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Bisphenol A imprinted polymer adsorbents with selective recognition and binding characteristics

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Abstract

Imprinted copolymers, which highly recognized and bound bisphenol A (Bis A), were synthesized by using covalent imprinting technique. Bisphenol A dimethacrylate (BADM) was used as a template monomer in the copolymerization with a crosslinkable monomer of divinyl benzene (DVB), ethylene glycol dimethacrylate (EGDM) or *N,N′*-methylenebisacrylamide (MBAA). The resultant copolymer was hydrolyzed in acidic or basic condition. It was found that the Bis A imprinted copolymers of EGDM and MBAA had no selectivity to Bis A, because the crosslinker dissociated by the hydrolysis reaction and thus comprehensive imprinted sites were not formed. On the other hand, imprinted copolymer of DVB showed excellent selectivity to differentiate Bis A from bisphenol E and bisphenol F (Bis F). Characterization of the copolymers suggested that the DVB copolymer had resistance to the acid and alkali conditions. Effect of recognition by the Bis F imprinted polymer was also compared with that of the Bis A imprinted polymer, when DVB and bisphenol F dimethacrylate were copolymerized. The Bis F imprinted copolymer was able to recognize Bis F in ethanol solution, however showed higher binding capacity for both Bis A and Bis F in water solution without recognition. Therefore, hydrophobic interaction between Bis A and the imprinted site enhanced the binding capacity with high selectively for the BADM-co-DVB imprinted copolymer.

Keywords: Molecular imprinting; Molecular recognition; Polymer adsorbent; Bisphenol A

1. Introduction

Bisphenol A (Bis A), which is known as endocrine disruptor, affects the reproduction and development of animal organism in extra-diluted concentration. Therefore, exposures to Bis A even in the ppb concentration range occur in human and animal body cause serious problems. In general, Bis A is eluted from plastics into foods or beverage [1,2], because Bis A is widely used for production of polycarbonates and epoxy raisins in an industrial scale, and consumed in large amounts. Therefore, the material, which recognizes and selectively absorbs Bis A, is surely required from the viewpoint of environmental conservation. For development of Bis A adsorbents, molecular imprinting has been very useful as alternative methods [3–5]. The imprinting techniques have found various applications in fields of separation and concentration. However, imprinted polymers with highly selective and largely adsorbed abilities to such endocrine disruptor still have been on progress. Therefore, in the near future, it is certainly necessary for such environmental conservation to utilize Bis A imprinted polymers, which selectively bind this chemical with high binding capacity. It is known that imprinting method gives both molecule recognition and binding polymer materials. Thus, resultant imprinting polymers memorizes the target molecule in shape and functionality. The non-covalent approach for Bis A imprinting mainly employed hydrogen bonding between a polymer and a Bis A molecule as the driving force for imprinting a target molecule [6]. Also, in covalent imprinting approach, recognition sites in imprinted polymers are constructed by means of common cross-linking polymerization in the presence of a template [4–7]. According to such template polymerization including a monomer-template complex, the resultant polymer matrix can be complementary to the template molecule. Recently, Bis A imprinted polymer was

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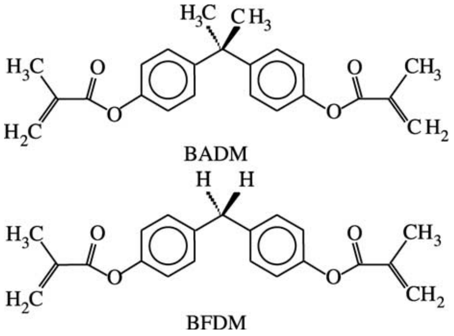


Scheme 1. Chemical structures of BADM and BFDM.

prepared by Takeuchi et al by applying to covalent technique [7]. They reported that copolymerization of functional monomer containing Bis A framework structure and ethylene glycol dimethacrylate (EGDM) as a crosslinking monomer gave Bis A imprinting materials. In this case, after the template was removed by alkali conditions, the Bis A imprinted polymer was prepared. However, recently, we confirmed the technique reported was unsuitable for highly recognizing the template molecules because the alkali treatment caused hydrolysis breakage of ester bonds for the crosslinked EGDM segments in the imprinted polymers. As a result, this was for cause and effect on increase of non-selective absorption by the imprinted polymers. Therefore, in the present work, we focused on selection of the crosslinkers and bisphenol monomers to discriminate bisphenol derivatives. Bisphenol A dimethacrylate (BADM) and Bisphenol F dimethacrylate (BFDM) (Scheme 1) were used as functional monomers. When the ester bonds of BADM copolymer are hydrolyzed, methacrylic acid segments and Bis A can be formed as shown in Scheme 2. The manner leaves the template trace as imprinted sites in the polymer matrix, which is capable to recognizing and binding only Bis A (Scheme 3). For Bis A imprinted polymers with EGDM, *N,N′*-methylenebisacrylamide (MBAA) and divinyl benzene (DVB), the stability of the copolymer was compared under the hydrolysis condition. We discussed binding and recognition of several Bis A analogs by using various imprinted copolymers crosslinked with DVB, EGDM and MBAA in order to discriminate Bis A analogs and phenol derivatives (Scheme 4).

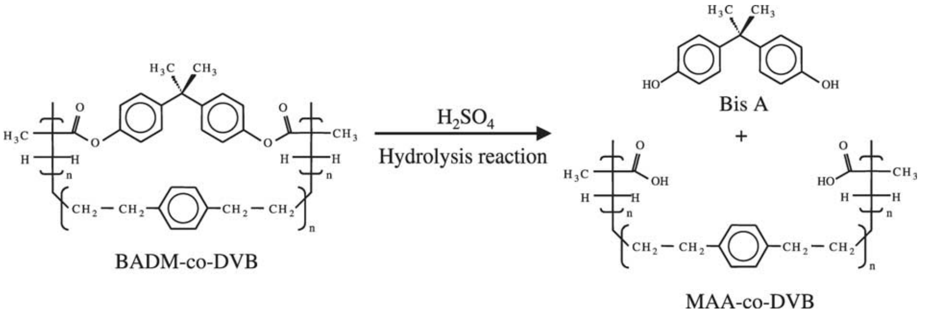
2. Experiments

2.1. Materials

Bisphenol A (Bis A), methacrylic acid (MAA), *N,N′*-methylenebisacrylamide (MBAA) and divinyl benzene (DVB) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Bisphenol A dimethacrylate was obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without purification. Ethylene glycol dimethacrylate (EGDM), 4-4′-ethylidenebisphenol (Bis E), 4,4′-dihydroxydiphenylmetane (Bis F), 2-(4-hydroxyphenyl)ethyl alcohol (HPEA) and resorcinol (RSO) were purchased from Tokyo Kasei Industry Co. (Tokyo, Japan).

2.2. Preparation of Bis A imprinted and non-imprinted polymers

Table 1 lists monomer feeds for copolymers of BADM synthesized with various crosslinked monomers. Copolymerization was carried out in toluene except for cases of MBAA. Due to non-soluble in toluene for MBAA, the polymerization was carried out in *N*-methyl-2-pyrrolidone (NMP). In polymerization, the monomer solution prepared was purged with nitrogen for 10 min and then 2,2′-azobis(isobutyronitrile) was added into the solution. The copolymerization was carried out at 55 °C for 12 h. The resulting copolymer was ground by pestle and mortar. Resultant copolymer granules were washed by solvent used in the copolymerization and then in tetrahydorofuran (THF). Then, dried under vacuum in desiccator was for copolymer granules. The content of BADM in each copolymer was estimated by using IR measurements of copolymers. The measurements of FT-IR spectrum were carried out by IR Prestige-21 FTIR-8400s (Shimadzu co.) using the KBr method. For example, the BADM content of 9.0 mol% in BADM-co-DVB was determined from the IR spectra of mixtures of PolyBADM and PolyDVB. Herein, the data of



Scheme 2. Synthetic reaction scheme of imprinted polymer including hydrolysis process of BADM segment.