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REVIEW ARTICLE

Ion-imprinted polymers for environmental monitoring of inorganic pollutants: synthesis, characterization, and applications

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Abstract Ion imprinting has become one of the fast-growing technologies that have gained a lot of attention recently especially in the area of materials science. One of them is called the ion-imprinted polymers (IIPs). The IIPs are synthesized on the principles of enzyme phenomenon whereby a polymer is altered by a polymerization that takes place in the presence of a template that will be later removed to create cavities that will recognize only the analyte of interest. This specific and selective affinity for the target species decreases the chances of competition with other different types of ions. The imprinting technique started with the discovery of the bulk polymerization method where by the monomer, initiator, crosslinker, and template are mixed together and allowed to polymerize, and then the resulting polymer is ground and sieved to get particles with sizes suitable for the polymer's application. The IIPs have got some attractive qualities for use in environmental applications which include their stability and inexpensiveness and have a wide range of synthesis options with each suiting a certain unique application. Apart from environmental work, IIPs have applications in many other areas such as in membranes, in drug delivery, and in biosensors as alternatives to antibodies just to mention a few. This review focuses on the synthesis, types of imprinting, characterization, and applications of IIPs.

Keywords Characterization · Ion-imprinted polymers · Immobilization · Imprinting

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Introduction

Generally, ion-imprinted polymers (IIPs) can be defined differently depending on the methods used to synthesize or fabricate them, functions they play, or the materials used for their synthesis. Saraji and Yousefi (2009) defined IIPs as a new class of highly selective materials that are highly recommended for analytical analysis, while Baghel et al. (2007) simply defines IIPs as "polymeric materials that are capable of higher ionic recognition". More accurately, IIPs are a new generation of materials with ionic recognition sites having high affinity towards the analytes of interest as compared to the competing species which may also be found in the same matrices (Baghel et al. 2007; Dhakal et al. 2005; Rao et al. 2006).

However, despite the fact that IIPs have exceptionally excellent qualities such as high selectivities, ease of preparation, easy storage, reusability, and harsh environment utility (Yoshida et al. 1999a, b, c), they also have some drawbacks which depend on the method of synthesis that was used. These limitations include slow rebinding which is a result of some of the recognition cavities being embedded deep in the polymer matrix as the case in 3-D imprinting, hence not easily accessible (Andac et al. 2004; Yoshida et al. 1999a, b). The application of IIPs for water soluble analytes contained in biological matrices presents another challenge as these materials may also be soluble; hence, difficulties for application in aqueous environments may also be witnessed (Chen et al. 2011). In some cases, the removal of the template was reported to be incomplete and therefore, affected the performance and the efficiency of the IIPs synthesized for their intended use (Sadeghi and Mofrad 2007; Say et al. 2003).

Despite the shortcomings that are associated with these materials, studies and subsequent documentation on IIPs have been on the rise over the last decade. For instance,

Liu et al. (2011) studied the use of α-Fe_2O_3-impregnated chitosan beads (As-IFICB) with As(III) as imprinted ions for the removal of As(III) from aqueous solutions. They found that the maximum adsorption capacity was 6.18 mg/g at pH5 and 30 °C, and these adsorptions were in agreement with Langmuir isotherms and also followed second-order kinetics. From this study, it was also evident that IIPs have the ability of being reused, as it was found that the As usage of these beads up to ten times did not have much change in the regeneration loss. Liu's work (Liu et al. 2011) was actually an improvement of the earlier work on increasing the adsorption capacities and selectivities towards analytes of interests (Abdel et al. 2011; Bleiman and Mishael 2010; Ito et al. 2003; Pancharoen et al. 2009). All the methods that have been studied showed various positive aspects, yet, some negatives hinder the utmost trust in these methods to play a huge role in sample cleanup and also in remediation studies (Feng et al. 2009a, b; Zhang et al. 2010a, b).

The imprinting technique has attracted attention after early investigations by Sellergren et al. (1988), Wulff (1984), Mosbach et al. (2001), and Ramström and Mosbach (1999) among others. Thereafter, modifications and improvements from the "traditional" imprinting developed earlier on followed (Deveci et al. 2009; He et al. 2007; Matsui et al. 1996; Su et al. 2008; Walsh et al. 2010). These were explored to solve the issues of slow rebinding kinetics, low selectivities, low reusage, and longer preparation times (Baghel et al. 2007; Chaitidou et al. 2009; Liu et al. 2007; Tada and Iwasawa 2003; Yoshida et al. 1999c). These have been successfully done by either altering the bonding between the template and the functional monomer or the polymerization medium (Chaitidou et al. 2009; Shamsipur et al. 2007; Wulff 2005).

The combination of the sol–gel processing and ion imprinting as reported by Quirarte-Escalante et al. (2009) gave polymers high mechanical strength as well as excellent chemical and thermal stabilities with improved metal uptakes. This is one way of the improving the traditional molecular and ion imprinting technique. Lead hybrid adsorbents have been synthesized using this method whereby organosilanes were hydrolyzed and co-condensed with crosslinking agents and also with mesoporous functionalized solids having high selectivities towards lead ions, and these were suitably used for the removal of lead from waste water (Quirarte-Escalante et al. 2009).

Ion imprinting has also been utilized in forming other analyte-specific materials known as ion-imprinted fibers (IIFs) (Li et al. 2011a, b). Here a metal-imprinted material is grafted into a support which can be silicon or polypropylene fiber, and these grafted materials show excellent properties and improved versatility as compared to the normal IIPs. All the available polymerization techniques can be used to prepare these IIFs. Li et al. (2011a, b) used a polypropylene fiber as support, and their surface is modified by functionalization, and the Cu(II) template was imprinted in them successfully.

The synthesis of these materials generally includes a monomer, crosslinker, initiator, and a template (Khajeh et al. 2011; Sadeghi and Mofrad 2007; Singh and Mishra 2010a). These IIP materials differ depending on the imprinting ion of choice, the type of polymerization to be used, and also the type of interaction between the template and the monomer. For example, in the report by Saraji (Saraji and Yousefi 2009), they used 4-vinylpyridine, EGDMA, 2,2′ AIBN and Ni-dithizone as monomer, crosslinker, initiator, and template, respectively, in preparing Ni(II)-IIPs. The same format is widely used even with other types of ions. However, Otero-Romani prepared Ni(II)-IIPs using 4-VP as monomer and vinylbenzene in the presence of Ni(II) alone or in the presence of Ni(II) and hydroxyquinoline as the crosslinker (Otero-Romaní et al. 2009). Many other monomers and crosslinkers have been reported by a number of researchers in various applications (Baggiani et al. 2012; Tada and Iwasawa 2003; Wei et al. 2005; Ye and Mosbach 2008).

Main steps in the imprinting technology

There are traditionally three steps involved in the ion imprinting process:

1. Complexation of a template to a polymerizable ligand: In this step, the union between the template (T) and the functional monomer, sometimes referred to as polymerizable ligand, is performed, and it is the basis of the preparation of this family of polymers (Cormack and Mosbach 1999; Denizli 2007). It also signifies the type of imprinting used and, hence, the type of polymers to be produced. In this step, the template of choice is made to interact with the monomer in one out of three possible ways (discussed later in this communication) to form a complex. In other words, the template is imprinted into the monomer.
2. Polymerization of this complex: After the successful complexation of the starting materials, this template-functional monomer complex is polymerized. This is where, if necessary and depending on the type of polymerization, the polymerization initiator and crosslinker are added (Cui et al. 2002; Singh and Mishra 2010a, b; Yoshida et al. 1999a, b). The crosslinker's role is to stabilize the "active sites" such that when the polymers are needed for reuse, they can still have intact and active sites ready and available for binding with the target molecules or ions (Singh and Mishra 2010a, b).
3. Removal of the template after polymerization: This is the final step in the polymerization process. It is

essential in that the "fake" analyte makes way for the target materials that are under investigation (Ramström and Mosbach 1999; Wulff 1984). After the removal of the template, cavities or active binding sites are left behind which are morphologically similar to the target materials hence making these prepared polymers to be analyte-specific and highly selective in the process (Khajeh et al. 2007; Tsoi et al. 2012). This and better enrichment factors which have since been associated with these IIPs. Scheme 1 shows the process of IIP synthesis.

Types of interactions in the IIP imprinting process

The type of interactions involved in the imprinting technique defines the type of imprinted polymer generated and hence the method of imprinting employed (Wulff 2005). Before choosing the type of interaction to be used, it is essential to take note of the following:

1. The interaction between the binding sites i.e., between the functional monomer and the template should be stable.
2. The leaching or the removal of the template after polymerization should be rapid and also, the rebinding and re-removal of analytes should be rapid so that the reuse of the polymer is hassle-free.
3. There should be a conducive medium for the template and monomer to "unite".

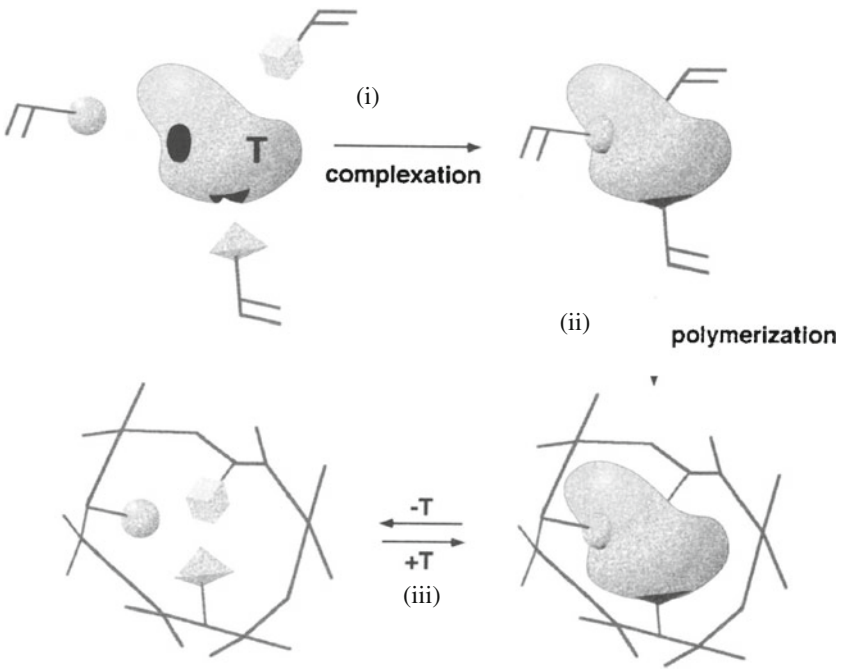
Before any polymerization takes place, the template and monomer should complex together, and the complexing is governed by interactions. The two main interactions are discussed in this communication.

Covalent interaction

In this type of interaction, the template and monomer are linked by rigid covalent bonds, though such bonds are limited in molecular imprinting (Vishnuvardhan et al. 2007; Wulff 2005). However, even though it provides a stable interaction between the monomer and template, it is highly inefficient as far as rebinding and reuse of the polymers to be synthesized is concerned. These interactions are too stable for the removal of the template and facilitate very slow rebinding kinetics (Caro et al. 2002). This prompted more research on other types of interactions to improve the ion imprinting technology. Scheme 2 shows the processes involved in the covalent imprinting process.

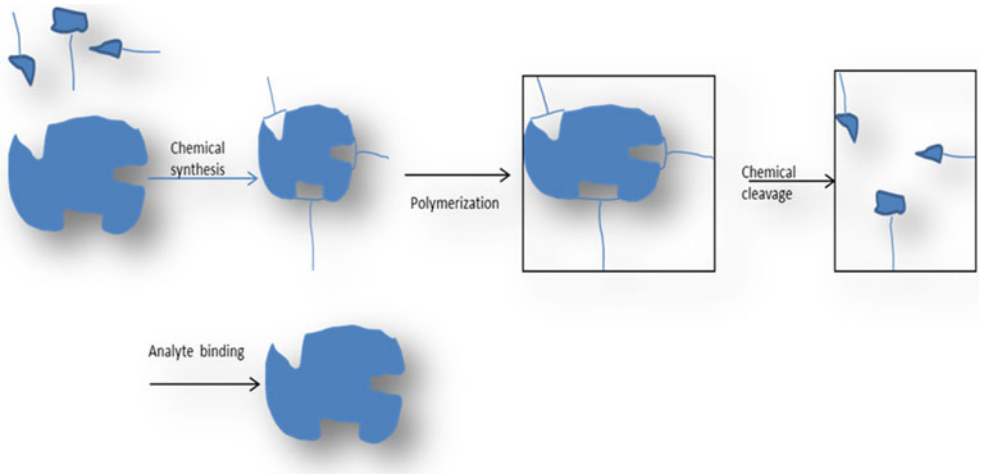
Non-covalent interaction

To achieve better rebinding kinetics and rapid template and monomer equilibrium, Mosbach et al. (2001) studied another generation of polymers based on non-covalent imprinting. In this method of imprinting, the template and monomer complex is formed by self-assembly. The monomer and template should be complementary, that is, the binding or complexation is based on the union of these two by a number of mechanisms such as hydrogen bonding, hydrophobic interactions, salt bridges, ionic interactions, and van der Waals forces (Ramström and Mosbach 1999; Wulff 2005). Scheme 3 is a diagrammatic representation of non-covalent imprinting.



Scheme 1 Scheme for the general synthesis of IIPs

Scheme 2 Covalent interaction in IIPs



Monomers, crosslinkers, and solvents for the imprinting procedure

Monomers

The proper selection of monomer, crosslinker, and solvent has an effect on the performance of the IIPs in their respective applications (Candan et al. 2009). The performance may be in terms of shelf life, utility, rebinding abilities, and reuse (Wulff 2002). In non-covalent imprinting, the durability of the polymer depends on the functional monomer and template interaction (Ramstrom et al. 1993). The monomer should have functional groups that will work towards strengthening the type of interaction between itself and the template and also the polymer matrix (Chen et al. 2011). In Fig. 1, examples of the mostly used monomer are shown.

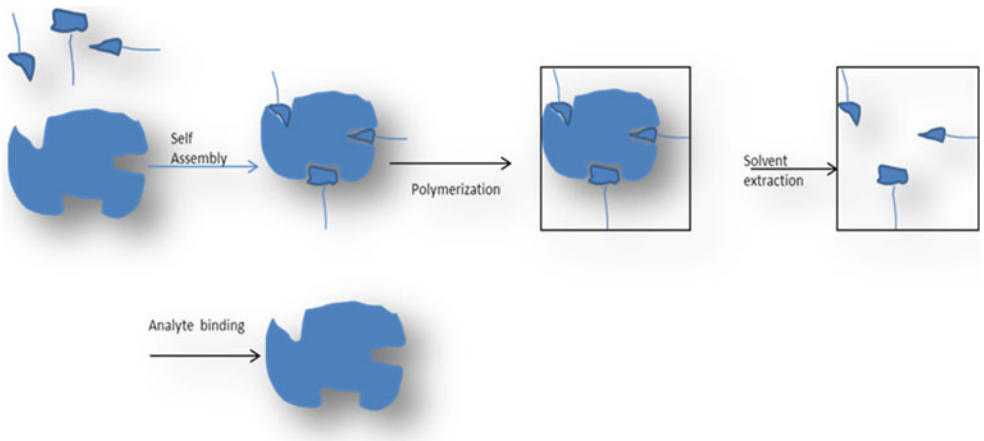
Crosslinkers

Crosslinkers play a major role in the imprinting process. What they do is create an environment whereby the orientation of the functional monomers and template favors formation of a rigid network where the template and, hence, the cavities are affixed (He et al. 2007). The more stable these cavities are the more useful the polymer will be. The crosslinkers should be in higher proportions in the final polymer, and the highly branched or high-molecular-weight crosslinkers have a tendency of producing such stable cavities (Matsui et al. 1996). For example, trimethylolpropane trimethacrylate (TRIM) (with three acrylate groups) has been reported to be a better crosslinker than EDMA (with two acrylate groups) (Glad et al. 1995). Figure 2 shows two mostly used crosslinkers.

Solvents

In most cases, solvents are used in the synthesis of IIPs. These include water, toluene, chloroform, acetonitrile, and many more (Su et al. 2008). A good solvent dissolves all the components of polymerization mixture and by extension contributes to the physical makeup of the polymer (Lubke et al. 2000). The usability of solvents may depend on the hydrogen bond parameter, dielectric constant, polarity, and solubility which may increase the durability or decrease the durability of that polymer (Li et al. 2011a, b; Matsui et al. 1996).

Scheme 3 Representation of non-covalent-based imprinting



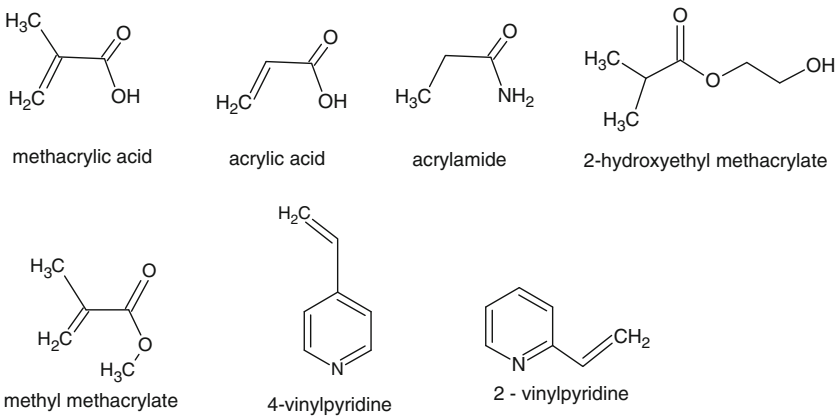


Fig. 1 Some frequently used monomers

Polymerization methods

There are generally four different polymerization methods used in the imprinting technique that have adequately been studied. Each has got more attractive features than the others. These polymerization methods include bulk polymerization (Mesquita et al. 2004; Saraji and Yousefi 2009; Yamasaki and Patrickios 2003), suspension polymerization (Dowding and Vincent 2000; Kaminoyama et al. 2005), precipitation polymerization (Chaitidou et al. 2009; Chimie 1918; Ho et al. 2005), and emulsion (surface) polymerization (Dai et al. 2012; Yoshida et al. 1999c). The polymerization and imprinting may also be classified further into two groups which are 2D and 3D (Daniel et al. 2005). As suggested by the terminology in 3D, the imprinting/polymerization happen in three dimensions, which means that the cavities are distributed in the "whole" surface of the polymer, and this inhibits easy site accessibility as compared to 2D (Yoshida et al. 1999a, b). It can be concluded that 3D is synonymous to bulk and suspension polymerization, while the 2D description is suitable for the surface polymerization which has more exposure of the active sites to the analytes of interest (Li et al. 2011a, b).

Bulk polymerization

Bulk polymerization has been mostly preferred in recent times by most researchers. Even though this approach may be having limitations such as nonuniform distribution of particle size, thermal instability (Khajeh et al. 2011; Saraji and Yousefi 2009), wasting of polymer on the grinding stage, and destruction of binding sites in the grinding stage (Gauczinski et al. 2010; Yoshida et al. 1999a, b), they are easy to prepare (Mosbach et al. 2001). The synthesis of IIPs via the bulk polymerization process includes the mixing all the materials: template, monomer, crosslinker, and initiator in a reaction vessel; sometimes the polymerization process is initiated by UV irradiation. Materials that are prepared in this way may not be ideal for utilization in systems like HPLC and solid-phase extraction (SPE) (Khajeh et al. 2007; Otero-Romaní et al. 2009) because of the irregular particle size. However, these are still in use even today, even though they have a yield of mostly less than 50 % after the grinding and sieving (Wulff 2005). Scheme 4 shows the graphical representation of bulk polymerization.

Precipitation polymerization

This type of polymerization emerges as a good alternative to bulk polymerization with a high yield and also forms particles that are rigid and cross-linked which helps them not to be easily coagulated (Chaitidou et al. 2009; Ramström and Mosbach 1999); hence, it needs no stabilizers and therefore shows specific binding properties because the particles are free of stabilizer molecules. This method gives particles at the 0.3–10 μm range (Ho et al. 2005), and these particles,

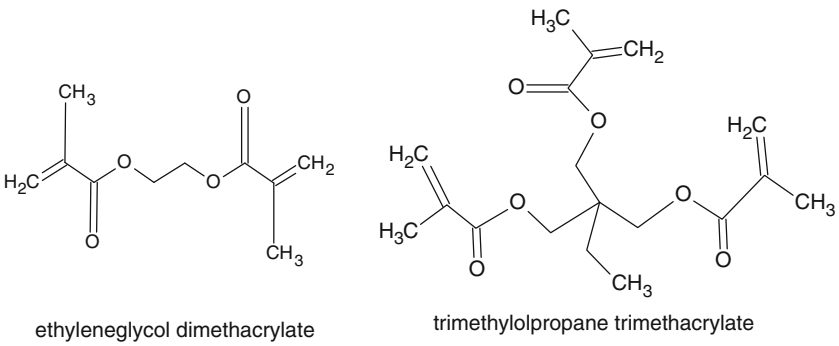
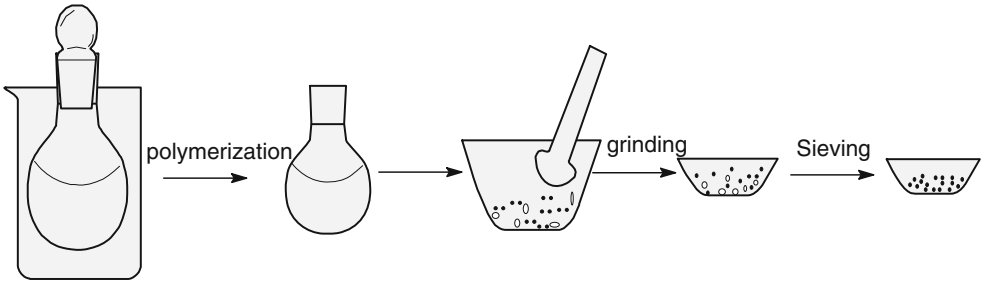


Fig. 2 Mostly used crosslinkers



Scheme 4 Schematic representation of bulk polymerization

which are highly cross-linked, are formed in excess amount of solvent (Chen et al. 2011).

Suspension polymerization

Generally, this is a heterogeneous process whereby the initiator is soluble in the monomer and these two are insoluble in the polymerization continuous phase which in most cases is water (Chen et al. 2011; Dowding and Vincent 2000). This method produces micro-beads of size distribution in the range 0.5–10 μm (Chen et al. 2011) which are enhanced by the rate of stirring. Droplets of the monomer and initiator are suspended (hence, the name suspension polymerization) in the continuous phase, in the presence of a stabilizer, then polymerized (Chen et al. 2011; Georgiadou and Brooks 2005). It is fast and reliable, and polymerization of particles may be achieved in a space of two hours (Dowding and Vincent 2000). This method has been put to test by Pérez-Moral and Mayes (2004) when he prepared micro-beads using liquid perfluorocarbon as the dispersing phase and got beads that showed that the size was indeed dependent on the stirring rate. Many of the same kind of polymers were later studied (Ansell and Mosbach 1997; Jiang et al. 2011; Walsh et al. 2010).

Surface (emulsion) polymerization

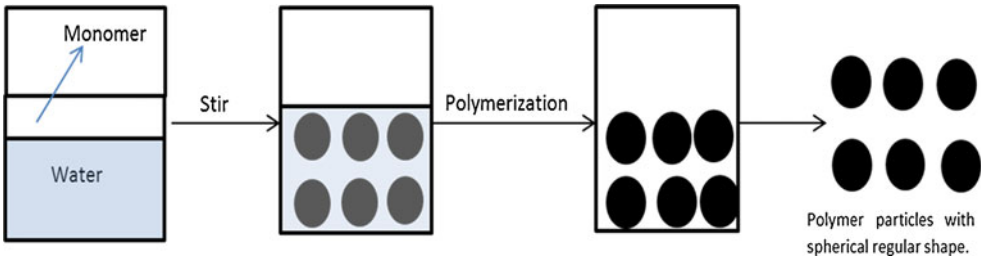
This is one of the highly used polymerization methods generally accounting for over 20×10^6 tons of the polymers that are produced per year (Ito et al. 2003; Ramström and Mosbach 1999). Surface polymerization has come in as a very good alternative to the other types of polymerization (Yoshida et al. 1999a, b). It comes with qualities such as complete removal of templates and offer very rapid adsorption and desorption kinetics (Chen et al. 2011). Surface polymerization also possesses good stability in acidic conditions which is good for metal removal, as most metals are soluble in acidic conditions, which may imply that better removals may take place in those conditions. This method is also able to produce polymers of high molecular weight which helps in the stability of the polymer and is also easy to control and to remove heat. The polymers produced may be conveniently obtained and easily handled and of direct usage. Also, particles of the polymers produced are small and able to prevent agglomeration (Chen et al. 2011; Kryscio and Peppas 2012). These positive aspects for this type of polymerization may be capitalized to use such synthesized polymers for online SPE applications and other column experiments. However, setbacks such as low yield, suspending agents turning into impurities, and possible inapplicability in water soluble matrices prevail (Liu et al. 2007). This may be tackled by modifying the synthesis by using surface-magnetic IIPs (Bach et al. 2012) which will have materials that will replace the centrifugation and filtration process conveniently and fairly economically. Scheme 5 shows the conceptual representation of surface polymerization. The summary of the polymerization techniques is presented in Table 1.

Characterization of IIPs

From a layman's point of view, characterization is simply the study of the "characters" of a certain material or object. In polymer chemistry, characterization is the in-depth study and investigation of the polymer properties (Zhao et al. 2011). This includes the size of the polymer particles, the morphology of the surface of the polymers, thermal stabilities/instabilities, functional groups present, and many other useful properties in the applications of that polymer under study. Characterization methods that have been used in the IIP technology include scanning electron microscopy (SEM), Brunauer–Teller–Emmett, Fourier transform Infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), X-ray diffractometry (XRD), thermal gravimetric analysis (TGA) and ultra violet–visible (UV–Vis) spectroscopy.

Scanning electron microscopy (SEM)

SEM has been used to get information about the surface of a wide range of materials (Christian-Albrechts University 2000; Reimschuessel 1972). To attain clear micrographs, the sample may need to be charged either by sprinkling a few particles of gold metal on the surface of the sample or any other method (Daniel et al. 2005; Reimschuessel 1972). The electron microscopy emits a beam of electrons which are



Scheme 5 Schematic representation of surface polymerization

directed to a probe that both scans across the surface of the specimen and the electrons react with the specimen which, in turn, emits electrons and photons. These electrons and photons are collected by the detector which then produces an image of the surface of the material (El-Gometi et al. 2011). In Fig. 3, an example of micrographs is shown.

Figure 3 shows an example of SEM micrographs of As-IIPs that were done in our lab. What it shows is the surface of these materials at a magnification of 10,000 times. It was able to show the imprints and the cavities after imprinting hence validating the presence of the imprints and cavities after the removal of the template (Daniel et al. 2005; Lu and Yan 2004; Rosatzin et al. 1991). In almost all the imprinting studies, SEM has been widely used (Cunliffe et al. 2005; Khajeh et al. 2007; Prasad et al. 2006; Tsoi et al. 2012; Wei et al. 2006) to show the difference in the surface before and after the removal of the template.

Fourier transform infrared (FT-IR)

Infrared spectroscopy is one rapid instrumental way of detecting or identifying functional groups in newly formed materials (Gebel et al. 2003; Prati et al. 2010). Infrared radiation is passed through a chemical compound which absorbs it and goes through a dipole moment change which induces molecular and lattice vibrations and rotations. A functional group of any given molecule is a combination of a specific arrangement of chemically bonded atoms, so the absorption of the infrared energy will be characteristic of the types of bonds and atoms present in the sample. The information is presented by an infrared spectroscopy which on correct interpretation will give the characteristic functional groups in the sample (Smith and Hinson-Smith 2003).

Quirarte-Escalante et al. (2009) synthesized lead IIPs to be used as suitable materials for the removal of lead from a number of metals and used FT-IR to study the functional groups that are in his materials. Likewise, Singh and Chaitidou (Chaitidou et al. 2009; Singh and Mishra 2009, 2010a, b) synthesized Ni(II)-IIPs and Co(II)-IIPs, respectively, and used FT-IR successfully to check the bonds and functional groups present and also confirm the formation or the polymerization of their materials.

Table 1 Summary of the polymerization techniques

Polymerization technique	Size distribution (μm)	Components
Bulk	20–50	Monomer
		Initiator
		Crosslinker
Precipitation	0.3–10	Monomer
		Solvent (optional)
Suspension	5–50	Monomer
		Continuous phase (usually water)
		Initiator (soluble in continuous phase)
		Surfactant
Emulsion	0.1–10	Monomer
		Continuous phase (usually water)
		Initiator (soluble in monomer)
		Stabilizer

Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is used to predict the most suitable template to functional monomer ratios, which dictates the feasibility and/or the efficiency of the materials being synthesized. This is a fast-growing technique that is being used in the imprinting technique. Farrington (Lubke et al. 2000) used the proton NMR experiments to combine with molecular modeling to study what really happens just before polymerization, and O'hamony (Deveci et al. 2009) used it to check if the ion-pair interactions and hydrophobicity do influence the selectivity in imprinted polymers.

X-ray diffraction (XRD)

The X-ray diffraction technique is used to characterize the crystal composition, grain size, preferred orientation, and identification of multiple phases in microcrystalline mixtures. It can also be used for the recognition of amorphous materials in partially crystalline mixtures (Su et al. 2008). The sample is exposed to an X-ray beam from the X-ray tube (source) which diffracts it into the secondary diffracted beams. The angle of diffraction (recorded as 2θ by convention) is

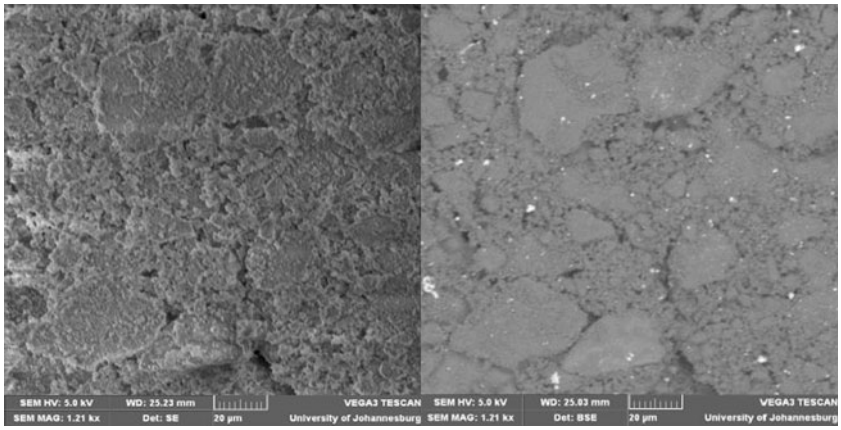


Fig. 3 SEM micrographs for arsenic-IIPs

related to the interplanar spacing, *d*, according to Bragg's law (Rao et al. 2006). The intensity of the diffraction maximum is related to the strength of those diffractions in the specimen. The angles and intensities of diffractions are recorded electronically using detector, electronics, and specialized software resulting in a plot of 2θ against intensity (Li et al. 2007).

In Zhan's work (Zhan et al. 2011), after preparing Cu(II)-surface-magnetic IIPs, XRD was used to check if the magnetite structure was changed for IIP and non-imprinted polymer (NIP). By comparing the XRD peaks for the Fe_3O_4, IIP, and NIP, it was concluded that the magnetite structure did not change because the peak positions were unchanged. However, Daniel et al. (2005) used XRD experiments to confirm the presence of Pd(II) in the IIPs prepared and also to see if after the removal of the template, there was any of the Pd(II) left.

Thermogravimetric analysis (TGA)

TGA measures changes in weight that occur to a sample as a function of temperature (degrees Celsius) over time (Dzunuzovic et al. 2008). These changes usually occur as a loss in weight, but a gain in weight can also be seen if the sample goes through an oxidation reaction. A sample of the test material is placed into a high alumina/ceramic cup that is supported in the furnace chamber. The balance is zeroed, and the sample cup with the specimen is heated according to a predetermined thermal cycle under an inert gas, oxygen, or air. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA signal is then converted to percent weight change and plotted against the set temperature range. TGA is very useful in characterizing polymers, organic or inorganic compounds, and other classes of common materials (Tang et al. 2008; Uezu et al. 1997; Zhao et al. 2007).

Daniel et al. (2005) used TGA studies on the Pd(II)-IIPs they were working on to study the thermal stabilities of the three types of polymerizations used to prepare Pd(II)-IIPs, i.e., bulk, precipitation, and suspension polymerizations. After the analysis of the TGA data, they came to the conclusion that all methods were thermally stable up to 290 °C. Similarly, Baghel et al. (2007) used TGA studies to come up with thermographs which, on interpretation, showed a similar degradation pattern for the NIP and CuP, while these were different for the IIP and the NIP.

Ultraviolet–visible spectrophotometry (UV–Vis)

UV–Vis studies are important in ion imprinting in compounds, complexes, or ions. Metals that are within the UV–Vis range are detected by the UV–Vis spectra and may be used to see the complete removal of the template, hence, confirm what have already been found out by AAS, XRD, etc. (Otero-Romaní et al. 2008, 2009).

When electromagnetic radiation in the UV and visible regions passes through a compound, a portion of it is usually absorbed by the compound. Therefore, a UV–Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions. The absorbed radiation promotes excitation within the electrons of the compounds' atoms, and electrons are excited from their highest occupied molecular orbital to the lowest unoccupied molecular orbital. Within the UV–Vis spectrophotometer the beam is split; one half is directed onto the reference cell (reference beam) containing the solvent, and the other half is directed onto the sample cell (sample beam) (Wong et al. 2005).

The instrument then makes a comparison between the intensities of the two beams as it scans over the region of desired wavelengths (ThermoSpectronic 1995). If the compound being analyzed absorbs light at a particular wavelength, the intensity of the sample beam will be lower than that of the reference beam. The instrument then indicates this by producing a graph of the plot of absorbance against the wavelength. This technique can be used to identify unknown compounds, since different molecules are only excited by specific light wavelengths that are characteristic of the functionality present in that compound. The amount of both unknown and known compounds can be quantified through the use of software ThermoSpectronic (1995).

Palladium imprinting and leaching after polymerization was tracked by UV–Vis spectroscopy by Daniel et al. (2005). This was satisfactory and complementary to the results obtained by the same group using XRD. On the other hand, Chaitidou et al. (2009) used the same method to study the pre-polymerization mixture to see if the complexation of z-Histidine with $Co(C_2H_3O_2)_2$ was satisfactory, and the results found were to the affirmative. This enables one to only continue into the polymerization once the complex is positively formed.

Brunauer–Emmett–Teller analysis

On the synthesis of materials with minute particle sizes, it is very essential to study the surface area of the particles, their morphology, and pore-size distribution. This may be done by the Brunauer–Emmett–Teller analysis. Knowing about the pore-size distribution and particle morphology helps to come up with reasons why parameters like selectivity and adsorption efficiencies are high or low in some materials.

The surface area of both NIP and IIP have been investigated using this characterization technique (Su et al. 2008); however, this technique is not only exclusive to the synthesis of IIPs, but it can also be used in other fields such as in exploring low-cost adsorbents (Abdel et al. 2011; Feng et al. 2009a, b).

Applications

Ever since the IIP technology came to the fore, a lot of studies on toxic metals in aqueous environments have been reported. These include but not limited to nickel, cadmium, lead, arsenic, cobalt, selenium, and mercury (Andac et al. 2006; Daniel et al. 2005; Denizli 2007; Khajeh et al. 2007; Otero-Romaní et al. 2008; Say et al. 2003; Tsoi et al. 2012). They have also been carried out for studies involving actinides and lanthanides with ease (Arbab-Zavar et al. 2011; Shirvani-Arani et al. 2008).

IIPs are generally a sample preparation tool which effectively preconcentrate and remove analytes of interest in a wide range of matrices; then the preconcentrated samples go for detection in analytical instruments such as ICP-OES, ICP-MS, GFAAS, FAAS, ETAAS, and HGAAS, depending on the analytes under investigation.

Andac et al. (2006) prepared Al-IIPs using suspension polymerization with polyvinyl alcohol and benzoyl peroxide as stabilizers, MAGA (*N*-methacrylolyl-L-glutamic acid) as the complexing monomer, and EDTA in removing the template. The IIPs showed more selectivity towards the aluminum ions and other ions such as Fe^{3+}, Ni^{2+}, and Cu^{2+}, which almost have the same ionic radius as Al^{3+}. The reusability of these materials was fairly good in that the polymers were able to remove 90 % of the aluminum ions and were also able to remove even on the fifth run. On the average, the Al (III)-IIP had removal efficiencies of at least 84 %.

Otero-Romani's group employed the precipitation polymerization technique to prepare Ni-IIPs using the template and the monomer (4-VP) and 8-hydroxyquinone as a non-vinylated chelating agent (Otero-Romaní et al. 2009). These polymers were then used as the packing in SPE cartridges which were used for Ni(II) enrichment in sea water and for detection, they used ICP-OES and ETAAS. They achieved very high enrichment factors of 40 and 100 which corresponded with detection limits of 137 ng/L and 52 ng/L respectively. These were a far improvement from those reported before (Feng and Fu 1998; Otero-Romaní et al. 2009; Wassink et al. 2000).

IIPs has often been used as stationary phases in most columns that can either be used for analytical separation or preconcentration (Jiajia et al. 2009; Singh and Mishra 2010a, b). Zhao et al. (2007) and others have synthesized Zn(II)-imprinted polymers which were then used as a stationary phase e.g., as SPE sorbents (Saraji and Yousefi 2009). They achieved a maximum of 3.9 mg/L at pH5.0. At these conditions, the Zn(II)-IIP showed high selectivities towards zinc than towards Cu(II), Ni(II), and Co(II).

Dispersion polymerization method has been reported by Say et al. (2003) in the preparation of Cu(II)-selective IIPs, such as poly(ethylene glycol dimethacrylate–methacryloylamidohistidine/Cu(II)) and poly(EGDMA–MAH/Cu(II)) micro-beads which were used as a solid-phase-extraction sorbent and in other chromatographic columns. The IIPs gave good separations because they had higher affinity for Cu(II) than for Zn(II) or Co(II) that were also introduced into the sample matrix.

Surface imprinting technique has been explored by Yoshida et al. (1999c) when they developed a suitable method for the removal and/or preconcentration of Zn(II) from aqueous samples. The resultant materials that were produced were used as metal adsorbents. In the synthesis of these resultant materials, TRIM and divinylbenzene (DVB) were tested as monomers for the successful preparation of highly rigid and selective materials towards Zn(II) with other metals of the same morphology as Zn(II). It was found that TRIM performs better than DVB as a monomer in that the polymers prepared using TRIM showed superiority than those of DVB in terms of adsorption performance. Actually, this performance by TRIM is no surprise, as TRIM has three polymerizable groups and has a high molecular weight which helps in the rigidness of the produced materials.

However, there are many such molecules that are investigated of their capabilities in as far as molecular imprinting is concerned. These include methacrylic acid, acrylic acid, 2- or 4-vinylpyridine, acrylamide, trifluoromethacrylic acid,

and 2-hydroxyethyl methacrylate to name just the mostly used in ion imprinting (Daniel et al. 2005; Ho et al. 2005; Otero-Romaní et al. 2009).

As outlined earlier in this communication, IIPs may also be used in the fabrication of ion-selective electrode (ISE) for the detection of metals which are electroactive. Prasad et al. (2006) lead a group of researchers who used this fact to develop IIP-based ISE for the determination of dysprosium (III). In this work, the analyte of interest reversibly binds to the IIP recognition element and a signal is generated. The electronic signal comes about as the electrodes detect a change in potential across the IIP which is then translated into an electronic signal. The developed ISE showed high selectivity towards the dysprosium(III). This technique of coupling IIPs and ISEs is still new and a lot can be improved in it, such as the proper choice of chelating ligand and monomers that can enhance the performance of this ensemble (Prasad et al. 2006).

Conclusions and recommendations

The introduction of IIPs has undoubtedly taken the sample preparation division of analytical chemistry to a next higher level. IIPs are applicable to a wider chemical picture and play a vital role in helping to quantify very low concentrations of toxicants such as arsenic, selenium, copper, nickel, cobalt, aluminum, and complexes of these elements and many more of the same. The selectivities shown by these materials make them one of the best to be used and also, their versatility helps them to be used for applications in a wider range of matrices and matrix conditions.

It is recommended that ion-imprinted polymers be employed in industrial scale for cleanup purposes, such as in waste water treatment, drinking water treatment, and drug delivery. This cannot be seen as an uphill battle because of their ease in preparation and handling. Alterations here and there may be necessary to bring the best out of these materials, such as the use of what is called ion-imprinted fibers and grafting of these ion-imprinted polymers on surfaces. Ion-imprinted polymers are here to stay and they are really doing a great job in improving the work that has been all along dominated by hollow fiber-supported liquid membranes, solid-phase extraction and coagulation, and many more.

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