



# Double imprinted photoresponsive polymer for simultaneous detection of phthalate esters in plastics

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## ABSTRACT

A double-phthalate-ester imprinted photoresponsive polymer was fabricated for simultaneous detection of phthalate esters. Specifically, three azobenzene derivatives with different steric characteristics (0, 2, and 4 methyl substituents at the *ortho* position) were used as functional monomers, supported by ZnO nanoscale support rods. Dibutyl phthalate and dicyclohexyl phthalate esters were used as double templates. The three photoresponsive molecularly imprinted polymers were fabricated with a triethanolamine trimethacrylate ester cross-linker, and were characterized by ultraviolet–visible absorption, Fourier-transform infrared spectroscopy, scanning and transmission electron microscopy, and N<sub>2</sub> adsorption–desorption analysis. Steric hindrance affected both photoresponsive properties and binding properties. As the steric hindrance increased, the *trans*→*cis* rate constant and the binding capacities decreased. Hence, the polymer with the least steric hindrance was used for the simultaneous detection of phthalate esters in plastic cups and toys. The doubly imprinted polymer was more effective for detection or extraction of the phthalate esters than was a single-phthalate-ester imprinted polymer.

## 1. Introduction

Phthalate esters are commonly used in industry as plasticizers, additives, and solvents [1]. The freely mobile plasticizer in packaging or bottling materials can migrate into food and beverages, including drinking water [2,3]. Because high doses of phthalate esters cause adverse effects on human health [3–7], monitoring and detection of phthalate esters in diverse plastics are needed.

Molecularly imprinted polymers (MIPs) are generally fabricated by copolymerization of a monomer and a cross-linking agent in the presence of a template molecule [8–15] or ion [16]. The subsequent removal of the template provides specific recognition sites with the shape, size, and functionality of the target templates [8]. Previous reports for phthalate ester targets utilized single phthalate ester templates [17–21] or single dummy templates [7,22]. These MIPs exhibited higher selectivity for the template than for its structural analogs [17,18]. However, several phthalate esters may be used in plastics. Double- and multi-template imprinted polymers were reported to exhibit better molecular recognition and a higher binding capacity for these templates [23–25]. This technique is well suited for detection of multiple phthalate esters in a plastic product.

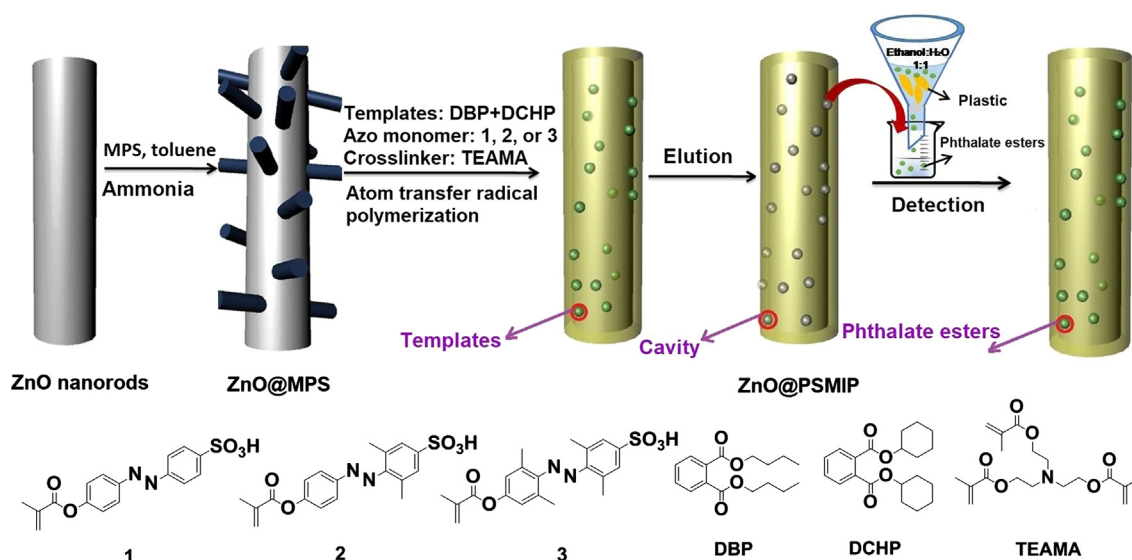
“Smart” MIPs can respond to external stimuli such as pH [25,26],

temperature [27,28], magnetic fields [17,29–31], or light [8,25]. Photoresponsive MIPs have the advantages of a clean stimulus source that can be remotely controlled. Azobenzene and its derivatives are commonly used monomers for photoresponsive MIPs because they exhibit rapid and reversible photoisomerization [8]. Photoresponsive MIPs based on azobenzenes have been widely used in photo-controlled drug release and uptake [32,33], drug [34], metabolite determinations [35], food additives [36,37] and food pollutants [38,39], solid-phase extraction [40,41], molecular recognition [42], and catalysis [43,44]. However, little is known on steric hindrance effects of azobenzene on photoresponsive MIPs.

In order to develop a photoresponsive MIP with good photoresponsive properties for simultaneous determination of phthalate esters in plastics, here, two phthalate esters [dicyclohexyl phthalate (DCHP) and dibutyl phthalate (DBP)] were used as double templates in three azobenzene derivative monomers (1, 2, and 3) with different steric characteristics (0, 2, and 4 *ortho*-methyl substituents, respectively, Scheme 1). The substrate consisted of ZnO nanorods. Using triethanolamine trimethacrylate (TEAMA) as the cross-linker, three photoresponsive surface molecularly imprinted polymers (ZnO@PSMIP<sub>1</sub>, ZnO@PSMIP<sub>2</sub>, and ZnO@PSMIP<sub>3</sub>) were fabricated. The effects of steric hindrance was studied, and the one with best properties was

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used for the simultaneous determination of phthalate esters in plastic cups and toys.

## 2. Experimental

### 2.1. Materials and instruments

Benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), diphenyl phthalate (DPhP), diisobutyl phthalate (DIBP), dicyclohexyl phthalate (DCHP), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), ethyl  $\alpha$ -bromoisobutyrate (98%), copper(I) bromide (99%), hexadecyltrimethylammonium bromide (CTAB), sodium hydroxide, zinc nitrate, 3-methacryloxypropyltrimethoxysilane (MPS), *N,N*-dimethylaminopyridine, triethanolamine, triethylamine, 3,5-dimethyl phenol, 2,6-dimethyl phenol, and methacrylic anhydride were purchased from Aladdin Co. Ltd., Shanghai, China. All chemical reagents and solvents were purchased from commercial suppliers and used without further purification. The crosslinker TEAMA and the azobenzene monomers (1, 2, 3) were synthesized according to previous methods [32,34,40,45].

Morphologies of the ZnO@PSMIPs (ZnO@PSMIP<sub>1</sub>, ZnO@PSMIP<sub>2</sub>, ZnO@PSMIP<sub>3</sub>) were characterized with scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM, Philips CM200 FEG, Dutch). The latter was operated at 200 kV. Fourier transform infrared (FT-IR) spectra, using a KBr pellet, were acquired with a Perkin-Elmer Model GX Spectrometer. Thermogravimetric analysis (TGA) was performed with a SDT Q600 thermal analyzer (USA) at a heating rate of 10 °C min<sup>-1</sup> up to 600 °C under flowing N<sub>2</sub> (100 ml min<sup>-1</sup>). Specific surface areas and pore diameters were respectively calculated by Brunauer-Emmett-Teller and Barrett-Joyne-Halenda models using N<sub>2</sub> adsorption-desorption data obtained at 77 K on an Autosorb-1 apparatus (Quantachrome, USA).

### 2.2. Synthesis of ZnO@PSMIPs

The synthesis of ZnO@PSMIPs involved three main steps (Scheme 1).

The ZnO and ZnO@MPS nanorods were synthesized according to a previous report [35].

The ZnO@PSMIP<sub>1</sub>, ZnO@PSMIP<sub>2</sub>, and ZnO@PSMIP<sub>3</sub> nanorods were fabricated via atom-transfer radical polymerization [46,47]. The following uses ZnO@PSMIP<sub>1</sub> as an example. To a 50-ml flask, ZnO@MPS nanorods (0.12 g) were dispersed in dimethyl formamide (10.0 ml) and

deionized water (10.0 ml) with ultrasonic stirring for 5 min. DCHP (9.5 mg, 29  $\mu$ mol), DBP (8.0 mg, 29  $\mu$ mol), and azobenzene monomer 1 (80.0 mg, 230  $\mu$ mol) were then sequentially introduced, and a clear homogeneous solution was obtained after the mixture was stirred at ambient temperature for 3 h in the dark. The solution was bubbled with nitrogen, to which TEAMA (253.8 mg, 5.0 mmol), PMDETA (17.3 mg, 0.10 mmol), CuBr (14.3 mg, 0.10 mmol), and ethyl  $\alpha$ -bromoisobutyrate (29.3 mg, 0.15 mmol) were sequentially added. The mixture was then stirred at 65 °C for 24 h. The ZnO@PSMIP<sub>1</sub> was collected by centrifugation and dried under vacuum at 50 °C for 24 h. Removal of templates was performed by Soxhlet extraction with 200 ml of a methanol/acetic acid mixture (8:2, v/v) for 48 h, followed by 200 ml of methanol for 12 h in the dark, and drying to a constant weight under vacuum at 40 °C. Azobenzene monomers 2 and 3 were respectively used to fabricate ZnO@PSMIP<sub>2</sub> and ZnO@PSMIP<sub>3</sub> using the same method. ZnO@PSMIP<sub>4</sub> was fabricated with the same method using DBP as the mono-template and functional azobenzene monomer 1 as a monomer.

The ZnO photoresponsive non-imprinted polymers ZnO@PSNIPs (ZnO@PSNIP<sub>1</sub>, ZnO@PSNIP<sub>2</sub>, ZnO@PSNIP<sub>3</sub>) were prepared in an identical fashion, except that no template was used during the polymerization.

### 2.3. Spectroscopic characterization and photoisomerization

Spectroscopic characterizations of the azobenzene monomers (1, 2, 3) and their corresponding ZnO@PSMIPs were performed in ethanol and deionized water (1:1, v:v) in a 1.0-cm-path-length quartz cuvette at room temperature on an UV-4802 spectrophotometer (UNICO (Shanghai) Instruments Co. Ltd., China). Suspensions of ZnO@PSMIPs were irradiated at 365 nm and then at 440 nm under magnetic stirring. Kinetics of the photoisomerization (*trans/cis*) were analyzed by Eq. (1) [36].

$$\ln \frac{(A_0 - A_\infty)}{(A_t - A_\infty)} = kt \quad (1)$$

in which  $A_0$ ,  $A_t$ , and  $A_\infty$  were the absorbances of the azobenzene chromophores at their corresponding wavelength at time 0,  $t$ , and at the photo-stationary stage, respectively, and  $k$  was the rate constant of the photoisomerization process.

### 2.4. Binding characteristics of ZnO@PSMIPs

To investigate the adsorption dynamics of ZnO@PSMIPs, 10.0 mg of

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