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Method for preparing a well-defined molecularly imprinted polymeric system via radiation-induced RAFT polymerization

Meshude Akbulut Söylemez, Olgun Güven, Murat Barsbay*

Department of Chemistry, Hacettepe University, 06800 Beytepe, Ankara, Turkey

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ABSTRACT

RAFT polymerization was utilized to imprint atrazine, a model herbicide, onto porous nonwoven fabric via surface-initiated polymerization of methacrylic acid (MAA) using γ-rays for the generation of radicals. Cumyl dithiobenzoate (CDB) and ethylene glycol dimethacrylate (EGDMA) were employed as the RAFT agent and crosslinker, respectively. The surface-imprinted PE/PP nonwoven fabric was characterized by ATR-FTIR, XPS, SEM and positron annihilation lifetime spectroscopy (PALS). Atrazine uptake measurements were carried out by HPLC. It was demonstrated that RAFT polymerization could be successfully utilized in conjunction with radiation-induced grafting technique for the preparation of well-defined MIPs. The MIP layer grafted onto the surface exhibited the same efficiency through the whole thickness range attained. The MIPs synthesized by RAFT method presented an increase of over 100% in binding capacity at low atrazine feed concentrations compared to those prepared by conventional free-radical polymerization method where no RAFT agent was employed.

1. Introduction

Molecular imprinting is a useful tool to prepare tailor made materials for specific recognition and separation of a wide range of template molecules such as ions [1], proteins [2], amino acids [3], drugs [4,5], herbicides [6], carbohydrates [7], etc. This method basically includes polymerization of functional monomers around a certain template molecule in the presence of a crosslinking agent. Removal of the template molecule leaves behind complementary binding sites in terms of size, shape and functionality in the polymeric network. These binding sites provide specific recognition of the template molecule selectively (see Scheme 1).

Molecular imprinting can be accomplished as covalent or non-covalent binding depending on the interactions between functional monomer and template molecule. In covalent imprinting, the molecular interactions are based on the formation of reversible covalent bonds, e.g. disulfide and coordination bonds [8]. This method provides homogeneous binding site distributions due to clear stoichiometry between the template and monomer. However, it cannot be applied to all kinds of templates and removal of the template from the final product is slow and needs chemical reactions, yielding a more difficult process compared to the latter. Non-covalent imprinting, on the other hand, is easier and it enables to imprint a wide range of template molecules. Although this method is by far the most applied, it causes heterogeneous binding site and affinity distributions [9,10] due to weaker and less specific interactions between functional monomers and template molecules [11].

Structural and distributional homogeneity and hence binding properties are also affected by the polymerization process applied during the preparation of molecularly imprinted polymers (MIP). Conventional free-radical polymerization (FRP) process largely applied in MIP preparations proceeds via uncontrolled polymerization and crosslinking reactions as inevitable consequences. The uncontrolled fashion encountered in conventional FRP is regarded as the main reason of many drawbacks of final imprinted product such as heterogeneous distribution of binding sites and affinity, low imprinting efficiency and heterogeneous inner morphology and porosity [12]. From the pioneering works of Boonpangrak et al. [13] and Vaughan et al. [14], the use of reversible-deactivation radical polymerization (RDRP) techniques in the imprinting studies is constantly increasing. In many publications to date the benefits of RDRP methods in terms of not only the structural uniformity and binding property improvements, but also the versatility of the process to prepare multifunctional materials that were otherwise difficult or impossible to obtain have been revealed [12].

RDRP techniques can be applied together with various MIP preparation methods such as bulk polymerization [15–18], surface imprinting via grafting [19–28], well-defined particle preparation using precipitation [29,30] or emulsion polymerization [19] and in-situ membrane synthesis [16]. Among these methods, grafting of molecularly imprinted polymers onto different support materials is quite

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* Corresponding author.
E-mail address: mbarsbay@hacettepe.edu.tr (M. Barsbay).

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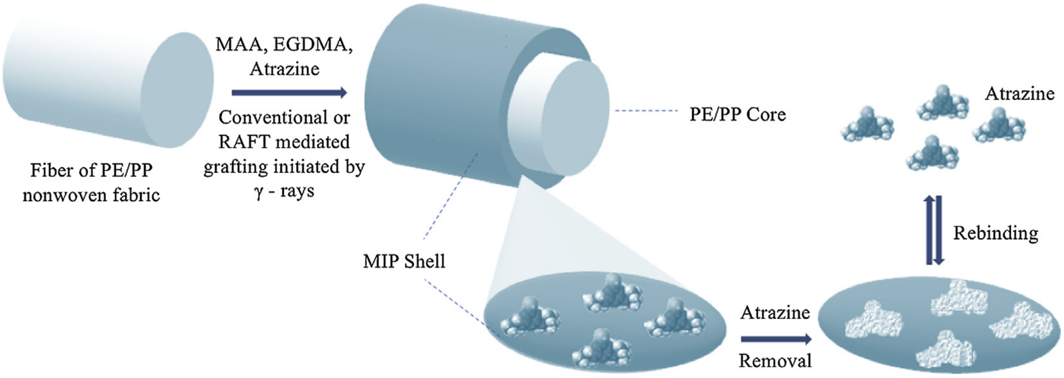

Scheme 1. Schematic representation of the radiation-induced grafting employed for the synthesis of MIPs.

promising as this method provides rapid uptake and removal of templates, fast binding kinetics and ease of accessibility of template molecule to the binding sites by allowing the imprinting at or beneath the surface. Among the RDRP methods, atom transfer radical polymerization (ATRP) has been widely used for the surface grafting of imprinted polymers to various support materials such as multiwalled carbon nanotubes [20], magnetic particles [19,21–24], silicon wafers [25], gold surfaces [26,27], spherical polymer particles [28,31] and dendrimeric structures [32]. Reversible addition fragmentation chain transfer [RAFT] polymerization has also been largely applied to the surface grafting of imprinted polymers [33–45].

A series of different approaches such as immobilizing a free radical initiator [39], a vinyl group [44], an ATRP initiator [25,46,47] or a RAFT agent [40–43] has been reported for the functionalization of a support material prior to surface grafting of imprinted polymers via RDRP methods. However, the use of ionizing radiation, one of the most promising methods for the surface modification of various substrates, has not yet been studied in detail in conjunction with a RDRP method for the preparation of surface grafted molecularly imprinted polymers. To the best of our knowledge, this study will be the most detailed report on the imprinting of a target molecule by radiation-induced RDRP method on a substrate. Among the RDRP methods, RAFT process is the only one that can be applied simultaneously with ionizing radiation such as γ-rays [48–50]. The use of ionizing radiation during the synthesis of MIPs further makes it possible to simultaneously graft them from polymeric surfaces introduced to the polymerization medium. Therefore ionizing radiation is promising not only to synthesize well-defined MIPs but also to simultaneously modify various substrates with these crosslinked polymers. In this study, γ-initiated RAFT polymerization was used for the synthesis of well-defined, surface-imprinted PE/PP nonwoven fabric for removal of atrazine, a model template molecule. Atrazine was chosen as its binding behavior has been studied in detail in many studies, which allows comparisons on the applied method. The substrate, nonwoven fabric, served as a porous durable supporting material with a large surface area.

2. Experimental

2.1. Materials

Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA) and cumyl dithiobenzoate (CDB) were obtained from Sigma-Aldrich (Milwaukee, USA) and employed as functional monomer, crosslinking agent and RAFT agent, respectively. Template molecule, atrazine, and its analogues, metribuzine and simazine, were obtained from Fluka. All the solvents were purchase from Sigma-Aldrich with highest purity.

2.2. Grafting of atrazine imprinted polymers onto nonwoven fabric via gamma radiation

Polyethylene/polypropylene (PE/PP) nonwoven fabric obtained from Kurashiki Sen-I Kako Co. Okayama, Japan was cut into circular pieces with 0.6 cm diameter (approximately 25 mg), washed with ethanol and water and dried in vacuum at ambient temperature. In a typical conventional MIP preparation process, a piece of fabric was dipped into a purgeable glass flask containing polymerization solution prepared by dissolving MAA (0.147 g; 1.70 mmol), EGDMA (2.21 g; 11.1 mmol) and atrazine (0.183 g; 0.85 mmol) in 15 mL DMF. The ratios of MAA/atrazine and MAA/EGDMA were adjusted to the optimum values which were previously set at 2/1 and 1/6.5, respectively [51]. The content was sealed and kept at ambient temperature for 1 h. The solutions were then purged with nitrogen for 10 min and placed into a Co-60 gamma cell at a dose rate of 0.026 kGy/h (Gammacell 220 Nordion, Canada) at room temperature. After irradiating the samples for various durations surface-imprinted PE/PP fabrics (MIPs) were removed from the polymerization solution, placed on a shaker and washed in a mixture of methanol:acetic acid:water (0.9:0.1:1 by volume). The solvent was changed periodically until no atrazine could be identified in the rinsing solution via HPLC analysis. In RAFT-mediated preparation process of MIPs, the RAFT agent (CDB) was also added to above-mentioned polymerization solution. The solutions were then treated similarly. Different MAA/CDB concentration ratios of 85, 165, 330, 665 and 1330 were used in syntheses carried out by RAFT polymerization. In both conventional and RAFT-mediated processes nonimprinted PE/PP fabrics (NIPs) were also prepared in parallel using the same procedure but in the absence of atrazine template. The synthesis procedure is summarized in the following overview scheme. For each sample attained at the end of synthesis the degree of grafting (Dg, wt%) was calculated using the following equation:

$$Dg = \frac{W_f - W_i}{W_i} \times 100$$

where W_i is the weight of the pristine fabric and W_f is the weight of the surface-imprinted nonwoven fabric after removal of the template.

2.3. Structural and chemical characterization of surface imprinted PE/PP nonwoven fabrics

2.3.1. Attenuated total reflectance Fourier transform infra-red spectroscopy

FTIR spectra were recorded in attenuated total reflectance (ATR) mode using a Thermo Nicolet iS10 model spectrometer. Spectra were obtained by cumulating 32 scans with a 4 cm^{-1} resolution.