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Molecularly Imprinted Ionomers

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ABSTRACT

Ionomers have been defined as copolymers that have a certain proportion of ionic groups. The ionic groups have a significant effect on the mechanical properties of the copolymers. This is generally due to aggregation of ions in a low dielectric medium. The primary result is to restrict chain motion and raise the glass transition temperature. These attributes have relevance to molecular imprinting, since restricted chain motion should help preserve the integrity of the binding site. The connection between ionomers and molecular imprinting has come from the production of metal ion imprinted resins. Metal ions are used in the production of molecularly imprinted polymer ion exchange resins and ionically permeable membranes. The polymers have applications as separations media, sequestering media and as ion selective sensors. Metal ions are also being used to form imprinted polymers based on metal mediated imprint binding. We have prepared ion exchange resins, selectively permeable polymer membranes, ion selective electrodes and ion selective optical sensors using a modified version of the molecular imprinting technique. The modification is a reduction in the amount of covalent crosslinking used to form the polymers. This reduction may be justified by the presence of residual metal ion crosslinking in the immediate region of the imprinted binding site. The effects of metal ions on the thermal and mechanical properties of the polymers, as well their impact on binding selectivity are critical variables.

INTRODUCTION

The production of selective metal ion sequestering and separation materials is a growing field with broad application and critical importance. Industry requires vast quantities of metals and generates tons of metal wastes. Nuclear energy production and past weapons production facilities have created unique challenges in the area of metal ions separation. Ultimately, technology must reach a point where all metal containing waste streams are treated as recoverable metal resources. Metal ion selective molecularly imprinted materials may be the means to realize this goal. An additional application of metal ion imprinted polymers is as sensors. The ability to detect a specific metal ion in a complex matrix is keenly appreciated.

Several issues need to be addressed in the design of molecularly imprinted ion complexing. Of primary concern is to make a rebinding site with good affinity. The binding selectivity afforded by metal ions is starting to be appreciated [1]. The large literature database of tabulated metal to ligand affinities forms a useful guide to the selection of the correct metal for a specific target [2]. Another useful aspect of metal ions in site production is the tendency of metal ions to exhibit directional bonding. The stereo-regularity of metal coordination geometries can be exploited to form a favorable geometry for secondary interactions. Many organic compounds have functional groups that are amenable to metal ion tethers. The selection of a metal ion with useful spectroscopic properties allows the imprinted polymer to be used as an optical sensor [3]. Metal ions can be spectroscopically useful by forming metal-analyte complexes that absorb specific wavelengths of light. Metal ions can be chosen that will not exhibit color unless coordinated by a target ligand. A metal can be chosen that forms a fluorescent complex, such as Zn^{2+} with benzoin. When the imprinted site is to sense a heavy metal ion, a fluorescent ligand may be induced to phosphoresce, via the external heavy atom effect, yielding an emission band that is Stokes shifted and longer lived than with the unbound molecule [4]. To prepare an anion sensing polymer, it is useful to choose a luminescent metal ion as a component of the binding site to acquire both a high thermodynamic binding affinity and a highly sensitive reporter [3].

Perhaps the greatest general utility in the use of metal ions to form imprinted polymers is the change in structural properties. The inclusion of cations into polymer acids to form polymer salts drastically changes the structural relaxation and other physical properties due to strong coulombic interchain interactions [5]. The effect is to raise the glass transition temperature and impede structural relaxation. When trying to produce a stable rebinding site in a polymer it is important to maintain site integrity. By using ionic crosslinks through metal ions the polymer chains become rigid and should maintain site integrity. Since metal ion crosslinking can have a greater effect on polymer properties than does covalent crosslinking, less total crosslinking can be used and some of the recoil effect described earlier may be avoided. This hypothesis is being examined in this work.

As stated previously, the chemical recognition element must be stable and reusable. A potential problem with MIPs as chemical recognition elements would be a gradual loss of specificity. The problem has not been directly addressed in the chemical literature but efforts to understand temperature effects on imprinted polymers have shown that selectivity can be destroyed by exposure to an elevated temperature for short periods. This sort of temperature study is analogous to the techniques used to artificially age materials. Chen et al. [6] showed a loss in selectivity with increasing time and temperature. Essentially, the selectivity was annealed away. These studies were performed on the usual highly covalently cross-linked polymers. No such studies have been performed on polymers with relatively low levels of covalent crosslinking or polymers, with low levels of covalent crosslinking supplemented by metal ion crosslinks or materials with only metal ion crosslinks.

EXPERIMENTAL DETAILS

The synthetic procedures involved in producing the polymers under investigation have been published previously [7-10]. The steps involved in acquiring the capacity data are shown in Figure 1. The data thus acquired are used in the equations that follow the Figure to calculate the metal ion capacity and selectivity parameters. In addition to the cation used to prepare the polymer, other cations with differing charges, sizes, coordination numbers, and/or coordination geometries are used in these selectivity quotient measurements to verify specificity. Measurements are also made using the polymers prepared with no metal cation (H^+ or NH_4^+). Measurements required for these studies are made using a pH meter for $[H^+]_a$ and elemental analysis (electro-thermal atomization atomic absorption, ETA-AAS or inductively coupled plasma mass spectrometry, ICP-MS) for $[M^{n+}]_a$.

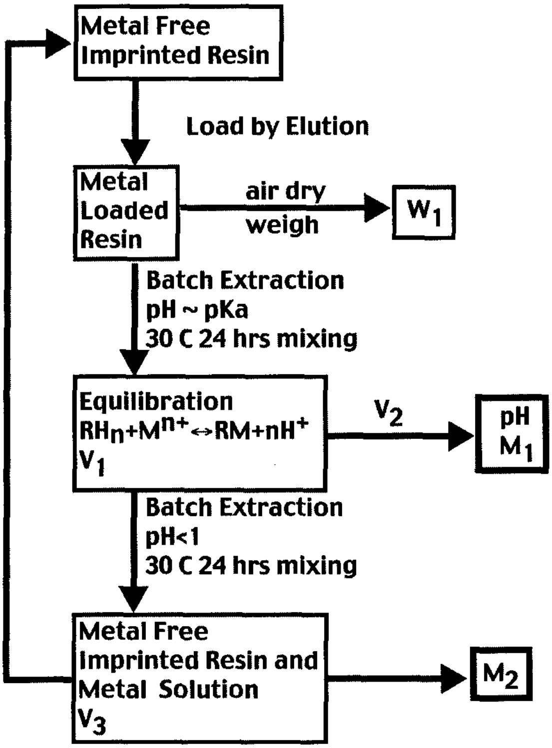

Figure 1. Steps involved in ascertaining resin capacity.

$$capacity = \frac{[M^{n+}]_1 V_2 + [M^{n+}]_2 V_3}{W_1} \tag{1}$$

$$K = \frac{[H^+]^n \left(capacity - [M^{n+}]_1 V_1 / W_1 \right)}{[M^{n+}]_1 \left(n[M^{n+}]_1 V_1 / W_1 \right)^n} \tag{2}$$

$$\alpha_{M_1, M_2} (selectivity) = \frac{capacity\ M_1}{capacity\ M_2} \tag{3}$$

The capacity of an imprinted polymer is affected by the amount of crosslinking. Polymers we have prepared with a fairly low level of crosslinking result in a maximum capacity at a certain level of crosslinking. Table I shows the effects of divinylbenezene (DVB) crosslinking on the capacities of lead imprinted styrenic resins and an unimprinted styrenic control resin. Although the unimprinted control (P-0) has double the amount of ligand (4-vinylbenzoic acid or VBA) as the imprinted resins, the Pb^{2+} capacities of all the imprinted resins are larger than the non-imprinted control resin. The capacity optimum of 2 % crosslinking suggests that a balance of site rigidity and accessibility can be obtained. In the case of Pb^{2+}, high levels of covalent crosslinking (>5 mole %) resulted in resins with no selectivity. In the case of styrenic Fe^{3+} resins, high levels of covalent crosslinking (85 mole %) gave reduced selectivity, but higher capacity, due to greater porosity (Figure 2).

Table I. The effect of cross-linking on lead ion capacity

polymer ID	mole % complex (mole % ligand)	mole % DVB	capacity (μmole/g)
P-0	(4)	1	0.112
P-1	1	1	0.179
P-2	1	2	0.231
P-3	1	4	0.127

In order to be certain as to the selectivity of the resins, experiments were performed to verify selectivity by the simultaneous loading of two or more metal ions. The results of one study are presented in Table II. As expected the Pb^{2+} imprinted polymer had better selectivity for Pb^{2+} ion.

Table II. Capacity and capacitive selectivity of unimprinted and Pb imprinted resins toward Pb, Cu and Cd in multiple exposure experiments

polymer ID	Pb capacity (μmole/g)	Cd capacity (μmole/g)	selectivity $\alpha_{Pb, Cd}$	Cu capacity (μmole/g)	selectivity $\alpha_{Pb, Cu}$
P-0	0.162	0.00463	35		
P-1	0.119	0.00220	54		
P-6	0.107	0.00120	90	0.00931	12

Further characterization included the determination of the acidity constants of some of the resins. The titration of a resin allows the determination of the number of ionogenic sites that have, during swelling and cleaning, become accessible to H^+ ion. This "capacity" is indicative of the relative amount of metal ion complex that has been incorporated in the copolymerization reaction. A calculation of the expected load of lead vinyl benzoate complex in a polymer containing 5.00 mole percent complex (with 1.00 percent crosslinking) is 416 μmole/gram. A titration of this copolymer yields a value of 20.2 μmole/gram for H^+ or just 10.1 μmole/gram of lead ion. This corresponds to only 2.50 percent of the metal ion complex being exchangeable into the copolymer. The remaining metal ion is locked in place and, for the reasons stated above, may contribute to the binding site rigidity.

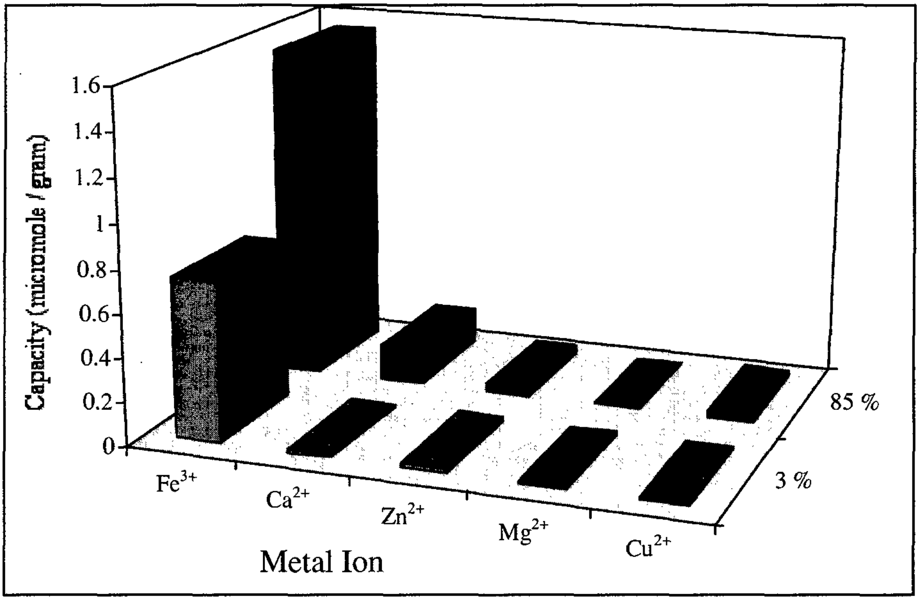

Figure 2. Ion loading capacity for Fe^{3+} imprinted polymers showing higher capacity but lower selectivity with high degrees of covalent crosslinking (% refers to divinyl benzene).

Blank resins, that are prepared without a template metal ion, exhibit a degree of selectivity based upon thermodynamic affinity. Thus, a comparison of the selectivity (α) values of the imprinted resins with those of the blank resins provides an estimate of the overall effect of imprinting on selectivity. Thus, a comparison of the selectivity (α) values of the imprinted resins with those of the blank resins provides an estimate of the overall effect of imprinting on selectivity. Thus the relative selectivity is:

$$\alpha' = \frac{\text{Selectivity of the imprinted Polymer}}{\text{Selectivity of the unimprinted Polymer}} \qquad (4)$$

where the unimprinted polymer is prepared without a metal ion template. The effect of imprinting is dramatic in the case of uranyl ion imprinted resins using VBA as the template ligand. In this case the selectivity of the blank polymers are favorable to first row transition metals. Thus, imprinting the resins results in selectivity values of 10 or greater for uranyl against ions tested; Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Fe^{3+} as compared to the 1 to 3 fold selectivity against exhibited by a blank polymer.

Table III. Effect of imprinting (α') of the uranyl templated 4-vinylbenzoate resins.*

Polymer Resin	α' UO_2^{2+}, Cd^{2+}	α' UO_2^{2+}, Cu^{2+}	α' UO_2^{2+}, Ni^{2+}
P12	19.1 ± 0.4	10.1± 0.2	24.5± 0.4
P22	21.4± 0.5	15.6± 0.4	29.5± 0.3
P32	33.0± 0.9	21.4± 0.3	33.5± 0.9
P42	37.2± 1.3	23.2± 0.5	36.2± 1.4

* The identity code for these polymers is as follows: the first digit is the mole % complex and the second digit is the mole % divinylbenzene.

The studies outlined above show that imprinted ion exchange resins made with small amounts of covalent crosslinking generally have much better selectivity but lower capacity than resins made by the conventional approach using large amounts of covalent crosslinking. This observation has been made by other practitioners. Harkins and Schweitzer, [11] first observed this phenomenon for Ni^{2+} and Cu^{2+} imprinted ion exchange resins. Lemaire, et al. observed this trend in their work with imprinting chelating resins for lanthanides [12]. We have observed this trend for Pb^{2+}, Fe^{3+} and UO_2^{2+} and intend to explore the implications of this observation and its ramifications to the field of molecular imprinting.

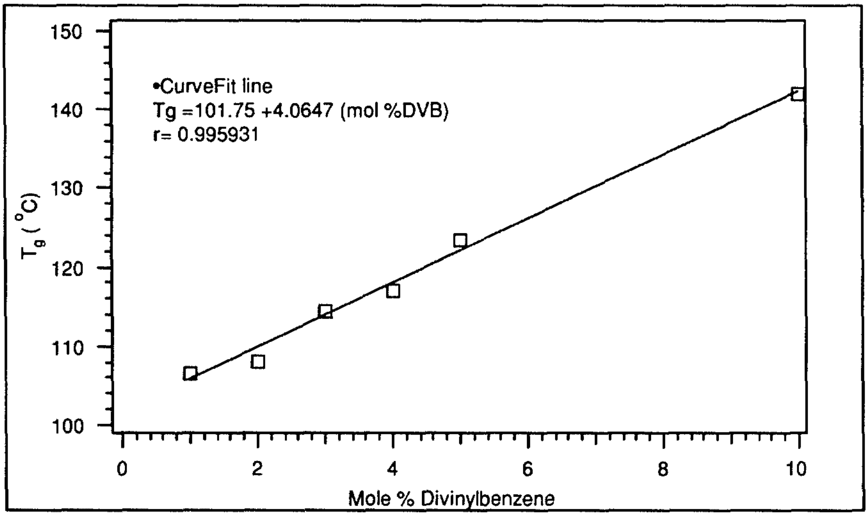

Figure 3. The glass transition temperatures of a series of polymers containing 1 mole % $Pb(VBA)_2$, equivalent to 0.41 mole % Pb, with increasing amounts of covalent crosslinking, as mole % DVB.

Differential scanning calorimetry (DSC) is a popular technique since it is capable of determining both thermodynamic properties and kinetic characteristics of thermal processes. The ability to define thermal transients in polymer relaxation, especially the glass transition temperature (Tg) and relaxation events that occur at temperatures other than Tg is of importance to this study. The relaxational transitions that occur at temperatures below the bulk Tg are referred to using Greek letters beginning with β, α being reserved for Tg. These lower temperature relaxational transitions may be important to the understanding of the stability and selectivity of the imprinted sites since they may represent motion at the site of the imprint. Figure 3 shows the effect that covalent crosslinking has on the Tg of a Pb^{2+} ion imprinted polymer.

A sufficient amount of metal ion crosslinking produces an additional transition at temperatures that are higher than the bulk, or "matrix" Tg. This higher temperature transition has been observed in certain cases by using DSC. It is much more readily apparent when using dynamic mechanical analysis (DMA). Thus, the high temperature transition induced by metal aggregation has a much greater effect on the mechanical properties than on the heat capacity of the bulk material. DMA can provide more information but requires a solid chunk of material as opposed to powders. This requirement makes it unsuitable to ascertain the differences in loaded and unloaded imprinted polymers. In the case of styrenic polymers similar to those we have produced, metal ion concentrations reach a threshold and the two glass transitions observed by DMA are seen as a single intermediate glass transition when measured by DSC. A plot of the DSC Tg values versus the amount of metal in a polymer gives an "s" shaped curve with the deviation from linearity being attributed to ion clustering (Figure 4). The bend of the "s" seems to occur when aggregation forms a new "cluster" Tg. This means that most of the investigation can be performed using the logistically simpler DSC with an occasional verification by DMA (Figure 5).

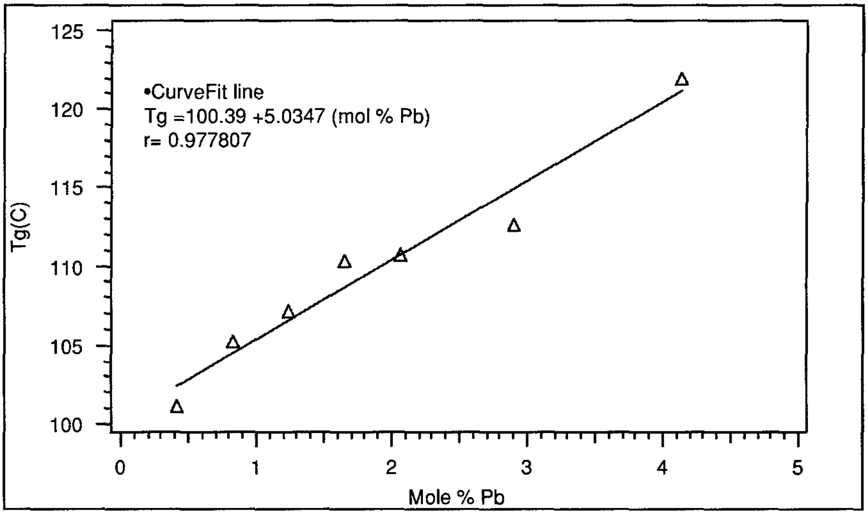

Figure 4. Graph of a series of polymers containing 1 mole % DVB with increasing amounts of ionic crosslinking, as $Pb(VBA)_2$.

The most recent development in scanning calorimetry is modulated DSC (MDSC). MDSC has advantages over conventional DSC that are of particular utility in the present investigation. Conventional DSC measures the sum of all the thermal events in the sample. This can be confusing when events overlap or are affected by fabrication. MDSC helps discriminate thermodynamic properties from thermal history and each of these from the other. For example, the glass transition is an enthalpic relaxation that can be affected by thermal history and in some instances may appear as a melting transition. Use of MDSC provides a means to discriminate against such artifacts. MDSC also has advantages in sensitivity and resolution, both critical in evaluating higher order transitions. We have begun to look at MDSC traces of Pb^{2+} and UO_2^{2+} imprinted polymers (Table IV). The data for uranyl imprinted ion exchange resins shows the expected increase in Tg with the increase in the amount of metal ion crosslinking. The abrupt jump at 5 mole % of the complex indicates that at this level complex aggregation has occurred. The thermal behavior has been examined in greater detail for the Pb^{2+} containing polymers.

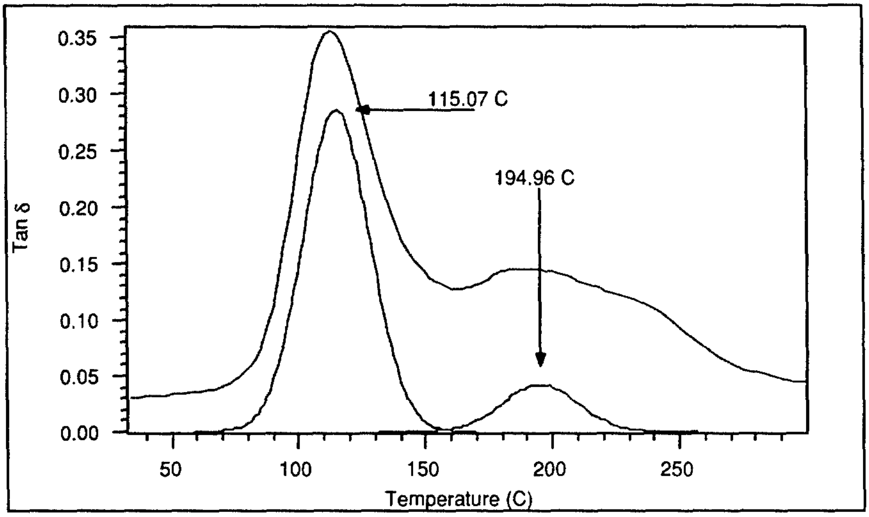

Figure 5. Dynamic Mechanical Analysis of the 4.1 mole % $Pb(VBA)_2$ containing polymer showing two glass transitions (upper trace smoothed data, lower trace Gaussian fit).

Table IV. Glass transition temperatures of uranyl vinylbenzoate imprinted polymers

Polymer ID	Tg by MDSC (°C)
polystyrene	102.56
P12	111
P22	112.24
P32	113.25
P42	113.89
P52	121.89

* For these polymers the identity code is: the first digit is the mole % complex and the second digit is the mole % divinylbenzene.

DISCUSSION

The discovery of the influence of metal ion crosslinking on molecular imprinting is a natural consequence of using the process to make ion exchange resins. The theory regarding the allowable reduction in the amount of covalent crosslinking was based on the expectation that in a highly crosslinked polymer matrix, the removal of the imprinting species will result in a recoil of the ligating atoms. The recoil occurs due to the relaxation of the polymer chains when the imprinting crosslink is broken. A highly crosslinked polymer is under a considerable amount of internal stress created during fabrication. The removal of the imprinting crosslink can relieve that stress by relaxation. A larger amount of covalent crosslinking restricts chain motion and a greater the amount of flexure stress is placed on the polymer chains during their growth. This theory predicts that higher levels of covalent crosslinking results in a larger amount of recoil and a greater loss in selectivity. The substitution of a small amount of ionic crosslinking has been shown to have dramatic effects on polymer properties. The benefits of ionic crosslinking on molecular imprinting are two-fold. First, ionic crosslinks have a greater effect on the localized rigidity of the binding sites through aggregation. Second, the crosslinks formed by a metal ion are by electrostatic attraction and may allow some rotational flexure at the crosslink, necessitating less adjustment in the region of the imprint and resulting in less selectivity loss when the imprint species is removed.

The properties of metal ion containing polymers have been studied from the materials science perspective for many years. Much of the work has appeared in a recent monograph by Eisenberg and Kim, entitled ,"Introduction to Ionomers" [13]. Of interest to this work is the characterization of the sodium salt of a copolymer of styrene and methacrylic acid. Several models for the structure of this copolymer have been developed. Central to these models is the concept of the aggregation of the ion pairs. Aggregation creates regions of reduced chain mobility in the manner of multiple crosslinks. When the amount of ion content is increased clusters of the aggregates cause regions of the polymer to behave differently and a second, higher glass transition temperature can be observed indicative of the effect of the clusters. As metal content continues to increase, the regions of restricted motion begin to overlap and a single, high glass transition temperature is observed. The metal ion aggregation is a result of dielectric constant and is similar to the processes involved in the production of reverse micelles.

Thus, the regions of greatest chain restriction are near the metal ion aggregates. The optimal placement of binding sites for imprinted polymers should also be near the metal ion aggregates. In the event that an ion exchange resin is being fabricated with low levels of covalent crosslinking, both of these criteria will be met, since some of the imprinting ions are left in the polymer after the ion exchange sites are liberated. We believe we have encountered this phenomenon in regard to Pb^{2+}, Fe^{3+} and UO_2^{2+}resins [7-10]

CONCLUSIONS

Metal ion imprinted polymers have yet to be characterized in sufficient detail. This lack of characterization is starting to be remedied. The associated field of ionomers gives clues toward the direction some of these new efforts should take. This is especially relevant since characterization of metal ion imprinted polymers has revealed that some of the metal ions are trapped in inaccessible locations or are bound too strongly to be released. This is especially true of resins formed with a non-complexing matrix monomer. Such resins possess residual metal ion crosslinks that may have a dramatic effect on the polymer properties. The effects of metal ion crosslinks on molecular imprinting are not well understood. The effects may help to explain why selectivity of some metal ion imprinted polymers is increased when the amount of covalent crosslinking is decreased.

ACKNOWLEDGEMENTS

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