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Insight into BPA–4-vinylpyridine interactions in molecularly imprinted polymers using complementary spectroscopy techniques

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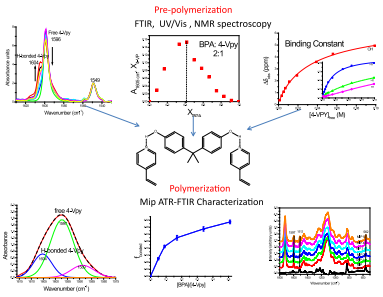
HIGHLIGHTS

- MIP ATR analysis confirmed BPA:4Vpy H-bonded complexes survived polymerization.
- MIP ATR analysis confirmed two functional groups in MIP binding sites.
- Reversible conformational changes explained the poor results in nonpolar solvents.
- Detailed description of rebinding mechanism in water based on MIP-ATR spectroscopy.
- Selectivity depended on analyte:monomer interactions, shape, solubility.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of solvent polarity on the nature and extent of non-covalent interactions responsible for BPA:4-Vinlypyridine complex formation has been investigated in the pre-polymerization mixture and correlated with polymer-ligand recognition. The combination of FTIR, ^{1}H NMR and UV–Vis spectroscopy has made possible the development of a more comprehensive understanding of pre-polymerization events at a molecular level, and how they govern the properties of subsequent polymerized MIPs. The MIP ATR characterization provides direct insight into the bonding within matrix-template system, confirming that monomer:template H-bonded complexes survived the polymerization process and the presence of two functional monomers in the binding sites. The polymer has shown an excellent affinity for BPA in aqueous solutions with poor recognition in organic solvents. Loss of affinity in organic solvents together with selectivity studies suggested that the binding mechanism depended critically on the conformation of the polymeric binding pockets, which when combined with H-bonding and weak electrostatic interactions allowed for selective recognition.

1. Introduction

Molecularly imprinted polymers (MIPs) synthesized via non-covalent self-assembly processes are biomimetic recognition materials selectively binding a target analyte in analogy to biological receptor–substrate interactions. Since non-covalent MIPs rely on complex formation between the target analyte and functional monomers in porogenic solution prior to radical copolymerization, the achievable selectivity is governed by the nature and stability of these complexes. Prior studies correlating polymer recognition properties with characteristics of the pre-polymerization mixture system can be found in the literature and include

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simulation via molecular modeling, UV spectroscopy, solution state NMR and FTIR [1,2]. These studies support the inherent correlation between the formation of pre-polymerization complexes and polymer affinity for specific substrates. Therefore, molecular-level investigations of the interactions governing complex formation and stability are crucial to fundamental rational understanding of designed biomimetic recognition materials.

The main non-covalent interactions responsible for molecular recognition in biomimetic systems are hydrogen bonding (H-bonding) and ion pairing. Furthermore, a number of weak interactions such as Coulombic attraction, charge transfer, and molecular stacking contribute to complex formation, especially in protic solvents partly compensating for the loss of polar interactions [1]. The analytical challenge is identifying methods for tracing complex formation in the pre-polymerization solution and to accurately evaluate how variable parameters influencing complex formation govern the properties of the subsequently formed imprinted polymers [2].

When applicable, UV–Vis spectroscopy will provide a simple and valuable tool for the rapid investigation of new monomer–target interactions. However, in order to use optical absorbance there must be either a shift in the wavelength of maximum absorbance or a change in A_{max} as a function of ligand concentration [3–6]. Solution NMR is probably the most widely used of the spectroscopic techniques as it affords high specificity and can yield structure information on the nature of the monomer:template complex: H-bonding [1,7,8] ionic, $\pi-\pi$ stacking interactions [9] and self-association [10,11]. Changes in the chemical shift values in NMR titration experiments have been used to establish the stoichiometry of complexes or the association constants between monomer: and template [12]. Concerning FTIR spectroscopy, despite being a powerful method for studying H-bonding, its application to analyze MIP pre-polymerization complexes is scarce in current literature [13–15]. With a few exceptions, the combination of spectroscopic methods for a more comprehensive understanding of pre-polymerization events has not been explored in detail [1,16–18].

Regarding polymer physical characterization, FTIR has already been demonstrated to be a valuable tool in the characterization of post-polymerization binding properties in MIPs both in the transmission [13,19–21] or the ATR-mode [22–24]. An additional advantage of this technique is the higher information content of the spectra that in some cases allows not only detecting but also to quantify the analyte [25] and study the mechanism of interaction of the template with the MIP matrix [26]. The utility of the method depends ultimately on a careful choice of template and MIP to avoid overlapping FTIR bands, thereby improving the sensitivity in detecting templates [27].

Another aspect to consider in relation with MIP-template interactions is that optimum binding occurs when the polymer is exposed to the same conditions used for polymerization. The reason for this lies in the postulated mechanism of template recognition by a MIP, which originates from two factors: shape of the imprinted cavity and the spatial positioning of the functional groups coordinated by the template and integrated into the polymer network during polymerization. The solvent polarity may affect the sorption capacity and selectivity in two ways. In the first place, the solvent competes with the template for both specific and non-specific sites [28]. Secondly, a solvent induced swelling/shrinking process can affect the shape of the cavity and the distance between functional groups and due to this MIP can lose its specificity when exposed to the "wrong conditions" [29].

By combining solution-state NMR, FTIR and UV–Vis spectroscopy and solid ATR-FTIR spectroscopy a more complete picture of the nature of the imprinted sites and of the interactions with an analyte may be obtained. We have made use of these tools for the characterization of a polymer imprinted with Bisphenol A (BPA). The potential toxicity (estrogen mimic) and abundance of BPA in environmental media and foodstuff have boosted the research for sensitive and selective methods for its determination in water samples. Therefore, numerous papers have been published dealing with the successful synthesis of BPA-imprinted polymers employing both covalent [28,30,31] and non-covalent imprinting techniques. Among the latter, most MIPs were prepared by non-aqueous bulk free radical polymerization and it has been proved that 4-vinylpyridine (4-Vpy) was the optimal functional polymer whereas ethylene glycol dimethacrylate (EGDMA) or trimethylolpropane trimethacrylate (TRIM) performed better than other crosslinkers [11,32–35]. Most of these MIPs have high selectivity but exhibit serious templates leakage and poor site accessibility. To avoid the leakage structural analogs of BPA were used as templates whereas surface imprinted materials improved transport properties [36–44].

Despite all this background information, apart the NMR titration data of Nguyen and Ansell [11] no detailed analysis either of the BPA-monomer–solvent interactions in the pre-polymerization solution or the mechanisms of recognition of the template with the polymer matrix have been undertaken. Hence such a study is presented here. Previous work within our research group involved a systematic chromatographic characterization of the adsorptive performance of a non-covalent BPA–4-Vpy-EGDMA MIP developed in the presence of a low volatile solvent, triethylenglycol dimethyl ether (TRIGLYME), in combination with a non reactive linear polymer, poly (vinyl acetate) (PVAc), as porogen. The results proved the large sorption capacity, high recognition ability and fast binding kinetics for BPA in water samples. The MIP selectivity demonstrated higher affinity for target BPA and BPA-analogs over other common water pollutants. Bisphenol F was chosen as a structural related molecule while paracetamol (phenolic compound) and caffeine (not phenolic compound) were selected between several contaminants usually found in natural waters [45].

This study further investigates the behavior of the pre-polymerization mixture of the selected template, BPA, its analog BPF and the aforementioned competitive compounds with 4-Vpy in organic solvents with a view to the potential use of spectroscopic techniques for understanding the process of binding site formation and selection of the most suitable rebinding conditions. First of all, the mechanism of analyte:monomer interaction was determined by comparing the shifts and/or broadening of the monomer and analyte infrared bands. After Job plot analysis of spectroscopic data (using IR, UV–Vis or ^{1}H NMR spectroscopy) provided information on the complex stoichiometry, FTIR titrations were carried out to calculate the apparent binding constants. In order to confirm the mechanism and compare the spectroscopic techniques, ^{1}H NMR titrations were also performed.

Additionally, ATR-FTIR studies enabled the detection and quantification of BPA, both in the pre-polymerization porogen solution and the polymer matrix. The template–monomer, template–template and template–crosslinker interactions and their effects on the polymerization reaction were further discussed. Accordingly, we examined whether the conversion profiles and copolymer composition could be altered significantly in the presence of an interacting template–monomer pair and if the solution complexes were translated into the polymer through the templating process. The ultimate goal of our research was to apply this direct detection technique to characterize the post-polymerization binding mechanism.