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Synthesis of Interpenetrating Polymer Networks as Metal Ion Complexing Agents

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ABSTRACT: The synthesis of an interpenetrating polymer network (IPN) comprised of aliphatic polymers with metal ion complexing ligands within an inert support network is presented. Conditions are defined that permit a maximum entanglement for minimum loss of the polymer from its support network upon continuous elution conditions. The synthesis of the polymerizable metal ion extractant diundecenyl phosphate (DUP) is detailed as well as its incorporation as a toluene solution at a given concentration into macroporous polystyrene beads. The performance of the system after polymerization to give the IPN is compared to that of an unpolymerized control wherein the DUP/toluene solution is simply absorbed into the network (polymer-absorbed extractant, PAE) and to the analogous polymer-trapped extractant (PTE) in which the styrene is polymerized around the extractant. With 50% aqueous ethanol as the eluting solvent, 0.5 M DUP was determined to be the critical entanglement concentration, i.e., the minimum concentration of polymerizable extractant that permits a degree of polymerization high enough so that disentanglement from the support is noticeably hindered relative to the unpolymerized PAE control. Under conditions where the IPN loses 30% of its extractant, the PAE loses 60% and the comparable PTE loses 71%. Evidence is presented that the key variable in determining monomeric extractant loss is the porosity of the support network, with porosities over 60 vol % losing more than 90% of their extractant. The PTE syntheses show that the extractant acts like a diluent during the formation of the polystyrene chains, leading to high degrees of porosity and, hence, large extractant loss rates. While the DUP/IPN and DUP/PAE absorb fewer mercury ions from aqueous solutions than a DUP/toluene solution, probably due to a loss in extractant ligand mobility within a polymer network, both still perform as well as the PAE made from the conventional liquid extractant bis(2-ethylhexyl) phosphate. Extension of this research into membrane supports is proposed.

Introduction

The complexation of metals to monomeric and polymer-supported ligands yields compounds with many important applications, including drug design, catalysis, and chromatographic separations.[1a] The synthesis of compounds that can complex metal ions is an area of continuing importance for ion-exchange chromatography[1b] and metal-recovery processes.[1c] With both scarcity and toxicity as important reasons for metal-recovery processes, research is still focused on developing the most efficient method for recovering and recycling metals from water.[2] The goal has been and continues to be optimizing the process whereby the metal-loaded aqueous phase is contacted with an organic phase containing ligands that can quantitatively complex with the metal ions of interest and concentrate them in the organic phase for eventual recovery with no concomitant loss of the organic phase to the aqueous effluent.

The study of small-molecule liquid extractants for metal ion complexation reactions has long received considerable attention.[3] The liquid–liquid extraction process is very versatile given that any organic solvent can be used in combination with any organophilic compound containing ligands that will complex metal ions. The extraction kinetics can be diffusion-controlled,[4] allowing for minimal contact time between the phases. The extractant can be varied according to the metal ion targeted for separation: hydroxy oximes for complexation with copper,[5] bis(2-ethylhexyl) phosphate for complexation with cobalt,[6] tricaprylylamine for complexation with tungsten,[7] and tributyl phosphate for complexation with chromium,[8] to cite only a very few examples.[9] The versatility and simplicity of the process make it industrially feasible, though an important disadvantage which remains involves loss of the extractant into the aqueous phase through solubility and entrainment,[10] leading to increased costs and environmental pollution. Entrainment losses are a more serious problem than solubility losses, and this has prompted research into understanding the phase-disengagement process.[11]

On the other end of the conceptual spectrum lies the solid–liquid complexation process, wherein the extractant ligands are covalently bonded to a polymer support in the form of either beads[12] or membranes.[13] An aqueous phase contacts the polymer-supported extractant and the metal ions are removed from the water, usually by ion exchange. What this process loses in versatility, it makes up for in the fact that solubility and entrainment losses are clearly obviated. The complexation kinetics are no longer necessarily diffusion-controlled, making the polymer synthesis an important variable, especially given the possibility of losses through polymer attrition if the support network is improperly produced. Much attention has been focused on polymer-supported extractants since the first ion-exchange resins were produced,[14] including examples of polymeric hydroxy oximes,[15] picolylamines,[16] phosphine oxides,[17] sulfonic acids,[18] and phosphinic acids.[19] Overall utility is hampered in many cases, though, by the cost of producing some of the more specialized polymers.

An attempt to combine the versatility of the liquid extractants with the elimination of entrainment losses offered by the polymeric extractants has been set forth by Warshawsky[20] and others[21] with what has been termed solvent-impregnated resins.[20] In this technique, a polymer support, which is either inert or contains covalently bonded ligands, is allowed to absorb a solution containing a conventional liquid extractant. The principal complexing agent thus remains the liquid extractant but the carrier is now solid, allowing for the entire organic phase to be handled as if it were a solid. In this manner, the widely available liquid extractants can be utilized in both chromatographic separations[21c] and metal ion recovery processes[20] with the elimination of phase disengagement problems in the latter. The polymer support that has been studied is commercially available in the form of polystyrene beads,[20] making the process an important option

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as compared to liquid–liquid extraction and ion-exchange resins. The process, though, clearly retains the disadvantage of extractant solubility in the aqueous phase, which especially hinders its large-scale adoption into membrane supports with their very large surface area. Dissolving the extractant in with the styrenic or acrylic monomers and thus trapping it into the polymer matrix during the copolymerization reaction[22] can allow for a longer term entanglement than simple absorption, though at a loss in versatility. The inability to extend this concept of polymer-trapped extractants[23] to polypropylene membranes also hinders its overall utility.

The object of this research is to combine the versatility of absorbing extractants into a polymer support with the higher degree of extractant retention conceptually possible with polymer-trapped extractants through the synthesis of interpenetrating polymer networks (IPN)[24] containing complexing ligands and to do so in such manner that the technique would be feasible in membranes as well as polymer beads. IPN's have been produced from a given polymer support into which is absorbed a compatible monomer followed by polymerization within the network to form a polymer within a polymer. Typical examples include polyacrylates in poly(styrenesulfonic acid)[24b] and poly(ethyl acrylate) in polystyrene.[24c] Our research extends this concept into the area of polymeric extractants for metal ion complexation: a readily available polymer support forms the initial matrix into which is absorbed a polymerizable monomer containing a ligand that can complex metal ions; free radical polymerization results in a polymeric extractant entangled within the original support network, thus giving an interpenetrating polymer network of extractant polymer within a support polymer. The entanglement obtained should dramatically reduce loss of the extractant into the aqueous phase, given especially that the molecular dimensions of the extractant have increased tremendously relative to the polymer pore size; results of experiments confirming this are presented below. For comparison purposes, resins have also been synthesized via the concept of polymer-trapped extractants in order to describe the relative extractant retention abilities of both techniques.

Essential to maintaining the general applicability of IPN's is that the support network be generally available and the polymerizable extractants be readily synthesized. The former consideration has been addressed by using polystyrene beads as the support in these initial experiments. Polystyrene is compatible with a wide range of compounds having varying polarities and is synthesized on a large scale for many uses, including the production of ion-exchange resins.[25] Given that polymeric membranes are an important alternative to polymers in bead form, we have also investigated the use of Celgard[26] and Accurel[27] polypropylene membranes as the support network in collaboration with Argonne National Laboratory;[28] we shall be reporting on this work in a future publication. Organophilic phosphoric acid derivatives have been used as metal ion extractants;[29] two much-studied examples are bis(2-ethylhexyl) phosphate[30] and di-*n*-octyl phosphate.[31] Given that an understanding of what to expect with such extractants already exists through literature precedent, it was decided to focus on polymerizable extractants containing the phosphoric acid ligand and the general type (RO)(R′O)P(O)OH, where either or both of the R groups are alkenyl. Absorption of the polymerizable phosphoric acid molecules within polystyrene beads, followed by polymerization through their vinyl groups, allows for the synthesis of an interpenetrating polymer network of extractant ligands through an inert matrix. The synthesis of such a system, the subsequent characterization, the analysis for extractant loss, and the system's utility for extracting mercury from solution form the subject of the present report.

Results and Discussion

The polymer support into which the extractant is absorbed was a polystyrene network cross-linked with 5% divinylbenzene (DVB) in the form of macroporous beads. The beads were synthesized by conventional suspension polymerization[32] with a solution containing 50% monomer (styrene, DVB) and 50% diluent (4-methyl-2-pentanol); upon polymerization, the diluent was steam-distilled out of the beads, leaving 500–1000-Å macrochannels in a network having approximately 50 vol % porosity.[33] This particular combination of channel size and porosity is representative of the membrane that will be studied, thus allowing for any differences in entanglement that are found between the extractant polymer and the support network to be due to the chemical nature of the support and not its physical nature.

The emphasis on disubstituted phosphoric acids, (RO)(R′O)P(O)OH, led to the synthesis of new extractants containing polymerizable double bonds. The substituents had to be sufficiently organophilic in order for the extractant to be absorbed by the polystyrene (and, later, polypropylene) support; organophilicity could be endowed by the R group, allowing for R′ to be a relatively small moiety (e.g., propyl). The advantage of both groups containing a double bond would be that a more extensive network could be formed given the difunctional nature of the monomer and the probability of cross-linking reactions. This advantage could turn into a disadvantage if a large degree of polymerization decreased the mobility of the extractant ligands to the point where the rate of the complexation process was affected; this would be particularly important with membranes where the permeability of the membrane is the key variable and would then require control of the polymer chain length during synthesis.

The synthetic effort has targeted an unsymmetrical and a symmetrical extractant, allyl 2-ethylhexyl phosphate (AEHP) and diundecenyl phosphate (DUP), respectively.

$$\underset{\text{AEHP}}{CH_2{=}CHCH_2OP(O)(OH)OCH_2CH(Et)CH_2CH_2CH_2CH_3}$$

$$\underset{\text{DUP}}{(CH_2{=}CH(CH_2)_9O)_2P(O)OH}$$

Such compounds are conceptually similar to those used in the synthesis of polymeric vesicles.[34] The allylic group can undergo oligomer formation (chain lengths <14)[35] rather than true polymer formation due to its effective chain-transfer mechanism, and this self-limiting process could prove ideal as we try to balance chain length with the kinetics of extraction.

The method of synthesis is similar for both AEHP and DUP, involving reaction of the precursor alcohols with $POCl_3$ followed by hydrolysis, as indicated in eq 1 and 2.

$$CH_3CH_2CH_2CH_2CH(Et)CH_2OH + POCl_3 \rightarrow CH_3CH_2CH_2CH_2CH(Et)CH_2OP(O)Cl_2 \xrightarrow{CH_2{=}CHCH_2OH} \xrightarrow{H_2O} \text{AEHP} \quad (1)$$

$$2CH_2{=}CH(CH_2)_9OH + POCl_3 \rightarrow \xrightarrow{H_2O} \text{DUP} \quad (2)$$

From the synthetic standpoint, AEHP is a difficult molecule to work with because the allyl group is prone to S_N2' rearrangement,[36] in this case from the intermediate phosphonyl chloride. The net result of this side reaction is the production of allyl chloride and a large amount of diacid, 2-ethylhexyl phosphate, from which separation of the monoacid in the desired purity has been found to be quite difficult. Current modifications in the synthetic technique, emphasizing especially the order of addition (the allyl alcohol being added after complete reaction of 0.25 M 2-ethylhexanol with 0.25 M $POCl_3$) has led to the isolation of AEHP, albeit in low yields to date. For this reason, it is the synthesis of DUP and its corresponding IPN's that will be described in the present report.

Monomer Preparation. The DUP synthesis can be divided into the following parts: reaction conditions (reactant stoichiometry, time/temperature, solvent), isolation of the crude monoacid, purification, and identification. Optimization of the reaction conditions is important because of the possibility of byproduct diacid and triester formation. Two factors that maximize monoacid yield have been found to be the use of pyridine as a cosolvent with ether and the utilization of an undecenol: $POCl_3$ ratio of 2.1:1. The presence of pyridine limits the amount of triester, as reported by Kosolapoff;[37] the 5% excess of alcohol relative to the ideal 2:1 ratio with $POCl_3$ limits the amount of diacid. Upon completion of the hydrolysis, which leads to the formation of the acid from the phosphonyl chloride, isolation of the monoacid from the reaction mixture usually entails a number of NaOH washes, but this is of limited utility with DUP where the difference in the hydrophobic character of the acids and the triester is small due to the dominant contribution of the long hydrocarbon chains. For this reason, developing an appropriate purification scheme was very important to the isolation of pure monoacid. We have found that precipitation of the cupric salt[38] allows for the isolation of the monoacid in 96% purity, as determined by titration curve. Key modifications to the published procedure[38] were necessary due to differences in behavior of DUP relative to bis(2-ethylhexyl) phosphate, for which the procedure was devised; these modifications are detailed in the Experimental Section. One pass through the copper technique is all that is required to give product in at least 96% purity. The product and its purity are identified through common spectroscopic techniques and a comparison of the acid capacity as determined by NaOEt titration with the capacity calculated from a phosphorus elemental analysis. Purification of the product has consistently led to agreement between the two values and the theoretically calculated value. In a typical synthesis, an acid capacity for the final product of 2.52 mequiv/g and a phosphorus capacity of 2.65 mequiv/g is obtained compared to a theoretical capacity of 2.48 mequiv/g.

IPN Preparation. In the initial synthesis of the IPN, 5% DVB polystyrene beads (−20+40 mesh) were placed in a 1 M DUP/toluene solution containing 2% AIBN (w/v) as the free radical initiator for 48 h in order to ensure complete swelling. Polymerization was then carried out at 60 °C for 96 h. Principal evidence for polymerization of the DUP and the successful attainment of an IPN is obtained by comparing the tendency of the polymerized extractant to elute out of the beads relative to an unpolymerized control wherein the monomeric extractant is absorbed into the polystyrene and utilized as such (to be referred to in what follows as a polymer-absorbed extractant, or PAE). Previous studies on DUP-like compounds by Fendler[34c] have shown that they undergo complete polymerization with AIBN as preformed vesicles through ^1H NMR analysis. While polymerizations of compounds in the vesicular state cannot be directly compared to the usual solution polymerizations, given that state's highly condensed nature,[34e] they do indicate the ability of allylic groups to polymerize at the reasonably high concentrations employed in the present study. A 2 M toluene solution of AEHP was found to undergo a 40% decrease in double bonds (by ^1H NMR[34c]) over 72 h with AIBN initiation. A 1 M DUP solution undergoes a significant extent of reaction over 96 h, as seen by HPLC analysis. Full characterization by vapor phase osmometry is currently in progress.

Extractant-containing resin was also synthesized by polymerizing styrene and DVB via bulk polymerization in the presence of DUP. Though it is possible that the DUP may be copolymerized into the styrenic backbone, an examination of allylic reactivity ratios[39] indicates that homopolymerization is more probable: for example, r_1(styrene) = 90 and r_2(allyl acetate) = 0 at 60 °C and r_1(styrene) = 31.5 and r_2(allyl chloride) = 0.016 at 70 °C. The polymer's elution characteristics should better define the degree of copolymerization. DUP solutions of 0.5 and 1 M were thus made in styrene with enough DVB to give 3% cross-linking. A slightly lower level of cross-linking was used than with the IPN's described above since the polymer could not be made macroporous here through the addition of an inert diluent (any attempt to remove it would also remove extractant). A 1 M bis(2-ethylhexyl) phosphate (DEHP) solution in styrene/DVB was also polymerized as a control to unambiguously give a polymer-trapped extractant (PTE). The polymerization utilizing 1 M extractant solutions phase separated[33] 15 min after reaching temperature, as evidenced by their changing from clear to opaque. The 0.5 M DUP solution became translucent after 1.5 h. After polymerization, the bulk polymers were ground to −20+40 mesh and used as described in the subsequent experiments.

Critical Entanglement Concentration. The degree of entanglement of the polymerized DUP through a given polystyrene network is clearly the most important variable in determining whether the extractant will be eluted from the beads. In order to establish the influence of extractant solution concentration on the extent of extractant loss upon elution and, hence, upon the extent of extractant entanglement within the polymer network, IPN's were prepared from polystyrene beads and 0.25, 0.50, 1.0, and 1.5 M DUP/toluene solutions. This leads to the definition of a new variable, the critical entanglement concentration (cec), which can be considered to be the minimum concentration of extractant required within a polymer support to yield an interpenetrating network upon polymerization; the effectiveness of the entanglement can be followed by an elution sequence relative to unpolymerized controls at the same extractant concentration.

Upon synthesis of the IPN's, the beads were Büchner-dried, rinsed with 25% ethanol to remove polymerized DUP from the surface, and placed in glass frit funnels for elution studies. An elution sequence was then established that would not only illustrate any difference between the polymerized sample and its unpolymerized control but also allow for extractant disentanglement to occur over a reasonable length of time. The extractant loss was followed by removing a small portion of the beads at hourly intervals and performing a phosphorus elemental analysis on them.

The simplest elution study involved continuously dripping water through a 20-mL resin bed volume over a period of 5 days. During that time, no loss in extractant was found from polymerized samples (IPN's) made from 0.5 and 1 M DUP solutions: the initial and final capacities for the former were 1.28 and 1.24 mequiv/g while for the

Table I
Elution Study on 0.5 M DUP/IPN and DUP/PAE with Aqueous Ethanol Solutions[a]

	ethanol,[b] vol %						
	0	5	10	15	25	50	95
DUP/IPN capacity[d]	1.21[c]	1.08	1.11	1.07	1.06	0.98	0.34
DUP/PAE capacity[d]	1.37[c]	1.22	1.01	0.97	0.92	0.74	0.45

[a] 1 L/h. [b] Aqueous solution. [c] Initial capacity prior to elution. [d] Units of mequiv/g.

Table II
Elution Study at 1 L/h on DUP/IPN and DUP/PAE with 50% Aqueous Ethanol

	no. elutions 1 L/h						
	0	1	2	3	4	5	6
0.25 M DUP/IPN[a]	0.69	0.52	0.41	0.42	0.35	0.31	0.31
0.25 M DUP/PAE	0.59	0.39	0.30	0.36	0.29	0.21	0.21
0.50 M DUP/IPN	1.31	1.01	1.02	0.75	0.70	0.78	0.70
0.50 M DUP/PAE	1.17	0.88	0.63	0.51	0.48	0.42	0.36
1.0 M DUP/IPN	1.34	1.17	1.01	0.95	0.92	0.92	0.89
1.0 M DUP/PAE	1.46	1.13	0.92	0.75	0.68	0.60	0.59
1.5 M DUP/IPN	1.71	1.66	1.44	1.41		1.31	1.32
1.5 M DUP/PAE	1.71	1.78	1.48	1.24	1.03	1.01	0.93

[a] Units of mequiv/g.

latter they were 1.30 and 1.24 mequiv/g. A definite extractant loss was found for an unpolymerized PAE control made from a 1 M DUP solution: 1.52 mequiv/g initial capacity, 1.07 mequiv/g final capacity. While pointing strongly toward an efficient entanglement upon formation of the IPN, aqueous ethanol solutions were utilized to accelerate extractant loss from an unpolymerized PAE and the corresponding IPN when no extractant loss was found with 8-L elutions (over 8 h) using solutions of 0.1 M HNO_3 in 0.1 M $NaNO_3$, 0.1 M NaOH in 0.5 M $NaNO_3$, and 1 M NaOH. With IPN beads produced from a 0.5 M DUP solution, the bead capacity was followed as a function of 1-L elutions with ethanol solutions having a decreasing aqueous content. The results, given in Table I, show that there is no difference in capacity of the IPN when eluting with 5%–25% ethanol solutions while a capacity decrease is observed with the PAE; the largest capacity difference between the two samples occurs when using 50% ethanol as the eluent with a small decrease in capacity observed with the IPN as well. An elution with 95% ethanol removes most of the extractant from both systems, proving that the entanglement is not an irreversible process. The first wash must be removing the most accessible extractant, presumably that just below the surface, as indicated by the resin capacity before and after elution with 5% ethanol. Given that later studies suggested that levels of ethanol greater than 70% are too nondiscriminatory between polymerized and nonpolymerized systems, 50% ethanol was used in the study of the entanglement influence on extractant loss.

A 1 M DUP/toluene solution was absorbed into two sets of beads, one of which was heated to form an IPN and the other kept at 25 °C as an unpolymerized PAE. Both were then eluted with 50% ethanol at a rate of 1 L/h for a total of 6 h. The effect of elution on the resin capacity is shown in Figure 1, wherein the PAE loses 60% of the extractant it contained originally while the IPN loses 30% of its original value. The influence of polymerization on the rate of extractant loss is thus established under the accelerated conditions utilized with 50% ethanol; given, then, the importance of entanglement, it next became necessary to establish the cec, as defined above.

Solutions of DUP in toluene were made up at concentrations of 0.25, 0.50, and 1.5 M. Six sets of polystyrene beads absorbed the solutions, three of which were heated to form IPN's and three of which remained as PAE's. The elution treatment using 50% ethanol was identical with each. The effect of ethanol elution on bead capacity is given in Table II. The conclusions that can be drawn from it are (a) there is little difference in the rate and extent of extractant loss when 0.25 M DUP is used for IPN synthesis relative to its control, and (b) the rate of extractant loss diminishes greatly after three ethanol washes with 0.5 and 1 M DUP/IPN's and after two ethanol washes with 1.5 M DUP/IPN. The cec, therefore, is established as 0.5 M DUP; i.e., 0.5 M is the minimum concentration that will allow the formation of a polymeric system through the polystyrene support large enough so that disentanglement via elution is noticeably hindered relative to the unpolymerized control. This is reflected in the percent decrease of extractant capacity for the polymerized and unpolymerized systems: 55% and 66% (0.25 M); 46% and 69% (0.5 M); 30% and 60% (1 M); 23% and 46% (1.5 M). In thus synthesizing IPN's from long-chain acids or bases for metal ion extraction processes where extended stability within the support network is a requirement, initial solution concentrations should be at least 0.5 M and preferably 1 M in the polymerizable extractant.

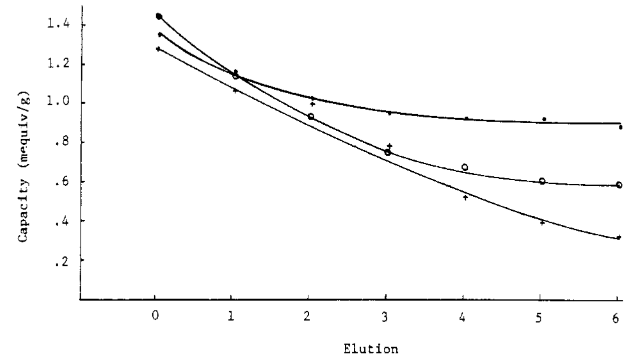

Figure 1. Bead capacity as a function of 50% aqueous ethanol elutions: (●) 1 M DUP/IPN; (○) 1 M DUP/PAE; (+) 1 M DUP/PTE.

Optimization of the Support Network. The next point studied was whether polymerizing the support network around the extractant to give a polymer-trapped extractant (PTE) held any advantage over simply absorbing a monomeric extractant into a preformed polymer network to give a polymer-absorbed extractant (PAE). As noted earlier, the DUP/PTE held the possibility of per-

Table III
Elution Study at 1 L/h on DUP/PTE, DEHP/PTE, and DEHP/PAE with 50% Aqueous Ethanol

	no. elutions 1 L/h						
	0	1	2	3	4	5	6
1.0 M DUP/PTE[a]	1.26	1.06	0.99	0.77	0.52	0.39	0.36
0.5 M DUP/PTE	0.65	0.34	0.28	0.32	0.26	0.25	0.26
1.0 M DEHP/PTE	1.12	0.76	0.47	0.45	0.42	0.40	0.40
1.0 M DEHP/PAE	1.41	1.21	0.73	0.40	0.35	0.38	0.30

[a] Units of mequiv/g.

manent incorporation through copolymerization (but without a high probability, given the reactivity ratios found for comparable systems). The elution study of extractant beads made from a 1 M solution of DUP in styrene (1 M DUP/PTE) is presented in Table III and best seen in Figure 1: the PTE is not nearly as good as the DUP/IPN in extractant retention and, worse still, loses extractant at a faster rate than the 1 M DUP/PAE. Whereas the 1 M DUP/IPN loses 30% of its capacity during the entire elution sequence and the 1 M DUP/PAE loses 60% of its capacity, the corresponding PTE loses no less than 71% of its capacity. That the capacity that remains in the PTE beads after the elutions (0.36 mequiv/g) is not due to copolymerization into the styrene backbone is shown by the fact that eluting the beads once with 500 mL of toluene leaves them with a capacity of 0.05 mequiv/g, reflecting a negligible incorporation. The elution data, supported by the reactivity ratios, show that the DUP does not copolymerize with styrene, and the rate of extractant loss further suggests that the DUP remains monomeric; the styrene must therefore homopolymerize and reach the gel point[40] before the DUP can itself homopolymerize. While this explains the rapid DUP loss in the PTE relative to the IPN, it does not explain the faster rate loss relative to the PAE; we shall return to this point shortly.

The conclusions made from studying the 1 M DUP systems are strengthened by the similarities found with the comparable 0.5 M DUP systems. As seen by comparing the 0.5 M DUP results in Tables II and III, the IPN and its PAE control lose 46% and 69%, respectively, of their extractant over the course of the elution sequence, while the PTE loses somewhat less than the PAE (62%). Again, the similarity in behavior between the PAE and the PTE supports the contention of no DUP polymerization (the resin capacity drops from 0.26 mequiv/g found with the last ethanol wash to 0.05 mequiv/g upon washing with toluene) and no additional entanglement obtained when the DUP is present during the formation of the polystyrene to hinder its loss upon elution.

The results obtained with 1 M DEHP as the extractant are given in Table III. The final capacity of the PTE resin is comparable to that from the 1 M DUP (0.40 vs. 0.36 mequiv, respectively) and only slightly higher than the 1 M DEHP/PAE resin (0.30 mequiv). Its residual capacity after washing with toluene is 0.005 mequiv/g, compared to 0.05 mequiv for the 1 M DUP/PTE, thus pointing to the possibility of a very low, though real, incorporation of the DUP into the polystyrene chains. The 1 M DEHP/PAE loses 79% of its extractant over the same time period that the analogous DUP resin loses 60%, indicating an inherently lower entanglement due to smaller side chains; the PTE loss is smaller for the DEHP than the DUP resin (64% vs. 71%, respectively), and this is a point to be addressed along with the rate of DUP loss in the PTE relative to its PAE.

An understanding of the elution kinetics of the PTE's and the corresponding relationship to the PAE's is obtained only by taking into account the nature of the polystyrene support as it forms around the extractant. The PTE's should not be considered simply as gel (i.e., microporous) polymers trapping extractants within their networks. The DUP and DEHP extractants are actually playing the role of diluent, much as 4-methyl-2-pentanol (4M2P) does during the synthesis of the polystyrene supports[33] for the PAE's. A macroporous polystyrene network is thus formed wherein the extractants are held both within the network and within the pores in exactly the same way that the PAE extractants operate. Direct evidence for the formation of a macroporous network is the observation of opacity noted earlier during the synthesis which is due to phase separation of the polystyrene chains from the surrounding solution of extractant and monomer and which is directly responsible for the macropores. The greater the polarity difference between the diluent and the growing polymer chain, the greater the diluent's efficiency in forming macropores at a given concentration due to earlier onset of phase separation;[41] this suggests that DUP and DEHP are more effective diluents than 4M2P, given their higher molecular weight and more polar nature, with DUP more so than DEHP due to its greater aliphatic character.[42] Within this context, then, it is important to note that the 1 M DUP/styrene solution consists of 46% DUP by weight, the 0.5 M DUP/styrene solution consists of 23 wt % DUP, and the 1 M DEHP/styrene solution consists of 37 wt % DEHP. The 46% DUP could act like 50–60% 4M2P during the styrene polymerization to give a more porous network than the 50% 4M2P used for the PAE's; the 37% DEHP could act like 40–50% 4M2P during the styrene polymerization to give a somewhat less porous network; and the 23% DUP could act like 25–35% 4M2P to give again a less porous network. These considerations would allow the elution kinetics to be explained by assuming porosity to be the key variable for loss of monomeric extractant: the more porous a network, perhaps above a certain level, the faster the extractant loss upon elution. The 1 M DUP/PTE should be a more porous network than the 1 M DUP/PAE, leading to a faster extractant loss for the former (−71% vs. −60%), thus explaining the relative ordering at the end of the elution sequence shown in Figure 1. The 0.5 M DUP/PTE should have less porosity than the 0.5 M DUP/PAE, leading to a lower rate of extractant loss for the former (−62% vs. −69%). The 1 M DEHP/PTE should have somewhat less porosity than the 1 M DEHP/PAE, leading to a somewhat lower extent of extractant loss for the former (−64% vs. −79%).

While a hypothesis centering on network porosity as the property that determines the extractant loss rate is consistent with experiment, it was examined through the following experiment: 5% DVB/styrene copolymers were synthesized at four levels of porosity with 30% (by weight) 4M2P, 50% 4M2P, 60% 4M2P, and 70% 4M2P. The diluent was washed out of the polymer network with ethanol; the polymer was then dried to give networks with increasing degrees of opacity as well as increasing friability in the order of increasing diluent concentration, sieved to

Table IV
Capacity[a] of 1 M DUP/PAE's Having Polystyrene Networks from Different Diluent Levels after 50% Aqueous Ethanol Elution at 1 L/h

	no. elutions 1 L/h						
	0	1	2	3	4	5	6
30% diluent network	0.62	0.35	0.21	0.20	0.23	0.23	0.23
50% diluent network	1.36	1.14	1.13	0.93	0.82	0.60	0.55
60% diluent network	1.39	1.18	0.35	0.14	0.096	0.095	0.096
70% diluent network	1.11	0.71	0.15	0.079	0.071	0.066	0.065

[a] Units of mequiv/g.

-20+40 mesh, allowed to swell in 1 M DUP toluene solution, and eluted with 50% aqueous ethanol to follow the rate of extractant loss as a function of network porosity. The results are given in Table IV and clearly support the overriding influence of network porosity on extractant loss. The network made from 30% 4M2P lost 63% of its extractant over the entire elution sequence, the 50% 4M2P network lost 60% (thus reproducing the 1 M DUP/PAE results given in Table II, which also show a 60% extractant loss), the 60% 4M2P network lost 93% of its extractant, and the 70% 4M2P network lost 94% of its extractant. Given the established relationship between diluent level and network porosity to approximate the value of the latter,[33,43] we conclude that networks with a level of porosity at or below 50 vol % (as obtained with 50% 4M2P) lose 60% of the extractant originally contained, and those with greater than 60 vol % porosity (as obtained with 60% 4M2P) lose more than 90% of the extractant originally contained. The direct relationship between percent diluent and percent porosity holds only for good nonsolvents like 4M2P.[43] We are currently working on establishing the correlation within our systems by porosimetry. The conclusions are, nonetheless, in line with the PTE results. The 1 M DUP/PTE can be expected to have 50–60 vol % porosity, thus yielding the 71% extractant loss (compared to 60% for the corresponding PAE, which has 50 vol % porosity), the 0.5 M DUP/PTE must have less than 50 vol % porosity, thus yielding the 62% extractant loss, and the 1 M DEHP/PTE, though not strictly on the same scale due to the expected lower level of chain entanglement, still has a porosity of 50 vol % or less, thus yielding an extractant loss of 64%. In the design, then, of extractant supports, there is no disadvantage to utilizing the simple PAE concept relative to the PTE concept as long as the support network does not exceed a porosity limit of 50 vol %. This conclusion should also be applicable to membranes and is under investigation.

Complexation of Mercury(II). After it was established that the IPN's can be expected to have a much longer lifetime than the unpolymerized analogues, the ability of IPN's to complex metal ions relative, again, to unpolymerized controls was studied. Mercury was chosen for this initial work because of its importance, availability, and ability to be quantified titrimetrically.[44]

The inherent affinity of DUP for mercury relative to the conventional liquid extractant DEHP was determined by contacting 10 mL each of 0.1 M DUP and 0.1 M DEHP solutions in toluene with 100 mL of 0.01 N mercuric nitrate (thus giving an initial ratio of $[\text{mequiv Hg(II)}]_i/[\text{mequiv H}^+]_i$ of 1) until equilibrium had been attained. Analysis of the aqueous phase showed that the DUP had absorbed 98% of the mercury while the DEHP had absorbed only 45%; the former had a final pH of 1.80 and the latter a pH of 2.00. The excellent complexing ability displayed by DUP is maintained when polymerized: when the polymerized DUP in toluene is contacted with mercury under the same conditions as above, 98% of the mercury is absorbed. The lower extent of extraction for DEHP has been observed in comparative studies with di-*n*-octyl phosphate, with very similar results obtained.[45]

The extraction ability of the IPN prepared from 1 M DUP solution with polystyrene beads was determined and compared with results obtained from the unpolymerized PAE (1 M DUP in polystyrene), as well as the 1 M DEHP/PAE. A 1-L solution of 0.01 N $Hg(NO_3)_2$ was passed through a given weight of each polymer with a 1-h elution time and the amount Hg(II) absorbed determined from analysis of the effluent. Given that the initial capacities of each, on a dry weight basis, were 1.37 mequiv/g (DUP/IPN), 1.34 mequiv/g (DUP/PAE), and 1.59 mequiv/g (DEHP/PAE), the ratio of total mequiv Hg(II) passed through each polymer bed to the total polymer exchange capacity was 1.6, 1.6, and 1.4, respectively.

The DEHP/PAE absorbed 34% of the Hg(II) in the eluent. Since 45% Hg(II) is absorbed under equilibrium conditions at an initial ratio (Hg:DEHP) of 1, the extent absorbed under equilibrium conditions with the current ratio (1.4) would be expected to be 32%, assuming that the same exchange capacity is maintained. The results thus suggest that the rapid kinetics known to be true with liquid–liquid extraction[4] are not necessarily affected when the extractant is within a polymer network. These results contrast with those found for the bulkier DUP, since the DUP/PAE absorbs 40% of the Hg(II). If the 98% loading observed in the equilibrium liquid–liquid extraction experiment is maintained at the 1.6 ratio used here, the maximum amount of Hg(II) that can be absorbed from solution is 62%; that the observed value is $^1/_3$ lower than the calculated value indicates that absorption of a bulky extractant within a polymer network may increase the time required to attain equilibrium. Polymerization of the extractant within a network has an additional effect on the extent of extraction, given that the DUP/IPN absorbs 32% of the Hg(II). The most likely explanation for this decrease is that the extractant ligands lose more of their mobility upon polymerization, which is reflected in a longer time to achieve equilibrium. Note, though, that even with a loss in mobility, the DUP performs as well as the DEHP. We have found with polymer-supported extractants that equilibrium times can be decreased by increasing support macroporosity,[46] but this avenue is not available to us here, given the increased extractant loss rate at higher porosities. Our current approach is to increase ligand mobility through lower degrees of polymerization and polymerization through one R group, allowing for a smaller R′ group to be utilized.

Conclusions

The concept of using interpenetrating polymer networks as metal ion complexing agents has been investigated through the synthesis of polymerizable liquid extractants and their subsequent free radical polymerization within a polystyrene network. Polymerization increases the retention of the extractant within the support, though with a concomitant impact on the metal ion extraction kinetics. The versatility of the process combined with the long-term stability of the extractant enhances the feasibility of the technique as a third option to liquid–liquid extraction and polymer-supported extractants for metal ion complexation. More comprehensive metal ion studies are currently being carried out in our laboratory. Syntheses of other extractants are aimed at examining the influence of increased ligand mobility through the polymerization of monofunctional extractants and the utilization of groups other than long-chain alkenyls.

Experimental Section

Macroporous Support Synthesis. Suspension polymerization is used to synthesize the support network in the form of beads having approximately 1-mm diameter. An aqueous phase consisting of 0.96 g of gelatin, 11.90 g of poly(diallyldimethylammonium chloride) (Calgon Corp.), and 6.33 g of boric acid in 316.5 mL of H_2O adjusted to pH 10.3 with 50% NaOH is poured into a 1-L round-bottom flask equipped with a condenser, nitrogen purge, thermometer, temperature control device (Instruments for Research and Industry; Cheltenham, PA), and an Eberbach Con-Torque stirrer. The organic phase (134.95 g of styrene (Aldrich), 13.55 g of divinylbenzene (55.4% DVB isomers, remainder as ethylstyrene isomers, Dow Chemical Co.), 1.50 g of benzoyl peroxide, and 150 g of 4-methyl-2-pentanol (Aldrich)) is then added to the flask; the suspension is set at a stir rate of 185 rpm, followed by heating to 80 °C over a 2 h period and holding at 80 °C for 10 h. The pentanol is removed from the polymer beads by steam distillation over 6 h. Upon cooling, they are water-washed, dried, and sieved.

DUP Synthesis. A solution of 42.93 g of $POCl_3$ (0.28 mol) and 110.7 g of pyridine (1.4 mol) in 1 L of anhydrous diethyl ether is poured into a flame-dried 2-L round-bottom flask equipped with thermometer, overhead stirrer, and addition funnel containing 250 mL of a 2.35 M 10-undecen-1-ol/ether solution. The alcohol is added over a period of 5 h in order to maintain a temperature of 25–30 °C. Stirring is continued for 16 h, followed by the addition of 350 mL of 3.42 N H_2SO_4 over 2 h. The ether phase is then taken on to the copper purification step.

Purification: $Cu(DUP)_2$ Formation. The ether phase is washed with 160 mL of 2 N NaOH in saturated $NaNO_3$ and then with saturated $NaNO_3$ solution until the washings are neutral. After the DUP is converted to its sodium salt form, 400 mL of 1 N $CuSO_4$ is added and the mixture shaken vigorously for 5 min. After the phases are separated, most of the ether is removed by evaporation under vacuum and the viscous liquid is added to 2 L of acetone. When the acetone solution is cooled with an ice water bath, a blue precipitate forms ($Cu(DUP)_2$), which is collected, washed with cold acetone, and air-dried at 25 °C for 24 h.

Purification: Reacidification of $Cu(DUP)_2$. The $Cu(DUP)_2$ is dissolved in 200 mL of ether and washed four times with 100 mL of 4 N HCl. The ether is removed, and the white solid is dissolved in 200 mL of anhydrous ether, which is again removed. The process is repeated until the DUP is free of any HCl odor. Pure DUP (mp 33.0–34.8 °C) can thus be obtained in 75% yield based on $POCl_3$.

Characterization: Base Titration. A weighed amount of DUP (approximately 0.700 g) is dissolved in 50 mL of 95% ethanol and titrated with 0.1 N NaOEt.

Characterization: % P Elemental Analysis.[47] A weighed amount of oven-dried DUP (20 mg) or resin (50 mg) is digested by heating with 5 mL of HNO_3/5 mL of 72% $HClO_4$ to a clear and colorless solution. After the mixture is cooled and diluted to 100 mL with water, a 10-mL aliquot is added to 3.5 mL of 72% $HClO_4$, 3.5 mL of ammonium molybdate solution (4.14 g in 50 mL of H_2O), and 4.5 mL of fresh amidol reagent (1 g of recrystallized amidol (Aldrich), 2.7 mL of H_2SO_4, and 10 g of Na_2SO_3 in 90 mL of H_2O). The solution is then further diluted to 50 mL and allowed to develop for 30 min. The absorbance is measured at 700 nm on a Bausch and Lomb Spectronic 21 and the % P calculated from a Beer's law plot with a series of KH_2PO_4 standards. All glassware must be rinsed completely free of phosphate detergents.

PAE Synthesis. The DUP/toluene solutions are made up at the concentrations reported (0.5–1.5 M) with 2% AIBN (w/v) added as the free radical initiator; the DEHP solutions are made up the same way except without the addition of AIBN. The PAE's are obtained after the beads are allowed to swell in the DUP solutions for 48 h.

IPN Synthesis. Polymerization of the DUP solutions within the beads is accomplished by placing the vial containing the DUP/PAE beads in an oil bath at 60 °C and holding at that temperature for 96 h.

PTE Synthesis. Into a 10 g batch of monomer (9.33 g of styrene, 0.570 g of 55.4% DVB solution (for 3% cross-linking), and 0.0978 g of benzoyl peroxide as initiator) is placed enough DUP to give a 0.5 or 1 M solution (3.017 g and 8.519 g, respectively); 5.938 g of DEHP is added to 10 g of monomer solution for the 1 M DEHP/PTE. The solutions are heated in an oil bath over a 2-h period to 80 °C, where they are held for 10 h. When cooled, the polymers are ground by using a micromill (Lab Apparatus Co., Cleveland, OH) to obtain a −20+40 mesh cut of fairly spherical particles. Prior to elution, the particles are swollen in a minimum amount of toluene in order to simulate the PAE's.

Elution Study. The polymers are suction-filtered to remove excess toluene solution, rinsed with 25% ethanol, and placed in glass-frit funnels. A sample is taken for % P analysis prior to any elution in order to determine the initial capacity. The polymers are then eluted with aqueous ethanol solutions (1 L/h) with samples taken hourly for % P analysis in order to quantify the rate of extractant loss. The first study was done with an elution sequence of 5, 10, 15, 25, 50, and 95% ethanol solutions (Table I); the later studies focused on 50% ethanol solutions over longer times (6 L/6 h).

Mercury Equilibrium Study. A 0.1 M DUP/toluene solution (10 mL) is shaken with 100 mL of 0.01 N mercuric nitrate for 17 h. A 50-mL aliquot from the aqueous phase is then taken and titrated for Hg(II) in order to determine the % Hg(II) absorbed.

Volhard Titration for Hg(II). An aliquot of known volume is added to 5 mL of 6 N HNO_3 and 5 mL of saturated ferric ammonium sulfate solution. Titration with 0.05 M NH_4SCN is to the first permanent burnt orange end point.

Mercury Elution Study. The polymers are treated initially as in the ethanol elution study. Once the sample is in the frit, 1 L of 0.01 N mercuric nitrate is passed through in 1 h and collected in a volumetric flask. A 100-mL aliquot is titrated as above in order to determine the mercury uptake.

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Registry No. DUP, 82280-44-2; DUP (homopolymer), 82280-45-3; $POCl_3$, 10025-87-3; (DVB)·(styrene) (copolymer), 9003-70-7; mercury, 7439-97-6; 10-undecen-1-ol, 112-43-6.

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Dual Mechanism Bifunctional Polymers: Polystyrene-Based Ion-Exchange/Redox Resins

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ABSTRACT: The synthesis of bifunctional phosphinic acid resins that consist of monoaryl (primary) and diaryl (secondary) phosphinic acid ligands supported on a polystyrene network was recently effected. This paper reports that these bifunctional polymers operate by a dual mechanism in that they will ion-exchange with a given metal ion at low pH and then reduce it to its zerovalent state if it has an appropriate reduction potential. The concept of *dual mechanism bifunctional polymers* is thus advanced to describe phosphinic acid resins and their derivatives. The reducing agent is the primary phosphinic acid ligand which becomes oxidized to the phosphonic acid, as shown by analysis with base. The phosphinic acid resins have a high capacity and are stable to prolonged contact with 4 N HNO_3 under ambient conditions. Extraction studies with zinc, mercury, silver, and gold are described. Comparative studies with phosphonic acid, sulfonic acid, and carboxylic acid resins clearly indicate the mechanism of action as well as an extraordinarily high affinity for the transition-metal ions by the phosphinic resins. For example, under very similar conditions, in the presence of excess sodium ions the phosphinic resins absorb 70% of the mercury(II) in solution as opposed to 25% by the sulfonic resins. The phosphinic resins operate by 100% redox of the metal ion absorbed until all of the primary sites are oxidized after which ion exchange occurs.

The complexation of metals to polymer supports yields reagents of tremendous utility. Polymer-supported metal catalysts[1] have been used in reactions as diverse as hydrogenation,[2] epoxidation,[3] hydroformylation,[4] oxidation,[5] and polymerization.[6] Polymer-supported metals have also been successfully applied to chromatographic separations of neutral molecules.[7,8] Polystyrene has proven to be a versatile support due to the large number of ligands that can be covalently bound to it. A judicious choice of ligands can lead to the synthesis of polymer-supported extractants

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