Soluble and Processable Phosphonate Sensing Star Molecularly Imprinted Polymers

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ABSTRACT: Soluble molecularly imprinted polymers (MIPs) were prepared by reversible addition fragmentation chain transfer (RAFT) polymerization followed by ring-closing metathesis (RCM). The polymerization was done in the presence of a template to generate a processable star MIP. The core of the star polymer was a dithiobenzoate-substituted tris(β-diketonate)europium(III) complex. The tris(β-diketonate)europium(III) complex served as a polymerization substrate for the three-armed RAFT-mediated star polymer and as a luminescent binding site for dicrotophos, an organophosphonate pesticide. The star arms were AB block copolymers. Block A was either 1-but-3-enyl-4-vinylbenzene or a mixture of 1-but-3-enyl-4-vinylbenzene and styrene. Block B was styrene or methyl methacrylate. The but-3-enyls of block A were reacted by RCM with a second generation Grubbs catalyst to give an intramolecularly cross-linked core. The intramolecularly cross-linked MIP was soluble in common organic solvents. The 30% cross-linked soluble and processable star MIP was applied to the determination of dicrotophos with sub-ppb level detection limits.

Introduction

Molecular imprinting is a technique for making a selective binding site for a specific chemical. The technique involves building a polymeric scaffold of molecular complements containing the target molecule. Subsequent removal of the target leaves a cavity with a structural "memory" of the target. MIPs can be employed as selective adsorbents of specific molecules or molecular functional groups. In addition, sensors for specific molecules can be made using optical transduction through lumiphores residing in the imprinted site. We have found that the use of metal ions as chromophores can improve selectivity due to selective complex formation. The combination of molecular imprinting and spectroscopic selectivity can result in sensors that are highly sensitive and nearly immune to interferences.[1]

A weakness of conventional MIPs with regard to processing is the insolubility of cross-linked polymers. Traditional MIPs are prepared as monoliths and ground into powders or are prepared in situ on a support. This limits the applicability of MIPs by imposing tedious or difficult processes for their inclusion in devices. This weakness could be avoided if a means were found to prepare individual macromolecules with cross-linked binding sites but otherwise soluble linear polymers arms. Zimmerman et al. have prepared a type of soluble cross-linked polymer by using a porphyrin encapsulated into a cross-linked core with multiple arms to enhance solubility.[2] This process is possible due to controlled free radical polymerization techniques that can form pseudo-living polymers. Modern techniques of controlled free radical polymerization also allow the preparation of block copolymers with potentially cross-linkable substituents in specific locations. The inclusion of cross-linkable mers proximate to the binding complex in the core of a star polymer allows the formation of molecularly imprinted macromolecules that are soluble and processable.

The mechanism we have used to detect organophosphates is to discern their effect on the luminescence of europium(III). The optical absorption and emission spectra of the triply charged free lanthanide ions, which are assignable to f → f transitions, generally consist of very narrow lines (0.1−0.01 nm). When ligands are placed around the lanthanide ions, there is often a shift in the spectral lines, splitting, and an intensity change. The exact character and degree of these changes are specific to the ligand environment with the major factors being the coordination number, the coordination symmetry (geometry), and the type(s) of ligands. Even though the ligand field is sufficient to produce these shifts, splits, and intensity alterations, the ligand to f electron coupling is generally not sufficient to result in broadening of the lines. Another consequence of the weak coupling and the interconfigurational nature of f → f transitions is that radiative lifetimes of lanthanide ions in compounds are quite long, on the order of milliseconds, simplifying time-resolved measurements that enhance sensitivity. The molar absorptivity of lanthanide ions is very low, but by judicious choice of coordinating ligand, the absorptivity and quantum efficiency can be enhanced by ligand-to-metal energy transfer. This allows the use of a broadband source, such as a light-emitting diode (LED), to pump the luminescence. In this study, europium(III) was selected since it has the simplest set of splitting and most favorable level structure for sensitization. The ion, europium(III) is one of the most useful lanthanides for chemical sensing. In the current application, reversible addition fragmentation chain transfer (RAFT) polymerization[3] was used to make an organophosphonate sensing MIP based on a tris(β-diketonate)europium(III) complex binding site.

Experimental Section

Reagents. Unless otherwise indicated, chemicals were obtained from commercial suppliers and used without further purification. Monomers were cleansed of inhibitors by filtration through alumina (Brockman Grade I). Analytical reagent grade chemicals were used along with deionized water to prepare solutions. The chemicals used were obtained from Aldrich (Aldrich, Milwaukee, WI) or Fisher Scientific (Pittsburgh, PA). The second generation Grubbs catalyst is benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium.[4] Dithiobenzoic acid, 1-but-3-enyl-4-vinylbenzene, and compounds **1**, **3**, and **5** were prepared according to the literature procedures.[6−8]

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Instrumentation. An in-house detection system was employed for screening lanthanide complexes that includes an Ar ion laser, model 543 head and model 170 power supply (Omnichrome, Chino, CA), and an *f*/4, 0.5 m monochromator (Chromex, Albuquerque, NM) equipped with a model ST-6 CCD detector (Santa Barbara Instrument Group, Inc., Santa Barbara, CA). KestrelSpec software (Rhea Corp. Wilmington, DE) was used to operate the CCD and record the compound luminescence. A Cary 50 UV/vis spectrophotometer (Varian, Walnut Creek, CA) was used to obtain absorbance spectra. The luminescence titrations were obtained using a model QM-2 fluorimeter/phosphorimeter (Photon Technologies International, Monmouth, NJ). A Hewlett-Packard model 5400 ICP-MS (Yokogawa Analytical Systems, Tokyo, Japan) was used to verify metal concentrations in all sample solutions. NMR was performed using a model EFT 90 MHz spectrometer (Anasazi Instruments, Indianapolis, IN). The purity of synthesized organics was established using a model QP 5050A GC/MS (Shimadzu, Columbia, MD). Microanalyses were performed by Desert Analytics, Inc. (Tuscon, AZ).

Gel Permeation Chromatography. The polymers were characterized by gel permeation chromatography on a Varian ProStar 330 photodiode array detector. Separation was completed using a Polymer Laboratories PL gel mixed bed column (4.6 mm × 250 mm) and a mixed bed guard column (4.6 mm × 50 mm) with a particle size of 5 μm at 30°. The mobile phase was 100% tetrahydrofuran with a flow rate of 0.3 mL/min. A 0.04 mg/mL sulfur solution was used as a flow marker and spiked into each sample and standard. This solution showed a retention time at about 15 min. Poly(methyl methacrylate) was characterized at 216 nm, and polystyrene was characterized at 250 nm. Calibrations were with near monodisperse polystyrene standards and near monodisperse poly(methyl methacrylate) standards purchased from Polymer Laboratories (Amherst, MA). Molecular weight averages and polydispersity indices were calculated using Galaxie software provided by Varian.

Compound Synthesis. Compound 4. Compound **2** (2.0 g, 8.25 mmol), dithiobenzoic acid (2.2 g, 12.5 mmol), and carbon tetrachloride (6 mL) were combined in a 15 mL round-bottomed flask equipped with a reflux condenser under an argon atmosphere. The reaction was heated at 70 °C for 16 h The solvent was removed under vacuum, and the final product was isolated by column chromatography using silica gel with 60/40 hexanes/chloroform as the eluent. Compound **4** was isolated as a viscous red oil (1.32 g, 40% yield). ^{1}H NMR (90 MHz, 25 °C, $CDCl_3$): δ 7.92−7.80 (m, 4 H), 7.55−7.18 (m, 5 H), 6.47 (s, 1 H), 5.23 (q, $J = 7.3$ Hz, 1 H), 1.75 (d, $J = 7.3$ Hz, 3H). Anal. Calcd for $C_{19}H_{15}F_3O_2S_2$: C, 57.56; H, 3.81. Found: C, 57.57; H, 3.73.

Compound 6. Compound **4** (1.32 g, 3.33 mmol) was dissolved in THF (5 mL) in a 15 mL round-bottomed flask, and 1.0 M sodium hydroxide (3.66 mL) was added dropwise. A solution of europium(III) chloride hexahydrate (0.41 g, 1.11 mmol) in water (2 mL) was added, and the flask was equipped with a reflux condenser. The reaction was heated at reflux for 3 h before excess methanol was added to end the reaction. The precipitate was removed by filtration, dried, dissolved in methylene chloride, filtered again, and precipitated into hexanes. The product was isolated as a red solid (0.78 g, 53% yield). Anal. Calcd for $(DBBTFA)_3Eu{\cdot}2H_2O{\cdot}CH_2Cl_2$, $C_{58}H_{46}Cl_2EuF_9O_8S_6$: C, 47.74; H, 3.22. Found: C, 47.73; H, 3.04.

Polymerization. Polymer 1, Block A (P-1$_A$). Compound **5** (40 mg, 26 μmol), 1-but-3-enyl-4-vinylbenzene (880 mg, 5.62 mmol), and 2,2′-azobis(2,4-dimethylvaleronitrile) (1.5 mg, 6 μmol) were placed into a reaction flask, and the flask was subjected to three freeze/pump/thaw cycles. The flask was left under an argon atmosphere and was heated ato 50 °C for 7 h when the excess 1-but-3-enyl-4-vinylbenzene was removed under vacuum.

Polymer 1, Block B (P-1$_{AB}$). Styrene (1.56 g, 15 mmol) was added to the reaction flask from the preceding reaction. The flask was subjected to three freeze/pump/thaw cycles and was heated at 100 °C for 72 h before the excess styrene was removed under vacuum. The residue was dissolved in CH_2Cl_2 and precipitated into methanol. A salmon-colored powder was obtained.

Table 1. Properties of Soluble and Processable MIPs

polymer	% 1-but-3-enyl-4-vinylbenzene	block A, time (h)[a]	% conv A[b]	block B, time (h)[c]	MW	M_n	MWD
P-1$_{AB}$[d]	100	7[f]	10	*g*,*h*	37 000	14 500	2.5
P-1$_{CR}$					56 800	18 400	3.1
P-2$_{AB}$[e]	3	7.5	40	8	33 900	26 600	1.28
P-2$_{CR}$					35 900	26 000	1.38
P-3$_{AB}$[e]	30	50	40	8	15 100	4 600	3.28
P-3$_{CR}$					15 300	5 200	3.23
P-4$_{AB}$[e]	100	50	41	8	23 200	6 500	3.58
P-4$_{CR}$					23 300	6 900	3.38

[a] Conditions: no initiator, 100 °C. [b] Determined gravimetrically. [c] Conditions: AIBN, 60 °C. [d] Core is **5**. [e] Core is **6**. [f] Conditions: Wako V-65, 50 °C. [g] Conditions: 60 °C 72 h, followed by 100 °C, 24 h. [h] Block B is styrene.

Polymer 1, Imprinting and Cross-Linking (P-1$_{CR}$). Polymer **1$_{AB}$** (500 mg), dicrotophos (13 mg, 55 μmol), and second Generation Grubbs catalyst (50 mg, 59 μmol) were placed in a Schlenk flask. The flask was evacuated and backfilled three times with argon. Anhydrous methylene chloride (150 mL) was added, and the solution was heated at reflux for 18 h and then at room temperature for an additional 6 h. The solution was filtered through silica gel, the solution concentrated, and the cross-linked polymer precipitated by addition to methanol. A white powder (350 mg, 70% yield) was collected.

Typical Polymerization for Polymers 2−5. Block A. The following procedure is demonstrated for a 30% cross-linked core. Compound **6** (40 mg, 29 μmol), 1-but-3-enyl-4-vinylbenzene (300 mg, 1.90 mmol), and styrene (700 mg, 6.72 mmol) were placed into a reaction flask, and the flask was subjected to three freeze/pump/thaw cycles. The flask was left under an argon atmosphere and was heated at 100 °C for the desired time (see Table 1) when the excess 1-but-3-enyl-4-vinylbenzene and styrene were removed by vacuum.

Typical Polymerization for Polymers 2−4. Block B. Methyl methacrylate (1.5 g, 15 mmol) and AIBN (1.5 mg, 9.1 μmol) were added to the flask from the preceding reaction. The flask was subjected to three freeze/pump/thaw cycles and was left under an argon atmosphere and was heated at 60 °C for 8 h when the excess methyl methacrylate was removed by vacuum. The residue was dissolved in CH_2Cl_2 and precipitated into methanol. A salmon-colored powder was obtained.

Cross-Linking and Imprinting of Polymers 2C−4C. Polymer **4$_{AB}$** (150 mg), second generation Grubbs catalyst (15 mg, 17 μmol), and dicrotophos (13 mg, 55 μmol) were placed in a 250 mL Schlenk flask. The flask was evacuated and backfilled three times with argon. Anhydrous methylene chloride (150 mL) was added, and the solution was heated at reflux for 18 h. The solution was filtered through silica gel, the solution concentrated, and the cross-linked polymer precipitated by addition to methanol. A white powder (122 mg, 81%) was collected.

Removal of Template. The dicrotophos-cross-linked polymer was washed by Soxhlet extraction with methanol for 4 h. The was solution was monitored by GC/MS for dictrotophos. The polymer was collected, dried in vacuo, and used in the binding and interference studies.

Binding and Interference Studies. The polymer was dissolved in anhydrous methylene chloride containing a trace amount of anhydrous calcium carbonate. Calcium carbonate both absorbs water and scavenges acids. The binding of dicrotophos was monitored by an increase in fluorescence at 612 nm. For all studies, polymer **P-4$_{CR}$** was used as a control. A solution of the model compound $Eu(NTFA)_3$ in methylene chloride was used to adjust for instrument changes.

Results and Discussion

Synthesis of Star Polymer Cores. The star polymer core consisted of a dithiobenzoate-substituted tris(β-diketonate)-

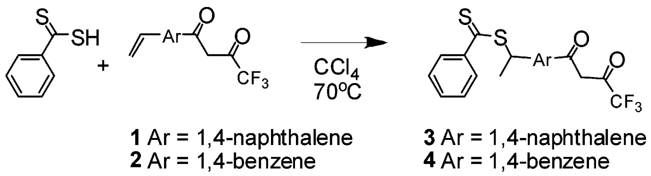

Figure 1. Preparation of the dithiobenzoate *β*-diketone ligands **3** and **4**.

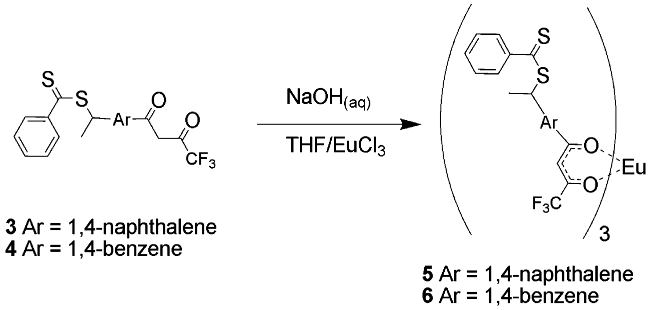

Figure 2. Preparation of the tris europium core complexes **5** and **6**.

europium(III) complex that was prepared in two steps. The dithiobenzoate *β*-diketone ligands **3**[8] and **4** were prepared by the condensation of equimolar amounts of dithiobenzoic acid with a vinyl-substituted *β*-diketone in carbon tetrachloride at 70 °C (Figure 1). The corresponding tris Eu(III) chelates **5**[8] and **6** were prepared by the addition of the diketonate anion to 0.33 equiv of $EuCl_3(aq)$ and refluxing for 3 h (Figure 2).

Polymerization. Previous work with bulk polymers prepared from styrene, divinylbenzene, and **5**, with toluene as a porogen and Wako V-65 as initiator, has been described.[8] The solutions were polymerized at 60 °C for 18 h. The polymerization was stopped by cooling to room temperature when toluene and unreacted monomer were removed under vacuum. The monolith was ground to a powder and washed with methanol and acetone to remove unreacted monomers and high boiling solvent. The method showed good incorporation of luminescent complex with no evidence of Eu(III) luminescence in the wash solutions. The gel effect was shown to be mitigated as demonstrated by their homogeneity. However, these polymers still required preparation in situ for sensor fabrication or application to a surface.

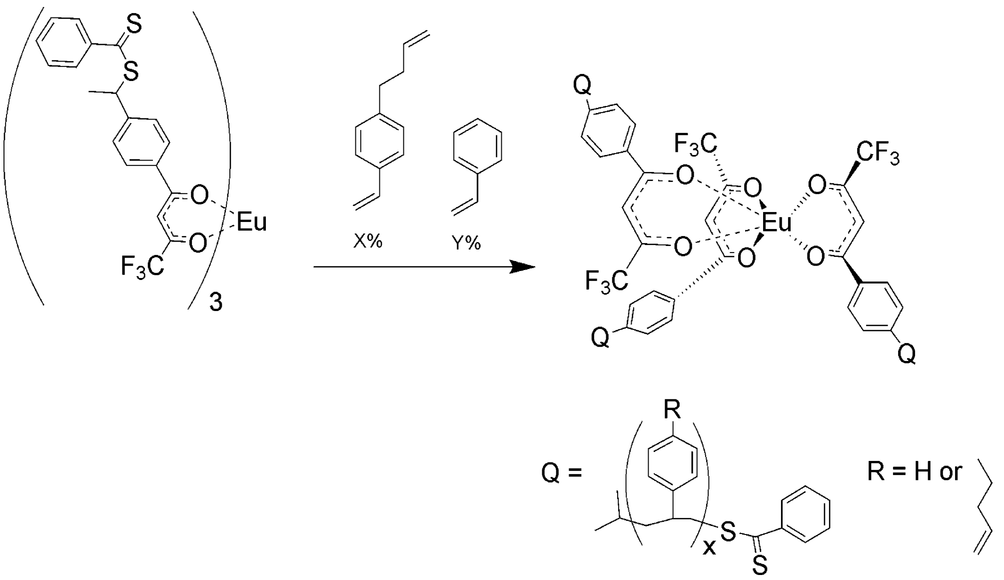

Figure 3. General synthetic scheme for block A formation using core **6**.

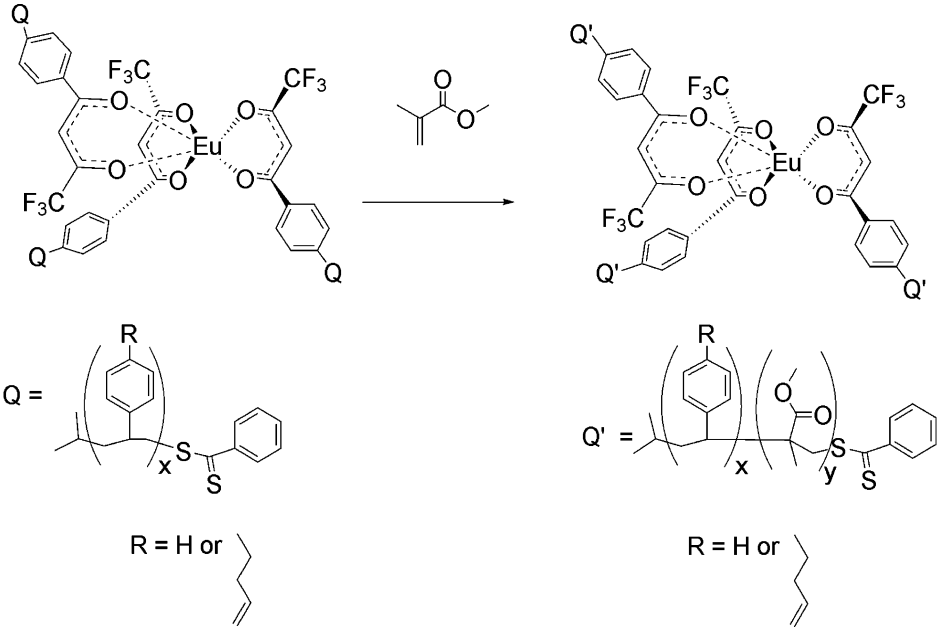

Figure 4. General synthetic scheme for block B formation using methyl methacrylate for making polymer "arms" with core **6**.

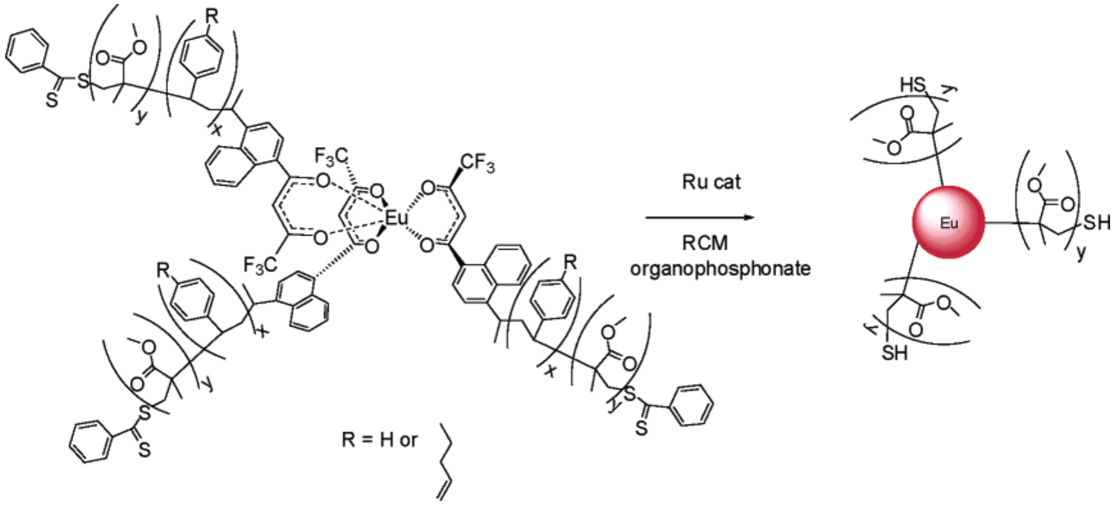

Figure 5. General scheme for cross-linking of the polymeric core using second generation Grubbs catalyst.

Additionally, it was desirable to cross-link the volume immediately surrounding the lumiphore to enhance its stability in the melt or in solution.

In this work, soluble, unimolecular, luminescent polymers were prepared by RAFT polymerization. The initial polymer used **5** as the core which served as the polymerization substrate for the three-armed RAFT-mediated polymer. The arms were AB block copolymers where block A was 1-but-3-enyl-4-vinylbenzene and block B was styrene, which imparts solubility upon subsequent intramolecular cross-linking by ring-closing metathesis (RCM).[6b] The monomer, 1-but-3-enyl-4-vinylbenzene, was chosen since it contains two reactive groups which have different reactivities. The vinyl groups are polymerizable under free-radical conditions, while the allylic but-3-enyl moiety remains stable under such conditions. However, the but-3-enyls are reactive under RCM conditions with second generation Grubbs catalyst which give an intramolecularly cross-linked core.[7]

P-1$_{\mathbf{A}}$ was prepared by addition of 1-but-3-enyl-4-vinylbenzene to **5**, with Wako V-65 initiator, at 50 °C for 7 h (Figure 3). The polymerization was stopped by cooling the polymerization flask in an ice bath. Approximately 10% of the monomer was consumed, which would correspond to addition of seven monomers/arm of the CTA substrate. **P-1$_{\mathbf{AB}}$** was polymerized at 60 °C for 72 h followed by 100 °C for another 24 h, and the polymerization stopped by addition to an ice bath after 70% of the monomer, styrene, was consumed (Figure 4). The M_n of **P-1$_{\mathbf{AB}}$** was found to be 14 500 g/mol, $M_w = 37\,000$ g/mol, and MWD = 2.5 by GPC analysis (Table 1). Luminescence titration of an aliquot of the un-cross-linked polymer with dimethylhydrogen phosphonate resulted in a molecular weight of 30 000 g/mol, consistent with GPC analysis.

P-1$_{\mathbf{AB}}$ was intramolecularly cross-linked in dilute methylene chloride under RCM conditions with second generation Grubbs catalyst, benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Figure 5). The RCM cross-linked polymer, **P-1$_{\mathbf{CR}}$**, was determined to have a $M_n = 18\,400$ g/mol, $M_w = 56\,800$ g/mol, and MWD = 3.1 by GPC analysis. It is clear that some intermolecular cross-linking occurred during RCM; however, intramolecular cross-linking predominated as evidenced by the relatively small change in molecular weight.

Cross-linking is consistent with the loss of free butenyl groups in the ^{1}H NMR. The free butenyls of the uncross-linked polymer were found to have peaks from 5 to 6 ppm, but the peaks disappeared upon reaction with RCM catalyst (Figure 6). Unexpectedly, the RCM catalyst also cleaved the dithioester end groups from the macromolecule as seen through the loss of the salmon color. The loss of color due to dithioester cleavage has also been observed by others.[7] The cross-linked polymers were soluble in methylene chloride and chloroform.

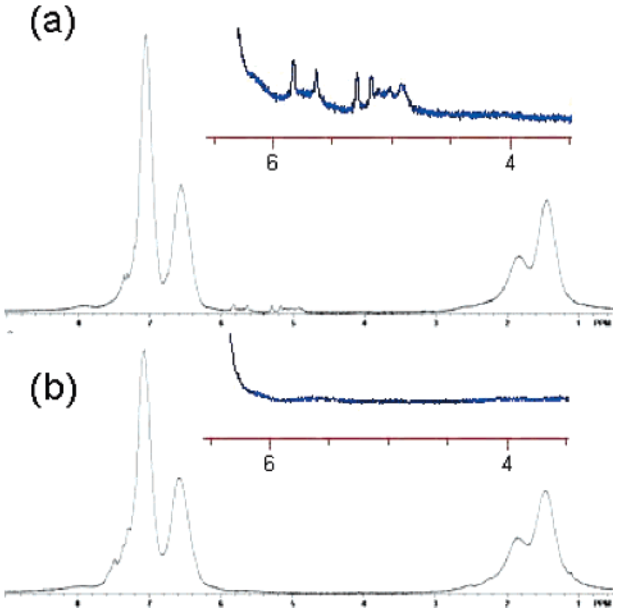

Figure 6. ^{1}H NMR spectrum of polymer **1**. (a) Before cross-linking by RCM. Note the presence of the vinyl absorbances of the butenyl moiety between 4.8 and 6 ppm. (b) After cross-linking by RCM. Note the absence of the vinyl absorbances of the butenyl moiety between 4.8 and 6 ppm.

It should be possible to follow the progress of the polymerization by fluorescence. Complexes **5** and **6** are weakly fluorescence due to the very strong dithioester chromophore absorbing the excitation wavelength of 390 nm. The polymerization reaction is visually evident by illumination with a long-wave UV lamp, revealing an increase in luminescence intensity during the reaction. The luminescence of the polymer increases dramatically as the distance between the dithioester chromophore and the europium increases. The luminescence of the star polymers is extremely bright. The pulsed gated spectra of 95 μg/mL of polymer **P-4$_{\mathbf{AB}}$** in CH_2Cl_2 are given in Figure 7. The spectra were obtained using a 20 μs delay and 100 μs integration times.

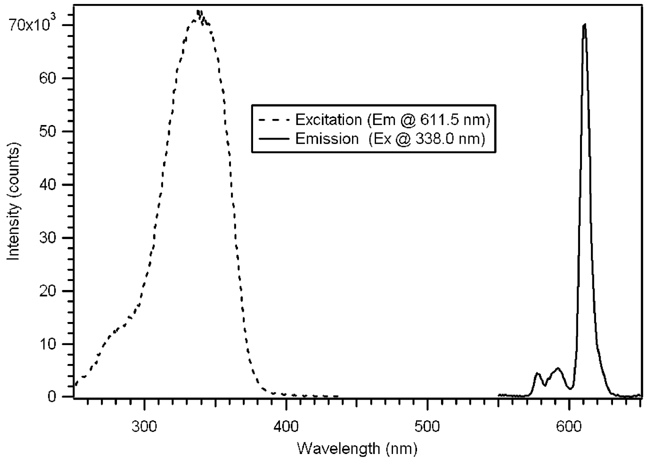

Figure 7. CW excitation and emission spectra of **P-4$_{AB}$** with absorbance maximum 338 nm and emission maximum at 611 nm.

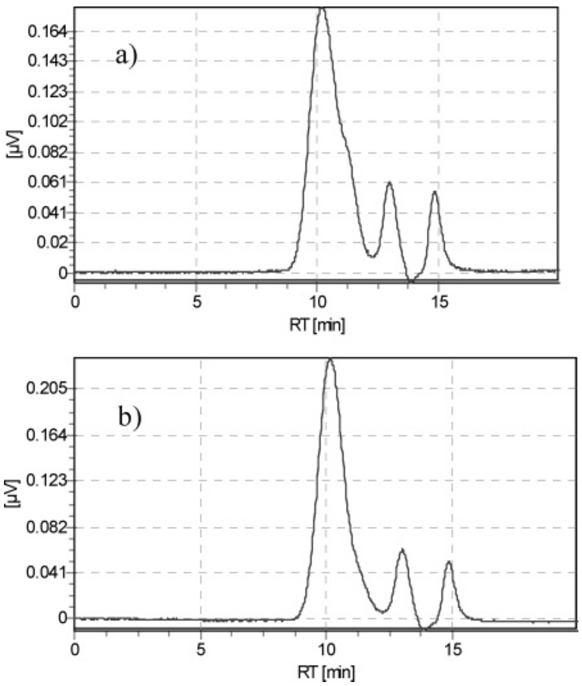

Figure 8. GPC trace of polymer **P-3$_{AB}$** (before cross-linking) and polymer **P-3$_{CR}$** (after cross-linking and Soxhlet extraction). The peak at 12 min is due to THF, and the peak at 15 min is due to the sulfur standard.

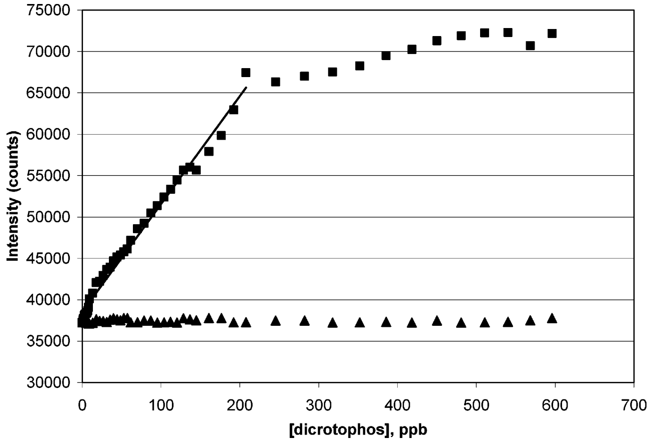

Figure 9. Luminescence titration of 0.1 mg/mL star MIP **P-3$_{CR}$** with 0.10 mM dicrotophos (squares). The control polymer **P-4$_{CR}$** is unchanged by the addition of dicrotophos (triangles). The line indicates a linear fit to the equation $y = 130x + 0.385$, $r^2 = 0.987$.

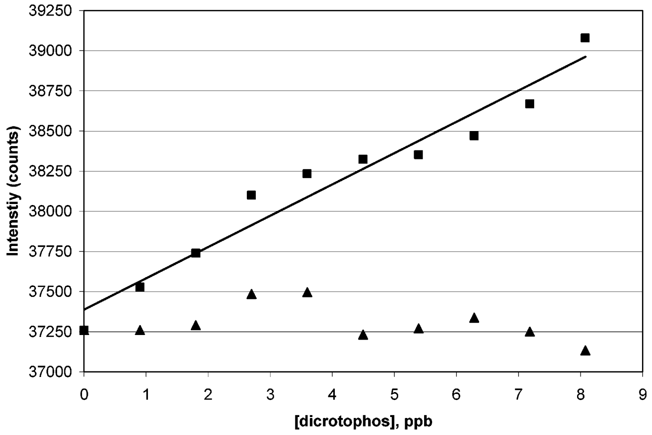

Figure 10. Expansion of the luminescence titration of 0.1 mg/mL star MIP **P-3$_{CR}$** with 0.1 mM dicrotophos showing a sub-ppb detection limit.

The polymers **1**−**4$_{AB}$** were cross-linked with dicrotophos through RCM. It was impossible to remove the dicrotophos in polymers **1** and **4**, even with extensive Soxhlet extraction, since the core was 100% 1-but-3-enyl-4-vinylbenzene and completely cross-linked. In order to give some degree of freedom to the cross-linked core, polymers in which block A was a copolymer of 1-but-3-enyl-4-vinylbenzene and styrene were prepared. We also switched to a core complex, **6**, due to ease of synthesis of **4** and stability of its precursors. Varying the degree of cross-linker in these polymers led to the preparation of luminescent, soluble, and processable imprinted polymers (Table 1). All of the polymers have a narrow molecular weight distribution. Polymer **1** was the first star MIP prepared. The MW of the cross-linked polymer increased significantly along with the polydispersity. This was due to running the cross-linking reaction in a solution that was too concentrated (3.33 mg/mL), resulting in intermolecular cross-linking. In polymers **2**−**4**, the polydispersities are similar between the un-cross-linked and cross-linked polymers since these cross-linking reactions were run at a 1 mg/mL (polymer) concentration. The GPC trace of polymer **P-3$_{AB}$** and **P-3$_{CR}$** is shown in Figure 8. The peak at 10 min corresponds to the polymer, while the peaks at 12 and 15 min correspond to THF and the added sulfur standard, respectively. Polymer **P-3$_{AB}$** was uncross-linked and shows a shoulder representative of low molecular weight oligomers. Polymer **P-3$_{CR}$** was cross-linked and Soxhlet extracted. The extraction removed the dicrotophos as well as the oligomers as indicated by the sharpening of the peak.

Binding and Interference Studies. Since the core of the star MIP has a lanthanide ion chromophore, luminescence can be used to verify that the polymer has useful properties. We have demonstrated that many organophosphonates bind to tris(β-diketonate)Eu(III) complexes with a 1:1 stoichiometry.[9]

We tested the rebinding of dicrotophos to the **P-3$_{CR}$**. The star MIP was dissolved in methylene chloride, and aliquots of a dicrotophos solution were added. Polymer **P-4$_{CR}$** was used as a control in the binding and interference studies. Polymer **P-4$_{CR}$** was chosen since it was exposed to the same conditions as **P-3$_{CR}$**. As seen in Figures 9 and 10, this polymer can be used as a sensor with a sub-ppb detection limit.

P-3$_{CR}$ was also highly selective for dicrotophos. We performed interference studies using dichlorvos, diazinon, and dimethyl methylphosphonate (Figure 11). The insecticide that is most similar to dicrotophos is dichlorvos. We chose diazinon due to the presences of nitrogen in the structure. We chose dimethyl methylphosphonate, since it is a common organophos-

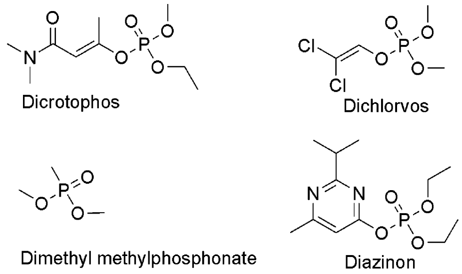

Figure 11. Structure of dicrotophos and tested potential interferents.

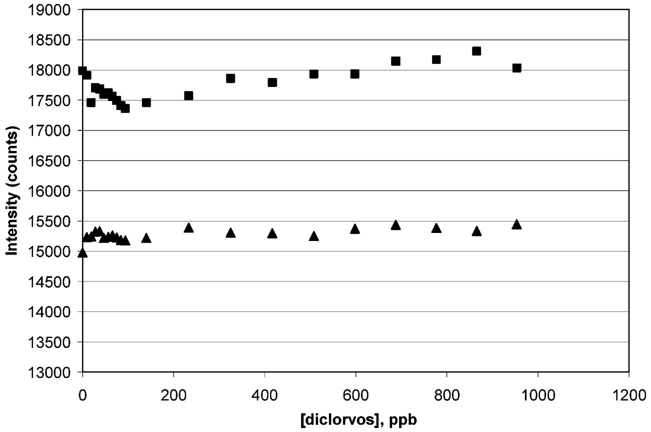

Figure 12. A dichlorvos luminescence interference test with star MIP **P-3$_{\mathrm{CR}}$** shows essentially no response up to 1 ppm or 1000 times the detection limit for dicrotophos (squares). The control polymer **P-4$_{\mathrm{CR}}$** is offset by 2500 counts for graphical clarity (triangles).

phate and its small size suggests it might be able to occupy a site imprinted with a larger molecule.

In these tests no interference was detected from the any of the three compounds, even when the polymer was subjected to concentrations 100−1000 times higher than the concentration of dicrotophos (Figure 12). The data for diazinon and dimethyl methylphosphonate were similar.

Conclusion

Soluble and processable molecularly imprinted polymers with good sensitivity (LOD's in the low ppb range) and very high selectivity (no interference from near identical interferents) have been prepared using RAFT polymerization. The polydispersities of the polymers were initially high (for example, **P-1$_{\mathrm{CR}}$**, MWD = 3.1) due to interstar cross-linking. By cross-linking in very dilute solution the polydispersity improved (**P-2$_{\mathrm{CR}}$**, MWD = 1.38). The process results in macromolecules with terminal thiol groups amenable to binding to gold. The soluble MIPs are a powerful step forward toward the production of synthetic antibodies, improved chemical sensors, or highly stable and efficient luminescent plastics.

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