



Molecularly imprinted polymer particles having coordinated hydrogen bonding in covalent-imprinting for efficient recognition towards vanillin



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ABSTRACT

This report explains the effects of vanillin-imprinted polymers showing hydrogen bonding coordinated in covalent-imprinting in core-shell particles. As new molecularly imprinted polymers (MIPs) for vanillin targets, this paper presents evidence for covalent-imprinting polymers having hydrogen-bonding coordination that is achieved using vanillin methacrylate (VMA) and methacrylic acid (MAA) for divinylbenzene (DVB) suspension polymerization. The stepwise polymerization can form core-shell uniform particles having about 0.3–2.5 μm diameter. The resultant vanillin-imprinted polymer containing VMA, MAA, and DVB segments enhanced separation of vanillin from other analogs, syringaldehyde and p-hydroxybenzaldehyde, showing a separation factor of 6.8. This result showed that the aid of hydrogen-bonded coordination of MAA in the covalent method with VMA imprinted the vanillin target. The influence of MAA in the imprinted polymer is shown by the separation performance having a high binding capacity and good selectivity, when both VMA and MAA segments were present in the polymer particles. Details of the effects of VMA and MAA amounts were investigated using target recognition by separation experiments.

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1. Introduction

Vanillin, known as 4-hydroxy-3-methoxybenzaldehyde and also known as vanilla, is an important compound used in food-related industries. Vanilla is obtainable from seed pods of *Vanilla planifolia*. Because of the exceptionally widespread utilization of vanillin in foods, cosmetics, pharmaceuticals, and fine chemical industries, vanilla has become an important aroma [1]. However, genuine vanilla extracted from pods is up to 200 times more expensive than synthetic vanillin. Fortunately, early in the twentieth century, chemists discovered that lignin can be a source of vanillin. Therefore, considerable attention has been devoted to the improvement of vanillin separation processes from waste lignin [2]. Lin and Dence reported that high macromolecular complexity of lignin was partially degraded via an oxidation process to obtain

the vanillin compound. This method was chosen as a standard method for lignin degradation because vanillin was produced as a major compound [3]. Although the vanillin obtained from the oxidation process contained high level of impurities [4], the purification of vanillin via oxidation processes was conducted in terms of a crystallization process [5]. Nevertheless, the crystallization process has still not yet purified the vanillin successfully, meaning that alternative technologies for vanillin are needed as new separation methods.

As a new separation technology, molecular imprinting has become widely developed with several polymers. It offers numerous benefits in artificial functional sorbents. Consequently, the utilization of molecular imprinting polymers (MIPs) has been widely exploited in diverse fields such as catalysis [6], chemical analysis [7], chromatography [8], capillary electrophoresis [9], hollow fiber separation [10], membrane separation [11], sensor technology [12], solid-phase extraction [13], and organic environment [14]. This exploitation for diverse applications results from the advantages of excellent selectivity and highly efficient absorptivity to the target molecules and ions, which enable easy design in a tailor-made fashion. Therefore, we applied MIP technology to encode vanillin in the present work. For imprinting vanillin, Wang et al. studied vanillin-imprinted polymers in a non-covalent approach using a bulk technique with preparation in different progen

Abbreviations: MIPs, molecularly imprinted polymers; VMA, vanillin methacrylate; MAA, methacrylic acid; DVB, divinylbenzene; MAC, methacryloyl chloride; TEA, triethylamine; THF, tetrahydrofuran; AIBN, 2,2'-azobisisobutyronitrile; CDCl_3 , deuterated chloroform; NMR, nuclear magnetic resonance; FT-IR, Fourier transform infrared; HPLC, high performance liquid chromatography; BA, binding amount; NIP, non-imprinted polymer; SA, syringaldehyde; HBA, p-hydroxybenzaldehyde; SEM, scanning electron microscope.

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solvents [15]. They compared MIP performances as stationary phases for HPLC columns. Results showed that the porogen exhibited a certain influence on adsorption performance of the polymer and that the cooperative hydrogen-bonding interaction between the imprinted molecule and the monomer enhanced the selectivity of the non-covalently imprinted polymers. Zhang et al. also applied non-covalent method in vanillin imprinted polymer membranes and displayed higher binding and separation capacity for vanillin [16]. In some polymers prepared using non-covalent imprinting, the simplicity of the imprinting process and the selection flexibility in terms of available functional monomers were beneficial for matching templates. Nevertheless, the non-covalent imprinted polymers showed lower binding affinity compared with that prepared using covalent one [17,18]. Unfortunately, only a few compounds can be imprinted using this approach for vanillin because the covalent imprinting entails difficulties in the synthesis of functional monomer for the tailor made production. However, this means that only insufficient technology exists for imprinting using a covalent-imprinting method.

Therefore, in this work, vanillin imprinted polymers were developed using a new monomer, vanillin methacrylate (VMA), in divinylbenzene. In our earlier research, post-addition functional polymerization was developed successfully as a new technique [19]. The core-shell MIP spheres included imprinting process with the precipitation polymerization of functional monomer used for covalent-imprinting on the surface of the polymerized DVB particles for bisphenol A target. Consequently, preparation of core-shell vanillin-imprinted polymers was designed for vanillin monomer (VMA) by covalent-imprinting to increase the separation process. For this purpose, it was found that the aid of co-monomer (methacrylic acid, MAA) coordinating hydrogen bonds with the VMA can show high recognition to the template by the imprinted polymer particles. The ability of the imprinted polymers in the recognition selectivity and binding activity were studied for the enhancement of vanillin separation.

2. Experimental

2.1. Materials

Vanillin ($\geq 98\%$) was purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA) and was purified with crystallization method [4]. Sodium hydroxide (Wako Pure Chemical Industries Ltd., Osaka, Japan), triethylamine (TEA) (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and methacryloyl chloride (MAC) (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) were used without further purification for synthesis of vanillin methacrylate. Magnesium sulfate was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Tetrahydrofuran (THF), chloroform, acetone, azobisisobutyronitrile (AIBN), acetonitrile (HPLC grade), methacrylic acid (MAA), acetic acid, sodium hydrogen carbonate and ethanol were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Divinylbenzene (DVB) (Nacalai Tesque Inc. (Kyoto, Japan)) was purified using a silica gel column to remove the inhibitor used earlier. The initiator of AIBN was purified by crystallization in methanol.

2.2. Preparation of vanillin-imprinted monomer

As a new monomer, vanillin methacrylate (VMA) (Fig. 1) was synthesized and used as a functional monomer for covalent vanillin imprinting. The synthesis approach was followed by esterification of vanillin (1.52 g, 10 mmol) with methacryloyl chloride (MAC) (4.18 g, 40 mmol). Then a methacrylate group was introduced to the vanillin framework in the presence of TEA. First, vanillin was added to THF solution (50 ml) and TEA (4.04 g, 40 mmol).

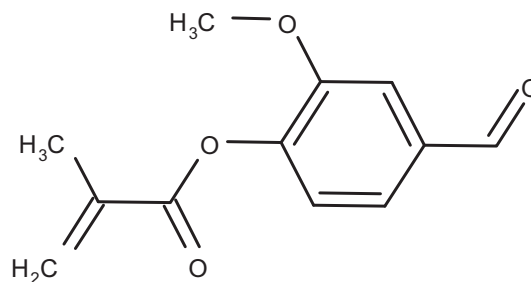


Fig. 1. Chemical structure of vanillin methacrylate.

Then, the vanillin was dissolved completely. To the solution, MAC was added dropwise under stirring. The esterification reaction was conducted overnight at room temperature for 24 h. Then, white precipitate of the TEA salt was removed by filtration and the THF solution was concentrated by evaporation. The resultant residue was dissolved in chloroform and washed with an aqueous solution of sodium hydrogen carbonate and finally with water to remove the salts and remaining of methacrylic acid produced with reaction of water and MAC completely. After drying of the THF solution over magnesium sulfate, the organic solvent was evaporated under vacuum. The resulting crude VMA was purified with a re-crystallization in ethanol to obtain a final product (white, 70.6% yield). ^1H NMR was used to characterize VMA: (CDCl_3) δ [ppm] = 1.98 (m; 3H, $\text{CH}_2 = \text{C}(\text{CH}_3)\text{C}=\text{O}-$), 3.84 (m; 3H, $-\text{OCH}_3$), 6.29–5.94 (d; 2H, CH_2), 9.76 (s; 1H, CHO). FT-IR in KBr was also applied: [cm^{-1}]: 1735 ($\text{C}=\text{O}$), 1701–1606 ($\text{C}=\text{O}$), 1506, 1458 and 1421 (OCH_3), 1598–1510 (aromatic ring of VMA), 1271–1153 (aromatic in-plane deformation), and 863–731 (aromatic out-of-plane deformation).

2.3. Preparation of vanillin-imprinted polymers

As Table 1 shows for several vanillin-imprinted polymers, copolymers of DVB and VMA, P(DVB-co-VMA) copolymer, were synthesized in the absence and presence of MAA. The terpolymers of DVB, MAA and VMA, P(DVB-co-MAA-co-VMA) were polymerized with 100 mmol of the DVB cross-linker. When the co-monomer MAA was added with 5, 10, and 20 mmol in the stepwise polymerization [19]. Briefly, the procedure for preparing the P(DVB-co-VMA) involved the mixture of 220 ml acetone, 30 ml water, DVB (50 mmol) and AIBN (1 mmol). The mixtures were poured into a 500 ml three-neck round bottom flask, which was kept in an oil bath and which was equipped with an agitator (BL 3000; Heidon/Shinto Scientific Co., Ltd.) and a condenser. The mixtures were de-gassed with nitrogen gas for 30 min at room temperature while the stirring speed was kept at 300 rpm. The flask temperature was increased to 65°C under continuous nitrogen atmosphere. At this stage, a white suspension of the DVB polymer appeared as seed particles in the flask after 3 h had passed. Then, VMA (10 mmol) in acetone (50 ml) was added to the suspension and the stepwise polymerization of VMA was conducted after the 3 h delay. When the VMA solution was added to the delayed time, the stepwise polymerization was maintained for another 24 h. Subsequently, the precipitated polymers were separated from the solution and washed with acetone/water mixture and dried under vacuum condition. The white powders of the resultant polymer were hydrolyzed with 1 M NaOH aqueous solution including a small amount of ethanol solution at 50°C for 12 h to remove the template [20]. Finally, the core-shell imprinted polymers were washed with water until neutral and dried under vacuum condition. For the P(DVB-co-MAA-co-VMA) terpolymer, a similar method was used with the copolymer for the polymerization process.

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