



GENERAL CHARACTERISTICS AND APPLICATIONS OF ION IMPRINTED POLYMERS

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Abstract

Molecular imprinting is a new interdisciplinary subject developed in recent years belonging to the area of host-guest chemistry and it plays significant role in the construction of molecular recognition sites in the polymer matrix. Ion imprinted polymers find wide applications in various fields. In this review article, we present a comprehensive overview of the general features of ion imprinted polymers and its applications.

Keywords-Ionimprinting, Polymers, Recognition

INTRODUCTION

The design of synthetic materials, which are able to mimic the recognition processes found in nature, became an important and active area of research¹⁻³. Molecular imprinting technology (MIT) is today a viable synthetic approach to design robust molecular recognition materials able to mimic natural recognition entities, such as antibodies and biological receptors⁴⁻⁶. MIT is considered a versatile and promising technique which is able to recognize both biological and chemical molecules including amino acids and proteins⁷⁻⁹, pollutants, drugs and food¹⁰⁻¹¹. Further, application areas include separation sciences and purification¹²⁻¹⁴, chemical sensors¹⁵, catalysis¹⁶, drug delivery¹⁷, and biological antibodies and receptor systems¹⁸.

Molecular imprinting technology is based on the formation of a complex between an analyte (template) and a functional monomer. In the presence of a large excess of crosslinking agent, a three-dimensional polymer network is formed. After polymerization process, the template is removed from the polymer leaving specific recognition sites complementary in shape, size and chemical functionality to molecule. Usually, intermolecular interactions like hydrogen bonds, dipole-dipole and ionic interactions between the template molecule and functional groups present in the polymer matrix drive the molecular recognition phenomena. Thus the resultant polymer recognizes and binds selectively only the template molecules.

Selective recognition of metal ions is a real challenge for a wide range of applications in analytical science. In that purpose, ion-imprinted polymers (IIPs) have been increasingly developed during the last years on the principle of molecularly imprinted polymers. Metal ion extraction in the aqueous environment remains a major issue because of their high toxicity, their persistence and susceptible carcinogenic effect¹⁹. Removal of metal ions from diverse water resources is essential. Various methods can be used for metal ion removal²⁰ from the most common liquid-liquid extraction and solid-liquid extraction or solid-phase extraction (SPE)²¹ to chemical precipitation²², membrane filtration²³, flotation²⁴, electrochemical²⁵ and biofiltration methods²⁶.

Solid phase extraction using ion exchange or chelating materials offers many advantages for metal ion separation since it simplifies the separation process and reduces the disposal costs as well as the solvent uses and exposure²⁷. Many synthetic polymers bearing various chelating functions have been studied²⁸. They can be prepared either by impregnation²⁹, by grafting of commercial sorbents or home-made copolymers, or by direct copolymerization of a functional monomer with a crosslinker³⁰.

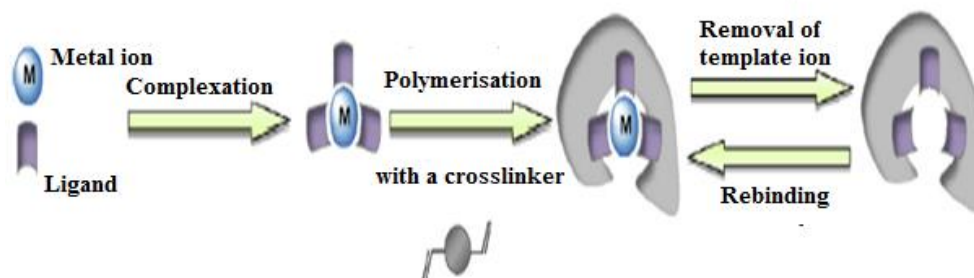


Fig.1. Schematic representation of synthesis of metal ion imprinted interpenetrating polymer networks

Ion-imprinted polymers (IIPs) have been introduced by Nishide et al. by crosslinking of poly(4-vinyl pyridine) with 1,4-dibromobutane in the presence of a metal ion³¹. This conception appears to be similar to the MIPs' by changing the template molecule to a metal ion (Fig.II.1). However, whereas MIPs generally interact with template molecules via classical functional monomers through hydrogen bonds or van der Waals interactions, a slight variation is the resort to coordination chemistry when IIPs are concerned. The preparation of IIPs generally requires a ligand to form a complex with the metal ion to produce selective binding sites after metal leaching. The first IIPs were described by Nishide et al. in 1976³² not so long after Wulff and Klotz prepared the first molecularly imprinted polymeric materials in 1972.

2. Ion imprinted polymers: General features

The general procedure for IIP elaboration consists in the preparation of a ligand-metal complex followed by copolymerization with a cross-linker in order to create three dimensional recognition cavities inside the polymer networks. Denizli et al. have detailed this process in three steps as follows³³: (i) complexation of the metal ion to a polymerizable ligand, (ii) polymerization of this complex, and (iii) removal of the template ion after polymerization. The polymerizable ligands are often named as bi-functional reagents: one functionality coming from their chelating ability and the other one from the vinyl function. A more simple method to prepare IIPs consists in using non-polymerizable ligand in which the ligand is embedded inside the polymer matrix through some trapping process³⁴. Whatever the choice to introduce the ligand, the interactions between the polymer framework and the complexed ion are based on coordinative bonds from some electron donating hetero atoms to the unfilled orbitals of the outer sphere of the metal ions.

The properties of ion-imprinted polymers are remarkable because of their high selectivity towards the target ion due to a memory effect resulting from their preparation process. The affinity of the ligand for the imprinted metal ion, the size and shape of the generated cavities are the two main factors responsible for high selectivity³⁵. As recognition sites are generated from the self assembly of some ligand(s) around the template ion and subsequent crosslinking, this arrangement enables the binding sites to match the charge, size and coordination number of the ion³⁶. Moreover, the complex geometry can be preserved through the crosslinking and leaching steps generating a favorable environment for the template ion rebinding. The functioning principle of IIP could be compared with ion-mediated biological self assembly processes such as intercellular junctions. In such ion-mediated biological self assembly processes, the recognition is mediated by calcium ions³⁷. Because they are highly crosslinked polymers, IIPs are durable and can be reused without loss of activity³⁸.

3. Reagents for molecular imprinting

Polymerization reaction is known as a very complex process, which could be affected by many factors, such as nature of monomer, crosslinker, initiator, temperature and time of polymerization, the presence or absence of magnetic field, and volume of the polymerization mixture. In order to obtain the ideal imprinted polymer, a variety of factors should be optimized. Thus synthesis of imprinted polymer is a time-consuming process. In order to prepare imprinted polymer with perfect properties, numerous attempts have been made to investigate such effects on the recognition properties of the polymeric materials³⁹. The selection of appropriate reagents is a crucial step in the molecular imprinting process. The functioning of an imprinted polymer is controlled by the type of template, ligand, functional monomer, crosslinkers, solvent and initiator used.

(3.1) Templates

Generally, template molecules are target compounds in analytical processes. An ideal template molecule should satisfy the following three requirements. First, it should not contain groups involved in or preventing polymerization. Second, it should exhibit excellent chemical stability during the polymerization reaction. Finally, it should contain functional groups well adapted to assemble with functional monomers. Most templates applied in molecular imprinting are derived from widespread environmental pollutants, which

can be grouped into three broad categories, including endocrine disrupting chemicals (EDC), pharmaceuticals and toxic metal ions⁴¹. Endocrine disrupting chemicals have attracted extensive attention when referring to global environmental problems because they can lead to the disturbance of central regulatory functions in humans and wild life. Worse still, some endocrine disrupting chemicals are even suspected to cause human infertility or stunt growth of children. Among those endocrine disrupting chemicals, hormone drugs,⁴⁰ triazine pesticides, and bisphenol A are the most widely concerning pollutants used in preparation of imprinted polymers. Pharmaceuticals have gained increasing attention and interest in the last few years due to their continuous release in the environment. Water compatible imprinted polymers have a significant development in the field of molecular imprinting technology.

(3.2) Ligand

The role of the ligand is the basic criterion since ion chelation is involved in the process of recognition. Since the template in ion imprinted polymers is an ion, reacting via its unfilled orbitals of the outer sphere, the major interactions with the polymer matrix will occur with some electron donating heteroatom. The general trend is to use ligand bearing one or more chelating groups. Some of the functionalized ligands used in the chemical immobilization approach are given in Fig.2.

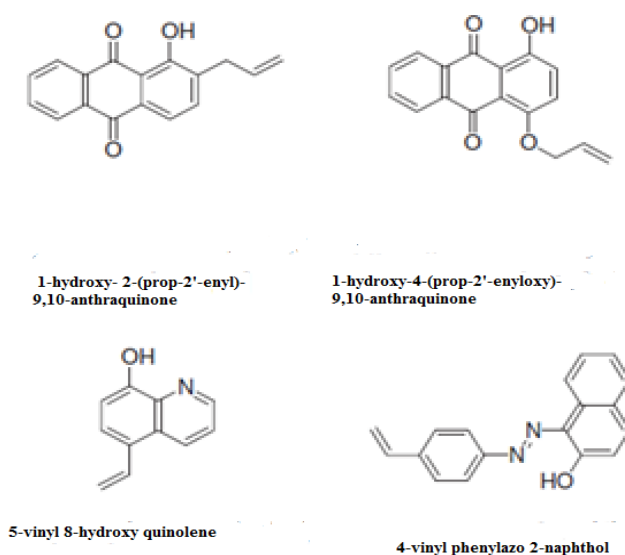


Fig.2. Functionalized ligands used in the synthesis of IIP

(3.3) Functional monomer

The role of the monomer is to provide functional groups which can form a complex with the template by covalent or non-covalent interactions. The use of a mono vinylated monomer, such as 4-vinylpyridine, has proved to be essential in the trapping approach to form a ternary complex with the metal ion. However, even when a functionalized ligand is used in the chemical approach, some other monomers may be introduced in the polymerization mixture. Commonly used monomers for molecular imprinting include methacrylic acid (MAA), acrylic acid (AA), 2- or 4-vinylpyridine (2- or 4-VP), acrylamide, trifluoro methacrylic acid and 2-hydroxyethyl methacrylate (HEMA). Methacrylic acid has been used as a “universal” functional monomer due to its unique characteristics, being capable to act as a hydrogen-bond donor and acceptor, and showing good suitability for ionic interactions⁴¹.

(3.4) Crosslinkers

The role of the crosslinker is to fix functional groups of functional monomers around imprinted molecules, and thereby form highly crosslinked rigid polymer. The crosslinker plays a major role in the ion imprinted polymers elaboration since it sparks off the binding sites creation. After removal of templates, the formed holes should completely complement to target molecules in shape and functional groups. Types and amounts of crosslinkers have profound influences on selectivity and binding capacity of molecularly imprinted polymers. When the dosage of crosslinkers is too low, molecularly imprinted polymers cannot maintain stable cavity configurations because of the low crosslinking degree. However, over-high amounts of crosslinkers will reduce the number of recognition sites per unit mass of molecularly imprinted polymers. Commonly used crosslinkers involve ethylene glycol dimethacrylate (EGDMA), trimethylolpropane trimethacrylate, divinylbenzene (DVB), etc.

(3.5) Solvent

Solvent is introduced during the synthesis of ion imprinted polymers in order to generate the porous structure. This porosity is essential for making a high number of binding sites accessible to the analytes. The porogen properties of such a solvent, commonly named a “porogen”, are depending on the difference between its solubility parameter and that of the monomers and polymer chains⁴¹. The solvating power of the medium will be varying along the polymerization process while monomers are consumed. All the polymerization components must be soluble in the porogen. For IIP preparation, this concerns not only the monomers and the initiator but also the ion template in a free form or entrapped in a complex. Porogenic solvent plays an important role in polymerization. Besides, it also influences the bonding strength between functional monomers and templates, the property and morphology of polymer, especially in non-covalent interaction system. Aprotic and low polar organic solvents, such as toluene, acetonitrile and chloroform are often used in non-covalent polymerization processes in order to obtain good imprinting efficiency. It is notable that imprinted polymers prepared in organic solvent work poorly in aqueous media because of the “solvent memory”.

(3.6) Initiators

The role of the initiator in radical polymerization is well-known as it is responsible for the creation of monomer radicals in order to propagate the polymer formation. The initiator is homolytically cleaved by thermal decomposition, photolysis or ionizing radiation. These two latter techniques are rarely used for ion imprinted polymer preparation. Any of the methods of initiation can be used to initiate free radical polymerization in presence of the template. If the template is photochemically or thermally unstable then initiators that can be triggered photochemically and thermally respectively would not be attractive. When complexation is driven by H-bonding then lower polymerization temperatures are preferred and under such circumstances photochemically active initiators are preferred. The rate of radical polymerization depends on the nature of the concentration of the initiator. 2, 2'-azo-bis-isobutyronitrile (AIBN) and potassium persulphate are the most efficient initiators. The choice of the initiator depends on the nature of the template.

4. Polymerization techniques

Ion imprinted polymers are generally synthesized by polycondensation, while organic ion imprinted polymers are mainly prepared by free radical polymerization. The formats of these ion imprinted polymers can vary according to the polymerization process. Bulk polymerization will lead to monolithic materials, whereas well-defined particles can be produced by heterogeneous (suspension or emulsion) or homogeneous (dispersion or precipitation) polymerization.

5. Different stages in the preparation of imprinted polymers

(5.1) Preorganization stage

Preorganized approach which uses covalent reversible bonds giving a rather homogeneous population of binding sites and reducing the non-specific sites. However, to remove the template from the polymer matrix, it is necessary to cleave the covalent bonds. The structure and stability of this complex indicate the behavior of the resulting molecular imprinted polymer.

(5.2) Covalent interactions

Covalent imprinting is distinguished by the use of templates which are covalently bound to one or more polymerizable groups. After polymerization the template is cleaved and the functionality left in the binding site is capable of binding the target molecule by re-establishment of the covalent bond. The advantage of this approach is that the functional groups are only associated with the template site. However only a limited number of compounds (alcohols, aldehydes, ketones, amines and carboxylic acids) can be imprinted with this approach.

(5.3) Non-covalent interactions

In non-covalent imprinting the interactions between functional monomer and template during polymerization are the same as those between polymer and template in the rebinding step. These are based on non-covalent forces such as H-bonding, ion-pairing and dipole-dipole interactions. This method was first introduced in organic polymers. Due to its simplicity this method is the most widely used to create imprinted polymers. To date the most common functional monomer employed is methacrylic acid, and adapted for the imprinting of 2,4-D, hydroquinidine, hormones, nucleotides and cyclic peptides.

6. Advantages of molecular imprinted polymers

The main advantages of molecularly imprinted polymers are their high selectivity and affinity for the target molecule used in the imprinting procedure. Imprinted polymers compared to biological systems such as proteins and nucleic acids, have higher physical robustness, strength, resistance to elevated temperature and pressure, and inertness towards acids, bases, metal ions and organic solvents. In addition, they are also

less expensive to be synthesized, and the storage life of the polymers is very high, keeping their recognition capacity for several years at room temperature.

7 Applications of molecular imprinted polymers

The peculiar properties of MIPs have made them a highly interesting tool for different application areas, including separation sciences and purification, sensors and biosensors, catalysis and drug delivery. Molecular imprinting chromatography is one of the most extensively studied application areas of MIPs, which are highly suitable for chromatographic separation, chiral separations, solid phase extraction, antibody and receptor mimicking, enzyme mimetic catalysis, organic synthesis and drug delivery.

(7.1) MIPs in separation techniques

Molecularly imprinted chromatography is one of the most traditional applications of molecularly imprinted polymers especially for liquid chromatography with imprinted polymers usually synthesized by bulk polymerization, ground and sieved mechanically and subsequently packed in a chromatographic column. However, the mechanical processing leads to irregular particles with relatively broad size distribution, resulting in packing of irreproducible quality. For this reason monolithic molecular imprinting columns have been recently prepared directly inside stainless steel columns or capillary columns. Experimental data suggest that not always uniform imprinted particles allow better chromatographic performances. For instance, precipitation polymerization was used to prepare spherical beads but with a total pore volume still lower compared to irregular particles obtained by bulk polymerization and it has been seen that the porosity of the beads strongly influences the chromatographic performance of these systems⁹⁰. The imprinted polymer sorbents, due to selective interactions exhibited, retain the analyte more strongly than the non-imprinted polymer materials⁴². Imprinted polymers are frequently used as chiral stationary phases in high performance liquid chromatography to obtain enantiomeric resolution of racemic mixtures such as amino acid derivatives⁴³ and drugs.

MIP based micro-columns for capillary electro chromatography (CEC) are recently realized for separation of several compounds. Solid phase extraction (SPE) is another important area of application of imprinted polymers in analytical chemistry. Molecular imprinted solid phase extraction (MISPE) was applied for extraction of several compounds in different sample matrices such as biological, environmental and also in food analysis. The first application of MISPE was made by Sellergren in 1994 who performed a selective extraction of pentamidine, a drug used for the treatment of acquired immune deficiency syndrome related disorders, in urine samples.

(7.2) As chemical sensors and biosensors

Recently chemical sensors and biosensors are of increasing interest in the field of modern analytical chemistry. This is due to the new demands that are appearing particularly in clinical diagnostics, environmental analysis and also in food analysis. A sensor is characterized by two important element, which has a specific interaction with an analyte which converts this interaction into a measuring effect. Recently the synthesis of artificial receptors capable of binding a target analyte with comparable affinity and selectivity to natural antibodies or enzymes has been done. Imprinted technology can also be used as antibody-like materials with high selectivity and sensitivity, owing to their long-term stability, chemical inertness and insolubility in water and organic solvents. In particular, the integration of imprinted polymers with sensors can be realized by *in situ* polymerization, using a photochemical or thermal initiator, or by surface grafting with chemical or UV initiation. The first generation of imprinted polymer sensors was prepared using imprinted polymers synthesized in the form of monoliths. The imprinted polymer sensor obtained was successfully employed to determine atropine concentrations in human serum and urine. Imprinted polymers were also widely employed as sensors for enantiomeric separation of different compounds. An interesting area of research was the preparation of mass sensitive imprinted polymer sensors for cells and viruses. Molecular imprinted polymer technology has been extensively studied for its potential applications in sensing.

(7.3) Catalysis

Considerable efforts have been made to investigate the possible use of imprinted polymer for catalytic applications. The high selectivity and strength of these polymers make them suitable to be used at elevated temperatures and pressures, in the presence of several organic solvents, and also under acidic and basic reaction conditions. For these reasons, MIPs can be employed instead of biomolecules, such as enzymes and natural catalytic antibodies which are highly vulnerable to certain conditions. The strategy using substrate analogues as template, involves the use of compounds that mimic the reaction complex between the substrate and the matrix. The catalytic groups will be introduced in the right positions into the cavities of the polymer and subsequently they will act as catalyst in presence of the true substrate. Finally, thermodynamic and kinetic studies were also carried out on MIPs catalytic systems with the aim of understanding molecular imprinting

and its specificity. Thus, the increasing rate and the larger induction, in logic, may be responsible for the specific recognition and catalysis.

(7.4) Drug delivery

Recently an area of great challenge in molecular imprinting technology is that of therapeutic agents, various imprinted polymers have been used as unusual synthetic polymeric carriers to prepare drug delivery systems. Recently, molecularly imprinted hydrogels for the recognition of cholesterol have been prepared by molecular design of methacrylate-based structures containing poly(ethylene glycol) in moderately and highly cross-linked networks. In recent years, many researchers have published about the use of MIPs in drug delivery applications given their physicochemical properties to protect the drug from degradation by enzymes during systemic trafficking in the body. The first report of imprinted polymers used as sustained release devices has been presented by Norell and co-workers.

(7.5) Selective removal of metal ions

An important application of the metal ion imprinted polymer is in the selective concentration of metal ions. The efforts in the selective concentration of the metal ions from aqueous solutions using IIP are steadily increasing. The selectivity depends on various factors: (i) the specific interaction of the ligands with metal ions; (ii) coordination number and coordination geometry of the metal ion; (iii) charge on the metal ion, and (iv) to some extent the size of the metal ion. However the conventional chelating ligands have encountered problems including low binding selectivity, slow rebinding kinetics and loss of selectivity with time.

Compared to this the metal ion-imprinted polymers exhibit rapid and usually strong complexation with metal ion resulting in high selectivity for the imprinted ion. The imprinted cavities in the polymers containing functional groups whose arrangement corresponds to that of the imprinted molecule. The selectivity for the optical resolution of racemates and separation of different diastereo isomers, configurational isomers and metal ion are quiet high. It is also possible to perform stereoselective reaction with the substrate bound inside the cavities. The advantages of the metal ion imprinted polymers over the conventional chelating polymers are: (i) the selectivity was further improved in every case; and (ii) the imprinted binding sites should be able to fix the growing polymer chain in a defined topology. After the removal of the imprinted molecule, it should be able to rebind the imprinted molecule. In all cases the structure of the polymer matrix and the macromolecular characteristics are of crucial importance in specificity and selectivity.

Ion imprinted polymers are generally used for treatment or analysis of water from tap, river, lake and ground waters⁴⁴. Their use can be extended to complex matrices such as sea water, industrial waste water. After some sample treatment, IIPs can be used to extract metal ions from solid samples such as food, soil and mine tailing samples, and human hair. As separation materials, IIP particles can also be incorporated in chromatographic columns. The applications of IIP are now extending to sensors. IIP particles can thus be mixed with some carbon paste or included in a polyvinyl chloride membrane to prepare ion-selective electrode. Recently IIPs have been combined with quartz crystal microbalances to design sensor devices.

8. Conclusion

Heavy metal exposures and poisoning are considered as hazardous which need to take the utmost care and precautions to prevent these toxins from entering our bodies. Thus ion imprinting technology offers an economically feasible technology for efficient removal and recovery of metals from aqueous solutions. The process has many attractive features including the selective removal of metal ions over a broad range of pH and temperature, its rapid kinetics of sorption and desorption and low capital and operational costs. The ion imprinted polymers can easily be produced using inexpensive growth media or obtained as a byproduct from some industry. The judicious choice of ion imprinted polymers can also out complete the commercial ion exchange polymers which have conventionally been used in the removal of metal ions. The increasing demand for sample treatments and quality control will be a major cause for the future development of the ion imprinting technology either as SPE sorbents or sensing devices in biomimetic sensors. The understanding of the mechanisms of interaction between the template metal ion and the polymer matrix is a fundamental challenge in ion imprinting method. It could be a useful tool in the design of performing ion imprinted polymers for the removal of hazardous metals from aqueous environment.

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