

Review

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*Industrial and Engineering Chemistry Research***

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100TH ANNIVERSARY REVIEW

Ion-Exchange Resins: A Retrospective from *Industrial and Engineering Chemistry Research*

Spiro D. Alexandratos*

Department of Chemistry, Hunter College of the City University of New York,
695 Park Avenue, New York, New York 10065

Ion-exchange resins comprise one of the most important scientific developments of the 20th century. Their applicability to water softening, environmental remediation, wastewater treatment, hydrometallurgy, chromatography, biomolecular separations, and catalysis was recognized in numerous publications. The principle of covalently bonding ligands to cross-linked polymer networks became the basis for the area of polymer-supported reagents. The journal *Industrial & Engineering Chemistry Research* and its predecessors have published some of the most important papers in this field. In celebration of its 100th anniversary, this review provides a retrospective of ion-exchange resins through publications appearing in this journal.

Introduction

Ion exchange consists of the interchange of ions between two phases. With ion-exchange resins, the resin—a cross-linked polymer network—is the insoluble phase to which an ion is electrostatically bound; when contacted with a solution containing ions of the same charge, an exchange can occur, the extent to which depends on the concentration of the ion(s) in solution and the affinity of the ion(s) for the insoluble phase relative to the solution phase (Figure 1). Both cation- and anion-exchange resins have been prepared. The different ion-exchange resins consist of different polymers and different ligands covalently bound to the polymers.

Ion-exchange resins are useful because of the insolubility of the resin phase. After contact with the ion-containing solution, the resin can be separated by filtration. They are also adaptable to continuous processes involving columns and chromatographic separations. Their insolubility renders them environmentally compatible since the cycle of loading/regeneration/reloading allows them to be used for many years. Ion-exchange resins have been used in water softening, removal of toxic metals from water in the environment, wastewater treatment, hydrometallurgy, sensors, chromatography, and biomolecular separations. They have also been used as catalysts, both in place of homogeneous catalysts such as sulfuric acid and to immobilize metallic catalysts.

Chronological Development. Over its 100-year history, *Industrial & Engineering Chemistry Research* has published some of the most significant papers on ion-exchange resins. This review provides a historical perspective of the field through a chronological examination of the concepts central to ion-exchange resins. As will be seen, the early papers develop applications with a limited number of resins while later papers expand the number of resins for new targeted applications.

Overview of 1909–1949. The phenol-formaldehyde polymer was introduced and cation exchange was ascribed to the phenolic

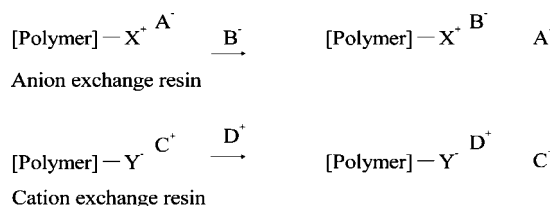
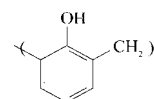


Figure 1. Exchange of ions between an insoluble (polymer) phase and a solution phase.

—OH group. The concept was extended to anion exchange by preparing a polymer from the reaction of formaldehyde with diaminobenzene. Industrial applications were developed, including catalysis and the recovery of natural products from dilute solutions. The discovery that ion-exchange ligands could be bonded to polystyrene led to a major shift away from the phenol-formaldehyde polymers. The polystyrene-based sulfonic acid cation-exchange resin and the trimethylammonium strong base anion-exchange resin were critical developments. The shift to polystyrene was due to the ability to form well defined beads via suspension polymerization and their applicability to column operations. Also developed was the methacrylate-based weak acid cation-exchange resin prepared as beads. The sugar industry became a major utilizer of ion-exchange resins for decolorization of sugar solutions.

Phenol-Formaldehyde Polymers. *Industrial & Engineering Chemistry* was there, in the beginning. The phenol-formaldehyde polymers were the first synthetic ion-exchange resins and Baekeland reported their synthesis in the first volume of *I&EC*.¹ The polymer, prepared under basic conditions and referred to as Bakelite, was already being applied to “more than forty different industries” and many additional applications were envisioned by Baekeland:



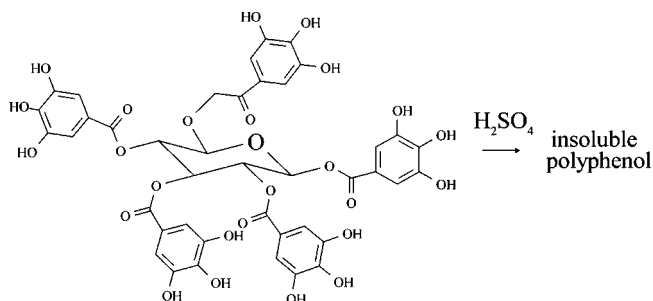
* To whom correspondence should be addressed. E-mail address: alexsd@hunter.cuny.edu.

"It makes excellent billiard balls of which the elasticity is very close to that of ivory, in short it can be used for similar purposes like knobs, buttons, knife handles, for which plastics are generally used. But its use for such fancy articles has not much appealed to my efforts as long as there are so many more important applications for engineering purposes."

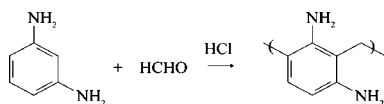
However, the application of Bakelite, and the phenol-formaldehyde polymer prepared under acidic conditions (referred to as Novolak) that was reported shortly thereafter,² to ion exchange was conceived not by Baekland but by Adams and Holmes almost three decades later (British Patents 450,308 and 450,309 (July 13, 1936); U.S. 2,104,501 (Jan. 4, 1938)). This led to an explosive development of the concept.

Alternate Polyphenols. A low-cost alternative to Bakelite was proposed when it was determined that tannins could be cross-linked with sulfuric acid to form an insoluble polyphenol.³ They were found to "...possess qualities such as cheapness, high exchange capacities, and resistance to aggressive waters..." and to "...exchange either sodium or hydrogen ions for calcium and magnesium...". A mechanism for the exchange was proposed:

"Why such materials exhibit base exchange is not definitely known. In the case of the polyhydric phenol-formaldehyde resins, it is probable that large molecules are built up in the way usual for phenol-formaldehyde condensations to produce substances which are capable of base exchanging in a manner similar to that of humus or lignin derivatives - that is, through functional phenolic groups."³



Anion Exchange. As use of the polyphenols for cation exchange increased, studies were begun to develop polymers for anion exchange. An early study described the preparation of polymers from the reaction of aniline, *m*-toluidine, *m*-phenylenediamine, or urea with formaldehyde, furfural, or furfuryl alcohol.⁴ The polymer found to have the best combination of final properties was that prepared with *m*-phenylenediamine and formaldehyde.



Water treatment was the primary application of these polymers:

"At present the chief interest in these methods of removing cations and anions from solutions comes from the field of water treatment, particularly from producers of boiler feed water for large, high-pressure, complete make-up steam power stations. The possibilities are such, however, that it is not unreasonable to expect that further applications will be found in the chemical industries."⁴

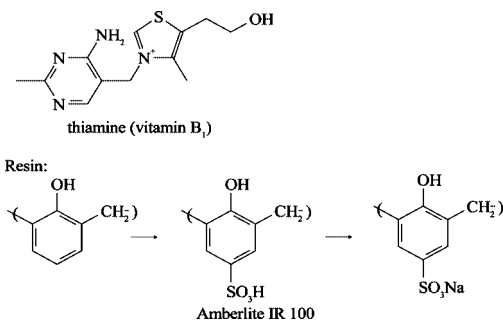


Figure 2. Thiamine and Amberlite IR-100.

Industrial Applications. The wide applicability of the new polymers to a range of industrial applications soon became evident:⁵

"Laboratory and field tests have proved the practicability of the use of resinous exchangers in the softening of water, the partial or complete removal of salts from water, sugar solutions, and protein solutions, in the recovery of traces of copper and other valuable metals, in the removal of iron and acids from industrial effluents and commercial products."⁵

Isotherm Studies. Amberlite IR-1, a phenol-formaldehyde polymer, and Amberlite IR-4, a polyamine-formaldehyde polymer, were identified as cation and anion-exchange polymers, commercially available from the Resinous Products and Chemical Company (a company set up with the participation of Otto Haas, later to become a division of the Rohm & Haas Company and then fully integrated into the company; Amberlite remains a trademark of the Rohm & Haas Company). Adsorption studies with acid and salt solutions showed that the polymers display Freundlich isotherms, typical of inorganic solids such as zeolites.⁶

Recovery of natural products. The potential of ion-exchange resins for the recovery of natural products was illustrated with the separation of thiamine from riboflavin.⁷ The ammonium site on the molecule allows for it to be bound onto a cation-exchange resin (Figure 2). Amberlite IR-100 in the sodium form was found to be effective. IR-100 is significant because it is a phenol-formaldehyde polymer that has been sulfonated. Sulfonation lowers the pH at which exchange can occur relative to exchange solely at the phenolic $-\text{OH}$. The process is useful for the recovery of thiamine from rice bran extracts.

Though the results are specific to thiamine, the concept is generally applicable to the analysis and recovery of natural products:

"The application of this method may proceed in two directions - as an analytical tool or in the recovery of thiamine from waste solutions. As an analytical tool the purity of the eluate is satisfactory. No interfering substances have been encountered. If desired, thiamine may be readily recrystallized from the eluate without extensive further purification. As a process tool to recover thiamine from natural sources, the resin offers a distinct potential advantage over zeolite BF an adsorbent: elution can be accomplished with a volatile acid instead of a salt which cannot be removed readily from the eluate."⁷

Functionalized Monomer Synthesis. An alternative route to the sulfonated phenol-formaldehyde polymer was detailed wherein the phenol was sulfonated first and that monomer then polymerized in the presence of formaldehyde (Figure 3). The product was referred to as Dowex 30 (Dowex

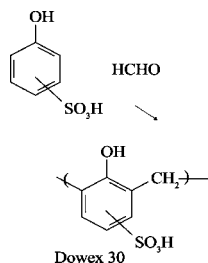
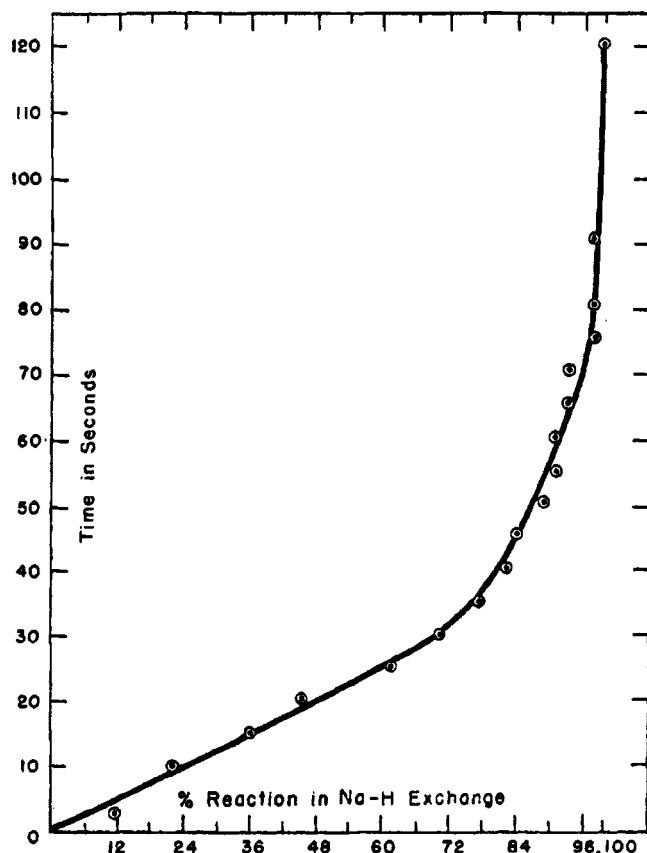


Figure 3. Preparation of Dowex 30.

Figure 4. Kinetics of Dowex 30 conversion from Na^+ to H^+ form. (Reprinted with permission from ref 8, Copyright 1946, American Chemical Society, Washington, DC.)

is a trademark of the Dow Chemical Company) and displays rapid kinetics of ion exchange (Figure 4).⁸

It was successfully applied to treating boiler feedwater:

"This resin has been installed in a boiler feed water purification plant for three years. In this application it softens lime-treated river water at 8–9 pH and maximum temperature of 100 °F from 60–70 ppm calcium carbonate hardness to less than 1 ppm. The resin has shown no volume loss, no increase in fines, and no loss of total capacity during this period."⁸

The two methodologies for the synthesis of ion-exchange resins was thus established sixty years ago: postfunctionalization of a polymer with ion-exchange ligands vs preparation of a functionalized monomer that is then polymerized. Whereas the latter technique ensures uniformity throughout the polymer, the former technique is usually easier to implement and, when done properly, yields a uniform polymer.

Catalysis by Cation-Exchange Resins. It was recognized that the sulfonated phenol-formaldehyde polymers could be used as catalysts, replacing homogeneous catalysts such as sulfuric

acid, in reactions that included ester formation, hydrolysis and alcoholysis, acetal formation and alcoholysis, and alcohol dehydration.⁹ Advantages to the use of the polymer are ones still being cited today: it can be used multiple times, compounds that polymerize in the presence of homogeneous acids readily undergo the targeted reaction, and the catalyst can be recovered by simple filtration. The esterification of oleic acid with butanol was found to proceed via second-order kinetics with a velocity constant that was directly proportional to the surface area of the catalyst.¹⁰

Strong Base Anion-Exchange Resins. The amine resins that had been developed with compounds such as *m*-phenylenediamine were capable of anion exchange only if the amine was protonated; that limited their use to acidic solutions. The presence of covalently bound quaternary ammonium sites on the polymer allowed anion exchange from neutral and alkaline solutions since the positive charge on the nitrogen did not depend upon protonation. These resins were referred to as strong base resins in order to distinguish them from the weak base resins that had tertiary amine sites in alkaline solutions. Amberlite IRA-400 was the strong base resin produced by the Rohm & Haas Co.¹¹ The affinity for a series of anions with this resin was determined to be: citrate > sulfate > oxalate > iodide > nitrate > chromate > bromide > thiocyanate > chloride > formate > hydroxyl > fluoride > acetate. Dowex 1 and Dowex 2 were the quaternary amine resins produced by the Dow Chemical Co. and reported to remove carbonic acid, silicic acid, amino acids, H_2S , and phenol from aqueous solutions.¹² Dowex 2 was applied in a plant that processed 2,500,000 gallons of water per day and it reduced the silica level to <0.05 ppm.¹³

Weak Acid Cation-Exchange Resins. The sulfonic acid ligand was an important addition to the phenol-formaldehyde polymers and its immobilization onto polystyrene beads led to the development of strong acid ion-exchange resins. The carboxylic acid ligand is a much weaker acid and it could be immobilized through the polymerization of methacrylic acid. A comparative study of the strong and weak acid cation-exchange resins (Amberlite IR-120 and IRC-50, respectively (Rohm & Haas)) demonstrated that the sulfonic acid ligand is capable of exchanging with alkali and alkaline earth ions but with relatively low selectivity while the carboxylic acid ligand is more selective for the divalent alkaline earth ions (Table 1).¹⁴

Resin Regeneration. The regeneration of exhausted cation resins was the major operating cost for their use.¹⁵ Variables in the regeneration were recognized to be H_2SO_4 vs HCl as the regenerant, amount and concentration of regenerant, flow rate, regeneration of the Na^+ vs the Ca^{2+} form of the resin, and downflow vs upflow.

Decolorization of Sugar Solutions. Refining crude sugar solutions became simplified by incorporating ion-exchange resins into the process.¹⁶ Passing the crude solution first

Table 1. Comparison of Cation-Exchange Equilibria of Carboxylic and Sulfonic Acid Cation-Exchange Resins

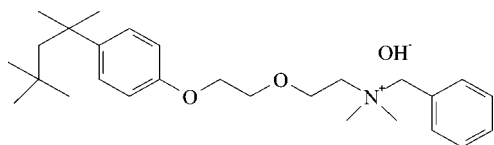
equilibria	Per Cent Exchange (Symmetry = 1)	
	Amberlite IRC-50	Amberlite IR-120
R-H + Na^+	0.004	46
R-H + Mg^{2+}	0.004	66
R-H + Ca^{2+}	0.012	69
R-Na + H^+	90	33
R-Ca + H^+	90	13
R-Na + Ca^{2+}	88	43
R-Na + Mg^{2+}	85	43
R-Ca + Na^+	10	15

through a cation-exchange resin removed inorganic cations, amine-containing bases and amphoteric compounds. A subsequent elution through an anion-exchange resin removed inorganic and organic acids. The final sugar solution was then found to be decolorized. Anionic, cationic and neutral compounds all contributed to the color of the solution, but anion-exchange resins decreased the color more than cation-exchange resins.

Separations with Metal-Containing Resin. Ion-exchange resins were modified in order to expand their applicability by binding a metal ion onto a resin through ion exchange and then reducing it to the zerovalent metal, making the metal the active site for subsequent separations. Thus, an amine-containing resin (Duolite A-3 from the Chemical Process Co.) was contacted with a solution of CuSO_4 to coordinate the Cu(II) to the amine, then the ion was reduced to Cu(0) with alkaline sodium hydrosulfite. The resulting copper-containing resin removed dissolved oxygen in water to <0.1 ppm.¹⁷

Overview of 1950–1959. It was proposed that ion-exchange resins could be selective for targeted ions by incorporating chelating groups into their structure. Applying the sulfonic acid cation-exchange resin as the catalyst for the inversion of sucrose showed that the degree to which the resin was cross-linked affected the kinetics thus marking the importance of reactant diffusion into the matrix as a variable. The application of the resins to deionization and wastewater treatment was developed further. Strong base anion-exchange resins were shown to be effective as catalysts in organic reactions and in the recovery of uranium from solutions.

Monobed Deionization. Deionization can require two resin beds by following one of two procedures: water can first pass through a cation-exchange resin to remove the cations and convert the salts into their corresponding acids, then pass through an anion-exchange resin to remove the anions; alternatively, water can pass through an anion resin then a cation resin, to again give deionized water. A third option was proposed:¹⁸ pass the water through one column consisting of both cation and anion-exchange resins to achieve deionization in a single pass. While regeneration was possible by separating the resin bed back to its constituent anion and cation resins, regenerating each separately, then recombining them, it was done without separation by passing HCl through the column to regenerate the cation-exchange resin, then using a regenerant for the anion resin, Hyamine 1622 (OH^-), which did not affect the cation resin. The unique feature of the regenerant is that the cation portion is too bulky to diffuse into the cation-exchange beads and thus they remain protonated as the reagent flows through the column while the OH^- ion regenerates the anion-exchange resin.



Inversion of Sucrose. The inversion of sucrose to glucose and fructose is catalyzed by HCl . The applicability of sulfonic and carboxylic acid resins to this process was studied and it was determined that the sulfonic acid resin is an effective catalyst. The rates of inversion increase as the particle size decreases and the resin porosity increases thus indicating that diffusion of sucrose through the resin bead and accessibility to the sulfonic acid ligand is the rate-determining step. Consistent with this, the rate of reaction decreases as the degree of cross-linking decreases (Figure 5).¹⁹

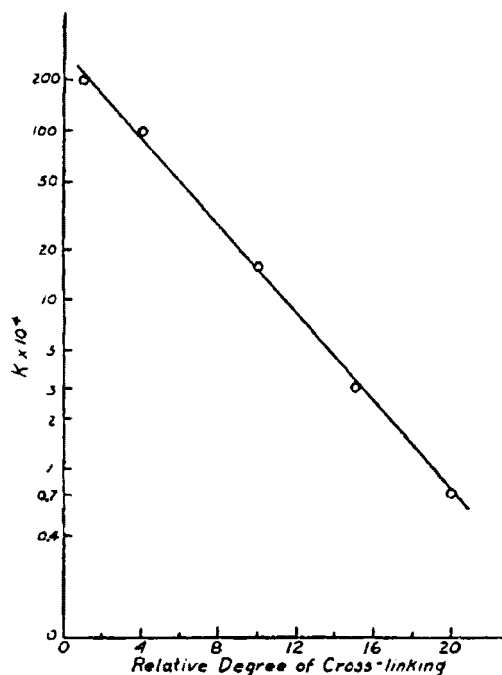
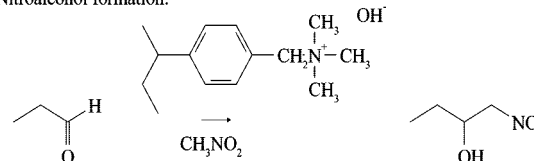


Figure 5. Variation in rate of sucrose inversion with degree of cross-linking. (Reprinted with permission from ref 19, Copyright 1951, American Chemical Society, Washington, DC.)

Wastewater Treatment. Wastewaters from electroplating operations offer an important opportunity for the recovery of metals that would otherwise go to waste and create disposal problems. Tin from wastewater containing sodium stannate from continuous sheet metal tinning mills was successfully recovered with a sulfonic acid cation-exchange resin by converting the soluble stannate salt (Na_2SnO_3) to insoluble metastannic acid (H_2SnO_3) which was a sludge that could, after settling for 8 h, be recovered by filtration; reconversion to a more concentrated sodium stannate solution allowed for the recovery of tin by electrolysis.²⁰

Catalysis by Anion-Exchange Resins. Appropriate anions ionically bound to strong base anion-exchange resins were applied as catalysts in organic reactions under conditions where exchange could not occur.²¹ The advantages are the same as those cited with cation-exchange resins as catalysts (multiple uses, applicable to column operations, pH-sensitive compounds are stable, and catalyst recovery by filtration). The resin in the hydroxide form was thus able to catalyze the formation of nitroalcohols from aldehydes and nitromethane (Figure 6). The OH^- abstracts a proton from the nitromethane, the resulting nucleophile attacks the aldehyde, and the OH^- is regenerated

Nitroalcohol formation:



Benzoin condensation:

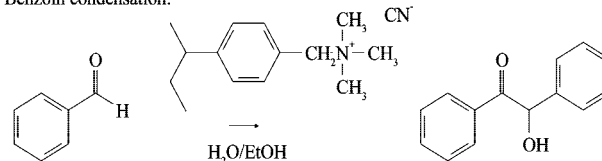


Figure 6. Anion-exchange resins as catalysts in organic synthesis.

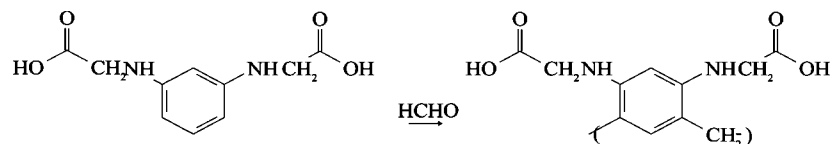


Figure 7. Polymerization of *m*-phenylene diglycine with formaldehyde.

in the subsequent step. The mechanism is generally applicable to the aldol²² and Knoevenagel²³ condensations. Catalytic activity is not limited to the hydroxide ion: ionically bound CN^- catalyzes the formation of benzoin from benzaldehyde (Figure 6).

Sugar Cane Juice Processing. Cation- and anion-exchange resins were used to process sugar cane juice for the removal of ash and salts. In a study with resins from different manufacturers (Amberlite, Dowex, Ionac, and Duolite resins), Dowex 50 was found to perform best.²⁴

Physical Stability of Cation-Exchange Resins. The continuous operation of cation-exchange resins through numerous load/regeneration cycles depends on their physical stability, i.e., the ability of the beads to resist fracture and disintegration into smaller irregular particles. It was found that the manner in which they are prepared from unfunctionalized polystyrene beads is critical to their stability.²⁵ The reaction with concentrated sulfuric acid must be done on beads that are fully swollen in an inert solvent; methylene chloride and trichloroethylene give good results since they are excellent swelling solvents. After sulfonation, the concentrated sulfuric acid in contact with the beads must not be diluted too rapidly with water because the swelling forces created by hydration of the sulfonic acid ligands will cause the beads to shatter; washing with sulfuric acid solutions of progressively lower acidity allows hydration to occur slowly. The resins must then be packed in a manner that maintains their complete hydration or they must be slowly hydrated prior to use.

Chelating Ion-Exchange Resins. The sulfonic acid resin is most valuable when different ions all need to be removed from water. The carboxylic acid resin is good at separating the alkaline earth from the alkali ions. Both cannot be applied if a particular transition metal ion needs to be removed from a solution containing different transition metal ions. A *specific ion-exchange resin* was thus defined as "one that under proper experimental conditions is characteristic of one ionic species only."²⁶ The preparation of a resin was described involving the condensation of *m*-phenylene diglycine dihydrochloride with formaldehyde (Figure 7). The ability of the resin to chelate metal ions through the carboxylate and amine groups led to greater selectivity among the divalent transition metal ions than was possible with the conventional ion-exchange resins. A later study of polymers from the reaction of formaldehyde with *o*-aminophenol, resorcinol, 2,4-dihydroxybenzoic acid, 2,4-dihydroxyacetophenone, and 8-quinolinol showed that the formaldehyde/quinolinol polymer had the highest selectivity for the ions tested.²⁷

Ion Exchange from Nonaqueous Solvents. Ion exchange can occur in solvents other than water though at slower rates. Sorption also depends on the ligand (as it does in water): Amberlite IR-120 (sulfonic acid) sorbs 4.00 mequiv Pb(II) per g resin while IRC-50 sorbs 0.06 mequiv per g.²⁸ (The Pb(II) was dissolved in the benzene as the naphthenate salt.) Ion exchange can be effective from isopropanol and this was applied to the treatment of waste solutions from the semiconductor industry by formulating a system to produce ultrapure isopropanol using anion and cation-exchange resins.²⁹

Sorption of Phenol. The removal of phenol and chlorinated phenols from wastewaters was known to be a serious problem. A strong base anion-exchange resin was reported to have a high capacity for phenols though the mechanism seems to have been sorption, rather than ion exchange, since ions were not released from the resin and the amounts sorbed exceeded its exchange capacity.³⁰ Sorption isotherms were similar to those obtained with charcoal. The phenols could be removed from the resin by elution with methanol. Resins with primary, secondary and quaternary amine sites sorb phenols but tertiary amine resins do not.³¹ Infrared spectra show binding between the amines and the phenols.

Uranium Recovery. Strong base anion-exchange resins were important to the recovery of uranium (as $\text{UO}_2(\text{SO}_4)_3^{4-}$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$) from processing operations. It was found that incorporating pyridinium groups along with the conventional trimethylammonium sites gave a resin with improved performance (Permutit SK and Permutit SKB).³² Regeneration and reuse of all strong base resins was critical to the economic viability of the process. Early breakthrough could be caused by the trapping of insoluble matter within the polymer network or by ions other than uranyl being strongly sorbed by the exchange sites. Silica, polythionate, cobaltcyanide, and molybdenum were identified as among the more prominent species responsible for poisoning of the resin. It was determined that the poisoning could be reversed by a slow elution with sulfuric acid as dilute as a 42.5% solution.³³

Overview of 1960–1979. Macroporous and ultrafine ion-exchange resins were introduced, greatly expanding their applicability. Resins were utilized for biomass conversion, the treatment of gaseous refinery streams, and the selective removal of boron from water.

Sorption of Gases. Dry anion-exchange resins were able to sorb SO_2 . In particular, Amberlite IRA-400 in the chloride form, had the potential to recover it from waste gas streams because of a high sorption rate.³⁴

Hydration of Olefins/Dehydration of Alcohols. In investigating how to get pure products from C_4 – C_5 refinery streams, it was determined that cation-exchange resins selectively hydrate the isoolefins in the stream to give tertiary alcohols.³⁵

Macroporous Resins. The introduction of macroporosity was a major advance in ion-exchange resin technology. The monomer phase used in the suspension polymerization was modified to include a porogen—a compound in which the monomer (e.g., styrene) was soluble but the polymer, as it formed, was not. This resulted in a change of bead morphology so that it became permanently porous. Sulfonation gave a macroporous strong acid cation-exchange resin. In one case (Amberlyst 15), the surface area of the resin was $42.5 \text{ m}^2/\text{g}$ (compared to $<0.1 \text{ m}^2/\text{g}$ for a conventional resin).³⁶ The advantage of macroporosity is shown in Figure 8. Whereas the conventional sulfonic acid resin (Amberlite IR-120) sorbs triethylamine from water at the same rate as the macroporous analogue (Amberlyst 15), the macroporous resin greatly outperforms the conventional resin in butanol and heptane. Thus, when the conventional resin is swollen (as in water), there is no need for a permanent porosity, but in nonswelling solvents, the porosity of the macroporous

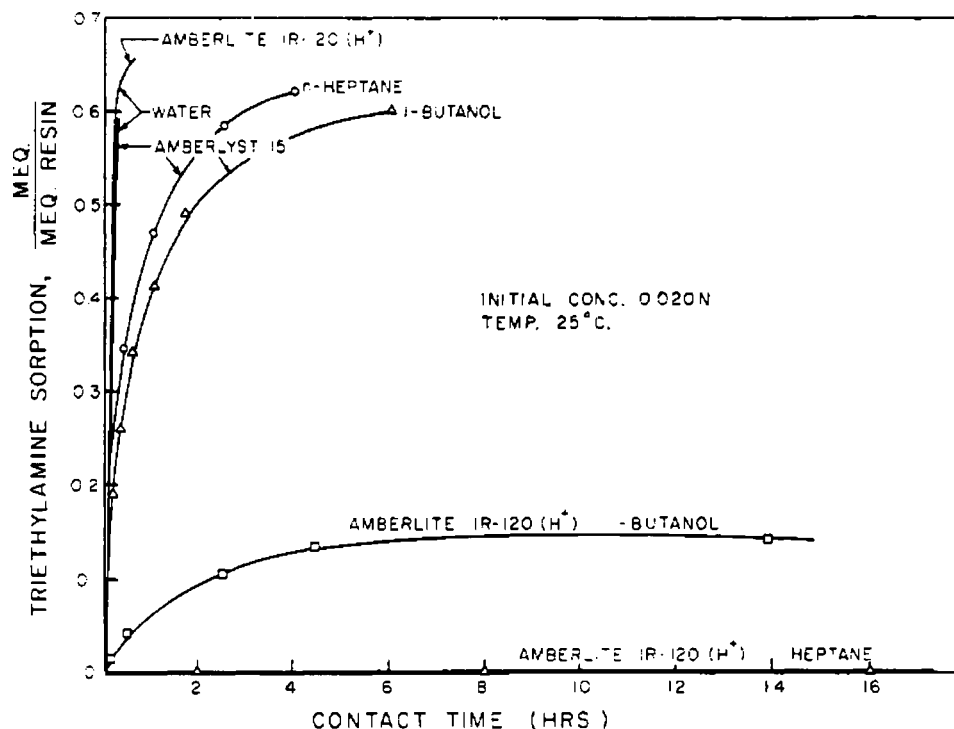


Figure 8. Comparative performance of conventional (Amberlite IR-120) vs macroporous (Amberlyst 15) resins in the sorption of triethylamine from different solvents. (Reprinted with permission from ref 36, Copyright 1962, American Chemical Society, Washington, DC.)

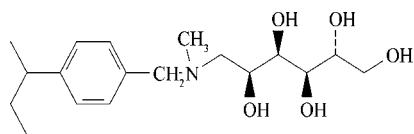


Figure 9. Immobilized *N*-methyl-D-glucamine as a boron-selective resin.

resin gives it an advantage in both the rate of sorption and the amount of substrate that is sorbed.

Boron-Selective Resin. Immobilizing *N*-methyl-D-glucamine onto chloromethylated polystyrene gave a resin (Figure 9) that was selective for the removal of boron as boric acid.³⁷ One intended application was the removal of boron from irrigation waters. In batch adsorption studies from a solution with 500 ppm NaCl and 10.8 ppm boron, the glucamine resin removed 100% of the boron initially present while a weak base resin removed almost none (final level of 10.7 ppm boron).

Ultrafine Resins. The particle size of ion-exchange resins was recognized as a variable that could limit the rates of reactions and the rates at which substrates were sorbed. A series of ion-exchange resins were thus prepared from polystyrene micropowders with a particle size of 0.5 to 1.5 μm (as compared to 450 μm for conventional ion-exchange resins).³⁸ Applications include their incorporation into paper for the rapid removal of organic pollutants from aqueous streams; and blending into plastics, films, coatings and fibers in order to impart antistatic activity, modify conductivity, control pH, improve dye retention, remove contaminating ions, absorb humidity, and act as a drug delivery agent.

Biomass Conversion. The following was written thirty-three years ago yet it is as relevant in 2008 as it was in 1975 (the lessons of history are often forgotten):

“Processes developed in the 1920’s to 1940’s for producing useful chemicals from farm products proved in most cases to be uneconomical because low cost natural gas and oil assured the success of a rapidly growing petrochemical industry. Recent events, how-

ever, have dramatized the need for replenishable raw materials such as farm products or, more particularly, waste materials from such products as alternate sources of industrial chemicals and polymers.”³⁹

Ion-exchange resins have played and continue to play a role in developing economical processes for converting biomass into valuable products. Sucrose can be converted to levulinic acid (5-oxopentanoic acid) with a strong acid ion-exchange resin. 5-Hydroxymethylfurfural is the intermediate and must stay in contact with the resin long enough to convert to levulinic acid. It was discovered that a sulfonic acid resin with small pores maximizes the yield of levulinic acid because the furfural is retained within the bead long enough for conversion to occur; resins with large pores permit the furfural to diffuse out of the bead and so decrease the yield of levulinic acid.

Deionization with Composite and Amphoteric Resins. Monobed deionization was one attempt to deionize water rapidly. Another attempt was the preparation of composite and amphoteric resins which placed the cation- and anion-exchange ligands in even closer contact.⁴⁰ A composite resin was prepared by grinding weak base anion-exchange and weak acid cation-exchange resins separately to a particle size of 10^{-5} m, mixing the resulting powders, and binding them together with polyvinyl alcohol and glutaraldehyde. Even greater contact of the functional groups was achieved by preparing a single resin with both carboxylic acid and secondary amine ligands; this amphoteric resin became commercially available as Amberlite XD-2. The amphoteric resin outperformed the composite resin by having a higher effective diffusivity for NaCl thus making it an appropriate resin for desalination processes.

Overview of 1980–1999. Chitosan, a ubiquitous form of biomass, was used as an alternative support for ion-selective resins. Bifunctional ion-exchange resins allowed for selectivity with rapid kinetics. Resins complexed with silver ions were used for olefin/paraffin separations. Metal ion separations were accomplished with different ligands.

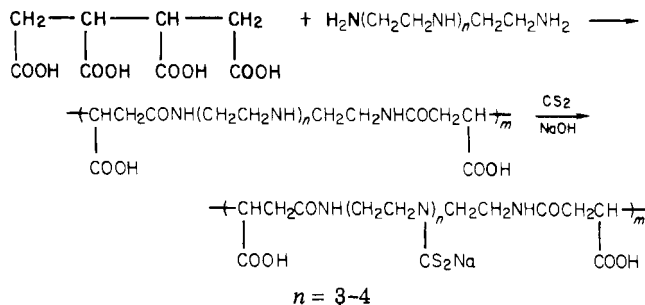


Figure 10. Chelating ion-exchange resin with carboxylic acid and dithiocarbamate ligands. (Reprinted with permission from ref 43, Copyright 1984, American Chemical Society, Washington, DC.)

Anion-Exchange Resins As Disinfectants. A strong base anion-exchange resin was used to ionically bind the triiodide, I_3^- , ion and it was effective as a broad spectrum bactericide and virucide in water.⁴¹ The I_5^- and I_7^- ions could also be supported on the resin.

Structural Variations in Anion-Exchange Resins. The great majority of ion-exchange resins use divinylbenzene (DVB) as the cross-linking agent to provide the resin with physical stability and insolubility. The preparation of macroporous resins requires the use of higher levels of DVB in order to obviate any problem with resin friability. It was proposed that copolymerizing styrene with low levels (1–2%) of hexahydro-1,3,5-triacryloyl-s-triazine (TAT) as an alternate cross-linking agent leads to anion-exchange resins (after chloromethylation and amination) with a range of morphological characteristics, controlled by the TAT and the chloromethylation conditions.⁴²

Uranium Recovery from Seawater. The recovery of uranium from seawater requires a highly selective resin due to the large number of ions present in much higher concentrations. A chelating ion-exchange resin with dithiocarbamate groups (Figure 10) was prepared and found to have a good affinity for uranium when contacted with seawater.⁴³ The resin is prepared by the reaction of butane-1,2,3,4-tetracarboxylic acid with tetraethylenepentamine and then converting a fraction of the secondary amines to dithiocarbamate with carbon disulfide. It was able to sorb 50 pg U/g resin per day from seawater that was then desorbed with 10% $(\text{NH}_4)_2\text{CO}_3$.

Using Biomass as an Alternate Support. The styrene-DVB copolymer is extremely versatile in being able to be modified with a large number of ligands. However, there has been research in identifying alternatives if they can be shown to have some advantage. Chitin (poly(*N*-acetyl-D-glucosamine)) is one

such alternative because it is abundantly available from the shells of crabs, shrimp and insects and is now handled as waste to be disposed. Deacetylation to give poly(D-glucosamine), otherwise known as chitosan, renders it soluble in acidic solutions through the primary amine group (Figure 11).⁴⁴ It can be used as a support for ligands by first rendering it insoluble with a cross-linking agent (e.g., ethylene glycol diglycidyl ether) and then reacting it with epichlorohydrin to give $-\text{CH}_2\text{Cl}$ groups. A subsequent reaction with poly(ethyleneimine) converts it into a chelating ion-exchange resin. From solutions at pH 7, it has an affinity order of $\text{Hg(II)} > \text{UO}_2(\text{II}) > \text{Cd(II)} > \text{Zn(II)} > \text{Cu(II)} > \text{Ni(II)}$. There is no affinity for Mg(II) , Ca(II) , Sr(II) , Ga(III) , and As(III) . Molybdate and vanadate anions in acidic solutions can be bound by chitosan that has been cross-linked with glutaraldehyde but whose amine group has not been further modified.⁴⁵

Selective Ion Exchange with Rapid Kinetics. Ion-selective complexants such as crown ethers are well-known but a significant problem has been that the rate of complexation of the immobilized ligands is not sufficiently rapid for large scale applications. Bifunctionality was determined to be a variable that could enhance the complexation kinetics of selective resins by incorporating a ligand into the polymer that would be responsible for an access mechanism of all ions into the matrix and coupling this to another ligand that would be responsible for the recognition mechanism. This was achieved by partially sulfonating microporous polystyrene beads to which had been immobilized the phosphinic acid ligand (Figure 12).⁴⁶ The monofunctional phosphinic acid resin cross-linked with 5% DVB complexed 53% of the Eu(III) present in a dilute solution at a 0.5 h contact time and 89% at 24 h. The bifunctional resin complexed 82% Eu(III) at 0.5 h. The contact studies with the monofunctional and bifunctional resins were done with the number of acid sites being kept constant at 1 mmol. Additional research confirmed that the increase in the extent of complexation was not due to the sulfonic acid ligands. A bifunctional diphosphonic acid/sulfonic acid resin performed well when applied to the separation of uranium from phosphoric acid solutions.⁴⁷

Olefin/Paraffin Separations. The separation of olefins from paraffins is important to the petrochemical industry. It is an energy-intensive process since it can involve distillation of compounds with similar boiling points. Metal ions such as Ag^+ complex olefins through their π -orbitals and thus provide an alternative route to separation.⁴⁸ a macroporous strong acid cation-exchange resin was partially (36.5%) exchanged with

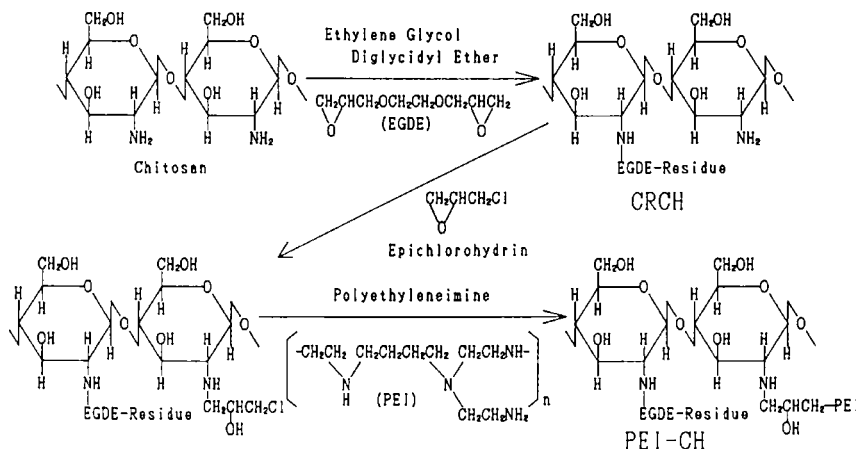


Figure 11. Chitosan as a support for chelating ion-exchange resins. (Reprinted with permission from ref 44, Copyright 1993, American Chemical Society, Washington, DC.)

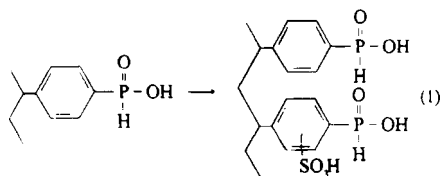


Figure 12. The bifunctional phosphinic/sulfonic acid ion-exchange resin. (Reprinted with permission from ref 46, Copyright 1995, American Chemical Society, Washington, DC.)

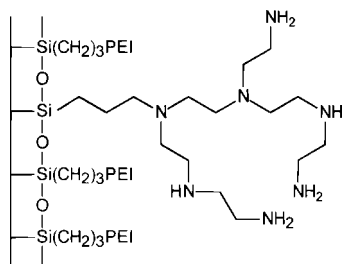


Figure 13. Polyethyleneimine-silica gel composite resin. (Reprinted with permission from ref 51, Copyright 1999, American Chemical Society, Washington, DC.)

silver ions and determined to sorb 1.48 mmol ethylene/g resin. The equilibrium ethylene/ethane sorption ratio was 6.4 at 25 °C and 1 atm pressure. The ethylene desorbed at 100–105 °C to regenerate the resin. The same concept was applied to Nafion membranes (a perfluorinated sulfonic acid polymer (Dupont)) that had been exchanged with Ag^+ . Starting with a feed solution of 1,5-hexadiene, 1-hexene, and *n*-hexane, the hexane was not transported through the membrane.⁴⁹

ABEC Resins. Aqueous Biphasic Extraction Chromatography resins selectively extract pertechnetate and iodide anions from alkaline radioactive wastes.⁵⁰ The resins consist of monomethylated polyethylene glycol (molecular weight of 2000 or 5000) bonded onto cross-linked poly(vinylbenzyl chloride) beads. After loading, they are regenerated by elution with water.

Polyethyleneimine Composite Resins. Polyethyleneimine is an important ligand because it can ion exchange in highly acidic solutions and chelate ions in less acidic solutions. A composite has been prepared where the ligand is bonded to silica gel (Figure 13).⁵¹ Intended applications are remediation of wastewater from mining operations and cooling water for power plants. In column studies, the composite had a high capacity for ions in the order $\text{Cu(II)} > \text{Co(II)} \sim \text{Ni(II)}$.

Overview of 2000–2008. Aminophosphonate, hydroxamic acid, and piperidine (for herbicide removal) were developed as ligands. The polymer support was prepared as a highly porous monolith. New resins were prepared via anionic polymerization and atom-transfer radical polymerization.

Monolith Polymers for Enhanced Kinetics. A monolith prepared from a high internal phase emulsion (HIPE) of an aqueous phase within a continuous phase of styrene/DVB (PolyHipe (Unilever)) is proposed as an alternative to beads with the advantage of lowering mass transfer limitations. The SEM is shown in Figure 14.⁵² The pore volume is 90% with a 30 μm cell diameter. The sulfonic acid ligand has been immobilized onto a polystyrene monolith cross-linked with 20% DVB and can act as a catalyst. It is expected that it will be most advantageous to use monoliths with very fast reactions where mass transfer into resin beads could be rate-limiting.

Aminophosphonate Resins. Aminophosphonate resins (Figure 15) have been commercialized. Ion-exchange equilibria were evaluated with surface complexation theory in order to better

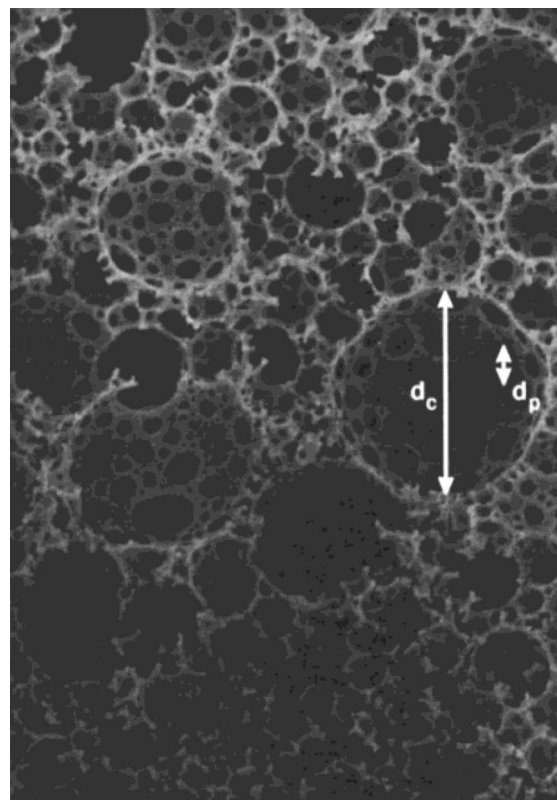


Figure 14. SEM of a PolyHipe monolith. (Reprinted with permission from ref 52, Copyright 2000, American Chemical Society, Washington, DC.)

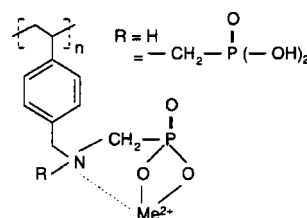


Figure 15. Polystyrene-based aminophosphonate resins. (Reprinted with permission from ref 53, Copyright 2001, American Chemical Society, Washington, DC.)

understand how to apply the resins to problems of industrial significance.⁵³ A good affinity is found for Cu^{2+} , Zn^{2+} , and Cd^{2+} .

Recovery of Gallium from the Bayer Process. The Bayer process is applied to bauxite ore for the separation of gallium, a metal important to the semiconductor industry. During the leaching process, gallium collects in what is termed the Bayer liquor and it is from there that it needs to be recovered. An ion-exchange resin with hydroxamic acid ligands (Figure 16) was developed for gallium recovery.⁵⁴ It was prepared from acrylonitrile with DVB as the cross-linking agent. Laboratory experiments indicate good selectivity for gallium from Bayer liquor.

Removal of Herbicides from Water. Atrazine is a chlorotriazine herbicide that is widely applied and so has been found in water in agricultural regions. Its removal from water is important due to its toxicity. Piperidine was covalently bound to commercially available amine-functionalized polystyrene resins and it removed atrazine from water by covalently binding, rather than sorbing, the atrazine (Figure 17).⁵⁵

Resins Modified by Anionic Polymerization. The preparation of supports for metals to be used as heterogeneous catalysts is of continuing importance. Poly(acrylic acid) grafted onto chloromethylated polystyrene gives a reagent with a high

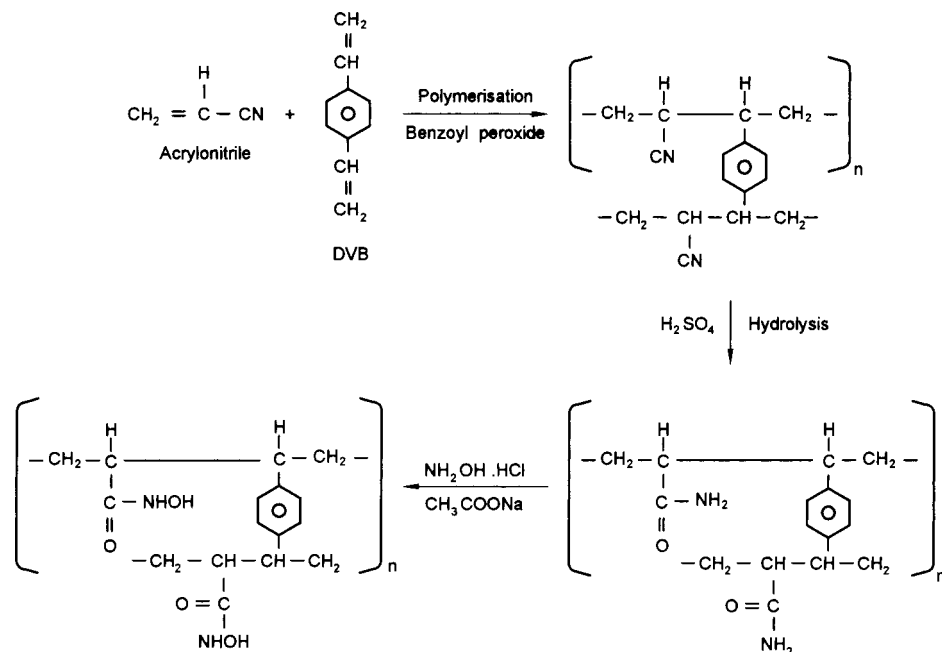


Figure 16. Poly(hydroxamic acid) resin applied to gallium recovery. (Reprinted with permission from ref 54, Copyright 2004, American Chemical Society, Washington, DC.)

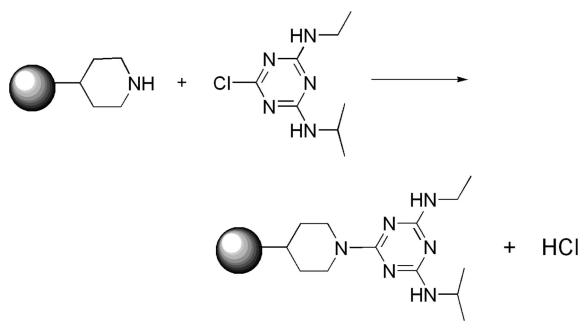


Figure 17. Reaction of piperidine-functionalized resin with atrazine. (Reprinted with permission from ref 55, Copyright 2005, American Chemical Society, Washington, DC.)

capacity for zerovalent metal. It was prepared by reacting the polystyrene support with phenyllithium, then grafting *t*-butyl acrylate to the resulting anion; deesterification gave a poly(acrylic acid) that was exchanged with palladium acetate and its reduction gave Pd metal (Figure 18).⁵⁶ The catalyst was used for the hydrogenation of alkenes, including cyclohexene, cinnamic acid, and 4-acetoxystyrene.

Ion-Exchange Resins by Atom-Transfer Radical Polymerization. The modification of poly(vinyl chloride) is interesting due to the wide availability of the polymer though it is more difficult to modify than poly(vinylbenzyl chloride). It was determined that poly(acrylic acid) could be grafted onto it by surface-initiated atom-transfer radical polymerization (Figure 19).⁵⁷ Hydroxyethyl acrylate was first grafted onto the poly(vinyl chloride) in a reaction catalyzed by Cu(I); hydrolysis gave the grafted poly(acrylic acid) with an acid capacity of 7.52 mmol/g. The polymer had an affinity of Cu(II) > Hg(II) ~ Zn(II) > Cd(II) from solutions at pH 5.

Conclusion—and a Brief Prospective

Research with ion-exchange resins is as fertile today as it was when it all first began. There is a renewed emphasis on water and wastewater treatment to remove both ions and

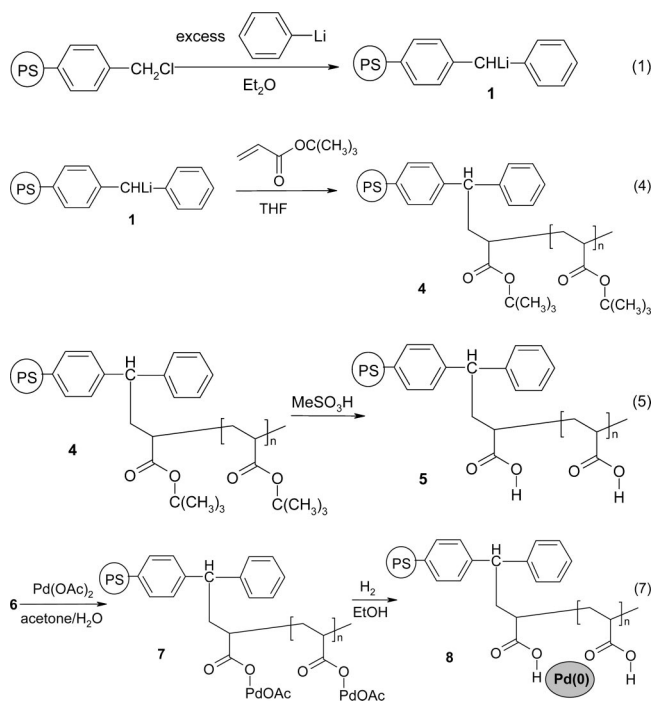


Figure 18. Preparation of grafted poly(acrylic acid) as a Pd(0)-loaded heterogeneous catalyst. (Reprinted with permission from ref 56, Copyright 2005, American Chemical Society, Washington, DC.)

molecules, and on catalytic applications. A search of *IECR* over its latest issues yields numerous publications, including: the kinetics of epoxidation of unsaturated triglycerides with Amberlite IR-120,⁵⁸ reaction rate models for the kinetics of *n*-hexyl acetate formation with Purolite resins,⁵⁹ recovery of the tungstate anion with Amberlite IRA-900,⁶⁰ perchlorate recovery with different anion-exchange resins,⁶¹ and Amberlyst 36 as a catalyst for the acetylation of ethylene glycol.⁶²

An important need is for the ability to design ion-exchange resins *a priori* that are selective for targeted substrates. This requires a better understanding of substrate - ligand interactions and the influence of the polymer support on those

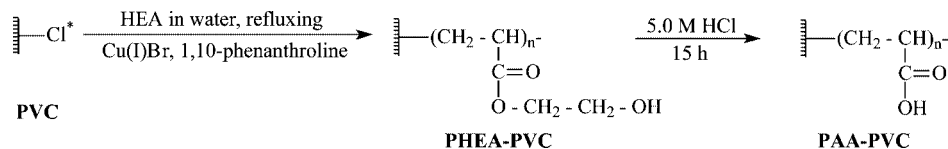


Figure 19. Atom-transfer radical polymerization for the preparation of functionalized PVC. (Reprinted with permission from ref 57, Copyright 2006, American Chemical Society, Washington, DC.)

interactions. Hard–soft acid–base theory is of great value as an organizing principle but a basic understanding of the effects of polarizability and molecular structure will require more research with molecular orbital theory. Beads as the physical form on which ion exchange occurs seems ideal—convenient for both batch and continuous process, easily handled, and stable—yet research will continue to develop polymer supports that minimize mass transfer limitations. Beads can be retained for this as xerogels and hypercrosslinked resins, but monoliths provide an interesting alternative as do membranes and linear polymers (coupled to ultrafiltration). Much of the promise of ion-exchange resins has been met—but the many important problems that remain suggest that there is still much to do with ion-exchange resins.

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