



Sorption behaviors and relation between selectivity and possible cavity shapes of the molecularly imprinted materials



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ABSTRACT

Molecular imprinted materials (MIP) were prepared through the phase inversion process after polymerization between sol-gel particles of triethoxy orthosilicate/3-(trimethoxysilyl)propyl methacrylate and mixture of styrene/acrylic acid. The sol-gel particles were rapidly precipitated by the addition of dilute NaCl solution. After removing NaCl and NH₄OH, the precipitated sol-gel particles were polymerized with two different mixtures of styrene/acrylic acid (5/1 and 10/1 ratios) in dioxane to prepare the corresponding sol-gel composites, which differ in the average length of styrene segments in-between carboxyl groups. The composites dispersed in dioxane were adsorbed with template until completing the complexation with functional groups, and then MIPs were prepared through the phase inversion process by the addition of non-solvent, H₂O. The relationship between the distribution of binding cavity shapes and the selectivity of MIP was considered depending on the length of styrene segments per one carboxyl group of MIP. The MIP of the longer styrene segment per one -COOH (10/1 of styrene/acrylic acid) showed higher selectivity than the shorter one (5/1 of styrene/acrylic acid). This can be explained by the higher proportion of the cavity shapes that surround completely template for the specific binding of the template. Langmuir isotherm described all the sorption data well suggesting that the sorption in these MIPs was mainly accomplished in monolayer. Scatchard analysis revealed that the sorption sites were heterogeneous for the template.

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1. Introduction

Molecular imprinting technique allows for effective separation of molecules and has various applications including the synthesis of stationary packing materials of HPLC [1,2], artificial enzymes [3–5], synthetic antibodies and receptors [6,7], molecular catalyst [8,9], and sensors [10,11]. Since the technique generates highly selective and sensitive binding cavities in the shape of a target molecule, it has been shown to be particularly useful in separating closely related molecules such as chiral compounds and structural isomers [12,13].

The molecularly imprinted polymers (MIPs) are generally prepared through co-polymerization of a functional monomer and divinyl monomer as a cross-linker in the presence of the template.

Functional monomer interacts with complementary functional groups of the template molecule to form a complex. The cross-linking monomer functions to solidify a three-dimensional cavity for the template in the MIPs. However, the use of cross-linker results in a very rigid polymer, which makes the removal of template difficult. Traditionally, researchers have had to ground the polymer into fine particles and sieve for the effective extraction of the template. This common method has several drawbacks: 1) some of the binding sites are still buried in the packed state without extraction even in the fine powder, thereby reducing the effective uptake capacity of the MIP, 2) the binding cavities are irregularly cracked by the grinding process, compromising the selectivity. Many efforts have been made to overcome these drawbacks, including aligning binding cavities on the surface of MIP [14,15] or using phase inversion process that bypasses the use of cross-linkers [16,17]. We recently reported a simple method to obtain a very porous MIP powder, which involves complexation between a polymer and a metal ion and phase inversion process [18]. However, the relationship between cavity shape and binding specificity

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has not been characterized to date. Understanding this relationship will contribute to the rational design of MIPs with higher specificity and improved performance [19,20].

In this work, we report the relationship between selectivity and possible binding cavity shapes of the MIPs prepared using the phase inversion process after polymerization between sol-gel particles of tetraethyl orthosilicate (TEOS)/3-(trimethoxysilyl)propyl methacrylate (MPS) and mixture of styrene/acrylic acid in dioxane. Sorption behaviors of MIPs against the isomers of ethylaniline are tested using the Langmuir isotherm and Scatchard analysis. In addition, we describe a method to rapidly precipitate the sol-gel particles from the milky suspension.

2. Experimental

2.1. Materials

Styrene(ST), acrylic acid (AA), 3-(trimethoxysilyl)propyl methacrylate (MPS), tetraethyl orthosilicate (TEOS), azo-bis-isobutyronitrile (AIBN), NH_4OH , ethanol, tetrahydrofuran (THF), and dioxane were purchased from Aldrich, and ethylanilines (2-, 3-, 4-EA) were purchased from Tokyo Chemical Industry. All reagents were used without further purification. The Chemical structures of the used materials were shown in Fig. 1.

2.2. Preparation of sol-gel particles

Mixture of TEOS and MPS (2 g, 1:1 in molar ratio) were mixed with 5 ml ethanol and 6 ml THF. After overnight shaking, 19 ml of 1:1 NH_4OH was added. The milky suspension was further incubated for 10 h with shaking. Then 1 ml of 20% NaCl solution was added to the suspension to accelerate the precipitation of sol-gel particles, and after 30 min, NaCl and NH_4OH were washed away several times. The suspension of the precipitate was easily re-precipitated during the washing out process. The wetted sol-gel particles after decantation were stored in a dark room.

2.3. Synthesis of polymer composite of sol-gel particles

The wetted sol-gel particles (approximately contained 1 g of dry particles and 3 ml of H_2O) were dispersed in 200 ml of dioxane and mixed with 1 g of the mixture of styrene/acrylic acid (5:1 or 10:1 in molar ratio) and 10 mg of AIBN in a round-bottom flask. After degassing with N_2 , the polymerization was conducted at 80 °C for 8 h with agitation. The polymer composites grafted on the sol-gel particles were obtained and designated as 5ST-1AA and 10ST-1AA, respectively, depending on the molar ratio of styrene and acrylic acid after the non-grafted copolymer of styrene-acrylic acid produced together in the polymerization process was removed from the polymerized mixture by dissolving several times with a plenty of dioxane.

2.4. Determination of maximum sorption of EA on to polymer composite

MIP in this work was prepared through the complexation between template and functional group of sol-gel composite in dioxane solvent and obtained using the phase inversion process via the addition of non-solvent. The maximum amount of template bound on the composite corresponds to the theoretical maximum number of binding sites in MIP. The uptake of the template, 4-EA, to the composite was measured in dioxane. 50 mg of the sol-gel polymer composite was mixed with 1, 3, 7, 10, 13, or 17 ml of the stock solution of 4-EA (50 mg/ml of dioxane), and pure dioxane was added to the final volume of 20 ml to produce different concentrations of 4-EA. After shaking for 12 h, the adsorption was measured with UV spectrometer at 286 nm.

2.5. Preparation of MIP and NIP

At the maximum uptake of the adsorption curve of sol-gel composite, all the carboxyl groups of the composite could be considered to form a complex with EA. Accordingly, 1 g of each polymer composite was suspended in 400 ml of dioxane and mixed with 16 g of 4-EA as a template, and shaken for 24 h. Then the non-solvent, H_2O , was added slowly to become a rigid state of the

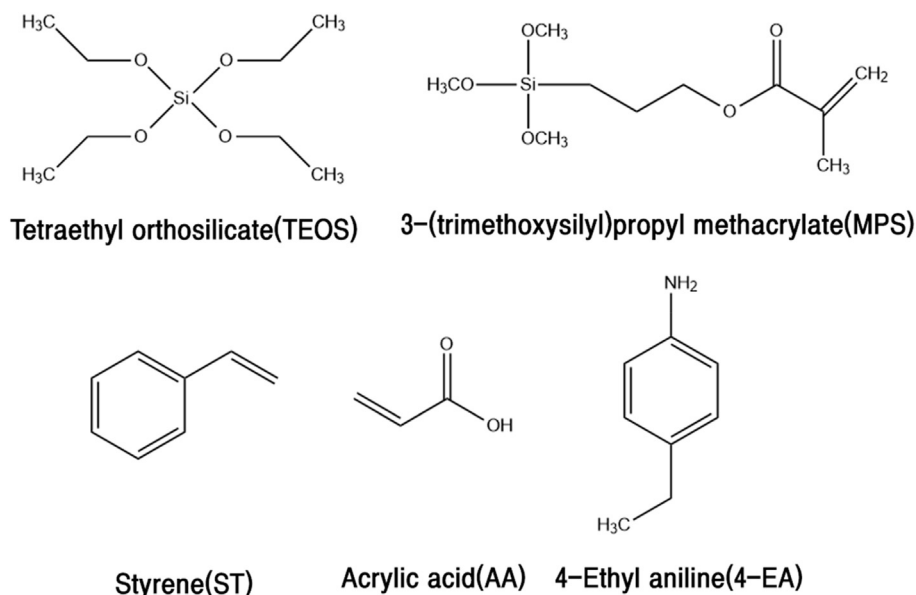


Fig. 1. Chemical Structures of the used materials.

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