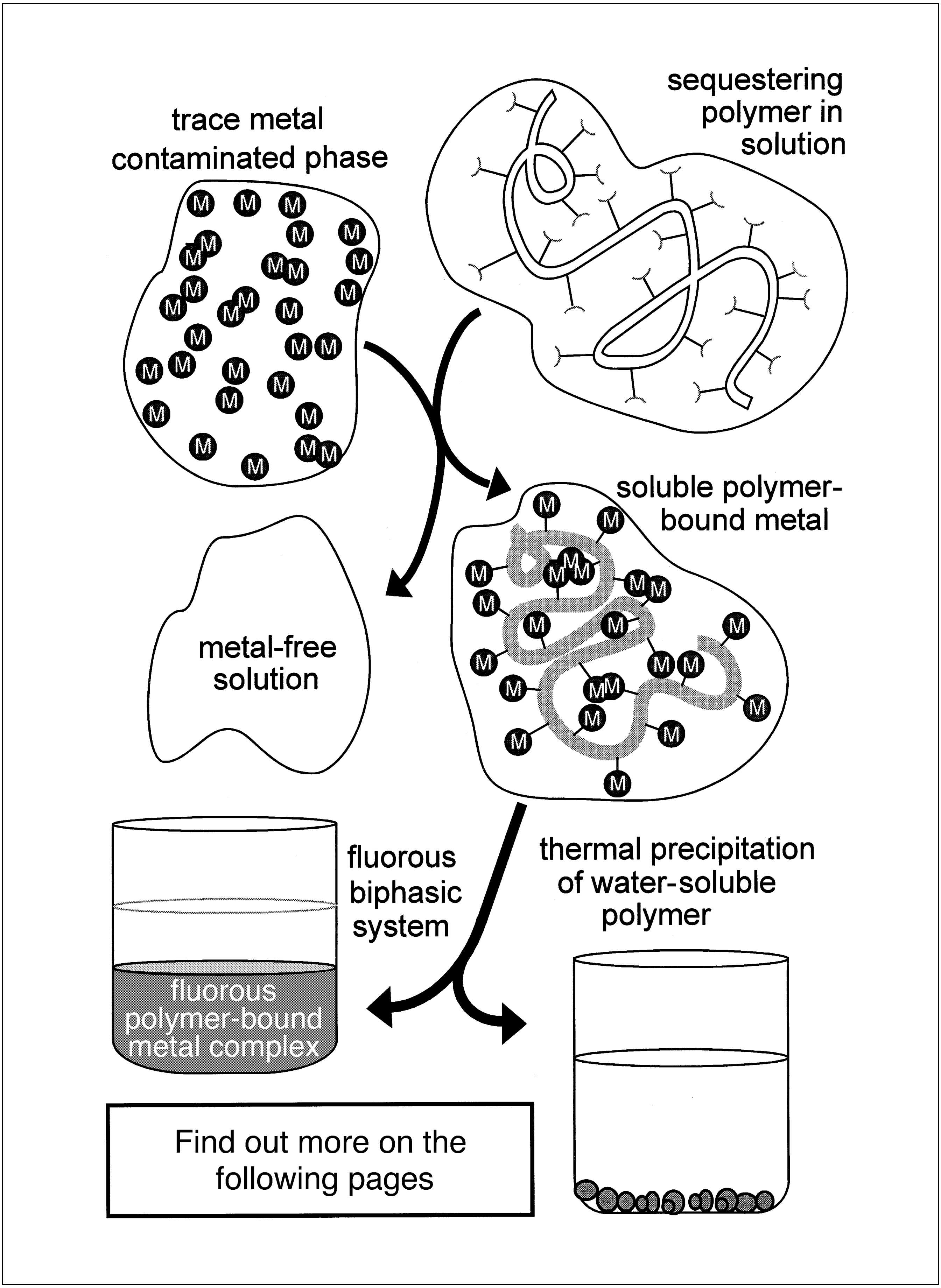
trace metal contaminated phase
sequestering polymer in solution
M
soluble polymer-bound metal
metal-free solution
fluorous biphasic system
thermal precipitation of water-soluble polymer
fluorous polymer-bound metal complex
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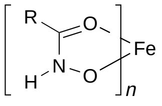
Sequestration of Trace Metals Using Water-Soluble and Fluorous Phase-Soluble Polymers[**]

David E. Bergbreiter,* Nirmal Koshti,
Justine G. Franchina, and Jonathon D. Frels

For several years now, our group has actively pursued the design and synthesis of soluble, polymer-bound ligands for transition metal catalysis.[1–5] Here we describe the extension of this chemistry to the design of functional polymers that are soluble in aqueous or fluorous phases, and that recover and remove trace metals from aqueous or organic solutions.

Soluble polymeric catalysts prepared from poly(*N*-isopropylacrylamide) have a lower critical solution temperature (LCST) and quantitatively phase separate from aqueous solution on heating. We have used this property to design "smart", water-soluble, reusable catalysts.[1, 3] We also showed that fluoroacrylate-bound reagents are selectively soluble in the fluorous phase of a fluorous biphasic system.[6] This work shows that these two types of polymers can be used as soluble ion-exchange resins for removal of trace metal from water or organic solvents, respectively.

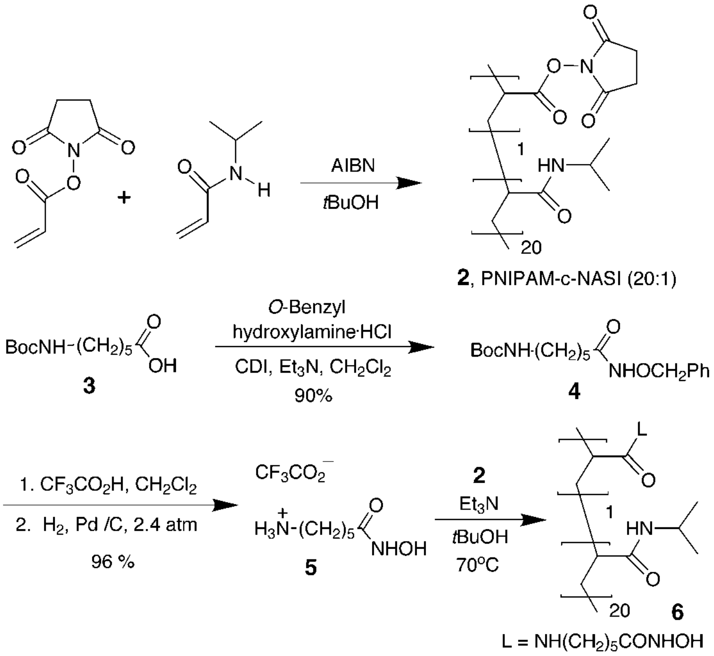
The studies reported here focus on the recovery of iron using polymeric hydroxamic acid ligands. Hydroxamic acids complex Fe^{III} to form red complexes (Scheme 1). The intense color of these complexes facilitates the determination of iron remaining in solution using UV/Vis spectroscopy.



Scheme 1. The hydroxamate complex of Fe^{III}.

The first polymeric ligand we studied was prepared by addition of **5** to a 20:1 poly(*N*-isopropyl acrylamide)-*co*-(*N*-acryloxy succinimide) copolymer (**2**, PNIPAM-c-NASI; Scheme 2). The polymer-bound hydroxamic acid **6** so formed had an LCST of 31 °C. A solution of 200 mg of **6** and 15.5 ppm of Fe^{III} in 25 mL of water formed a red hydroxamate complex that precipitated above 31 °C leaving a colorless supernatant. Addition of an excess of **5** to the supernatant produced a colorless solution ($A < 0.002$), showing that over 99 % of the Fe^{III} had been removed from solution by thermal sequestration by **6** above the LCST of **6**. Inductively coupled plasma (ICP) analysis of the supernatant affirmed this result, showing that the 15.5 ppm Fe^{III} concentration was reduced to 116 ppb.

Substrates or catalysts attached to PNIPAM have little reactivity above their LCST.[2] Likewise, Fe^{III} complexed to **6** does not readily exchange Fe^{III} with **5** above the LCST of **6**. When an aqueous red suspension of 200 mg of **6** containing 18.5 ppm of Fe^{III} at 50 °C was stirred with 5 mg of **5** at 50 °C for 12 h, no detectable Fe^{III} was seen in the supernatant. The failure of **5** to bind Fe^{III} at 50 °C when soluble **5** was mixed with insoluble Fe^{III}-containing **6** shows that Fe^{III} is not readily leached from the precipitated polymer even when soluble ligands are present.



Scheme 2. Synthesis of a poly(*N*-isopropylacrylamide)-bound hydroxamic acid. AIBN = azobisisobutyronitrile, Boc = *tert*-butoxycarbonyl, CDI = *N,N'*-carbonyl diimidazole.

Figure 1 shows that **6** (the PNIPAM-bound hydroxamic acid) recovers Fe^{III} from water even in the presence of **5**. This occurs if a single polymeric hydroxamic ligand on the Fe^{III} is enough to insure precipitation of the hydroxamate–Fe^{III} complex. The results in Figure 1 show that more than 99 % of the Fe^{III} is sequestered by **6** if the ratio of the **5**:**6** is less than 1.

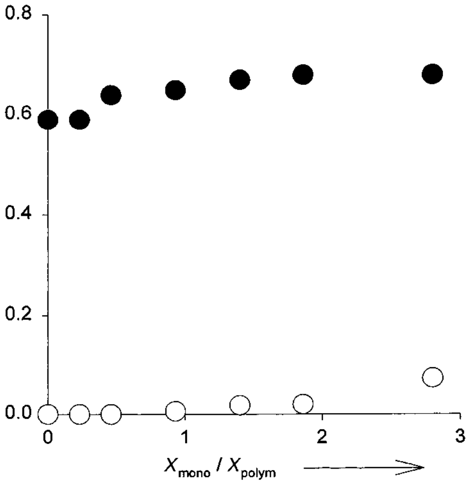


Figure 1. Absorbance A at 439 nm of a solution with varying ratios of **5** and **6** in a 15 ppm Fe^{III} solution (●) and of its supernatant after precipitation of **6** (○).

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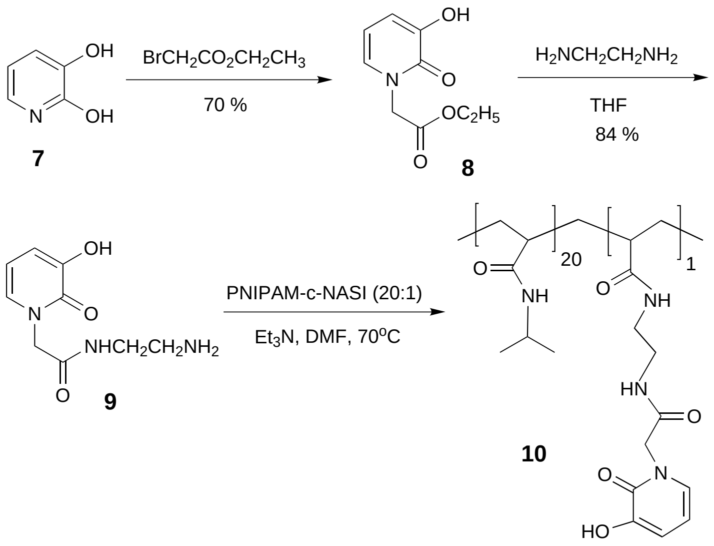
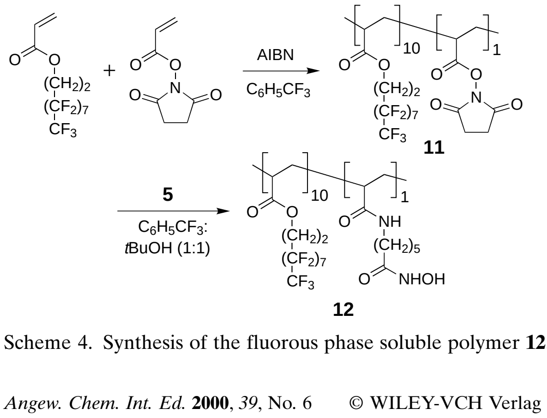
PNIPAM copolymers containing other ligands also bind Fe^{III} or Cu^{II}. 3-Hydroxy-2-pyridinone ligands on PNIPAM were prepared as shown in Scheme 3. Imidazole-containing copolymers were prepared by copolymerization of vinyl imidazole and **1**.[7, 8] Experiments like those with **5** showed that 0.15 g of **10** in 25 mL of water binds 14.4 ppm of Fe^{III} (at 25 °C: $A = 1.109$, $\lambda_{max} = 578$ nm). Heating results in precipitation of **10** and over 99 % of the Fe^{III}, based on the residual absorbance of less than 0.002 for the supernatant after treatment with **9**. Similarly, 1.23 g of a 10:1 NIPAM–vinyl imidazole copolymer binds 98 % of a 269.2 ppm Cu^{II} solution ($CuSO_4$) on heating above the LCST (35 °C). Addition of imidazole to the supernatant resulted in a residual absorbance of 2 % at 658 nm.



Scheme 3. Synthesis of polymer-bound 3-hydroxy-2-pyridinone.

While PNIPAM copolymers recover trace metals from water, similar LCST behavior cannot be used at a convenient temperature to recover trace metals from an organic solvent. To address this issue, we prepared a fluorous phase soluble hydroxamic acid polymer (Scheme 4). Prior work has shown the utility of fluorous biphasic chemistry for separations involving organic solvents,[9, 10] and we have reported that derivatives of polymers like **11** are fluorous phase soluble polymer supports.[6] In this case, amidation of **11** by **5** in trifluorophenylmethane yields the fluorous phase soluble, metal-binding polymer **12**. When 140 ppm of **12** were dissolved in 10 mL of FC-77 (a perfluorinated ether) and then shaken with 10 mL of CH_3OH containing 28 ppm of Fe^{III} for 15 min, a red fluorous phase formed. Centrifugation and liquid/liquid separation of the fluorous phase resulted in a CH_3OH phase that contained no detectable Fe^{III}, based on the absence of a detectable absorbance on addition of **5** to this solution (> 99.5 % Fe^{III} extraction).



Scheme 4. Synthesis of the fluorous phase soluble polymer **12**.

Treatment with ethylenediaminetetraacetate (EDTA) regenerates these soluble polymer complexing agents. When an aqueous solution of Fe^{III}-containing **6** was stirred with disodium EDTA, the solution became colorless. Competitive binding of Fe^{III} by EDTA reformed metal-free **6**, which was isolated by two thermal precipitation/dissolution cycles. Recovered **6** was as effective as the original **6** at sequestering Fe^{III} from water. Likewise, when the red fluorous phase containing the Fe^{III} complex of **12** was shaken with a solution of disodium EDTA in CH_3OH, the fluorous phase decolorized. Once decolorized, the fluorous phase soluble **12** was successfully used again to remove Fe^{III} from a fresh Fe^{III} solution in CH_3OH.

We have shown that near quantitative metal recovery from aqueous solution is possible with water-soluble PNIPAM copolymers that by design contain metal-binding agents. Chelated metal does not readily leach from the precipitated polymer. A variety of ligands can be employed. Similar fluorous phase soluble polymers also complex trace amounts of Fe^{III} from organic solutions in a fluorous biphasic system. In both cases the iron-complexing agents are regenerable. These soluble ion-exchange resins provide two simple ways to complex and remove trace amounts of metal from solution. In water, the resin is recovered as a solid after mild heating. In organic solvents, a fluorous phase containing a fluorinated polymer is used under fluorous biphasic conditions with separation being effected by liquid/liquid phase separation. Such materials are alternatives to the existing arsenal of cross-linked, insoluble ion-exchange resins and may be useful in other solvents too (e.g. supercritical CO_2). The polymers described here function differently and under milder conditions than the thermally regenerable Sirotherm resins.[11] Further studies of this chemistry continue in our group to establish the generality and limitations of these techniques.

Experimental Section

The PNIPAM copolymers were prepared from **1** and *N*-acryloxysuccinimide (NASI) or vinyl imidazole using AIBN initiation in *t*BuOH.[2, 7, 12] Amines containing hydroxamic acid or 3-hydroxy-2-pyridinone were prepared using unexceptional chemistry, and then coupled to the active ester groups on **2**. In a typical metal-binding experiment, 200 mg of **6** were added to 25 mL of an aqueous solution containing 15.5 ppm ferric chloride to give a red solution at 25 °C ($A = 0.65$, $\lambda = 439$ nm). Heating to 40 °C produced a red precipitate. Centrifugation (above 35 °C) yielded a clear solution whose absorbance at 439 nm was less than 0.002 after treatment with **5**. Hydroxamic-containing fluorous phase soluble polymers were prepared from a previously reported reactive fluoroacrylate copolymer (prepared by AIBN-initiated polymerization of NASI and 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate).[6, 13]

Detailed experimental procedures for the synthesis of **6**, **10**, and **12** are available in the Supporting Information.

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π-Allylpalladium-Mediated Catalytic Synthesis of Functionalized Allenes**

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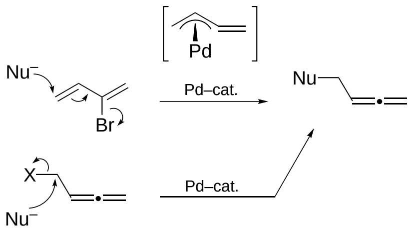
Allenes have attracted attention as useful synthons for synthetic organic chemistry.[1] The interesting reactivity of allenes originates mainly from their unique strained structure, and thus continuous efforts have been made to construct the 1,2-dienic moieties. Standard methods of allene synthesis are based on the S_N2'-type substitution of propargylic compounds [Eq. (1)].[1, 2] However, the products from these synthetic methods are often contaminated with the corresponding propargyl compounds or 1,3-dienes, and purification steps become problematic. Recently, some highly selective synthetic methods for the formation of allenes were reported,[3] however, the yields of the allenic products were not always satisfactory. In addition, these procedures require reactive reagents, such as Grignard reagents or organolithium species, and are unable to handle substrates or products with susceptible functional groups. We describe herein a novel synthetic method for synthesizing a variety of functionalized allenes.

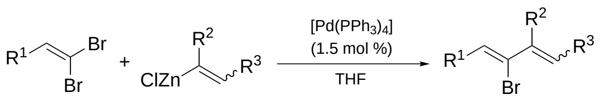
(1)

Our strategy is a formal S_N2' substitution of 2-bromo-1,3-butadienes, which is catalyzed by a palladium complex [Eq. (2), top]. The reaction proceeds under very mild conditions via a π-allylpalladium intermediate[4] and gives the clean products in excellent yields. The reaction described here has some analogies to the Pd-catalyzed functionalization of allenyl esters with "soft" carbon nucleophiles reported by Gore and co-workers in 1984 [Eq. (2), bottom].[5] They suggested an analogous intermediate to the one established in this report. However, the substrates they employed possess 1,2-dienic moieties and thus, tedious procedures are required to construct the allenic skeletons prior to the functionalization step, which greatly reduces the synthetic usefulness of the reaction. The advantages of our approach described here are: 1) easy access to the 1,3-dienyl substrates, which enables us to introduce a wide range of substituents in the substrates and the allenic products, and 2) a variety of nucleophilic reagents, including N, O, and P nucleophiles, can be used. The reaction also represents a rare example of a transition metal catalyzed transformation to give allenes.[6]



(2)

The substrates, (*Z*)-2-bromo-1,3-butadienes (**1**), are readily available in 63–90% yield by palladium-catalyzed regio- and stereoselective cross-coupling of 1,1-dibromo-1-alkenes[7] with the corresponding vinylzinc reagents (Scheme 1).[8] The choice of the organometallic reagent is important for this step; while $(CH_2{=}CH)ZnCl$ gives the coupling product in satisfactory yield, the less-reactive vinyltin reagent $Bu_3Sn(CH{=}CH_2)$ gives the same product in very low yield (<20%). More basic Grignard reagents enhance the elimination of HBr from **1** to give a considerable amount of $R^1C{\equiv}C{-}CH{=}CH_2$ as a by-product. When R^1 is an alkyl substituent, a second cross-coupling proceeds to a certain extent to give a triene, $R^1CH{=}C(CH{=}CH_2)_2$, as a by-product (≈15%). The triene does not affect the allene formation, thus, a mixture of **1** and the triene can be employed in the following step without further purification.



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Scheme 1. Palladium-catalyzed selective cross-coupling of dibromoalkenes with organozinc reagents.

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