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Synthesis and Characterization of Bifunctional Phosphinic Acid Resins

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ABSTRACT: A new bifunctional polymer-supported extractant for use in metal ion recovery has been synthesized incorporating primary phosphinic acid/secondary phosphine oxide, as well as primary and secondary phosphinic acid ligands, depending on the method of synthesis. Emphasis is on polystyrene in bead form as the polymer support at various divinylbenzene cross-link levels and either with or without macroporosity. Functionalization is with PCl_3 and various levels of $AlCl_3$ as catalyst at temperatures ranging from −78 to +73 °C. From a study of the resin properties as a function of the synthetic variables, we make the following mechanistic conclusions: (1) under mild conditions (≤0 °C), 20% substitution to primary phosphinic acid groups occurs; (2) with increasing temperature (23 °C), the extent of reaction increases to 50% with a combination of primary acid and triarylphosphine oxide groups which arise from Friedel–Crafts secondary cross-linking; (3) under forcing conditions (73 °C, high $AlCl_3$ level), 100% substitution occurs with dichlorophosphine groups followed by a disproportionation reaction giving rise to primary acid and secondary oxide groups; (4) secondary phosphine oxide groups can be further hydrolyzed to secondary phosphinic acid with strong base. Macroporosity has an influence at higher cross-link levels on both extent of functionalization and reagent accessibility: complete functionalization and reagent accessibility is maintained only with macroporous resins when more than 8% divinylbenzene is utilized for cross-linking.

Introduction

The concept of immobilizing reagents onto polymer supports for use in organic reactions has received a good deal of attention;[1] utilizations include polymers as phase-transfer catalysts,[2] protecting groups,[3] acid catalysts,[4] resolving agents,[5] photosensitizers,[6] and metal ion complexing agents in asymmetric synthesis.[7] Polymers as metal ion complexing agents have also seen important use in solvent extraction chemistry.[8,9a] Principles that are understood in liquid–liquid extraction processes are extrapolated to solid–liquid extraction processes by the synthesis of polymers to which extractant ligands are covalently bonded[9b] or in which extractants are physically entangled;[9c] it is our research into the former concept that is the subject of this report[10] (our research into the latter concept will be reported in due course).

Commercial styrene-based ion-exchange resins, such as Amberlite IR-120 (a sulfonic resin),[11] Duolite C-63 (a phosphonic resin),[12] Dowex A-1 (a carboxylic resin),[13] and Amberlite IRA-900 (a quaternary ammonium ion resin),[14] can be used as metal ion extractants, as can polymeric neutral extractants such as poly(diallyl allylphosphonate)[15] and poly(styrene-*g*-phenyltrimethylenephosphine oxide).[16] Other examples include the polymeric 8-hydroxyquinolines,[17] carbamates,[18] acrylates,[19] and crown ethers.[20] Our research objectives in the synthesis of polymer-supported extractants can be summarized as follows:

(1) Develop an understanding of the role of the polymer support in the extraction process and define conditions in which the polymer can enhance the selectivity displayed by the extractant ligand.

(2) Develop commercially useful resins which show good selectivity in acidic solutions.

(3) Develop bifunctional extractants which contain acid and oxide moieties within the same polymer network. In some liquid systems, use of both an ionic and a neutral extractant within the same solution allows for synergistic extraction in which more metal is extracted than either extractant would complex alone;[8] the successful synthesis of an analogous polymeric system would allow for the first example of polymer-supported synergistic extraction.

In following our first objective, we decided to focus on polystyrene as the polymer support. Polystyrene is an industrial polymer with an economical synthesis; it is resistant to degradation by acid/base/oxygen under ordinary conditions; aromatic substitution reactions allow for the synthesis of a wide variety of high-capacity resins; adjustment of the synthetic variables allows for variation in the attrition–diffusion properties of the polymer network;

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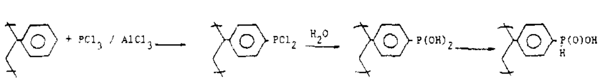
and the synthetic variables allow for a wide enough variation in network characteristics to study the effect of the polymer backbone on the selectivity displayed by the extractant ligand.

In light of our second objective, all of our initial studies have centered on phosphorus-based acids. Polymeric phosphonic acids are known to have inherently greater selectivity than the sulfonic acids while ion exchanging at significantly lower pH values than the carboxylic acids.[21] The focus on phosphorus-based acids also permitted significant progress toward our third objective: the scheme we devised allowed for the synthesis of a phosphinic acid/phosphine oxide bifunctional ion-exchange resin which may lead to the observation of polymer-supported synergistic extraction.

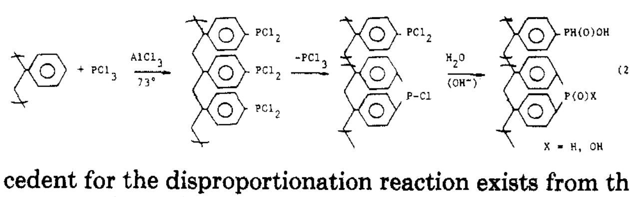
Results and Discussion

Synthesis. The polystyrene support was synthesized by suspension polymerization:[22] 2–30 wt % divinylbenzene (DVB) was added along with styrene to an aqueous layer containing polyelectrolytes as suspension stabilizers; the polymerization (80 °C/10 h) yielded beads approximately 1 mm in diameter. Addition of DVB as cross-link agent is critical because as the % DVB increases, the matrix strengthens and allows for greater attrition resistance; on the other hand, the matrix also becomes less flexible, which leads to decreased exchange kinetics and reagent accessibility. Consequently the second critical parameter, macroporosity, was introduced: addition of a given level of 4-methyl-2-pentanol to the monomer mix allows for the synthesis of macroporous (or macroreticular (MR)) beads which contain approximately 50 vol % porosity and 500–1000-Å macrochannels.[23] As macroporosity increases, the matrix becomes more open, leading to increased exchange kinetics and reagent accessibility, but this comes at the cost of increased friability. It, therefore, becomes important to balance the cross-linking–macroporosity requirements of the system to maximize bead strength and exchange kinetics/reagent accessibility.

The functionalization of polymer supports to phosphonic acid resins has been studied. They are readily produced by the Friedel–Crafts reaction of PCl_3 onto polystyrene with an $AlCl_3$ catalyst followed by either chlorination then hydrolysis[12,24] or hydrolysis then oxidation with hot concentrated nitric acid.[25-29] Hydrolysis only of the intermediate dichlorophosphine allows for the isolation of a phosphinic acid resin (eq 1).[24,27] At one time, a phosphinic resin was commercially available as Duolite C-62.[27] It was our hypothesis, though, that if the phoshination with PCl_3 was allowed to go to completion, a disproportionation reaction should occur upon continued heating which would yield upon hydrolysis the primary (or monoaryl) phosphinic acid as well as a phosphine oxide which could further hydrolyze to a secondary (or diaryl) phosphinic acid depending on the experimental conditions (eq 2).[30] Precedent for the disproportionation reaction exists from the monomeric analogues: Brown and Silver found that dichlorophenylphosphine gave monochlorodiphenylphosphine with loss of PCl_3 upon heating with $AlCl_3$;[31] Kosolapoff and Huber isolated dichlorophenyl- and monochlorodiphenylphosphine in a 3:2 ratio upon refluxing benzene with PCl_3 in the presence of $AlCl_3$;[32] and Frank concluded that the hydrolysis of monochlorodiarylphosphine gave the phosphine oxide if the aromatic group was bulky (e.g., mesityl) and the secondary phosphinic acid if it was not bulky (e.g., phenyl).[33] If, then, the polymer backbone acts like the ultimate hindered substituent, the primary phosphinic acid/phosphine oxide ligands should be formed; if each phenyl group acts independently and does not hinder the hydrolysis, the primary/secondary phosphinic acid ligands should be formed but mild hydrolytic conditions could cause the reaction to stop at the phosphine oxide intermediate.



(1)



(2)

Given these considerations, we synthesized the polystyrene support at cross-link levels of 2–30 wt % DVB and with either no macroporosity (gel beads) or 50 vol % macroporosity (MR beads). The beads were functionalized with PCl_3 and various levels of $AlCl_3$ as catalyst at various temperatures (−78 to +73 °C) over a 4-h reaction time. Unless otherwise noted, the functionalized beads were hydrolyzed in 1 N NaOH to give the cation-exchange phosphorus resin. Hydrolysis goes to completion given that no residual chlorine is found in the resin by chlorine elemental analysis. The resin was conditioned to the acid form and the capacity analyzed by NaOH titration to give total acidity, elemental phosphorus analysis to give total substitution by phosphorus moieties, and iodine oxidation to quantify the presence of oxidizable P–H bonds (phosphine oxide and/or primary phosphinic acid). The gel resins were consistently found to absorb approximately 0.50 g of H_2O/(g of dry resin) while the MR resins absorb 0.75 g of H_2O/(g of dry resin). MR resins with levels of cross-linking as low as 2% DVB (made from a level of 4-methyl-2-pentanol comparable to ours) have been found to be macroporous by scanning electron micrographs.[34]

The syntheses were thought to lead to resins falling into one of the following three categories: (I) total acidity (OH) = total capacity (%P) > I_2 oxidation if primary/secondary acids present; (II) total acidity (OH) = total capacity (%P) = I_2 oxidation if only primary acid present; (III) total acidity (OH) < total capacity (%P) = I_2 oxidation if primary acid/oxide groups present. Note that the NaOH analysis is done on the intact beads while the %P analysis is done on beads solubilized with perchloric acid; the latter is a better indicator of total extent of functionalization. A comparison of the two values allows for conclusions on reagent accessibility: if total acidity (OH) is less than total capacity (%P) regardless of bead size in the NaOH analysis, then reagent accessibility through the cross-link network may or may not be a limiting factor.

Variable Cross-Link Level in MR Resins. Initial studies dealt with a 2% DVB MR resin functionalized with PCl_3 and 0.77 mol of $AlCl_3$/(mol of copolymer) at 73 °C/4 h; hydrolysis with 1 N NaOH gave a white opaque resin which analyzed as follows:

$$\text{total OH} = 4.41 \text{ mequiv/g}$$
$$\text{total \%P} = 4.61 \text{ mequiv/g}$$
$$I_2 \text{ oxidation} = 2.31 \text{ mequiv/g}$$

The results are consistent with case I listed above: the resin consists of primary and secondary phosphinic acid groups (2.31 and 2.10 mequiv/g, respectively). Assuming complete styrene substitution and the experimental value for extent of primary acid, the theoretical total acidity calculates to 4.46 mequiv, in agreement with experiment. Repeat analyses with different resins made under identical

Table I
Effect of Cross-Link Level on MR Capacity[a]

		capacity, mequiv/g					
		acid					
resin		primary	secondary	primary/secondary	total OH	total %P	theory
MS14A	2% DVB	2.31	2.10	0.91	4.41	4.61	4.46
MS14B	5% DVB	2.54	1.59	0.63	4.13	4.59	4.40
MS14C	10% DVB	2.45	1.50	0.61	3.95	4.29	4.09
MS14D	15% DVB	2.48	1.42	0.57	3.90	3.83	3.87
	PhPH(O)OH				7.08	7.19	7.04
	$PhP(O)(OH)_2$				12.84	6.45	6.33

[a] Functionalization with 0.77 mol of $AlCl_3$/73 °C.

Table II
Effect of Temperature on Capacity of 2% DVB MR Resins[a]

		capacity, mequiv/g					
		acid					
resin	temp, °C	primary	secondary	total OH	total %P	theory	reactn, %
DR8A	−78	1.33	0	*b*	1.12	5.77	19.4
DR8B	0	1.45	0	1.22[b]	1.30	5.77	22.5
DR8C	23	2.08	0	2.01	2.69	5.77	34.8
DR8D	73	2.31	2.28	4.75	4.59	4.46	100
MS14A	73	2.31	2.10	4.41	4.61		

[a] 0.77 mol of $AlCl_3$. [b] OH^- accessibility is limiting at lowest capacity; %P is a better measure of functionality.

conditions show reproducibility to ±0.2 mequiv/g; repeat analyses with the same resin show reproducibility to ±0.05 mequiv/g. That the acidic moieties are monoprotic is clearly indicated in Figure 1, which shows the pH titration curves of the 2% DVB resin and the model compounds phenylphosphinic acid and phenylphosphonic acid. The diprotic nature of phenylphosphonic acid is found while the curves for phenylphosphinic acid and the resin are quite similar; the polymeric phosphonic acid formed after the I_2 oxidation showed diprotic character identical with the model compound, and curves in the literature further support the ability to distinguish between a monoprotic and diprotic polymeric acid.[35] Long-term stability of the primary phosphinic acid sites was determined by NaOH titration and I_2 analyses on the same resin batch over the course of 1 year: the pH curve was consistently monoprotic and the I_2 oxidation value constant to ±0.2 mequiv/g. Diprotic phosphonic acid could be found only after the I_2 oxidation reaction. The stability of secondary phosphine oxide sites was established in the same manner. It is also important to note, especially for future metal ion extraction studies, that contacting the resin with 4 N HNO_3 for 17 h at room temperature results in no change in the functionality as determined by a NaOH titration curve.

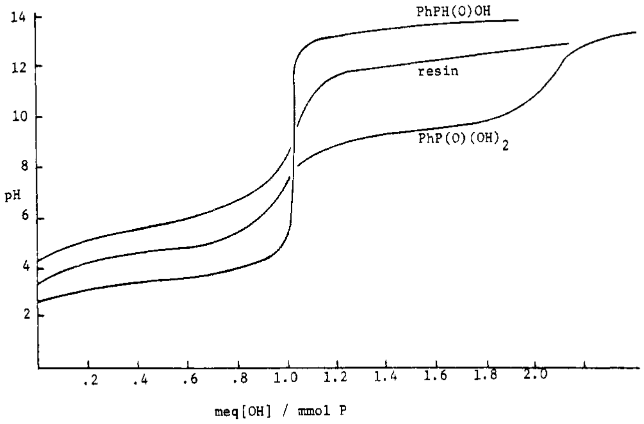


Figure 1. Titration curves for the polymeric resin, phenylphosphinic acid, and phenylphosphonic acid.

Table I shows the effect of cross-link level on the acidity of MR resins functionalized with 0.77 mol of $AlCl_3$/(mol of copolymer) at 73 °C; results for the NaOH and %P analyses of the model compounds are also shown to indicate the reliability of our experimental technique. The data permit the following conclusions for MR resins cross-linked with 2–15% DVB:

(1) Only primary and secondary acid groups are present; the primary acid capacity is constant (2.45 ± 0.10 mequiv/g).

(2) Comparison of the total acidity (OH) and the total (%P) capacity shows no reagent accessibility problem with the MR resins up to 15% DVB; additionally, comparison with theoretical values shows that levels up to 15% DVB do not hinder 100% functionalization at 73 °C.

(3) The ratio of secondary to primary acid sites falls by 40% as cross-linking increases from 2% to 15% DVB: secondary cross-linking via disproportionation becomes less favorable as the matrix becomes more rigid, consistent with the concept of increased site–site isolation as the cross-link level increases.[36]

(4) Cross-link levels up to 15% DVB are allowed in MR resins if required for bead strength without critical loss in observed capacity.

Temperature as a Variable in Resin Synthesis. Table II summarizes the effect of temperature on the acidity of MR resins cross-linked with 2% DVB and functionalized with 0.77 mol of $AlCl_3$/(mol of copolymer); the temperatures employed were −78, 0, 23, and 73 °C. Analyses are presented for two different resins functionalized at 73 °C in order to indicate the reproducibility of the experimental values. The data show the following:

(1) Only primary acid is formed at temperatures ≤23 °C given the equality in total (OH) acidity (or total (%P) capacity at −78 °C) and the I_2 oxidation analysis; the theoretical values are determined on that basis for DR8ABC.

(2) Accessibility by OH^- is limited at low functionality (≤0 °C) due to resin hydrophobicity; powdering DR8B and then titrating with NaOH yields 1.22 vs. 1.30 mequiv/g by %P analysis. (Insufficient sample prevented the same analysis with DR8A.)

(3) At 23 °C, the total (OH) acidity reproducibly agrees with the I_2 oxidation value but both are consistently lower

Table III
Effect of $AlCl_3$ Catalyst Level on Capacity of 2% DVB MR Resins[a]

		capacity, mequiv/g			
		acid			
resin	$AlCl_3$	primary	secondary	total OH	total %P
AW06A	0.2	2.43	0	2.02	2.39
AW06B	0.5	2.63	1.68	4.31	4.20
MS14A	0.77	2.31	2.10	4.41	4.61
AW06C	0.9	2.51	2.07	4.58	5.17
AW06D	1.2	2.26	2.69	4.95	5.17

[a] 73 °C.

Table IV
Effect of $AlCl_3$ Catalyst Level on Capacity of 2% DVB MR Resins[a]

		capacity, mequiv/g			
		acid			
resin	$AlCl_3$	primary	secondary	total OH	total %P
AW12A	0.2	1.61	0	*b*	1.21
AW12B	0.5	1.42	0	*b*	1.12
DR8C	0.77	2.08	0	2.01	2.69
AW12C	0.9	2.41	0	2.32	3.09
AW12D	1.2	2.28	0	2.09	3.01

[a] 23 °C. [b] OH^- accessibility is limiting at lowest capacity; %P is a better measure of functionality.

than the total %P value by approximately 0.7 mequiv/g; apparently some group is present which is inert to both I_2 and OH^- (v.i.).

(4) At 73 °C, both primary and secondary acid groups are present.

Overall, then, as the temperature of functionalization increases, the extent of reaction to acid sites monotonically increases.

Catalyst Level as a Variable in Resin Synthesis. The effect of $AlCl_3$ catalyst level on the acidity of 2% DVB cross-linked MR resins is summarized in Table III for functionalization at 73 °C and Table IV for functionalization at 23 °C. The results at 73 °C clearly show that increasing the catalyst level increases the acid capacity through formation of secondary acid groups; thus, the degree of secondary cross-linking to give the secondary acid groups increases as the amount of catalyst increases. Less forcing conditions such as lowering the temperature to 23 °C yields resins with only primary phosphinic acid sites as also indicated in Table II. This conclusion seems to be independent of the $AlCl_3$ level as shown by comparing the I_2 oxidation and total OH values in TableIV. Under mild conditions at 23 °C ($AlCl_3$ levels of 0.2, 0.5 mol/mol), only primary acid groups are present given the reasonable agreement between the I_2 oxidation and total %P analyses though the hydrophobicity of the resins makes wet chemical analysis difficult. At higher $AlCl_3$ level, the acid functionality increases over what is found at lower levels, but seems to remain constant within the range studied (0.77–1.2 mol/mol: 2.26 ± 0.16 mequiv/g). The increased hydrophilicity allows OH^- accessibility as shown by the close agreement with the I_2 oxidation values (total $(OH)_{av}$ = 2.14 ± 0.16 mequiv/g). Grinding the beads to 400 mesh size and redoing the OH^- analysis further shows that accessibility is not a problem: agreement with the bead values is to ±0.05 mequiv/g. Once more, the most striking difference is between the total OH and total %P values; given the agreement possible between the two techniques (cf. Tables I and II) and the ease of reagent accessibility, the difference should be considered chemical and require a mechanistic explanation.

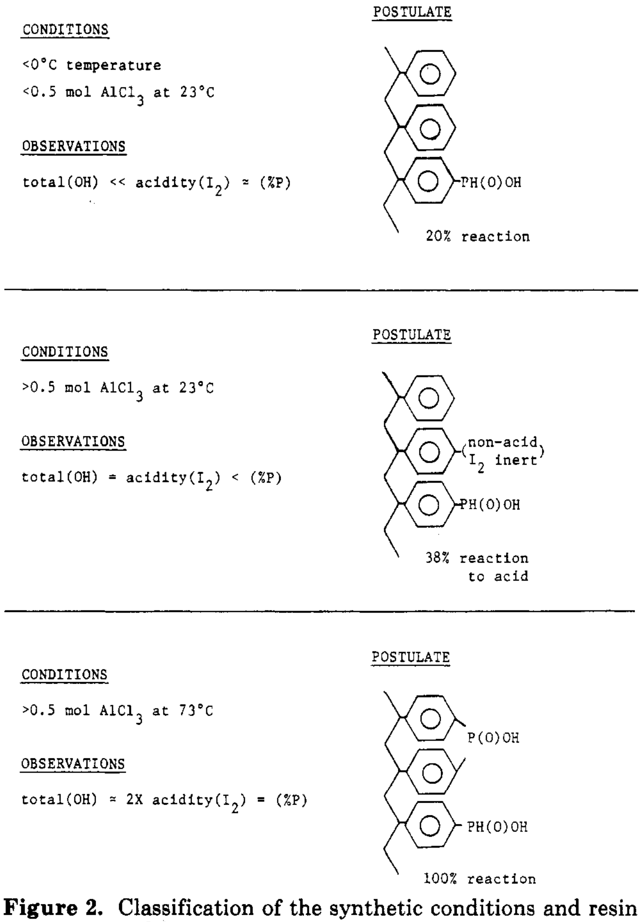


Figure 2. Classification of the synthetic conditions and resin structure resulting.

Mechanism. The synthetic conditions can be put into one of three categories, each with its own set of observations and corresponding postulate as to the nature of the resulting resin (Figure 2). Under mild conditions (very low temperature, low $AlCl_3$), the total acidity (via I_2 oxidation) is close to the value predicted by the %P analysis; this indicates only primary phosphinic acid sites with approximately 20% substitution on the phenyl rings occurring. The lowest energy process is thus monosubstitution to primary acid sites. With increasing temperature and/or increasing catalyst level, the extent of reaction increases to 50% with primary acid sites and a nonacidic/I_2-inert moiety: the total acidity found by NaOH ti-

Table V
Results from the Functionalization of Linear Polystyrene

resin	temp, °C	reactn with PCl_3	capacity, mequiv/g		
			total OH	total %P	total %P from beads
AW105A	−78	no gelation		0.79	1.12 (primary acid only)
AW105B	0	no gelation		0.71	1.30 (primary acid only)
AW86C	21	polymer gelled slightly		3.19	2.69 (primary acid/ tertiary oxide)
AW61B	73	gel to elastic polymer	4.52	4.95	4.59 (primary/ secondary acid)

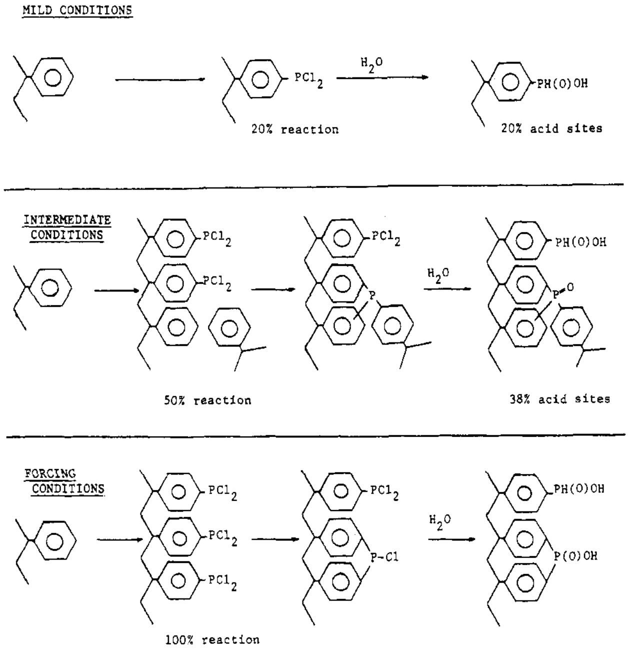


Figure 3. Mechanism of the functionalization reaction.

tration is equivalent to that found by I_2 oxidation and both are lower than the %P analysis by 0.7 mequiv/g; consistent with this observation would be the presence of tertiary phosphine oxide arising from Friedel–Crafts cross-linking. Precedence for Friedel–Crafts cross-linking comes from a study of chloromethylation reactions.[37] Under forcing conditions (high $AlCl_3$ and high temperature), 100% substitution occurs with PCl_2 moieties followed by disproportionation giving rise to the primary and secondary phosphinic acid sites. The mechanism of functionalization is summarized in Figure 3. We are currently studying temperatures between 20 and 73 °C in order to determine the point at which the disproportionation reaction becomes evident.

Secondary Cross-Linking in Linear Polystyrene. The resins synthesized under forcing conditions are of greatest utility because they have the highest capacity and greatest hydrophilicity allowing for good reagent accessibility with minimum resin bed volumes. Additionally, the conclusion as regards secondary cross-linking via disproportionation becomes, perhaps, the most important finding of this work: by proper control of the synthetic conditions, it is conceivable that the phosphine oxide (precursor to the secondary phosphinic acid) can be isolated on the resin and utilized for metal ion extractions. Evidence for the presence of the secondary sites comes from comparison of the I_2, NaOH, and %P analyses; further support for this concept comes from experiments with linear polystyrene. Linear polystyrene and PCl_3 form a homogeneous solution; if secondary cross-linking occurs, the linear polymer should become insoluble and a precipitate found even prior to hydrolysis. The experiments were carried out at concentrations as in Table II at temperatures of −78 to +73 °C.

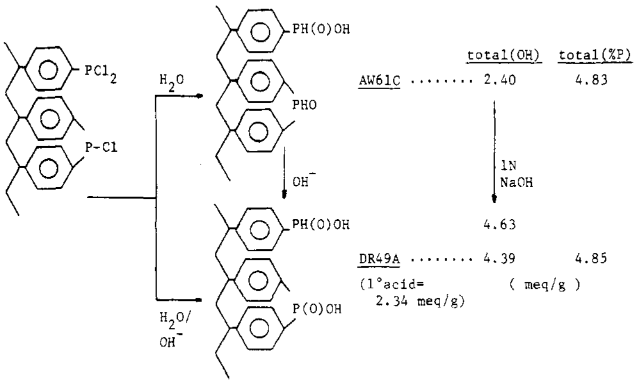


Figure 4. Synthesis of a bifunctional phosphinic acid/phosphine oxide resin. The value for total OH was obtained by titration with 0.1 N NaOH.

The results, given in Table V, show the following: where only primary acid is postulated (≤0 °C), no precipitate is formed during the reaction with PCl_3; on the other hand, the polymer gelled to an elastic, insoluble mass upon reaction at 73 °C. The unhydrolyzed elastic polymer was found to be insoluble in a variety of solvents including toluene, acetone, ethanol, and aqueous NaOH (where it hydrolyzed and swelled fourfold but never dissolved). The polymer gelled, but to a lesser extent, upon reaction at 21 °C. Gel formation can thus be taken as macroscopic evidence of secondary cross-linking.

Polymeric Acid/Oxide Extractant Synthesis. The concept of secondary cross-linking leading to the phosphinic acid caused us to concentrate our efforts on the adjustment of the synthetic conditions to allow for the isolation of the phosphine oxide in conjunction with the primary phosphinic acid. It soon became clear that the monochlorophosphine was being hydrolyzed directly to the acid by the action of the 1 N NaOH in the final step: hydrolysis in distilled water allowed for the isolation of a resin containing primary acid and secondary oxide sites. As summarized in Figure 4, resins synthesized under identical conditions (2% DVB gel copolymer beads; 0.77 mol of $AlCl_3$/73 °C) except for the final hydrolysis step showed identical %P elemental analyses (4.83 and 4.85 mequiv/g) but different OH^- titration values: 2.40 mequiv/g for resin hydrolyzed in H_2O and 4.39 mequiv/g for resin hydrolyzed in 1 N NaOH. The OH^- titration was carried out with 0.1 N NaOH and results indicate that the rate of neutralization is much faster than the rate of oxidation. The value of 2.40 mequiv/g, which must be due to the primary phosphinic acid sites, correlates well with the value for the primary sites by I_2 oxidation of the NaOH-hydrolyzed resin (2.34 mequiv/g). Additionally, stirring the H_2O-hydrolyzed resin with 1 N NaOH converts it to a total acidity of 4.63 mequiv/g, in agreement with its elemental analysis and results from NaOH-hydrolyzed resin. This system thus represents the first example of a bifunctional phosphinic acid/phosphine oxide polymeric extractant; a complete study of its metal ion extraction capability is currently under study.

Table VI
Effect of Cross-Link Level on Gel Acidity[a]

resin		capacity, mequiv/g		
		primary acid	total OH	total %P
DR49A	2% DVB	2.34	4.39 (4.41)[b]	4.85 (4.61)[b]
AW41A	5% DVB		4.31 (4.13)	4.41 (4.59)
DR49B	10% DVB	1.94	3.26 (3.95)	3.77 (4.29)
DR49C	15% DVB	1.13	1.39 (3.90)	2.45 (3.83)
DR49D	30% DVB	0.53		0.72

[a] Functionalization with 0.77 mol of $AlCl_3$/73 °C. [b] Comparable MR values.

Variable Cross-Link Level in Gel Resins. In order to define the effect of macroporosity prior to metal ion extraction studies, gel resins were synthesized at the same cross-link levels used for the MR resins. Table VI summarizes the data on the acidity of the resins functionalized with 0.77 mol of $AlCl_3$/(mol of copolymer) at 73 °C. The data permit the following conclusions for the gel resins cross-linked with 2–30% DVB:

(1) Comparison of the total capacities by %P elemental analysis shows that levels only up to 10% DVB allow for 100% functionalization at 73 °C.

(2) At 15% DVB, functionalization decreases (cf. %P analysis of gel vs. MR) as does reagent accessibility (cf. gel acidities obtained from OH^- vs. %P analysis).

(3) Reagent accessibility is lessened at 10% and 15% DVB levels for gel resins due to the tightness of the matrix; powdering the resins yields OH^- values in agreement with the %P analysis, thus emphasizing the importance of macroporosity at higher cross-link levels.

(4) At 30% DVB, functionalization decreases to 15% of maximum and the matrix is inaccessible to OH^-. A plot of acid capacity vs. %DVB shows that MR resins should be preferred at levels >8% DVB in order to avoid loss of active capacity and minimize resin bed volumes. Thus, macroporosity has an influence at higher cross-link levels on both extent of functionalization and reagent accessibility; its influence on the extent of metal ion extraction will be reported in a subsequent publication.[38]

Experimental Section

All reagents were purchased commercially and used without further purification unless otherwise noted.

Copolymer Synthesis. Styrene/DVB copolymer beads are synthesized by suspension polymerization.[22] In a typical preparation, gelatin (0.96 g), poly(diallyldimethylammonium chloride) (11.90 g, Calgon Corp.), and boric acid (6.33 g) are dissolved in 316.5 mL of H_2O. The pH is adjusted to 10.3 with 50% NaOH. The aqueous phase is poured into a 1-L round-bottom flask equipped with a condenser, dry nitrogen purge, a thermometer to which is attached a Therm-O-Watch temperature-control device (Instruments for Research and Industry, Cheltenham, PA), and an Eberbach Con-Torque stirrer with double-paddle stir shaft. The monomer mix is then added (286.7 g of styrene (Aldrich), 10.3 g of technical DVB (Dow Chemical Co.; analyzed to be 55.4% *m*- and *p*-DVB) for 2% cross-linking, and 3.00 g of benzoyl peroxide); the stir speed is set at 250 rpm. The suspension is heated over a 2-h period to 80 °C and the temperature held for 10 h. Complete polymerization is ensured by heating the system at 100 °C for 2 h. The beads are then washed 4 times with water and dried. MR beads are synthesized by replacing half the monomer mix with 4-methyl-2-pentanol (Aldrich) and adjusting the stir rate to 200 rpm. A 6-h steam distillation to remove the alcohol replaces the 2-h finish-off employed with gel synthesis.

Polymer-Supported Phosphorus Acid Resin. Copolymer beads (10 g, 0.10 mol, −20 +40 mesh) are placed with 130 mL of PCl_3 (Aldrich) into a 250-mL round-bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. The copolymer is allowed to swell with the PCl_3 for 1 h. The $AlCl_3$ catalyst (Aldrich) is added at the levels indicated in the paper and the system taken to the desired temperature over a 1-h period. The temperature is held for 4 h and then taken to room temperature. The beads are isolated from the PCl_3 solution and hydrolysis is effected at 0 °C with 500 mL of 1 N NaOH or H_2O saturated with NaCl. The resin is washed with H_2O until neutral, placed in a glass frit funnel, and conditioned with 1 L of H_2O, 1 N NaOH, H_2O, 1 N HCl, and H_2O, each with 1-h elution times. The NaOH elution must be omitted if the phosphine oxide groups are to be maintained. The resin is then suction dried at 720 mmHg/5 min. A weighed sample is dried at 110 °C/16 h in order to determine the amount of water absorbed by the resin.

NaOH Titration Analysis. A suction-dried (hydrated) resin sample corresponding to 0.5-g dry weight is placed with 50 mL of H_2O into a beaker and titrated with 0.1 N NaOH. Additions of 1.0 mL are made hourly (45 min is usually required for full exchange per addition) with the neutralization followed by a Corning Model 130 pH meter.

Phosphorus Elemental Analysis.[39] Oven-dried and powdered resin (20 mg) is digested by heating with 5 mL of HNO_3/(5 mL of 72% $HClO_4$) to a clear and colorless solution. The solution is cooled and diluted to 100 mL with H_2O. To a 10-mL aliquot is added 3.5 mL of 72% $HClO_4$, 4.5 mL of fresh amidol reagent (1 g of recrystallized amidol (Aldrich), 2.7 mL of H_2SO_4, 10 g of Na_2SO_3, and 90 mL of H_2O), and 3.5 mL of ammonium molybdate solution (4.14 g in 50 mL of H_2O). The solution is diluted to 50 mL and allowed to develop for 30 min. Its absorbance is then measured at 700 nm on a Bausch and Lomb Spectronic 21 and the %P determined from a Beer's law plot using a series of KH_2PO_4 standards. Excellent reproducibility is found as long as complete digestion is obtained and all glassware is rinsed completely free of phosphate detergents.

Iodine Oxidation Analysis.[40] A suction-dried (hydrated) resin sample corresponding to 0.5-g dry weight is placed with 20 mL of 0.2 N KI_3 and 2 mL of pyridine into a 100-mL bottle. The bottle is shaken vigorously for 22 h. Excess KI_3 is titrated with standard $Na_2S_2O_3$ and the P–H capacity calculated.

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Metal Ion Extraction Capability of Phosphinic Acid Resins: Comparative Study of Phosphinic, Sulfonic, and Carboxylic Resins Using Zinc Ions

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ABSTRACT: Bifunctional cation-exchange resins were evaluated as zinc ion extractants. Bifunctionality consisted of either primary and secondary phosphinic acid ligands or primary phosphinic acid/secondary phosphine oxide ligands. The performance of these phosphinic resins was compared to the zinc extraction ability of comparably cross-linked polystyrene-based sulfonic and carboxylic resins. For the phosphinic resins, the degree of extraction is determined by the initial ratio (R_i) of zinc ions to be absorbed and acid sites to carry out the exchange; the equilibrium point is independent of matrix rigidity to 15% divinylbenzene (DVB). Further, there is no dependence of zinc extraction ability on the total capacity or the presence of primary/secondary vs. primary only phosphinic acid groups vs. primary acid/secondary phosphine oxide groups at any given R_i level. For sulfonic resins, on the other hand, the zinc loading on the resin decreases at a given R_i as the amount of DVB increases from 2% to 15%. A similar conclusion is valid for the carboxylic resins although the zinc extraction is lower under similar conditions. In general, the phosphinic resins display superior extraction ability under comparable conditions. The unique dependence on R_i alone displayed by the phosphinic ligands is explained on the basis of ion pair formation. Current studies show that *phosphinic acid resins operate by both an ion-exchange and redox mechanism* depending on the reduction potential of the metal.

Introduction

The application of commercial ion-exchange resins to metal ion recovery from aqueous solutions is a concept which has received extensive study.[1] Strong acid cation exchangers are produced by covalent bonding of sulfonic acid groups usually to a cross-linked polystyrene network.[2] Contact with an aqueous solution of a metal ion allows for cation exchange to occur and the metal can then be recovered from the polymer by elution with an aqueous mineral acid solution. The ion-exchange effectiveness of a strong acid resin can be offset by a lack of selectivity, especially when the metal ion of interest is in trace amounts relative to common metals such as the alkali metal ions.[3] Selectivity is enhanced with the weak acid cation-exchange resins wherein carboxylate groups are bonded to either a styrenic or ethylenic network,[4] but this leads to a decreased ability to exchange in the acidic pH region (which is usually the region of interest in waste metal recovery).[5] Novel ion-exchange resins have been synthesized by bonding selective ligands onto commercial supports for the purpose of recovering specific metals;[6] such resins illustrate important principles, but are usually not commercially feasible due to their cost.

In liquid–liquid extractions, a cation-containing aqueous phase at a given pH is contacted with an extractant-containing organic phase; the organic phase consists of an

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