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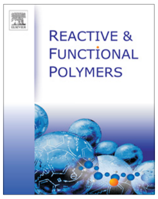

Review

Recent advances on ion-imprinted polymers

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ABSTRACT

Selective recognition of metal ions is a real challenge for a large range of applications in the analytical field (from extraction to detection and quantification). For that purpose, ion-imprinted polymers (IIPs) have been increasingly developed during the last 15 years on the principle of molecularly imprinted polymers (MIPs). Those imprinted materials are designed to mimic the binding sites of biological entities and assure an improved recognition of the template species. The aim of this review is to give the current state of the art in the conception of IIPs from the components to the polymerization process. Some applications of those materials will be also discussed.

Contents

Abbreviations: AIBN, azobisisobutyronitrile; BPO, benzoylperoxide; DVB, divinylbenzene; DMF, dimethylformamide; DMSO, dimethylsulfoxide; EDMA, ethylene glycol dimethacrylate; FTIR, Fourier-Transformed Infrared; HEMA, 2-hydroxyethylmethacrylate; IIP, ion-imprinted polymer; MAA, methacrylic acid; MBA, N,N′-methylene-bis(acrylamide); MIP, molecularly imprinted polymer; MMA, methyl methacrylate; NIP, non-imprinted polymer; SEM, scanning electron microscopy; SPE, solid-phase extraction; THF, tetrahydrofuran; VP, vinylpyridine.

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1. Introduction

Metal ion extraction and quantification in the aqueous environment remains a major issue because of their high toxicity, their persistence and susceptible carcinogenic effect [1]. Legislations now require the control and/or reduction of metal species in diverse water resources. Various methods can be used for metal ion separation [2] from the most common liquid–liquid extraction and solid–liquid extraction (or solid–phase extraction, SPE) [3] to chemical precipitation [4], membrane filtration [5], flotation [6], electrochemical [7] and biofiltration methods [8].

SPE 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 exposure [9]. Many synthetic polymers bearing various chelating functions have been studied [10]. They can be prepared either by impregnation [11,12], by grafting of commercial sorbents [13–16] or home-made copolymers [17,18], or by direct copolymerization of a functional monomer with a crosslinker [19–22].

Although selectivity is a challenging concern for both water treatment and sample preparation for quantification, it is difficult to achieve with the previously mentioned materials. A similar difficulty has been encountered for the selective recognition of organic compounds. To overcome this problem, chemists have mimicked biological hosts and their specific receptors based on molecular recognition. Molecularly imprinted polymers (MIPs) have been designed on a similar molecular recognition process [23]. In the non-covalent approach, a template molecule interacts with a functional monomer and a crosslinker in a porogen solvent [24]. After polymerization, the removal of the template generates the recognition cavities inside the three-dimensional copolymer network. Indications for the conception of MIPs can be found in many reviews and book chapters [25–27] and their binding properties have been modelized and characterized thoroughly [28,29]. For several years, MIPs are widely studied as new materials for chromatographic applications [30], SPE [31], sensor devices [32], in vitro diagnostic [33], chiral separations [34] and catalysis [35,36].

Ion-imprinted polymers (IIPs) have been introduced by Nishide et al. by crosslinking of poly(4-vinylpyridine) with 1,4-dibromobutane in the presence of a metal ion [37]. The conception appears to be similar to the MIPs' by changing the template molecule in a metal ion. However, whereas MIPs generally interact with template molecules via classical functional monomers (such as AA, MAA, HEMA or VP) 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. [37] in 1976 not so long after Wulff and Klotz independently published their preparation of the first molecularly polymer imprinted materials in 1972 [38,39]. Nevertheless, their real development is more recent and a considerable increase of the number of publications dealing with IIPs can be observed on the last 10 years (Fig. 1). Two review articles have been dedicated to IIPs in 2004 and 2006 by Rao et al. [40,41]. They were mainly focused on the principle and applications of IIPs. More recently, two review papers have been dedicated to IIPs. Mafu et al. only reviewed some aspects of their characterization and applications [42] and Wu focused on anion imprinted polymers [43]. The present survey will thus focus on IIPs for cation species recognition, emphasizing the papers published from 2006. The aim of this review is to help chemists in their conception of organic IIPs by giving general indications on the principle, the characterization, the design and the different accessible formats of these materials.

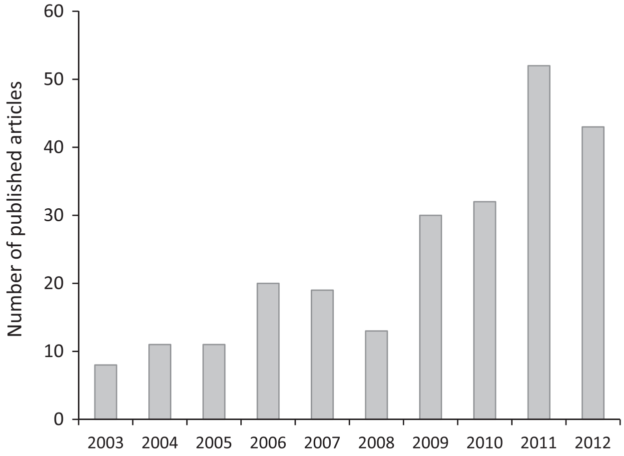

Fig. 1. Number of published papers on IIP over the last 10 years.

2. IIP general features

The general procedure for IIP elaboration consists in the preparation of a ligand-metal complex and its copolymerization with a cross-linker in order to create three dimensional recognition cavities inside the polymer network. Denizli et al. have detailed this process in three steps as follows (Fig. 2) [44]: (1) complexation of the metal ion to a polymerizable ligand, (2) polymerization of this complex and (3) removal of the template ion after polymerization. As organic imprinted polymers are mainly prepared by free radical polymerization, vinyl groups are the classic type of polymerizable functions suiting for this purpose. The polymerizable ligands are often named as bi-functional reagents: one functionality coming from their chelating ability and the other one from their vinyl function.

Although this approach has been widely performed, a simpler method to prepare IIPs consists in using non-polymerizable ligand. In this case, the ligand is embedded inside the polymer matrix through some trapping process [41]. These different ways for incorporating the ligand will be detailed in the next section. 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 heteroatoms (such as oxygen, nitrogen or sulphur) to the unfilled orbitals of the outer sphere of the metal ions.

Ion-imprinted polymers properties are remarkable because of their high selectivity towards the target ion due to a memory effect resulting from their preparation process. Two main factors are

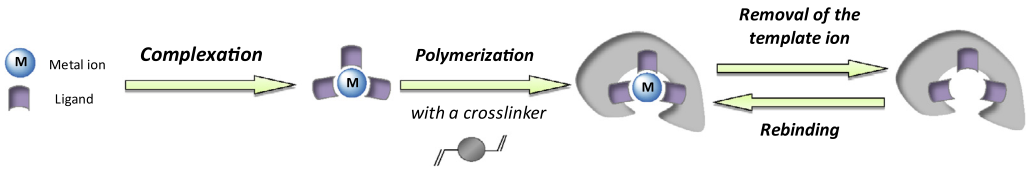

Fig. 2. Schematic representation of an IIP synthesis.