Synthesis of Bifunctional Ion-Exchange Resins through the Arbusov Reaction: Effect on Selectivity and Kinetics

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SYNOPSIS

Bifunctional ion-exchange resins are synthesized from vinylbenzyl chloride–styrene co-polymers. The two types of functional groups are introduced by an Arbusov reaction followed by sulfonation. The effect of ligand ratios, macroporosity, and matrix rigidity on the complexation of Eu(III) from solutions of low pH is quantified. It is found that ion complexation kinetics and selectivity are maximized with resins having both sulfonic and phosphonic acid ligands. Maximum metal ion complexation rates depend on a balance between chemical interactions (i.e., a bifunctional network interacting with a given substrate through an access and a recognition mechanism) and physical parameters (i.e., matrix porosity and rigidity). Structural integrity must be maintained through an appropriate crosslink level in order for the advantage of bifunctionality to be maintained in low-pH solutions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer-supported reagents have been applied to many aspects of chemistry, including organic synthesis, catalysis, and substrate recognition.[1] There have been many studies aimed at understanding which polymeric reagents are most appropriate to the recognition of targeted metal ions.[2] Such studies are especially important in environmental separations for the isolation of radionuclides and other toxic metal ions present in aqueous media.

Metal-specific ligands which have been immobilized on polymer supports include crown ethers,[3] 8-hydroxyquinoline,[4] dioximes,[5] and carbamoylmethylphosphonates.[6] Polymer-supported reagents, however, often have slow rates of complexation, especially in highly acidic solutions where ion exchange is suppressed[7]; additionally, purely complexing ligands, though highly selective, tend to be hydrophobic, thus further limiting access into the polymer[8] and lowering the rate of complexation.

In studying how best to couple substrate recognition between a polymer-supported reagent and a soluble guest with rapid rates of complexation, the concept of dual-mechanism bifunctional polymers has been introduced whereby two different types of ligands operating through two different mechanisms (an access mechanism and a recognition mechanism) display high substrate selectivity.[9]

Polymers with phosphorus-based ligands display unique selectivities for metal ions. In the current research, we have introduced phosphonic acid ligands onto polystyrene through the Arbusov reaction.[10] The effect of bifunctionality on metal ion kinetics and selectivity was examined by immobilizing sulfonic acid groups onto a network already partially functionalized with phosphonic acid ligands; it was anticipated that the strongly acidic sulfonate group would enhance access of the ions into the polymer network while the phosphonate group would be responsible for an increased selectivity.

EXPERIMENTAL

Synthesis

Copolymers of vinylbenzyl chloride (VBC), styrene (St), and divinylbenzene (DVB) are prepared by suspension polymerization at various monomer ratios with 0.5% benzoyl peroxide as initiator. Copolymers prepared with equal volumes of monomers

and toluene–dodecane in a 1 : 9 ratio are macroporous; a 1 : 1 ratio gives an expanded gel structure. Copolymers with no added diluent are microporous (i.e., standard gel) resins. The copolymers are phosphorylated with an excess of triethyl, tri(isopropyl), or tributyl phosphite. The reaction involves a 24-h reflux, filtering, and washing with acetone, acetone–water, and water. Part of each batch is hydrolyzed with concentrated HCl (3 g resin to 50 mL HCl) and part is chlorosulfonated [3 g resin is swollen in 15 mL ethylene dichloride (EDC) for 1 h, 15 mL 10% chlorosulfonic acid in EDC is added, and the reaction is stirred at room temperature for 1 h]. The hydrolyzed and chlorosulfonated resins are conditioned with 1 L 1M HCl, water, 1M NaOH, water, 1M HCl, and water.

Characterization

The phosphorus capacity is determined by digesting 20 mg resin in a solution of HNO_3–$HClO_4$ (1 : 2 v/v) and developing with amidol and ammonium molybdate. The acid capacity is measured by contacting 0.5 g resin for 24 h with 0.1M NaOH in 5% NaCl and titrating a 50-mL aliquot with 0.05M H_2SO_4.

The percent solids is the ratio of dry to wet resin weight and is determined by centrifuging the excess water off the resin, weighing, and then oven drying to a constant weight.

The true and apparent densities of resins prepared in the presence of diluents are measured pycnometrically in methanol and mercury, respectively. The porosity is calculated as $1 - r_0/r$, where r_0 is the apparent and r the true density.

Metal ion study

The resins are contacted with $10^{-4}M$ Eu(NO_3)$_3$ solutions in 0.04M and 1M HNO_3 as well as 1M HNO_3/0.04M $NaNO_3$. Enough resin to give 0.05 mM phosphorus is shaken with 5 mL of the given solution for 0.5 and 24 h. The solutions are then filtered and the Eu(III) concentration is determined via atomic emission on a Perkin-Elmer model 3100 spectrophotometer with the wavelength set at 459.4 nm.

RESULTS AND DISCUSSION

The phosphorylation of VBC–St copolymers cross-linked with 2 and 5% DVB goes to completion within 24 h. All copolymers are functionalized with

tri(isopropyl) phosphite; the copolymer with 2% DVB and a 2 : 1 molar ratio of VBC–St is also functionalized with triethyl and tributyl phosphite. The reaction scheme is given in Figure 1.

The polymers were hydrolyzed with concentrated HCl in order to obtain resins with phosphonic acid ligands. The properties of the resins are given in Table I. The acid capacities are almost exactly equal to twice the phosphorus capacity, indicating complete ester hydrolysis. For polymers functionalized with triethyl and tributyl phosphite, the phosphorus capacities are 3.70 and 3.68 mmol/g, respectively, and the acid capacities are 7.08 and 7.12 mmol/g, respectively, again indicating a quantitative hydrolysis of the ester groups.

The hydrolyzed resins are moderately hydrophilic: the solids percentage is expected to be lower at the lower crosslinking level but is considerably higher for the resin with a 1 : 2 VBC–St ratio. Among resins with 5% DVB, the lowest solids percentage is shown by the macroporous resin (apparent density 0.71 g/mL, true density 1.35 g/mL, calculated porosity 47.4%) obtained with toluene–dodecane (1 : 9); most of the water, however, is found in the pores, not the gel phase. The volume fractions of
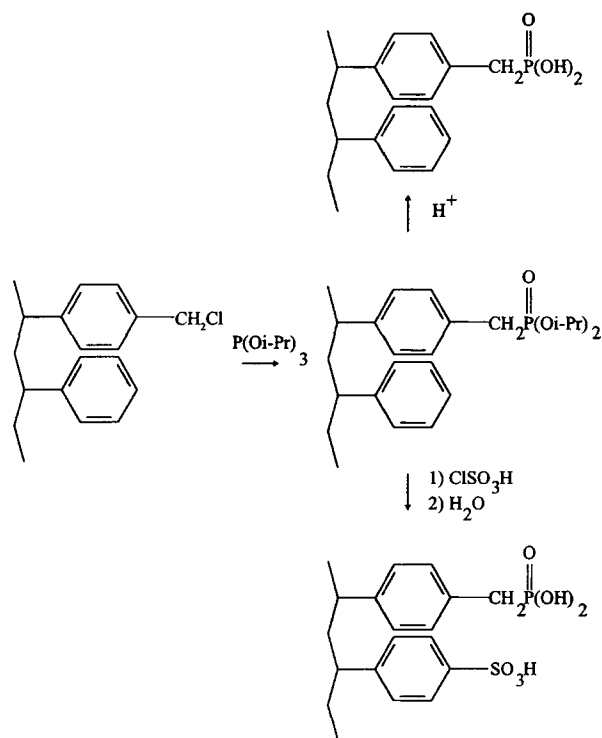
Figure 1 Synthesis of phosphonic acid ion-exchange resin or bifunctional phosphonate–sulfonate resin from the phosphonate ester resin prepared by the Arbusov reaction.

Table I   Ion-Exchange Resins via the Arbusov Reaction with Tri(isopropyl) Phosphite on VBC–St–DVB Copolymers and Subsequent Hydrolysis

Percent DVB	VBC St	Porosity	Capacity (mmol/g)			Percent Solids > Hydr.[d]	Water Uptake (g/g)
			Phosphorus < Hydr.[c]	Phosphorus > Hydr.[d]	Acid		
2	1 : 0	Gel	3.36	4.74	9.66	51.05	0.96
2	2 : 1	Gel	2.93	3.72	7.58	51.54	0.94
2	1 : 2	Gel	1.97	2.45	4.60	71.66	0.40
5	2 : 1	Gel	2.79	3.75	7.00	66.64	0.50
5	2 : 1	Exp[a]	2.63	3.22	6.26	61.29	0.63
5	2 : 1	MR[b]	2.72	3.36	6.85	36.40	1.75

[a] Expanded gel structure obtained by using 50% diluent (toluene–dodecane, 1 : 1 ratio).
[b] Macroporous structure obtained by using 50% diluent (toluene–dodecane, 1 : 9 ratio).
[c] Before hydrolysis.
[d] After hydrolysis.

polymer in the three hydrated resins crosslinked with 5% DVB (gel, expanded gel, and macroporous) are 0.60, 0.60, and 0.57, respectively. Thus, in spite of the low solids percentage for the macroporous resin, accessibility into the gel phase is approximately constant for the three resins.

Bifunctional ion-exchange/coordination resins were prepared from the Arbusov-modified VBC–St–DVB polymers by subsequent modification with chlorosulfonic acid (Table II). Functionalization with sulfonic acid groups decreases the phosphorus capacity per gram of polymer (due to the net increase in weight) and increases the acid capacity. Resins prepared with a 2 : 1 VBC–St ratio have an acid capacity which is greater than twice the phosphorus capacity by 2.8 mmol/g; this value represents the sulfonate group capacity, which is over and above the phosphonate group contribution to the total acid capacity. The resin prepared from the 1 : 2 VBC–St ratio has 4.30 mmol sulfonate groups and 1.67

mmol phosphonate groups per gram polymer. Interestingly, the resin made from the VBC–DVB copolymer contains 1.24 mmol sulfonate groups/g, indicating that chlorosulfonation occurs on phosphonated aryl sites or, more probably, on the ethylstyrene moieties present from the technical-grade DVB.

The solids percentage is lower for each chlorosulfonated resin relative to the corresponding precursors. The largest difference is displayed by the resin with the 1 : 2 VBC–St comonomer ratio (71.66% solids before chlorosulfonation and 18.72% solids afterward), which indicates that the strong-acid capacity acts to maximize hydrophilicity.

Chlorosulfonation of resins with 2% DVB and a 2 : 1 VBC–St ratio modified with either P(OEt)$_3$ or P(OBu)$_3$ gives resins with a phosphorus content of 2.88 and 2.39 mmol/g, respectively, but acid capacities of only 2.73 and 1.22 mmol/g, respectively. Chlorosulfonation thus does not lead to concurrent

Table II   Bifunctional Resins via the Arbusov Reaction with Tri(isopropyl) Phosphite on VBC–St–DVB Copolymers and Subsequent Chlorosulfonation

Percent DVB	VBC St	Porosity	Capacity (mmol/g)		Percent Solids	Water Uptake
			Phosphorus	Acid		
2	1 : 0	Gel	4.00	9.24	20.42	3.90
2	2 : 1	Gel	2.86	8.60	26.00	2.85
2	1 : 2	Gel	1.67	7.64	18.72	4.34
5	2 : 1	Gel	2.70	8.13	42.77	1.34
5	2 : 1	Exp.[a]	2.48	7.76	26.55	2.92
5	2 : 1	MR[a]	2.51	7.89	27.78	2.60

[a] See Table I for definitions.

hydrolysis of diethyl and dibutyl phosphonate esters as it does with di(isopropyl) esters, which is consistent with the lower sensitivity of primary alcohol esters toward acid hydrolysis relative to secondary esters.

The complexation of Eu(III) by monofunctional phosphonic acid resins prepared by hydrolysis is found to be quantitative from $0.04 M$ HNO_3 solution within 30 min of contact (Table III). The sole exception is the resin with the 1 : 2 VBC–St ratio, and this is also the most hydrophobic resin (Table I). In $1 M$ HNO_3, dissociation of the phosphonic acid groups is suppressed and Eu(III) complexation does not exceed 9% for all hydrolyzed resins. Differences in crosslink level and porosity have a negligible influence on the level of complexation. Increasing the contact time to 24 h has minimal influence.

Bifunctionality is found to have a dominant influence on the ion-complexing ability of the resins. In each case, the bifunctional resins, prepared by sulfonation, complex two to eight times the amount of Eu(III) relative to the hydrolyzed resins (Table III). As much as 51.0% Eu(III) complexation occurs from $1 M$ HNO_3 within 30 min. In order to quantify how much of the complexation is due to ion exchange with the sulfonic acid ligands, experiments were performed with Eu(III) in $1 M$ HNO_3–$0.4 M$ $NaNO_3$. The Na^+ ions, present in vast excess over the trace amount of Eu(III), will exchange with the nonselective sulfonic acid ligands, and whatever amount of Eu(III) is complexed from this solution will be mostly from complexation with the more selective

phosphorus ligands. Table III shows that Eu(III) uptake remains significantly greater from the $NaNO_3$ solutions with the bifunctional resins relative to the monofunctional resins, indicating that the mechanism of complexation is one of access by the sulfonate ligands and recognition by the phosphonate groups.

In order to further evaluate the contribution of sulfonic acid groups to Eu(III) complexation under competitive conditions using the $1 M$ HNO_3–$0.4 M$ $NaNO_3$ solution, three chlorosulfonated resins were synthesized from 2% DVB (gel), 5% DVB (gel), and 5% DVB (macroporous) copolymers with a 2 : 1 VBC–St ratio. The resins complexed 20.3, 21.2, and 23.3% Eu(III) at 30 min contact and 21.2, 22.5, and 24.5% Eu(III) at 24 h contact. These values can be compared with the values for the monofunctional phosphonic acid resins under identical conditions. Assuming additivity in the behavior of the two ligands, the sum of the amount of europium complexed by each monofunctional resin should equal that complexed by the corresponding bifunctional resin. At 30 min contact time, this is the case (within experimental error) for the 2% DVB gel and 5% DVB macroporous resins. The former must be crosslinked lightly enough to yield a flexible matrix which maximizes access through the micropores, at least to the level indicated (24%); the latter, as expected, allows for maximum access through the macropores. Cooperatively, however, is indicated by the 5% DVB gel resin, wherein the sulfonic acid groups increase ionic accessibility into the polymer network,

Table III   Ion-Complexing Properties of Resins Prepared with the Arbusov Reaction

| | | | | Percent Eu(III) Complexed from $HNO_3/NaNO_3$ (M/M) | | | | | |
| | | | | At 30 Min | | | At 24 h | | |
Percent DVB	VBC–St	Porosity	H/S[a]	$0.04M/—$	$1M/—$	$1M/0.4M$	$0.04M/—$	$1M/—$	$1M/0.4M$
2	1 : 0	Gel	H	100.0	5.7	8.7	100.0	10.5	4.2
2	2 : 1	Gel	H	100.0	6.9	7.0	100.0	19.0	27.1
2	1 : 2	Gel	H	91.2	5.3	7.3	100.0	8.5	2.2
5	2 : 1	Gel	H	100.0	5.5	7.0	100.0	9.0	4.4
5	2 : 1	Exp.[b]	H	100.0	6.5	6.6	100.0	8.0	3.8
5	2 : 1	MR[b]	H	100.0	8.0	8.0	100.0	11.5	16.5
2	1 : 0	Gel	S	100.0	14.7	16.0	100.0	22.5	22.2
2	2 : 1	Gel	S	100.0	28.5	24.0	100.0	40.0	22.2
2	1 : 2	Gel	S	100.0	32.4	25.8	100.0	37.0	31.6
5	2 : 1	Gel	S	100.0	51.0	36.6	100.0	65.0	45.1
5	2 : 1	Exp.[b]	S	100.0	39.5	26.8	100.0	46.5	33.7
5	2 : 1	MR[b]	S	100.0	49.5	34.5	100.0	56.5	41.6

[a] Hydrolyzed/sulfonated.
[b] See Table I for definitions.

allowing for more europium to be complexed (36.6%) than expected from the two ligands acting alone (28.2%). This is confirmed by the results at 24 h contact time: the 5% DVB gel resin complexes almost 70% more europium than expected from the sum of the ligands acting alone. The 5% DVB macroporous resin again complexes almost exactly the amount calculated from the two monofunctional resins. The 2% DVB gel resin actually complexes much less than expected, and this points to an important influence that a flexible network can impose on ligand accessibility: a decrease in ligand accessibility at a low crosslink level is possible due to a collapse of the microporous structure in highly acidic solutions. This is indicated by comparing the uptake of water versus the uptake of $1 M$ HNO_3. For the 2% DVB gel, 5% DVB gel, and 5% DVB macroporous resins, the uptake of water is 2.85, 1.34, and 2.60 g/g, respectively, while the uptake of $1 M$ HNO_3 is 1.87, 1.13, and 2.31 g/g, respectively. The decrease in solvent uptake upon going from water to $1 M$ HNO_3 is thus 0.98, 0.21, and 0.29 g/g. The resin crosslinked with 2% DVB does not have sufficient structural integrity to maintain its microporosity in the more ionic nitric acid solution; this collapse leads to a decrease in ligand accessibility and thus a relatively low level of metal ion complexation. The more highly crosslinked resin, however, does not require complete solvation of the ligands in order to maximize its microporosity, thus allowing for a more efficient complexation of metal ions from acidic solutions in the case of the bifunctional resin.

CONCLUSION

The results show that maximized metal ion kinetics depends on a balance between chemical interactions (i.e., a bifunctional network interacting with a given substrate through an access and a recognition mechanism) and physical parameters (i.e., matrix porosity and rigidity).

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