfate from an aqueous stream through barium sulfate precipitation. A significant problem with the monofunctional resins, though, is that clogging of the micropores leads to a low apparent capacity while attempts to separate the precipitate from the resin in a continuous flow system requires very careful control of the flow rate and other solution variables.

The third class of dual mechanism bifunctional polymers combines the ion exchange and precipitation reactions within the same support network in order to facilitate intra-bead formation of the insoluble metal salt.[67] This, then, would localize the precipitate within each particle and allow for its recovery through resolubilization into a concentrated solution. Potential problems with resin clogging clearly indicate the need for a support network with significant micro- or macroporosity. The central idea behind the Class III resins is that a cation exchange ligand will activate the access mechanism by ion exchanging with the metal ion in solution bringing it near another ligand to which an anion would be electrostatically bound. The anion, in turn, would be chosen so that contact with the cation would activate the recognition mechanism leading to the formation of an insoluble salt.

Synthesis

As with the Class II resins described above, the ion exchange ligand in the Class III resins is the phosphonic acid group. The classic anion exchange ligand, which is also appropriate in the current situation, is the quaternary amine group. The synthesis from poly(vinylbenzyl chloride) is summarized in equation (9). The initial support is crosslinked with 2% DVB in order to maximize the available microporosity. The parallel with the diacid/amine resin is apparent; the principal difference is amination with a tertiary instead of a secondary amine. The resins synthesized to date have had an approximately equal mix of phosphorus and amine sites. As seen in equation (9),


(9)

the chloride ion is ionically bound to the resin. Through different acid or soluble salt elutions, the supported anion can be changed according to the metal ion targeted for recovery via the precipitation reaction.

Metal ion studies

Important variables which have been studied to date are: (1) the effect of varying the hydrophobic nature of the amine moiety from trimethyl to tributylamine; (2) the effect of varying the anion for precipitation of a targeted metal cation; and (3) the effect of varying the solution-resin contact time. The experiments have been carried out under batch conditions which should thus indicate how susceptible the resins are to clogging. Along with the bifunctional trimethylamine/diacid and tributylamine/diacid resins, control experiments were run with the monofunctional amine and phosphonic acid resins, each pretreated under exactly the same conditions as the bifunctional resin prior to the metal ion experiments. Results involving the removal of silver ions from water via AgCl and AgSCN precipitation are presented in Table II. In each case, 100 mL of approximately 0.01N metal nitrate solution was shaken for the indicated contact time with enough resin to yield 1 mequiv phosphorus and/or amine sites; thus, the initial ratio of mequiv metal ion in solution to mequiv resin active sites was 1. The resins were placed in the indicated anionic form by elution with 1L/h of either 1N HCl or 1N KSCN. A 1L/h water wash followed each elution. The phosphonic acid resin was

TABLE II

%Ag(I) ABSORBED FROM SOLUTION AS A FUNCTION OF TIME FOR MONOFUNCTIONAL AND BIFUNCTIONAL AMINE/ACID RESINS

	Resin						
	$PO(OH)_2$	NMe_3X	NMe_3X/acid		NBu_3X	NBu_3X/acid	
time			calc	expt		calc	expt
	Anion (X): Cl^- via HCl elution						
5min	31.1	89.5	65.4	67.6	17.3	25.0	57.7
1h	30.7	98.8	70.7	68.4	76.1	50.6	60.8
24h	31.6	98.5	70.9	69.6	98.7	61.0	60.6
	Anion (X): SCN^- via KSCN elution						
5min	43.4	37.4	39.9	43.7	2.4	25.4	32.5
1h	44.0	85.3	68.3	68.4	4.6	26.7	40.3
24h	43.7	98.3	75.8	71.7	25.6[a]	35.8	67.6

[a] 17h data point which is equivalent to the 6h point

also eluted in order to ensure that the diacid ligands were in the same ionic form as in the bifunctional resin.

The results clearly show that very high levels of metal ion recovery are indeed possible through the precipitation reaction. Focusing first on the AgCl reaction, we note that the bifunctional trimethylamine/acid resin removes more Ag(I) from solution than the monofunctional phosphonic acid resin (68.4% vs. 30.7% after 1h) and that both display rapid rates of reaction (<5 minutes to equilibrium). That cation exchange/precipitation is not the only mechanism of action for the bifunctional resin is seen from the monofunctional amine resin: essentially quantitative silver removal occurs within 5 to 10 minutes via anion exchange between the resin chloride anion and the solution nitrate anion followed by solution precipitation of AgCl. Given the results from the two monofunctional resins, we can calculate the performance to be expected from the bifunctional resin if the two groups are acting independently. This may be done by summing the quotient of each group's mole fraction in the bifunctional resin with its monofunctional resin performance. Doing so allows us to conclude that the two groups are indeed acting independently when on the same polymer backbone; for example, at 5 minutes, the calculated %Ag absorbed is 65.4 while experimentally it is 67.6. Increasing the resin organophilicity by substituting tributyl groups for the trimethyl groups on the amine moiety decreases the rate of chloride-nitrate exchange in the monofunctional amine resin (17.3% Ag absorbed at 5 minutes vs. 89.5% with the trimethylamine resin). On the other hand, the bifunctional tributylamine/acid resin shows no concomitant drop in reaction rate: the equilibrium value of 60% Ag absorbed is attained, again, within approximately 5 minutes. This is the first indication of bifunctional group cooperativity leading to **polymer-supported synergistic extraction** wherein both groups operating together extract greater amounts of metal than either one could alone. This is verified by calculating the %Ag absorbed based on the monofunctional resin results and comparing it to the bifunctional resin performance. At 5 minutes contact, 25.0% Ag absorbed is expected while more than twice that (57.7%) is found. It is important to note that the same equilibrium value is attained (61% calculated and found) at 24 hours which indicates that solution anion exchange has been slowed but not eliminated.

A resin/anion system which would significantly suppress solution anion exchange so that the precipitation reaction could be localized almost entirely within the resin bead was defined by utilizing the relatively organophilic thiocyanate anion for the precipitation reaction (Table II). It was reasoned that a more organophilic anion would tend to remain on the resin rather than ion exchange into the aqueous solution but still be available for the precipitation reaction once cation exchange occurred. The thiocyanate anion seemed to be an ideal candidate because it is a soft, polarizable anion which should prefer an organophilic support more than the hydrophilic nitrate anion, it forms the insoluble AgSCN salt, and it is readily supported onto the resins via KSCN elution. Results with the monofunctional trimethylamine resin show that the polymer ligand controls the overall reaction since anion exchange still occurs given that quantitative AgSCN precipitation occurs. Calculation of the bifunctional resin performance shows that experiment parallels independent functional group behavior. The situation, though, changes dramatically when the organophilic thiocyanate anion is supported onto the organophilic tributylamine moiety. The corresponding monofunctional resin shows that the anion exchange reaction is slowed to such an extent that, at equilibrium, only 25% Ag is removed from solution compared to quantitative reaction with the trimethylamine resin. It is therefore very significant that the bifunctional tributylamine/acid resin consistently exceeds the calculated performance. Bifunctional group cooperativity leads once more to polymer-supported synergistic extraction but now over the entire time studied so that cation exchange of the Ag(I) into the resin activates the precipitation reaction with the thiocyanate anion to yield intra-bead AgSCN salt formation. The key point is that a soft anion must be supported on an organophilic moiety for bifunctional group cooperativity to be evident; this will then lead to insoluble metal salt formation localized within the resin bead. For polymer-supported synergistic extraction to be observed, as it is in this case, conditions must be chosen within the resin so that the recognition mechanism is inactive until a set metal ion is absorbed into the resin at which point it intervenes with the net effect of creating a highly specific polymer bead for the targeted metal ion.

CONTINUING STUDIES

Research is continuing with all three classes of the dual mechanism bifunctional polymers. The Class I resins are being studied in order to establish the kinetics of the redox reaction relative to the ion exchange reaction for different metal ions. Novel Class II resins are being synthesized with an emphasis on sulfur-containing ligands. Equilibrium studies with both resin classes are being carried out with a variety of metal ions in order to establish the inherent coordinative ability of the different phosphoryl ligands utilizing the principles of hard-soft acid-base theory. The net effect of varying macroporosity levels in the polymer support for the Class III resins is being studied in order to establish the influence on the kinetics and the ease of salt recovery.

Concurrent with the synthesis and characterization of new DMBP's for metal ion complexation reactions is the application of these polymers, and the development of others, for bioseparations.

CONCLUSION

Multifunctional polymers as enhanced molecular/ionic recognition agents are being synthesized and characterized within different separation processes. The underlying concept maintains that specificity in polymer to molecule/ion interactions is dependent upon multi-point attachments of varying strength. With metal ions, dual mechanism bifunctional polymers have been found to impart specificity to metal ion recovery reactions through the superpositioning of recognition mechanisms (redox, coordination, and precipitation) onto the access mechanism (ion exchange). Such polymers, as well as others with higher functionality, are being studied for the purification of proteins.

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