



Study of the morphology and the adsorption behavior of molecularly imprinted polymers prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization process based on two functionalized β -cyclodextrin as monomers



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ARTICLE INFO

Article history:

Received 21 July 2015

Received in revised form 29 November 2015

Accepted 30 November 2015

Available online xxxx

Keywords:

Molecularly imprinted polymer

RAFT polymerization

Morphology

Adsorption behavior

ABSTRACT

The adsorption behavior of molecularly imprinted polymers (MIPs) prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization process through the effect of polymer morphologies was described. In this study, two kinds of RAFT-MIPs were synthesized based on methacrylic acid functionalized β -cyclodextrin (MAA- β -CD) and 2-hydroxyethyl methacrylate functionalized β -cyclodextrin (HEMA- β -CD) monomers, represented as RAFT-MMIP and RAFT-HMIP, respectively. The results of RAFT-MIPs were respectively compared with MMIP and HMIP prepared by free radical polymerization (FRP) process (without RAFT agent). The Field Emission Scanning Electron Microscope (FESEM) images showed that the RAFT-MMIP had slightly spherical and spongy-porous structure, and the MMIP had rough surface structure. Besides, the surface area of RAFT-MMIP was larger than MMIP. In contrast, the RAFT-HMIP formed non-porous particles with a smooth surface structure, while the HMIP formed a porous structure with a large surface area size. Through their physical characteristics, it proved that the morphological properties played an important factor which affected the adsorption behavior properties of MIPs, including kinetic, isotherm and thermodynamic studies. The superior physical characteristics of RAFT-MMIP demonstrated the greater equilibrium contact time, fast kinetic adsorption, higher adsorption rate, enhanced adsorption capacity and higher binding affinity. However, the non-porous RAFT-HMIP structure was poor in the adsorption behavior system. The RAFT polymerization successfully worked depending on the monomer used to generate potential MIPs.

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1. Introduction

Molecularly imprinted polymers (MIPs) are a cross-linked polymeric material that exhibits high selectivity and great affinity against a target molecule (template) purposely present during the synthesis process. The resulting MIPs have favorable mechanical, thermal and chemical stabilities which make MIPs very promising adsorbents for many separation applications such as chromatographic [1,2], solid-phase extraction [3,4], and membrane separation [5,6]. The principle of MIPs synthesis technique involves; (1) the self-assembly of monomer-template molecules, (2) the polymerization of template-monomer complex with cross-linking agent, and (3) the template removal to afford the imprinted polymer.

Usually, MIPs are prepared using traditional free radical polymerization (FRP) mechanism, whereas the rate of chain propagation and termination cannot be controlled, resulting in a heterogeneous polymer structures [7]. This result would greatly affect the internal binding sites and give several drawbacks of MIPs, such as the broad binding sites' heterogeneity, relatively low affinity and reduced selectivity [8]. The introduction of reversible addition-fragmentation chain transfer (RAFT) polymerization method into the molecular strategy has attracted significant interest, which can solve the problem of FRP. RAFT polymerization is one of the most versatile living/control radical polymerization (LRP) methods, especially in terms of providing living characteristics to the radical polymerization [9,10] making it compatible with almost all FRP monomers [11] and it does not involve any metal catalyst [12,13]. The controllability of RAFT polymerization could be attributed to the use of RAFT agent (normally a dithioester) and the resulting fast and equilibrium between active species (propagating radicals) and dormant species (thiocarbonylthio-terminated chains) [8]. Additionally, it is thermodynamically controlled with

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negligible chain termination and constant slow chain growth, which remarkably improve the match in the chain growth and chain relaxation rates. Thus, it leads to homogeneous network polymer compared to FRP, which results in higher target affinity [14] and improves the binding properties of MIPs.

Therefore, the RAFT polymerization has been widely used by several researches in various MIP polymerization methods, such as surface grafting [15,16], suspension [17], precipitation [8,18] and core-shell polymerizations [13,19]. However, our previous work [20] demonstrated that the MIP obtained using RAFT polymerization in bulk polymerization method showed lower binding capacity and affinity compared to the ones obtained from the FRP bulk polymerization. Ma et al. [21] also found similar observations. There is speculation that the fast gelation during polymerization process leads to heavily interrupted equilibrium between the dormant species and active radicals in the RAFT mechanism. So, it was proven that the application of RAFT polymerization in molecular imprinting does not always improve the binding properties of the MIPs.

In our previous work, we studied the potential of applying RAFT polymerization in two different kinds of RAFT-MIPs based on the influence of monomer-template interaction, and the effectiveness of RAFT agent on the selective binding properties [20] on a molecular level. Nevertheless, the performance of MIPs is not only dictated on a molecular level, but also by the physical make-up of the polymer on a macromolecular level. MIPs are generally insoluble materials whose subsequent use depends on their morphology in terms of the particle shape and size, and the porous texture of the materials [22]. Therefore, we focused on studying the relationship between the polymer morphologies and corresponding polymer adsorption behaviors on a macromolecular level. To our best knowledge, this is the first report that describes the consequences of polymer morphology on the adsorption behavior of MIPs prepared by RAFT polymerization process.

Herein, two kinds of reversible addition-fragmentation chain transfer molecularly imprinted polymers (RAFT-MIPs) were synthesized by RAFT polymerization process in bulk polymerization method. In order to synthesize those RAFT-MIPs, two different conventional monomers, such as methacrylic acid (MAA) and 2-hydroxyethyl methacrylate (HEMA) were initially modified with β -cyclodextrin (β -CD) to become functionalized β -CD-monomers. The produce of functionalized β -CD-monomers was methacrylic acid functionalized β -cyclodextrin (MAA- β -CD) and 2-hydroxyethyl methacrylate functionalized β -cyclodextrin (HEMA- β -CD). β -CD is a series of cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic cavity capable of binding the hydrophobic structures of guest. It is well-known to form inclusion complexes with various substrate compounds. Compared to single MIPs monomer, the functionalized β -CD-monomers could increase a number of possible bonds between the template and the monomer, which improve the recognition ability and binding capacity of MIPs [23,24].

The resulting RAFT-MIPs are represented as reversible addition-fragmentation chain transfer molecularly imprinted polymer methacrylic acid functionalized β -cyclodextrin (RAFT-MMIP) and reversible addition-fragmentation chain transfer molecularly imprinted polymer 2-hydroxyethyl methacrylate functionalized β -cyclodextrin (RAFT-HMIP) were then obtained. Hence, batch kinetic, equilibrium adsorption and thermodynamic experiments for the adsorption of benzylparaben (BzP) analyte were conducted. The results of this sorption studies would contribute to better understanding of the sorption behavior of RAFT-MIPs with commensurate polymer morphology towards BzP uptake. A typical MIPs prepared by FRP polymerization (omitted RAFT agent) were synthesized as corresponding MIPs.

2. Experimental

2.1. Materials

β -cyclodextrin (β -CD) was purchased from Acros (Geel, Belgium). Methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA),

toluene-2,4-diisocyanate (TDI), trimethylolpropane trimethacrylate (TRIM), benzoyl peroxide (BPO), dimethylacetamide (DMAC), cumyl dithiobenzoate (CDB), dibutyltin dilaurate (DBTDL), methanol, acetic acid and toluene were purchased from Sigma-Aldrich (St. Louis, MO, USA). Other solvents were analytical reagent grade and were used as received without further purification. Distilled water was used throughout the experiments.

2.2. Synthesis of MAA- β -CD and HEMA- β -CD monomers

Methacrylic acid functionalized β -cyclodextrin (MAA- β -CD) and 2-hydroxyethyl methacrylate functionalized β -cyclodextrin (HEMA- β -CD) monomers were synthesized based on our previous work [20].

2.3. Synthesis of molecularly imprinted polymers (MIPs)

The MIPs were synthesized based on our previous work [20]. As for the synthesis of RAFT-MIP(MAA- β -CD), as RAFT-MMIP, the BzP template (0.14 mmol) was dissolved in 10 mL of DMAC solvent in a flask, containing MAA- β -CD monomer (0.56 mmol, 0.757 g), TRIM cross-linker (2.80 mmol, 0.894 mL), CDB as RAFT agent (1.24 mmol, 0.327 g) and BPO initiator (0.6, 0.145 g). The synthesis of RAFT-MIP(HEMA- β -CD) as RAFT-HMIP was carried out under similar conditions, using HEMA- β -CD monomer (0.56 mmol, 0.806 g). The solution was sealed and purged with nitrogen gas for at least 10 min. Then, the mixture was allowed to polymerize in a water bath at 70 °C for overnight. The successful bulk RAFT-MIPs were extensively crushed, ground and wet-sieved. The extraction process was then carried out with a mixture of methanol/acetic acid (v/v, 9/1) to leach out the BzP template from RAFT-MIPs particles, until no BzP template in the eluate could be detected at wavelength of 258 nm by the UV-Vis spectrophotometer. The RAFT-MIPs particles were finally washed with methanol to remove any residual acetic acid and dried under vacuum at 80 °C. The MIPs synthesized without CDB which were molecularly imprinted polymer-methacrylic acid functionalized β -cyclodextrin, MIP(MAA- β -CD) as MMIP, and molecularly imprinted polymer 2-hydroxyethyl methacrylate functionalized β -cyclodextrin, MIP(HEMA- β -CD) as HMIP were synthesized as comparison.

2.4. Characterization of MIPs

The percentages of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) elements of MIPs were measured using elemental analyzer UM TRUSPEC MICRO CHNS LECO (Perkin Elmer, Waltham, MA, USA). The surface morphologies of MIPs were determined using Quanta FEG 450 Field Emission Scanning Electron Microscope (FESEM) from FEI (Hillsboro, OR, USA). Meanwhile, the surface area and pore size distribution of MIPs were measured by nitrogen adsorption-desorption analysis at 77 K using Quantachrome Autosorb Automated Gas Sorption system (Quantachrome, Boynton Beach, FL, USA). Prior to nitrogen sorption measurements, the MIPs were previously degassed at 393 K for 24 h to remove adsorbed gases and moisture. The values of specific surface area, average pore size and pore volume of MIPs were calculated from Brunauer-Emmett-Teller (BET) method, Barrett-Joyner-Halenda (BJH) method and Dubinin-Radushkevich (DR) plot, respectively. The concentration of BzP in the aqueous solution was analyzed using a Shimadzu Ultraviolet-Visible spectroscopy (UV-Vis) recording spectrophotometer (Shimadzu, Tokyo, Japan), equipped with 1 cm quartz cells, at a maximum wavelength of the BzP ($\lambda_{\max} = 258$ nm).

2.5. Batch adsorption studies

2.5.1. Kinetic study

Kinetic studies were applied to study the effect of contact time and to calculate the kinetic parameter. To determine the effect of time on the BzP uptake, the adsorption process was conducted for the time

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