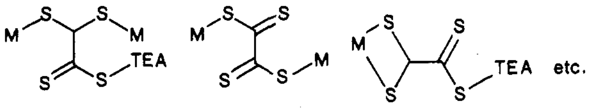
130, 803. (e) Lodmell, J. C.; Anderson, W. C.; Hurley, M. F.; Chambers, J. Q. *Anal. Chim. Acta* **1981**, *129*, 49.

(37) (a) Jeroschewski, P. *Z. Chem.* **1981**, *21*, 412. (b) Lund, J.; Hoyer, E.; Hazell, R. G. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 207.

(38) Reynolds, J. R.; Karasz, F. E.; Lillya, C. P.; Chien, J. C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 268.

(39) The poly(MTO)s are difficult to characterize because of their insolubility and infusability. They are also not easy to analyze. There are no hydrogens for NMR and only one type of carbon. Analysis of sulfur and metals are performed both at the Microanalytical Laboratory of the University of Massachusetts and by Galbraith for confirmation. The errors of their analysis are generally greater than considered acceptable for C and H. A referee objected to the structures postulated for the poly(MTO)s. However, the X-ray structures have been obtained[40] for the related bimetallic catena μ-dithiooxalates compounds $\mathrm{AMn(S_2C_2O_2)_2(H_2O)\cdot 4.5H_2O}$ (A = Cu, Ni, Pd, Pt). Our proposed structures are the same as these. The referee suggested the following alternative structures:



They seem improbable because of their low coordinate states.

(40) (a) Gleizes, A.; Verdaguer, M. *J. Am. Chem. Soc.* **1984**, *106*, 3727. (b) Verdaguer, M.; Gleizes, A.; Renard, J. P.; Seiden, J. *Phys. Rev. B: Condens. Matter* **1984**, *29*, 5144.

(41) Alacacer, L.; Novais, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3.

(42) Wnek, G. E. Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1980.

(43) Chien, J. C. W.; Warakomski, J. M.; Karasz, F. E.; Chia, W. L.; Lillya, C. P. *Phys. Rev. B: Condens. Matter* **1983**, *28*, 6937.

(44) A referee pointed out that in the polymers containing Cu, Ni, and Pd there may exist a small amount of metal in the +1 oxidation state. Now conduction could occur via intermolecular redox reactions between M^{1+} and M^{2+}, i.e., mixed-valence states. The n-type conductivity can be explained when M^{2+} is in excess; the M^{1+} is electron excessive in a "sea" of M^{2+} and hence an n carrier moves.[45] Just the reverse would be true for an excess of M^{1+} for p-type conductivity. The former may be an explanation for the n-type conductivity for poly(PtTTO), though Pt^{1+} is not a common oxidation state. It is difficult to imagine that the M^{1+} states are present in excess for poly(CuTTO) and poly(NiTTO).

(45) Hansen, K. W. *J. Electrochem. Soc.* **1965**, *112*, 995.

(46) Chien, J. C. W.; Schen, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2447.

(47) Schen, M. A.; Karasz, F. E.; Chien, J. C. W. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 217.

(48) Wan, W.; Wang, P.; Cao, Y.; Qian, R.; Wang, F.; Zhao, X.; Gong, Z. *Solid State Commun.* **1947**, *47*, 759.

(49) Kume, K.; Masubuchi, S.; Mizoguchi, K.; Mizuno, K.; Shirakawa, H. Proceedings of ICSM 86, to be published in *Synth. Met.*

(50) (a) Groff, R. P.; Suna, A.; Merrifield, R. E. *Phys. Rev. Lett.* **1974**, *33*, 418. (b) Khanna, S. K.; Ehrenfreund, E.; Garito, A. F.; Heeger, A. J. *Phys. Rev. B: Solid State* **1974**, *10*, 2205. (c) Ferraris, J. P.; Finnegan, T. F. *Solid State Commun.* **1976**, *18*, 1169. (d) Cooper, J. R.; Jerome, D.; Weger, M.; Etemad, S. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, L219. (e) Bloch, A. N.; Cowan, D. O.; Bechgaard, K.; Pyle, R. E.; Banks, R. H.; Poehler, T. O. *Phys. Rev. Lett.* **1975**, *24*, 1561. (f) Javadi, H. H. S.; Sridhar, S.; Gruner, G.; Chiang, L.; Wudl, F. *Phys. Rev. Lett.* **1985**, *55*, 1216.

Synthesis and Characterization of Bifunctional Ion-Exchange/Coordination Resins

Spiro D. Alexandratos,* Donna R. Quillen, and Marie E. Bates

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600.

Received October 6, 1986

ABSTRACT: The synthesis of bifunctional resins that complex metal ions via the mechanisms of ion exchange and coordination is detailed. These resins form the second class of polymer-supported complexing agents for specific metal ion extractions within the recently detailed dual mechanism bifunctional polymer category. This series of resins incorporates phosphonic acid groups as the ion-exchange ligand and a varying coordination ligand that allows the different resins to be selective for different metal ions. The development of resins with phosphonic acid/phosphonate ester ligands and phosphonic acid/tertiary amine ligands on a polystyrene support is described.

Introduction

The selective complexation of a targeted metal ion by a given ligand is an important objective for many applications, including catalytic,[1] chromatographic,[2] and metal ion recovery[3] processes. The ion-exchange reaction is an extremely versatile reaction and one that is well-suited to the complexation of cations and anions through electrostatic binding. The strongly acidic sulfonic acid cation-exchange resin has played a central role in metal recovery processes due to its exchange strength in acidic solutions.[4] The classic works of Boyd and his co-workers,[5] though, have shown that the ion-exchange reaction alone does not have a wide enough range in the free energy of reaction to allow for selectivity: for example, the change in enthalpy of reaction for the sulfonic resins with alkali metal ions is only 1.5 kcal/mol. The inability of the sulfonic resin to differentiate among many ions for a given ion can thus obviate its use for practical recovery processes[6] requiring the selective absorption of valuable or toxic metal ions in a background of innocuous ions present at much higher concentrations. Additionally, a small value for the free energy of reaction implies that the metal ion can be lost to the environment in catalytic applications since the binding would be relatively weak. Ion-exchange resins are very important to metal ion complexation reactions due to their hydrophilicity, accessibility, and high capacity, but the synthesis of a polymer with a greater degree of selectivity would prove important to different applications.

Ions are capable of undergoing many reactions in addition to simple ion exchange such as reduction, coordination/chelation, and precipitation.[7] These reactions can be quite specific for certain metal ions depending on the coreactant: for example, with a series of reducing agents, a metal ion can be unaffected, be reduced to a lower ionic valence state, or be removed from solution in its metallic form; with a series of anions, a metal ion can remain free (i.e., solvated), complexed to various degrees, or precipitate from solution. It therefore follows that the introduction

0024-9297/87/2220-1191$01.50/0

of significant selectivity to ion-exchange resins can be expected when a reaction additional to ion exchange is allowed to occur.[8] Mechanistically, the ion-exchange process can draw the dissolved metal ions into the polymer while the resin's additional reaction can be a sink for one of the ions, displacing its equilibrium until only that ion can be found within the resin for its subsequent recovery. The ion-exchange ligand ensures the metal ion's accessibility while the additional reaction ensures selectivity.

With these theoretical considerations as background, we have recently introduced a category of resins that have been termed *dual mechanism bifunctional polymers*[9] wherein two different ligands are bound to a polymer support and operate by two different mechanisms for the selective complexation of metal ions. One ligand operates by ion exchange; the second ligand varies according to the desired reaction thus defining the class within this category. The first class that has been described is the phosphinic acid resin, which operates by the ion-exchange and redox mechanisms via primary and secondary phosphinic acid ligands. The redox reaction makes the resins much more selective for reducible ions such as Hg(II) than for relatively nonreducible ions such as Zn(II) and allows for the isolation of pure metal from a solution of its ions.

Other research aimed at introducing specificity into polymeric reagents has emphasized the immobilization of specific ligands.[10] One of the more successful examples is the production of copper-selective resins based on picolylamine[11] and hydroxyoximes.[12] Dithiocarbamate derivatives have a high affinity for silver ions,[13] and, in general, sulfur-containing resins have been found to be more selective toward the noble and heavy metals than resins with nitrogen- or oxygen-based ligands.[14] In line with this, isothiouronium[15] and thioglycolate[16] resins are specific for mercury, silver, and gold complexation.[17] The iminodiacetic acid resin is a commercially available chelating resin (Dowex A-1, Chelex-100) and shows high affinity for divalent ions.[18] Polystyrene-supported acetylacetone[19] and crown ethers[20] have been prepared and also found to be good chelating resins. In many cases, the syntheses are quite elegant but lead to resins with a number of drawbacks: selectivity dependent on a carboxylic acid or hydroxylic ligand requires a relatively high pH solution for the exchange to occur while a purely coordinative resin has insufficient hydrophilicity to allow for rapid ionic accessibility and hence shows a low apparent capacity. The ideal situation would entail a completely hydrophilic resin due to the presence of a relatively strong acid ion-exchange ligand and a high coordinative ability for specificity; just such a situation is described by our second class of dual mechanism bifunctional polymers—ion exchange/coordination resins.

Phosphoryl-containing resins are an especially important type of resin due to their inherent coordinative ability.[21] The phosphinic resin can thus be expected to display a good deal of selectivity even with nonreducible multivalent ions, relative to the sulfonic resin, due to the significant Lewis basicity of the phosphoryl oxygen. In fact, such a selectivity has been observed in trace level extraction studies of europium and various actinides: in the presence of a large excess of sodium ions, the phosphinic resin has a distribution coefficient that is as much as 3 orders of magnitude greater than that for the sulfonic resin.[22] The importance of the coordinative interaction is evident in the specificity displayed by coordinating compounds for various metal ions. Examples include the affinity of bipyridine for Cu(II),[23] nitrated aromatic amines for potassium ions,[24] bis(2-mercapto)anilinoglyoxal for gold,[25] thiourea for mercury,[26] and crown ethers for the alkali ions.[27] The coordinative interaction can be significant enough that it alone can be used in the recovery of metal ions from dilute aqueous solutions. Phosphoryl compounds such as tributyl phosphate[28] and trioctylphosphine oxide[29] and amines such as quinoline[30] play prominent roles in metal ion recovery processes. Additionally, it has been observed in certain extractions that combining a purely coordinative extractant with a liquid ion-exchange extractant in a given organic phase results in a greater level of metal ion recovery than expected from each extractant operating separately. This phenomenon of synergism or synergistic extraction[31] arises from an increase in the organophilicity of the metal complex as the neutral extractant coordinates with the metal ion and either replaces waters of hydration (thus making the extraction entropically favored) or expands the coordination sphere of the metal.[32] It is precisely this type of dual mechanism of action that the ion-exchange/coordination resins will be particularly well suited for due to the proximity of the two types of ligands. The coordination reaction would therefore bring about selectivity to the ion-exchange process, as discussed earlier, and possibly enhance the amount of metal extracted from solution in what would thus be polymer-supported synergistic extraction.

The purpose of the present report is to describe how the coordinative interaction can be utilized within the scheme of dual mechanism bifunctional polymers. Within this series of ion-exchange/coordination resins, the ion-exchange ligand will remain the same while the coordinating ligand will be varied to give the greatest specificity for a targeted metal ion. Thus, the ion-exchange phosphonic acid ligand will endow the polymer with hydrophilicity and ionic accessibility while the coordinating ligand will allow for complexing specificity. Given the extensive research carried out to date on solvent extraction systems using neutral phosphoryl compounds and amines, both alone and in conjunction with liquid ion-exchange extractants, we have developed syntheses of resins with phosphonic acid/phosphonate ester ligands and phosphonic acid/tertiary amine ligands on a polystyrene support. The syntheses and initial metal ion extraction studies are presented here, with a detailed metal ion selectivity series to be presented in a subsequent publication.[33]

Results and Discussion

Polystyrene is one of the most important support polymers due to its versatility as a reactant[34] and its physical/chemical stability. Its chloromethylene derivative, poly(vinylbenzyl chloride), is also extremely useful because it allows for the preparation of polymer-supported reagents best synthesized through nucleophilic reactions, as exemplified by the strong and weak base anion-exchange resins.[35] Having the objective to prepare an amine-containing resin, it was decided to use poly(vinylbenzyl chloride) as the starting point for both bifunctional resins since a comparative study of the extracting ability of different resins should keep the polymer support structure as constant as possible.[36] The polymer was prepared by suspension polymerization[37] of vinylbenzyl chloride to give gel beads approximately 0.5 mm in diameter and cross-linked with 2% divinylbenzene in order to maintain structural integrity.

Phosphonic Acid/Phosphonate Ester Resins. The synthesis of the phosphonic acid/phosphonate ester resins (IV–IX) is summarized in Scheme I as is the synthesis of the phosphonic acid (I), phosphonate monoester (II), and phosphonate diester (III) resins to be used as controls in the subsequent extraction study. The initial reaction of

Scheme I

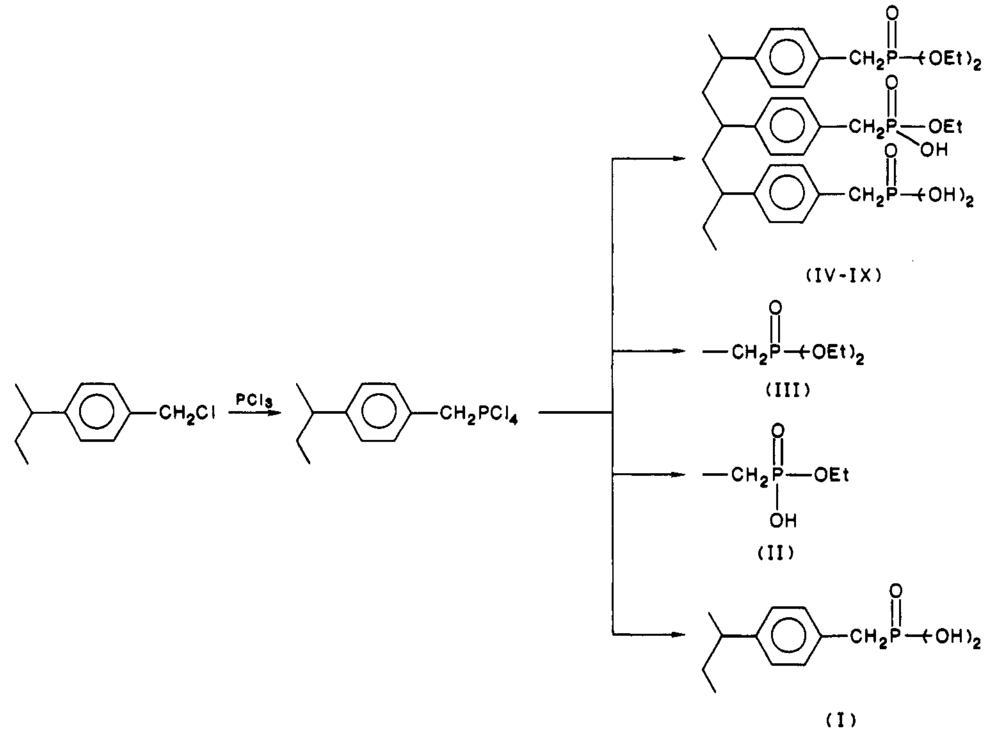


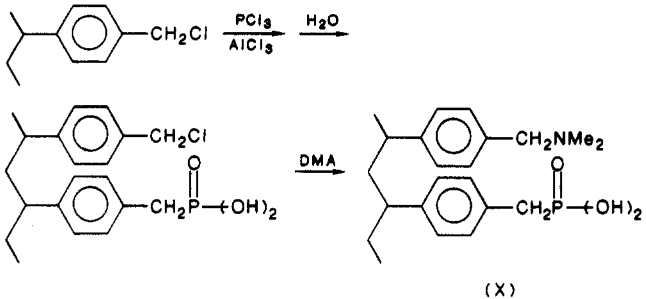
Table I
Characterization of the Acid/Ester Resins

resin	phosphorus, mequiv/g	acid capacity, mequiv/g	total ester, %	diester content, %	monoester content, %	diacid content, %
phosphonic acid (I)	3.36	6.51	0			100
monoester (II)	3.44	3.42	50		100	
diester (III)	1.88	0.00	100	100		
mixed ester						
(IV)	3.43	1.11	83.8	66	34	0
(V)	3.49	1.06	84.8	76	17	7
(VI)	3.56	0.65	90.9	83	17	0
(VII)	3.98	4.97	37.6	13	49	38
(VIII)	3.51	4.56	35.0	17	36	47
(IX)	3.82	5.71	25.3	7	37	56

PCl_3 on the polymer has precedence from the small-molecule studies by Clay[38] as well as Kinnear and Perren[39] on various chlorides. We found that the $AlCl_3$ level is critical in determining the extent of reaction since it remains complexed to the PCl_4 moiety after the substitution reaction. A level of 1.2 mole of $AlCl_3$ per mole of CH_2Cl groups coupled with a temperature of 73 °C was found to ensure a high degree of functionalization. The type of resin obtained depends upon the solvolytic conditions. The slow addition of water leads directly to the formation of the phosphonic resin (I). The pure diester resin (III) is obtained only by carefully controlling the exothermicity of the quench reaction with ethanol. Very mild quench conditions are attained only through partial functionalization of the polystyrene support and the slow subsequent addition of anhydrous ethanol to maintain a quench temperature of 0 °C. A rapid ethanol addition leads to the buildup of heat from the highly exothermic reaction, which allows some of the liberated HCl to react with the ethoxy groups to form ethyl chloride and monoprotic or diprotic phosphorus ligands. A controlled heatup to 80 °C leads to the isolation of resin, which is almost entirely monoester benzylethylphosphonic acid (II). Different mixed diester/monoester/diacid resins (IV–IX) are produced by the addition of ethanol/water in various mole ratios.

The resin properties are summarized in Table I. A phosphorus elemental analysis yields the total degree of functionalization by comparison to the theoretical values (approximately 5.0 mequiv/g for the phosphonic acid, 3.9 mequiv/g for the diester and 4.4 mequiv/g for the monoester resin). The table thus shows that each resin is 70–80% functionalized except for the diester, which is closer to 50% functionalized due to the milder reaction conditions (see Experimental Section). The total percent esterification is obtained by a base analysis for the resin's total acid capacity, dividing half that value by the phosphorus capacity and subtracting from unity. A pH titration curve serves to quantify the three ligands on the resin: comparing the milliequivalents at the break to the total milliequivalents from the base analysis quantifies the amount of diacid to monoacid while comparison to the phosphorus analysis gives the amount of diester by difference. (The second proton on the phosphonic acid does not yield a well-defined break point.) Quantifying the ligands by this procedure is important to an understanding of the ester resins' metal ion extraction performance.

Phosphonic Acid/Amine Resin. The synthesis of the phosphonic acid/tertiary amine resin is summarized by eq 1. The critical feature of this preparation is the adjustment required in the initial PCl_3 functionalization conditions to permit about half of the CH_2 moieties to remain unreacted for the subsequent amination. As was done in the preparation of the pure diester resin, maintaining an $AlCl_3$ level of 0.77 mol/mol CH_2Cl groups and a 40 °C



(X)

(1)

reaction temperature allowed that objective to be achieved. The phosphonic acid/amine resin thus obtained had a phosphorus capacity of 2.03 mequiv/g and an amine capacity of 2.20 mequiv/g. Its metal ion extraction ability under highly acidic conditions was studied and compared to the corresponding phosphonic acid and amine resins.

The structure of the resin as given in eq 1 (structure X) is written in the free amine/diacid form. It should be noted that in pure water the functional groups exist, at least to some extent, as zwitterions. The extent of zwitterion formation is probably determined by the ability of the two groups to be in near enough proximity to permit ionic stabilization. In the low pH solutions employed for the extraction study, the amine moieties are all undoubtedly protonated with, in this case, nitric acid.

Initial Metal Ion Extraction Studies: Americium. The different coordinative abilities of the various resins can be quantified through a comparative metal ion extraction study. Initial work has focused on americium complexation with the resins under conditions that have been detailed previously.[22] Studies such as the current one, carried out with trace levels of the metal ion of interest, are best correlated in terms of the distribution coefficient, D, as a function of the solution pH,[22] where D equals the concentration of metal in the resin at equilibrium divided by the concentration of metal in the aqueous phase. The slope of the log D/pH graph is then the charge of the exchanging ion if only ion exchange is occurring. Values less than the ionic charge are indicative of a coordinative extraction mechanism, and a value of zero implies the absence of ion exchange with extraction occurring only through coordination with the neutral salt. All log D/pH correlations were carried out in constant ionic strength solutions (4 M nitrate ion) through the addition of varying amounts of $NaNO_3$ as the nitric acid concentration was adjusted to give different pH solutions.

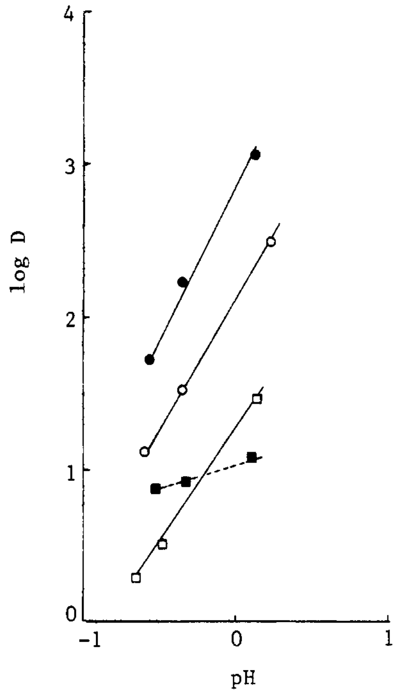


Figure 1. Effect of resin ligand acidity on americium extraction in the presence of excess sodium: (●) phosphinic acid, (○) phosphonate monoester, (□) phosphonic acid, (■) sulfonic acid.

Figure 1 shows the log D/pH correlation for resins uniformly substituted with one moiety: phosphinic acid, phosphonate monoester, phosphonic acid, and sulfonic acid. The trend indicates that increasing the acid strength of the phosphorus ligand increases the extent of americium extraction. The slopes of the three phosphorus resins are comparable (1.90, 1.71, and 1.73 for the resins as listed above, respectively), indicating that the coordinative component is an important part of the extraction mechanism. The phosphorus resins are probably extracting the Am(III) ion and neutral $Am(NO_3)_3$ salt in such a proportion as to give the observed slope. This conclusion is preferred over alternate explanations when one notes that the sulfonic acid resin under conditions of changing pH only (i.e., no sodium ions present in solution) has a slope of 3.0 for Am(III) extraction,[22] thus showing the absence of intermediate nitrate salts. That ligand acid strength alone is not sufficient to ensure a high degree of extraction may be seen by the performance of the sulfonic resin in the presence of sodium (Figure 1). High ligand acidity coupled with low coordinative ability, as is typical of the sulfonic acid group, leads to low selectivity for the americium in the presence of a large excess of sodium. The relative coordinative ability of the phosphoryl oxygen in the three phosphorus resins is probably critical to establishing the extraction order since the acid strength can be seen from model compounds to follow the order shown but within a rather small range (pK_a values of 3.49 for phenylphosphinic acid,[40] 3.96 for phenylphosphonic acid,[41] and 3.83 for cyclohexylphenyl phosphonate monoester[41]). Qualitative arguments support the order phosphinic, phosphonate monoester, and phosphonic acid for one of decreasing coordinative ability: the electron-withdrawing ability of oxygen reduces the basicity of the phosphoryl oxygen in the monoester and phosphonic acid relative to the phosphinic acid while the effect in the monoester is moderated by the electron-donating ability of the ethyl group, making it thus a somewhat better coordinator than the phosphonic acid.

As given in Table I, the ester resins of mixed functionality fall into two categories: those consisting of diester/monoester moieties and those consisting principally of diacid/monoester moieties. Figure 2 shows that the monoester ligand dominates the results in the diester/monoester resins. The trend parallels that of the resin's monoester content with the 100% monoester resin extracting the most americium over the pH range studied. This behavior implies that the diester ligand in these resins is not participating in the americium extraction; studies with the pure diester resin are consistent with this conclusion since it is found to extract very low levels of americium (see Figure 2). Resins comprised of more than approximately 40% diacid ligands all perform in the same manner that the pure diacid resin performs (Figure 2). The amine/diacid resin also falls on the diacid correlation, indicating that the amine moiety plays no role in the americium extraction, as also seen by the poor performance of the pure amine resin. It is important to note, though, that conclusions involving metal ion extractions with coordinating ligands alone can be expected to be dependent upon the counterion since they must allow for close enough

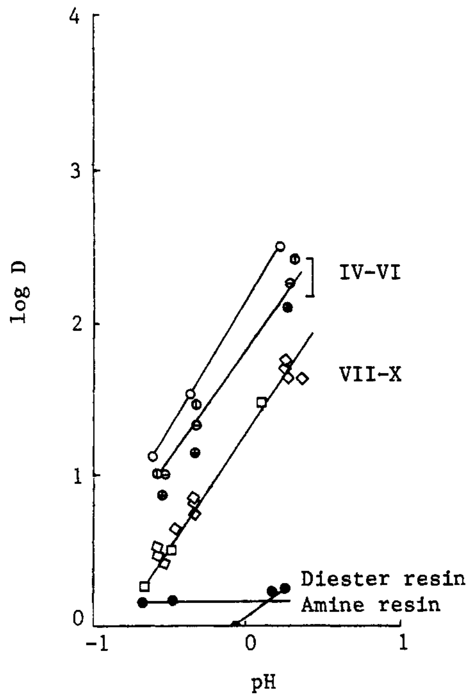


Figure 2. Americium extraction with mixed acid/ester resins in the presence of excess sodium: (○) phosphonate monoester, (⦶) resin IV, (⊖) resin V, (⊕) resin VI, (□) phosphonic acid, (◇) resins VII–X.

contact with the metal ion to give the extraction of a neutral species. The behavior, thus, of the pure diester and amine resins with americium holds only for nitrate solutions and will probably be different with counterions that allow for contact ion pairing. We are currently studying the influence of the counterion on the extent of transition-metal ion extractions.

Conclusion

The synthesis of new bifunctional ion-exchange/coordination resins containing phosphonic acid ligands for ion exchange and either phosphonate ester or amine ligands for coordination to the metal ion has been described. A comparative study is under way.[33] The kinetics, elution characteristics, and counterion effect are also being studied.

Experimental Section

The synthesis of the 2% divinylbenzene cross-linked poly(vinylbenzyl chloride) gel beads via suspension polymerization has been described, as has the acid analysis and phosphorus elemental analysis.[42] The details of the americium extraction procedure have also been presented.[22]

Phosphonic Acid/Phosphonate Ester Resins. Poly(vinylbenzyl chloride) beads (−20 + 40 mesh, 20 g) are placed in a 500-mL round-bottom flask equipped with an overhead stirrer, condenser, and thermometer, to which are added 160 mL of PCl_3 (1 h swell time) and 21.05 g of $AlCl_3$. The reaction is heated to 73 °C over 1 h and held there for 4 h, after which time it is cooled to room temperature. The resin is then washed free of PCl_3 with toluene and cooled to 0 °C with 50 mL of toluene added for fluidity. Aqueous ethanol is slowly added at a rate that maintains the temperature below 10 °C. The aqueous ethanol composition varies according to the desired resin: the greater the percent esterification, the more ethanol used. Thus, an 8:1 mole ratio of ethanol to water yields a resin with 84.8% esterification, while a 2:1 ratio yields 25.3% esterification, and a 0:1 ratio yields the phosphonic acid resin. Enough of the aqueous ethanol solution is added to contact the resin with a total of 1.4 mol of ethanol plus water. The resin/quench solution is stirred for 1 h, the solution is siphoned off, and a second quench solution is added. In order to ensure complete removal of the HCl that forms, four washings with 500 mL of 95% ethanol and eight washings with 500 mL of 50% ethanol are carried out. The resin is then conditioned with successive elutions (1 L/h) of H_2O, 1 N NaOH, H_2O, 1 N HCl, and H_2O. The resin is analyzed by NaOH titration and a phosphorus elemental analysis.

The pure diester resin is prepared as above except that the functionalization conditions are milder (13.5 g $AlCl_3$ and a 40 °C reaction temperature), and the quench solution, consisting solely of anhydrous ethanol, is added at a much slower rate in order to maintain a quench temperature of 0 °C.

The pure monoester resin is prepared in the same manner as the mixed ester resins except for quenching with absolute ethanol and heating the second ethanol quench solution at 80 °C for 16 h.

Phosphonic Acid/Amine Resin. The initial functionalization reaction is as with the pure diester resin. Water alone is used in the quench. After conditioning the resin as above, phosphorus and chlorine elemental analyses are done to quantify the partial conversion of the resin to phosphonic acid moieties. The phosphonic resin (13.5 g dry weight) is then aminated by converting it to its sodium salt form, placing it in a 500-mL flask equipped with an overhead stirrer, dry ice condenser, and thermometer, and refluxing with 250 mL of 40 wt % aqueous dimethylamine (Aldrich) containing 0.5 g of NaOH for 4 h. After cooling, the resin is conditioned with the elution sequence specified for the ester resins. The amine capacity is determined by eluting the resin with 1 N HCl followed by 1 L/h of water and 4 wt % $NaNO_3$. The $NaNO_3$ eluent is analyzed for chloride ion by a Mohr titration. A pure amine resin is prepared and analyzed in the same manner, except, of course, that amination occurs on the original poly(vinylbenzyl chloride) beads. The water wash removes no ionically bound HCl: the amine capacity determined by Mohr titration exactly matches the resin chlorine content determined by elemental analysis prior to an additional 1.5 L H_2O/3 h and $NaNO_3$ elution.

Acknowledgment. We gratefully acknowledge the support of the Department of Energy, Office of Basic Energy Sciences (DE-AS05-83ER13113). The americium studies were carried out at the Oak Ridge National Laboratory with the cooperation of W. Jack McDowell of the Separation Science Group (Chemistry Division). We gratefully acknowledge his help and the fact that we are collaborating with him on the complete transition-metal ion study.

Registry No. Na, 7440-23-5; Am, 7440-35-9.

References and Notes

(1) Hirai, H.; Toshima, N. In *Tailored Metal Catalysts*; Iwasawa, Y., Ed.; Reidel: Dordrect, 1986.
(2) Helfferich, F. *J. Am. Chem. Soc.* **1962**, *84*, 3237.
(3) Marhol, M. *Ion Exchangers in Analytical Chemistry*; Svehla, G., Ed.; Elsevier: Amsterdam, 1982; *Compr. Anal. Chem. 14*.
(4) Strelow, F. W. E.; Rethemeyer, R.; Bothma, C. J. C. *Anal. Chem.* **1965**, *37*, 106.
(5) Boyd, G. E.; Vaslow, F.; Lindenbaum, S. *J. Phys. Chem.* **1967**, *71*, 2214.
(6) Dorfner, K. *Ion Exchangers*; Ann Arbor Science: Ann Arbor, MI, 1972; Chapter 4.
(7) Helfferich, F. *J. Phys. Chem.* **1965**, *69*, 1178.
(8) Janauer, G. E.; Gibbons, R. E., Jr.; Bernier, W. E. in *Ion Exchange and Solvent Extraction*; Marinsky, J. A., Marcus, Y., Eds.; Marcel Dekker: New York, 1985; Vol. 9, Chapter 2.
(9) Alexandratos, S. D.; Wilson, D. L. *Macromolecules* **1986**, *19*, 280.
(10) Vernon, F. *Sel. Annu. Rev. Anal. Sci.* **1972**, *2*, 83.
(11) Grinstead, R. R. *J. Met.* **1979**, 13.
(12) (a) Vernon, F.; Nyo, K. M. *Anal. Chim. Acta* **1977**, *93*, 203. (b) Walsh, D. J.; Crosby, P.; Dalton, R. F. *Polymer* **1983**, *24*, 423.
(13) (a) Leyden, D. E.; Luttrell, G. H. *Anal. Chem.* **1975**, *47*, 1612. (b) Hiratani, K.; Onishi, Y.; Nakagawa, T. *J. Appl. Polym. Sci.* **1981**, *26*, 1475.
(14) Moyers, E. M.; Fritz, J. S. *Anal. Chem.* **1976**, *48*, 1117.
(15) Blount, C. W.; Tomas, T. L.; Gwill, S. M. *Anal. Chem.* **1975**, *45*, 1045.
(16) (a) Phillips, R. J.; Fritz, J. S. *Anal. Chem.* **1978**, *50*, 1504. (b) Fritz, J. S.; Gillette, R. K.; Mishmash, H. E. *Anal. Chem.* **1966**, *38*, 1869.
(17) Pollard, F. H.; Nickless, G.; Burton, K.; Hubbard, J. *Microchem. J.* **1966**, *10*, 131.

(18) Fritz, J. S.; Moyers, E. M. *Talanta* **1976**, *23*, 590.
(19) Yeh, H. C.; Eichinger, B. E.; Anderson, N. H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2575.
(20) Blasius, E.; Janzen, K. P. *Isr. J. Chem.* **1985**, *26*, 25.
(21) Sekine, T.; Hasegawa, Y. *Solvent Extraction Chemistry*; Marcel Dekker: New York, 1977; p 464.
(22) Alexandratos, S. D.; Quillen, D. R.; McDowell, W. J. *Sep. Sci. Technol.* **1987**, *22*, 983.
(23) Roche, T. S.; Wilkins, R. G. *Chem. Commun.* **1970**, 1681.
(24) Kielland, J. German Patent 715 200, 1941.
(25) Bayer, E.; Fiedler, H.; Hock, K. L.; Otterbach, D.; Schenk, G.; Voelter, W. *Angew. Chem.* **1964**, *76*, 76.
(26) Sugil, A.; Ogawa, N.; Hashizume, H. *Talanta* **1980**, *27*, 627.
(27) Takagi, M.; Ueno, K. In *Top. Curr. Chem.* **1984**, *121*.
(28) Agett, J.; Udy, D. J. *J. Inorg. Chem.* **1970**, *32*, 2802.
(29) Harmon, H. D.; Peterson, J. R.; McDowell, W. J.; Coleman, C. F. *J. Inorg. Nucl. Chem.* **1976**, *38*, 155.
(30) Antikainene, P. J.; Dyrssen, D. *Acta Chem. Scand.* **1960**, *14*, 86.
(31) Mathur, J. N. *Solvent Extr. Ion Exch.* **1983**, *1*, 349.
(32) Choppin, G. R. *Sep. Sci. Technol.* **1981**, *16*, 1113.
(33) Alexandratos, S. D.; Painton, C. D. C.; Quillen, D. R.; McDowell, W. J. *Sep. Sci. Technol.*, submitted.
(34) Farrall, M. J.; Frechet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877.
(35) Millar, J. R. In *Mass Transfer and Kinetics of Ion Exchange*; Liberti, L, Helfferich, F. G., Eds.; Martinus Nijhoff: The Hague, 1983; Chapter 1.
(36) Green, B. R.; Hancock, R. D. *Hydrometallurgy* **1981**, *6*, 353.
(37) Barrett, J. H. U.S. Patent 3 843 566, 1974.
(38) Clay, J. P. *J. Org. Chem.* **1951**, *16*, 892.
(39) Kinnear, A. M.; Perren, E. A. *J. Chem. Soc.* **1952**, 3437.
(40) Alexandratos, S. D.; Strand, M. A.; Quillen, D. R.; Walder, A. J. *Macromolecules* **1985**, *18*, 829.
(41) Peppard, D. F.; Mason, G. W.; Andrejasich, C. M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 697.
(42) Alexandratos, S. D.; Wilson, D. L.; Strand, M. A.; Quillen, D. R.; Walder, A. J.; McDowell, W. J. *Macromolecules* **1985**, *18*, 835.

Cis–Trans Isomerization of Alkyl-Substituted Allylic Ion Pairs. 2. Isomerization of Oligobutadienyllithium and Oligobutadienylsodium and of *n*-Butylallylpotassium and Its Relation to Anionic Butadiene Polymerization in Tetrahydrofuran

R. T. McDonald, S. Bywater,* and P. Black

Chemistry Division, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9. *Received August 21, 1986*

ABSTRACT: The allylic active centers present in the anionic polymerization of dienes exist in cis and trans forms. In THF the cis form is the more stable but is not normally formed in the transition state. Measurements of trans → cis isomerization rates are required to adequately describe the mechanism. These have been determined for oligobutadienyllithium and -sodium and for *n*-butylallylpotassium over a temperature range. The order of rates is $Li \gg Na > K$ as previously observed for neopentylallyl compounds. A bulky end-group effect was found important mainly for lithium. The results are correlated with changes of microstructure of polybutadiene observed as a function of temperature and counterion.

Anionic polymerization of dienes in polar or nonpolar solvents proceeds via active centers which can exist in either cis or trans form. The geometrical isomer immediately formed in the transition state is normally not the thermodynamically stable one. Competition between monomer addition and relaxation to the stable form determines which isomer reacts with monomer and influences the reactivity and stereospecificity of the reaction.[1] It is, therefore, important to measure anion-pair isomerization rates in order to fully understand the polymerization mechanism. In a recent publication,[2] we presented data on the trans to cis isomerization rates in tetrahydrofuran of a series of neopentylallyl–alkali metal salts with counterions, lithium, sodium, and potassium. These compounds which are easily prepared have been extensively characterized by spectroscopic techniques[3] and used as models for the growing active centers in anionic polymerization. The presence of a neopentyl substituent on the allylic system may, due to its bulky nature, affect some properties of such systems. There is no evidence that it affects significantly the equilibrium cis/trans ratio; this appears to require the *tert*-butyl group to be directly substituted on the allylic system.[4] A difference in cis,trans isomerization rates between 2-methylneopentylallyllithium and oligomers formed by isoprene addition to it was however observed in the first measured rates of isomerization of an aliphatic allylic compound in heptane.[5] It is important, therefore, to investigate end-group effects on isomerization rates in tetrahydrofuran, particularly if these results are to be used in the interpretation of microstructure changes in anionic polymerization.

Experimental Section

The preparation of suitable lithium compounds can be easily achieved by modification of the standard preparation of neopentylallyllithium.[2,6] Instead of equimolar amounts of butadiene and *tert*-butyllithium, a 3–4-fold excess of butadiene was used in benzene as solvent. The *tert*-butyllithium concentration used was $\sim 10^{-2}$ M, so that the microstructure of the enchained butadiene units will be largely, 1,4.[7] The benzene was removed in vacuum by freeze-drying and the product dissolved in tetrahydrofuran (THF) at $\sim$-90 to -95 °C.

For comparison purposes between the present experiments and those carried out earlier on neopentylallyllithium, the preparation of *n*-pentylallyllithium was attempted. Due to the much slower initiation rate, it cannot be prepared from equivalent amounts of *n*-butyllithium and butadiene. An 80% (mol) yield, however, together with 20% higher molecular weight products (mostly dimer) was obtained from $\sim 10^{-2}$ mol of *n*-butyllithium and a quarter of the number of moles of butadiene in $\sim$10 mL of benzene. The butadiene was distilled slowly from a side arm held at $\sim$-35 °C to a well-stirred solution of the initiator cooled to 5 °C.

A suitable allylic sodium compound could be made by starting with neopentylallylsodium prepared from neopentylallyllithium as described previously.[2] Addition of about 3 mol equiv of butadiene at low temperature in THF would produce a compound with a less bulky substituent on the allylsodium and primarily in the trans form.[9] Suggestions[10] that the small amount of residual lithium compounds present could have some effect on rates of similar processes led us to attempt a direct metalation of

0024-9297/87/2220-1196$01.50/0