

Synthesis of Novel Photoresponsive Molecularly Imprinted Polymer Microspheres with Special Binding Properties

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ABSTRACT: An azobenzene-containing molecularly imprinting polymer microsphere with photoresponsive binding properties toward 2,4-dichlorophenoxyacetic acid (2,4-D) was successfully prepared via silica surface polymerization. The number-average diameters of silica and imprinting polymer microsphere are 0.5 and 0.7 μm , respectively. The static adsorption, binding and selectivity experiments were performed to investigate the adsorption properties and recognition characteristics of the polymers for 2,4-D. The equilibrium adsorptive experiments indicated that 2,4-D-SMIP (surface molecularly imprinted polymers) has significantly higher adsorption capacity for 2,4-D than its nonimprinted polymers (SNIP). The binding constant K_d and apparent maximum number Q_{max} of the imprinted polymer were determined by Scatchard analysis as 0.054 mmol L^{-1} and 0.167 mmol g^{-1} , respectively. The result of photo-regulated release and uptake of 2,4-D experiment demonstrated that azo-containing SMIP can make use of light and change it into mechanical properties to release and take up the template molecules. It means that the SMIP can be controlled by light. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 869–876, 2013

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INTRODUCTION

Recent years, molecularly imprinted materials had received extensive attention. Molecularly imprinted polymers (MIPs) are artificially synthesized materials with prearrangement of their structure to imitate natural molecular recognition.¹ The artificial receptors of molecular imprinted polymers can duplicate tailor-made molecular recognition binding sites.² Because of their prearrangement of structure, molecularly imprinted polymers have many potential applications and advantages in many fields, including separation, chemical sensors, antibody mimics, biomimetic catalysis, drug delivery, drug development, and so on.^{3–9}

Although tremendous progress has been made in the molecular imprinting field, there are still many challenges, especially the elution of template and the design of advanced MIP materials imitating the biological receptors.^{10–12} The biological receptors have many interesting characteristics such as their high responsive toward external stimuli such as the temperature, pH and so on. The developed MIPs are normally difficult to deform to modify their binding properties because a high fraction of crosslinker is usually used in molecular imprinting to stabilize the binding sites. Recently, the rational use of certain co-functional monomers and azobenzene monomers in molecular

imprinting, together with the appropriate choice of the amounts of the crosslinkers, made it possible to obtain responsive MIPs toward different stimuli such as temperature, pH, and light.^{13,14}

Photoirradiation is one of the most frequently adopted external stimuli for stimuli-responsive materials (SRMs). As clean energy, light can be manipulated precisely, rapidly and remotely. Numerous well-established photoresponsive molecular systems were available.^{15–17} Among the PH, temperature, ionic, solvent composition, and photoirradiation,¹⁸ the UV–vis photoirradiated trans–cis isomerization of azobenzene and its derivatives are probably the most extensively studied. Trans–cis photoisomerization of azobenzene brings great changes in geometry and dipole moment to chromophore.^{19,20}

Surface imprinting technology²¹ that controls templates to be situated on the surface or in the proximity of material surface had received significant attention over the past few years. The imprinted materials prepared with these approaches had significant advantages compared to the materials by traditional imprinting technology, such as complete removal of template molecules, good accessibility to the target species, controllable size, regular shape, and good recyclable performance.¹

In this article, a new photoresponsive imprinting polymer was prepared via the surface imprinting technique by using modified

silica particles as supporting materials, azo-containing compounds as functional monomers, EGDMA as crosslinker, and AIBN as initiator. To investigate the properties of imprinted particles, a series of adsorption studies were conducted. The results demonstrated that 2,4-D surface molecular-imprinted polymer(2,4-D-SMIP) had quicker separation, higher selectivity, faster binding kinetics and better adsorption properties than SNIP. The 2,4-D-SMIP materials were able to release and take up 2,4-D upon irradiation at 365 and 440 nm, respectively.

EXPERIMENTAL

Materials and Reagents

Materials. 3-Iodopropyltrimethoxysilane was purchased from Sigma, USA.. 2,4-D, p-acetylphenylamine, Ethylene glycol dimethacrylate (EGDMA) were purchased from Shanghai Aladdin chemical factory (Shanghai, China) .(4-chloro-2-methylphenoxy)acetic acid (MCPAc), Phenoxyacetic acid (POAc) were obtained from J & K Chemical Limited (Beijing, China). 2, 2'-Azobisisobutyronitrile (AIBN) was purchased from Shanghai NO.4 reagent and H. V. Chemical Co. (Shanghai, China). Tetraethoxysilane (TEOS), was purchased from Alfa Aesar Chemical Company. EGDMA was distilled under vacuum before use. AIBN was purified by recrystallization from ethanol. All other reagents used were all of analytical chemical grade.

Instruments. The instruments used in this study were as follows: UV-2450 Ultraviolet-visible Spectrophotometer (Shimadzu, Japan); SHZ-82 constant temperature bath oscillator (Zhongda Instrument, Jiangsu, China); KQ2200DB ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Jiangsu, China); YXJ-II high-speed centrifuge (Zhongda Instrument, Jiangsu, China); fourier transform infrared spectra (FT-IR) (Nicolet, America). The scanning electron microscope (SEM) micrographs of the sorbents were obtained at 20.0 kV on a JSM-5610LV scanning electron microscopy (JEOL, Japan). The ¹H NMR spectra were recorded by a AV-400 spectrometer (Bruker, Germany). Elemental analysis was carried out by a PerkinElmer 2400 elemental analyzer.

Synthesis of Azo-Containing Functional Monomer and 2,4-D-SMIP

Synthesis of 4-Hydroxy-4'-acetylazobenzene. To 10 mmol of p-acetylphenylamine, 2.7 mL of concentrated hydrochloric acid and 20 mL of water were added. The mixture was placed in the ice bath. To the cooled mixture, a solution of 10 mmol of sodium nitrite in 3 mL of water was added dropwise and the resulting solution was stirred at a temperature between 0 and 5°C within 15 min. Subsequently, the solution containing 10 mmol of phenol in 6 mL of methanol was added dropwise. The reaction was stirred for 30 min and was neutralized with sodium acetate. After the temperature was raised to room temperature, the mixture was stirred for 1 h.²² The product was filtered, washed with large amount of water and dried under vacuum at 50°C. (yield: 81%) ¹H NMR (DMSO-d₆): δ_H 2.5 (s, 3H, -CH₃), 6.95-7.85 (m, 4H, Ph); 7.9- 8.12 (m, 4H, Ph) 10.45 (s, 1H, -OH); m/z 240 [M-H]⁻; Elemental analysis results (calculated (found)): C, 68.90 (69.9); H, 6 (5.03); N, 10.96 (11.66); O, 14.02 (13.32); IR (KBr), ν/cm⁻¹: 845.57, 1434.09, 1470.30, 1504.46, 1591.96, 333.27

Synthesis of Silica Gel Particles

Silica gel particles were obtained using a Stöber method.²³ To a solution of 0.65 mL of TEOS in 11.35 mL of ethanol, 3 mL of a 16.7% (which was obtained by adding 5 mL water into a 15 mL 25% ammonia solution) ammonium hydroxide solution was added rapidly. The resulting solution was stirred vigorously with magnetic stirrer for 24 h and a suspension of silica gel particles was obtained ethyl alcohol and ammonium hydroxide were removed under vacuum and particles were kept in the aqueous suspension. In order to increase the content of -OH, silica particles were activated by dipping into 6 mol L⁻¹ hydrochloric acid for 24 h, then filtered and washed repeatedly with distilled water. Such treated silica particles were dried at 110°C to constant weight. The diameter of the silica gel is 500 nm. IR (KBr), ν/cm⁻¹: 1101.65, 947.35, 3423.68. Elemental analysis results: Si, 76.03; O, 23.91

Synthesis of 4-(3-(Trimethoxysily)propoxy)benzaldehyde

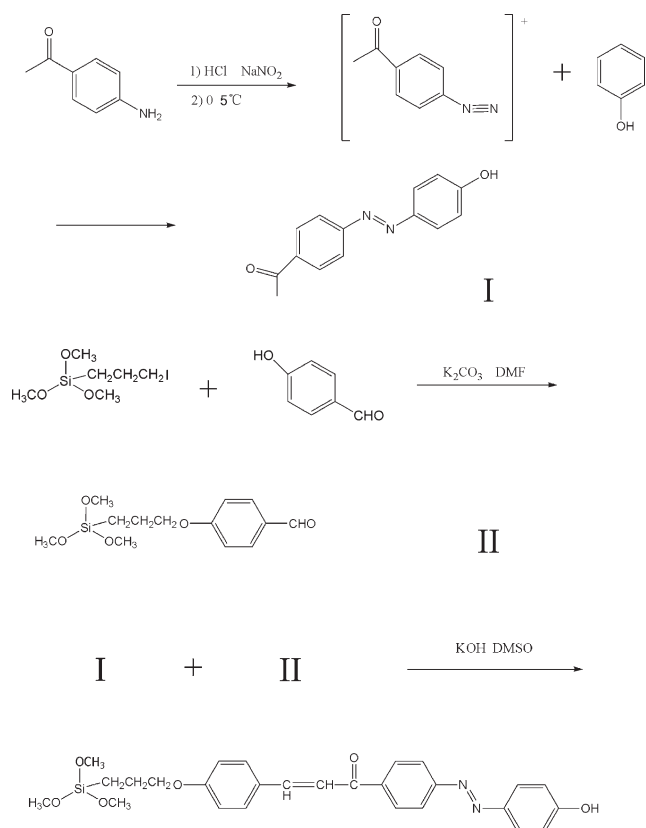
A mixture of p-hydroxybenzaldehyde (0.5 mmol), 3-iodopropyltrimethoxysilane (0.5 mmol) and K₂CO₃ (0.148 g) were placed in dry DMF (15 mL). After 16 h at 80°C, the reaction mixture was washed with a certain amount of water, the white product was obtained. The product was dried under vacuum at 50°C for 24 h. (yield: 41%). ¹H-NMR (DMSO-d₆): δ_H 0.58 (t, 2H, -CH₂-), 1.75 (m, 2H, -CH₂-), 3.32 (s, 9H, -OCH₃); 3.92 (t, 2H, -CH₂-); 7.0 (d, 2H, Ph); 7.78 (d, 2H, Ph) 9.87 (s, 1H, -CHO); m/z 284 [M-H]⁻; Elemental analysis results (calculated (found)): C, 59.01 (59.91); H, 6 (7.09); O, 27.94 (28.13); Si 12.06 (9.88); IR (KBr), ν/cm⁻¹: 2930, 1660, 1590, 1470, 1430, 1250, 1140, 1010, 845.

Synthesis of Azo-Containing Functional Monomer

The azo-containing functional monomer was obtained by aldol condensation.²⁴ 1mmol 4-hydroxy-4'-acetylazobenzene was placed in dry DMSO, and 2mmol KOH aqueous was added. Aqueous PH was adjusted to 13-14, then the mixture aqueous were stirred about 2 h. Subsequently a solution of 4-(3-(trimethoxysily)propoxy)benzaldehyde was added dropwise. The mixture was kept at room temperature for 8 h and then it was acidified with 10% HCl aqueous and washed with a certain amount of water. The product precipitate out as solid. The obtained solid was filtered and washed with water, dried, and purified by recrystallization. (yield: 47%). ¹H-NMR (DMSO-d₆): δ_H 0.53 (t, 2H, -CH₂-), 1.77 (m, 2H, -CH₂-), 3.30 (s, 9H, -OCH₃); 3.92 (t, 2H, -CH₂-); 7.0 (m, 4H); 7.68 (m, 5H); 7.9 (d, 1H); 8.1 (m, 4H); 10.21 (s, 1H, -OH). m/z 506 [M-H]⁻; Elemental analysis results (calculated (found)): C, 63.21 (64.01); H, 6 (5.97); O, 18.15 (18.95); Si 5.21 (5.54); N, 5.62 (5.53); IR (KBr), ν/cm⁻¹: 792.92, 1103.62, 1408.08, 1480.24, 1506.58, 1602.82, 1669.36, 3439.36.

Introduction of Vinyl Groups on the Surface of Silica Particles

The activated silica (AS) was obtained by drying in vacuum at 60°C to eliminate surface water and activate the surface silanol groups for silanization. Dried activated silica (0.96 g) was dispersed in absolutely dry toluene (50 mL) in round bottomed flask under the atmosphere of nitrogen with continuous stirring. Subsequently, azo-containing functional monomer (0.24 mmol) and triethylamine (1 mL) were added into the flask. The



Scheme 1. Preparation of the functionalized azobenzene monomer.

reaction was refluxed and stirred at 90°C for 24 h. The beads were then separated from the mixture via filtration and washed with toluene, acetone, and methanol, respectively. The product was dried under vacuum at 80°C for 24 h. IR (KBr), ν/cm^{-1} : 1101.65, 3423.68, 1669.36, 1602.82, 1506.58, 1408.08.

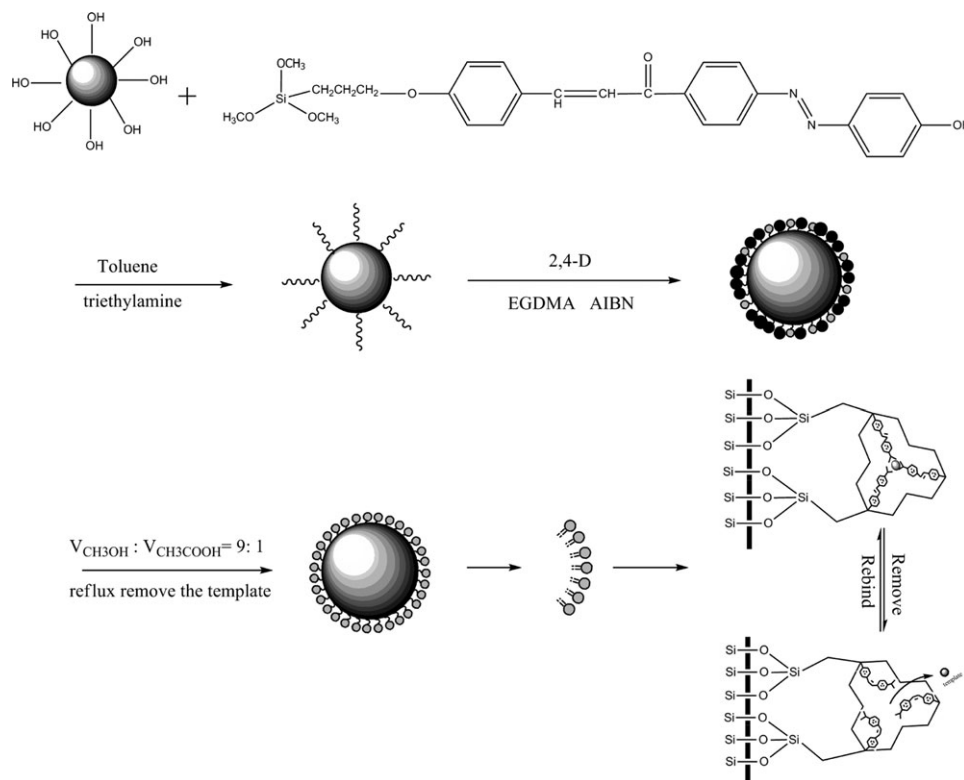
Synthesis of 2,4-D-SMIP and Nonimprinted Polymers (SNIP)

The template 2,4-D (0.23 mmol) was dissolved in acetonitrile and the silica modified with azo-containing functional monomer (0.16 g) was added in acetonitrile (35.0 mL) in a glass vial (150 mL volume). After stirring for 3 h at room temperature, EGDMA (2 mmol), AIBN (40mg) were added into the solution. The polymerization was thermal initiated in a water bath at 50°C for 6 h, and then continued at 60°C for 18 h. All the experiments were operated in the dark. The product particles were washed repeatedly with a mixed solvent of methanol and acetic acid ($V_{\text{CH}_3\text{OH}} : V_{\text{CH}_3\text{COOH}} = 9 : 1$) to remove the template 2,4-D and the remaining monomer. 2,4-D-SMIP was obtained by filtration and drying. As a control, SNIP were prepared in the absence of the template and treated with the same method. Both materials were stored at room temperature in the dark.

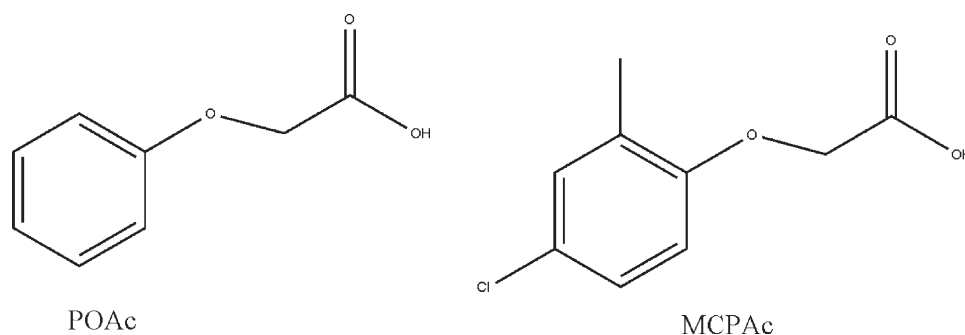
The synthesis process of functional monomer and SMIP was shown in Schemes 1 and 2.

Photochemical Isomerization Test

The photochemical isomerization of azo-containing functional monomer was investigated by irradiating firstly with a 365nm UV lamp and then with a 440 nm visible light lamp. All



Scheme 2. Preparation of 2,4-D-SMIP and the photoregulated uptake and release of 2,4-D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]



Scheme 3. The related test compounds of the template.

photoisomerization studies were performed with 1.0 mg of azo-containing functional monomer in 5.0 mL of methanol.

Photoregulated Release and Take Up Studies

The studies on the photoregulated release and uptake of the template 2,4-D and its analogues by SMIP/SNIP microspheres were performed by alternately switching on and turning off the UV light irradiation on the mixtures of SMIP/SNIP microspheres and a solution of analytes: A series of samples were prepared by adding 10.0 mg of SMIP/SNIP microspheres and a mixed solution of 2,4-D, MCPAc and POAc in methanol into plastic tubes (5 mL), respectively, which were subsequently sealed and put into an incubator equipped with a 365 nm UV lamp (16 W). After their incubation at room temperature in the dark for 16 h, one sample was taken out from the incubator and centrifuged to determine the amounts of analytes bound by the SMIP/SNIP microspheres (by HPLC). The UV light was then switched on in the incubator to irradiate the remaining samples immediately after the first sample was taken out. After 6 h of UV light irradiation with incubation for the samples at room temperature, the UV light was switched off and the second sample was taken out for the determination of the binding of the analytes. The remaining samples were then incubated at room temperature in the dark for 16 h, and the third sample was taken out for the determination of the binding of the analytes. The above photoswitching procedures (i.e., UV light on for 6 h and UV light off for 16 h alternately) were repeated until all of the samples were measured.

The studies on the photoregulated release and uptake of the template 2,4-D, MCPAc and POAc by SMIP/SNIP microspheres irradiation with 365 nm UV lamp and 440 nm visible light were carried out similarly (440 nm for 3 h and 365 nm for 6 h). The result was shown in Figure 7.

Binding Experiments

The capacity of the adsorbent for 2,4-D was determined in batch mode, involving adsorption dynamics. A certain amount of 2,4-D-SMIP (50.0 mg) or SNIP (50.0 mg) was accurately taken into a 20 mL brown bottle, and then 10 mL of 2,4-D solution in methanol with different concentrations were added. The mixture was agitated in a shaken bed. At different time intervals, the mixture was centrifuged at 4000 rpm for 10 min, and the supernatant solutions were collected. Finally, the concentrations of 2,4-D were determined by UV spectrophotometer.

The adsorption quantity (Q), which was defined as mmol of template molecule 2,4-D bound per gram polymers were calculated by the following eq. (1).

$$Q = \frac{(C_0 - C) \cdot V}{W} \quad (1)$$

where Q (mmol g^{-1}) is the adsorbed amount of 2,4-D, C_0 (mmol L^{-1}) is the initial concentration of 2,4-D, C (mmol L^{-1}) is the supernatant solution's concentration of 2,4-D, V (L) and W (g) are the volume of the solution and the amount of the polymer, respectively.

Selectivity Experiments

To examine the recognition selectivity of 2,4-D-SMIP particles toward 2,4-D, POAc and MCPAc (Scheme 3) were selected as a contrast substance in this study. The adsorption capacity of the template or the competition species was calculated as above. The distribution coefficient for each substance was calculated according to eq. (2),

$$K = C_p / C \quad (2)$$

where K represents the distribution of 2,4-D (mL g^{-1}), C_p (mmol g^{-1}) is the equilibrium combining quantity, and C (mmol mL^{-1}) is the equilibrium concentration.

RESULTS AND DISCUSSION

Characteristics of SMIP

The SEM photographs reveal that almost perfectly spherical silica gel particles are formed with very smooth surface [Figure 1(a)]. The particles are very uniform in size with no smaller structures agglomerated on their surface.²⁵ Comparing a with b can clearly indicate the surface of silica been cladding by a layer of film. It can be seen from the two SEM images that the shape of the polymer was uniform to that of the silica particles and the size of the polymer is bigger than that of silica particles. The possible reason was that the thickness of polymerization membrane on the surface of silica particles was very well-distributed.

FTIR spectra of the four kinds of particles modified SiO_2 , $\text{SiO}_2(\text{AS})$, SMIP, and SNIP were determined with KBr pellet method (Figure 2), and their FTIR spectra were shown as a, b, c, and d in Figure 2, respectively. The observed features around 1078 and 974 cm^{-1} indicated Si—O—Si and Si—O—H stretching

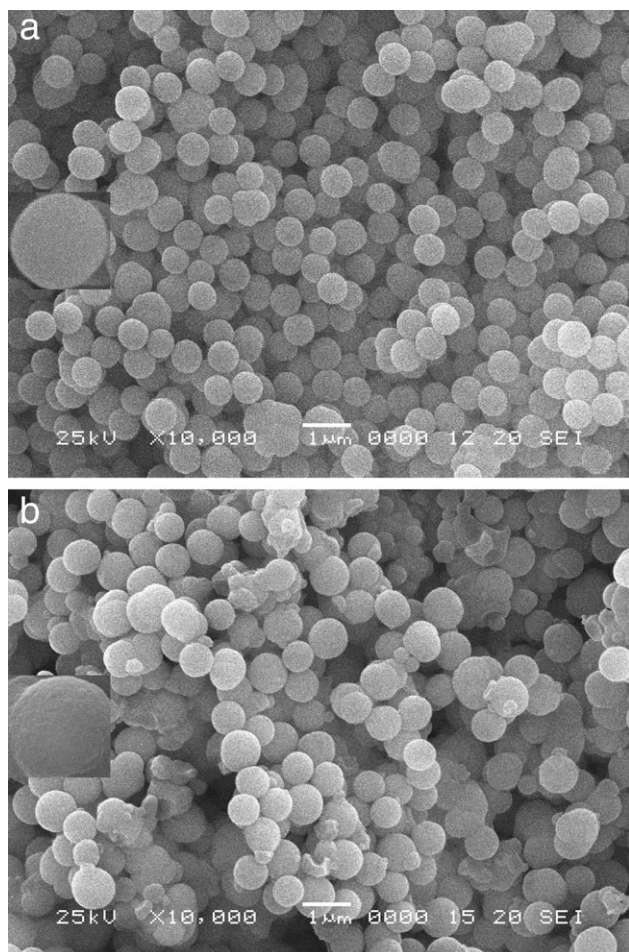


Figure 1. SEM micrographs: (a) silica particle; (b) SMIP.

vibrations, respectively. The band around 800.29 resulted from Si—O vibrations. When compared with the spectra of a and b, the stretching vibration of O—H appearing at around 3439.36 cm^{-1} indicated that silanol groups were not silanized com-

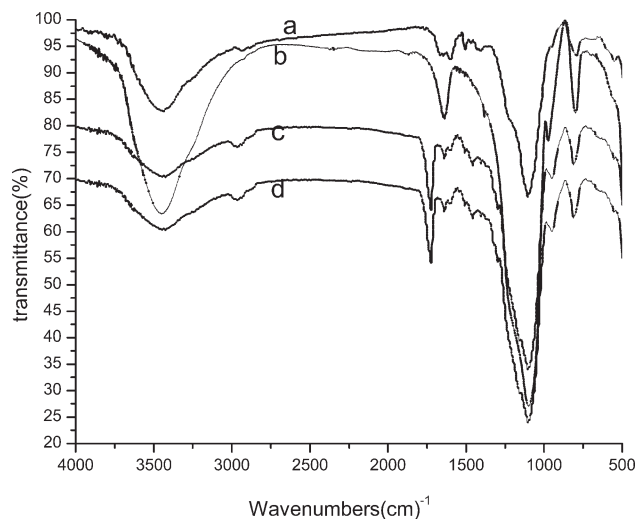


Figure 2. FTIR spectra of modified SiO_2 (a), SiO_2 (b), SMIP(c), SNIP(d).

pletely. The vinyl groups introduced onto the surface of the activated silica by immobilization of a long chain group played a space-shield effect on the surrounding silanol groups, which was why so many silanol groups were still not bonded.

The spectrum of MD- SiO_2 (modified SiO_2) showed the new bands at 2920 cm^{-1} and 1669.36 cm^{-1} , which were attributed to the stretching vibration absorption of saturated C—H band and carbonyl C=O band, respectively. Because of polymerization crosslinking process, the carbonyl (C=O) absorption of c moved to 1723.16 cm^{-1} . The infrared data indicated that the surface of SiO_2 had been modified by silane reagent. Imprinted and nonimprinted material showed similar locations and appearances of the major bonds. This result suggested that the polymerization had been successfully carried out.

Adsorption Capacity of SMIP and SNIP of 2,4-D and Scatchard Analysis

The template recognition ability of 2,4-D-SMIP was studied in static equilibrium binding experiments. The adsorption capacities of the polymers for 2,4-D with diverse initial concentration of the template were shown in Figure 3.

It can be seen from Figure 3, 2,4-D-SMIP shows a higher capacity for 2,4-D than SNIP at either low or high concentration. The binding capacity of the polymers increased gradually with increase of 2,4-D concentration. The difference of adsorption between 2,4-D-SMIP and SNIP was getting larger with the increasing concentration of the template. The possible reason was that the low concentration of 2,4-D was not enough to saturate the specific binding cavities. The results indicated that the two polymers were significant different in their space-structure. The nonselective physical adsorption occurred between SNIP and 2,4-D. The 2,4-D-SMIP adsorbed much more template molecules than that of SNIP because 2,4-D-SMIP had generated specific recognition sites in imprinting cavities.

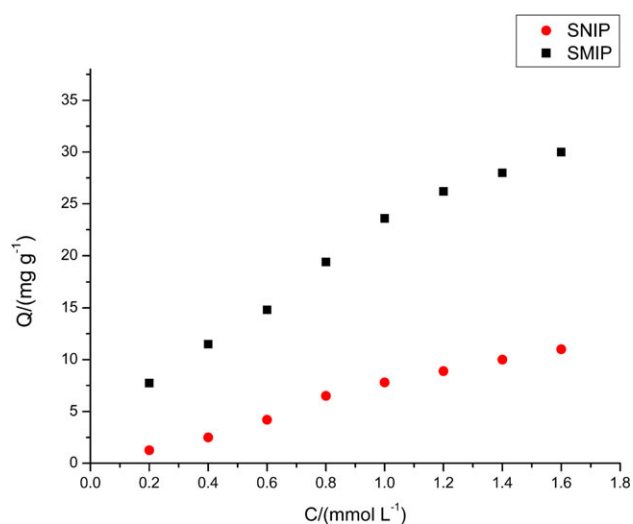


Figure 3. Adsorption isotherm of 2,4-D-SMIP and SNIP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

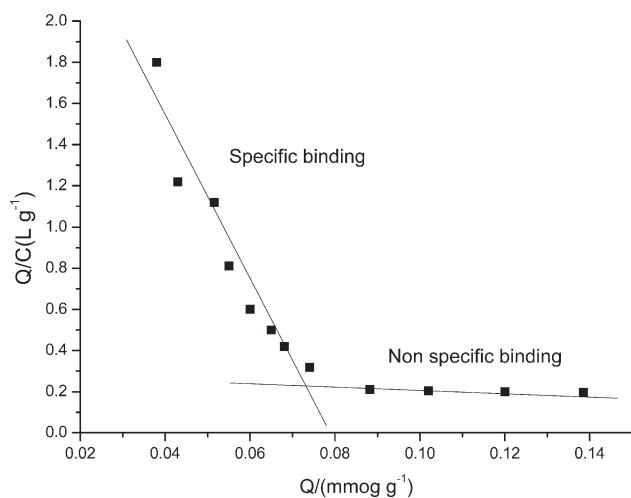


Figure 4. Scatchard curves of SMIP for 2,4-D.

It was hypothesized that the binding sites which were complementary in size, geometry and functional groups orientation to the 2,4-D were successfully produced in the SMIP. To prove this hypothesis, the Scatchard equation was used to further evaluate the SMIP's properties. The equation is as follows:

$$\frac{Q}{C_e} = \frac{Q_{\max} - Q}{K_d}$$

where Q_{\max} (mmol g^{-1}) represents the maximal chemical binding capacity of the SMIP for 2,4-D, Q (mmol g^{-1}) was the equilibrium adsorption capacity of 2,4-D bound to the polymers, C_e (mmol L^{-1}) was the equilibrium concentration of 2,4-D in the solution and K_d (mmol L^{-1}) was the dissociation constant. Scatchard curves were obtained by taking Q as the x -coordinate and Q/C_e as the y -coordinate.

The chemical binding characteristics of the SMIP for 2,4-D obtained using the Scatchard equation are shown in Figure 4. The study was carried out in the dark. It can be observed that Figure 4 exhibits a nonlinear relationship. The plot shows two intersecting lines with different slopes corresponding to the high- and low-affinity populations of binding sites. The relatively low binding strength is likely to be caused by the interruption of the hydrogen-bond interactions by the solvent media. It called nonspecific binding. The affinity of the imprinted receptor sites in the SMIP material for 2,4-D is probably based exclusively on host-guest shape recognition. From the slope and the intercept of the Scatchard plots, the specific binding K_d and Q_{\max} have been calculated to be $0.054 \text{ mmol L}^{-1}$ and $0.167 \text{ mmol g}^{-1}$.

The Binding Selectivity of the SMIP and SNIP

The binding selectivity of the SMIP and SNIP microspheres was studied by measuring their competitive binding capacities toward 2,4-D and two structurally similar compounds POAc and MCPAc (Scheme 3), which have the same functionality (i.e., carboxyl group) but a little difference either in the distance between the functional group and the benzene ring or in the numbers of substituents on the benzene ring.

As shown in Figure 5, the SMIP exhibited significantly higher binding capacities toward 2,4-D than POAc and MCPAc, the binding capacities of MCPAc is higher than POAc. The reason may be that the structure of MCPAc is similar to 2,4-D. It still can be seen clearly that the SNIP have a certain adsorption of those analytes, but the difference is not large. Due to the higher selectivity of the SMIP, it can be applied in sample treatment.

Photoisomerization Properties of the azo-Containing Functional Monomer

The UV-vis spectrum of the azo-containing functional monomer is dominated by a peak at 316nm and a small shoulder at 432 nm. These can be assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the azobenzene chromophore, respectively.²⁶ Figure 6 shows the UV-vis spectroscopic responses of the azo-containing functional monomer at 365 nm and 440 nm. Irradiating at 440 nm, the less thermodynamically stable *cis*- azo-containing functional monomer transformed the spectral changes and at 365 nm it transformed slowly from *trans* to *cis*. These spectral changes are attributed to the *trans*→*cis* isomerization of the azobenzene chromophore. Putting the azo-containing functional monomer in dark, it can be changed *cis* to *trans* slowly. The possible reason is that the *trans* conformation is more stable than the *cis* conformation. All of this indicates that the photoinduced isomerization is reversible.

Photoregulated Release and Uptake of 2,4-D

Figure 7 shows the change of the binding capacities of 2,4-D-SMIP and SNIP microspheres toward 2,4-D and its analogues MCPAc and POAc under repetitive photoswitching conditions. As expected, the SMIP microspheres showed significantly higher binding capacities toward 2,4-D than toward MCPAc and POAc, revealed once again the high selectivity of the SMIP microspheres toward the template molecular. Irradiation at 365 nm caused a decrease in the amount of 2,4-D in the methanol solution. A majority of 2,4-D were released from the 2,4-D-SMIP material, leaving partially of the SMIP receptor sites still occupied by 2,4-D. This photoregulated release of bound 2,4-D from the SMIP material by 365 nm irradiation can be attributed to the photoinduced *trans*→*cis* isomerization of azobenzene chromophores in the SMIP receptor sites, resulting in a change

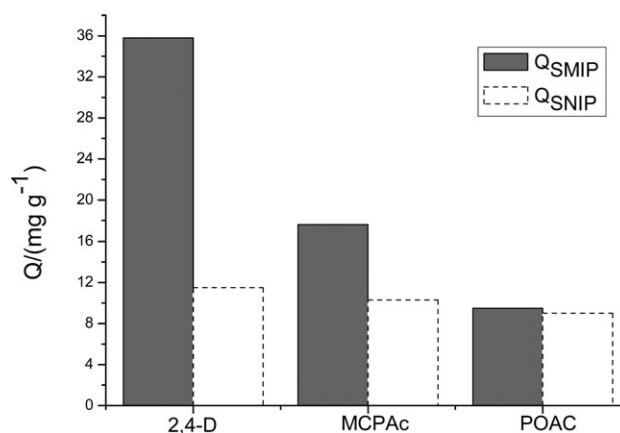


Figure 5. Selective bindings of the 2,4-D-SMIP and SNIP microspheres toward 2,4-D, MCPAc, POAc.

in the receptor geometry. The host-guest interaction become weakened, and the bound 2,4-D is released back into the solution. Irradiation of the SMIP material at 440 nm or in dark after the completion of the photoregulated 2,4-D release caused the uptake of 2,4-D back into the SMIP material. This near-quantitative uptake of the released 2,4-D is evidence of the reversibility of the receptor-site configuration and substrate affinity in the course of photoswitching of the azobenzene chromophores.

Repeating the photoswitching cycles resulted in the release and uptake of 2,4-D in quantities very similar to those of the previous cycles, which clearly demonstrated the reversibility of the binding site configuration and substrate affinity in the course of photoswitching of azo chromophores. Although the SMIP microspheres were still able to photoregulated release and uptake of the structural analogues of the template MCPAc and POAc, their amounts were significantly lower than that of 2,4-D under the similar experimental conditions. This indicated that

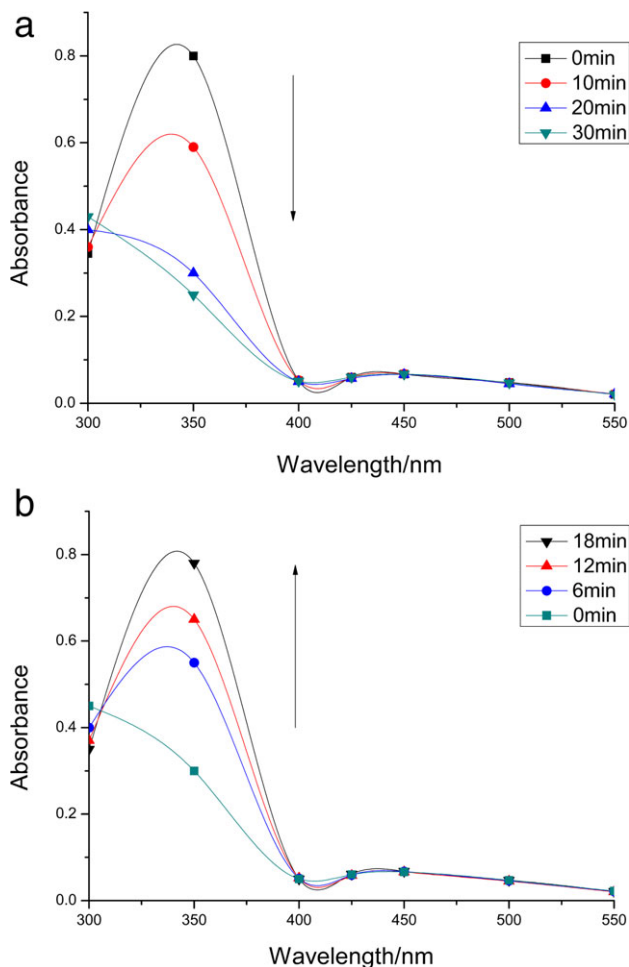


Figure 6. UV-vis spectroscopic responses of the photoisomerization of azobenzene monomer in Methanol:(a) trans-to-cis isomerization upon irradiation at 365 nm and (b) cis-to trans isomerization by irradiation at 440 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

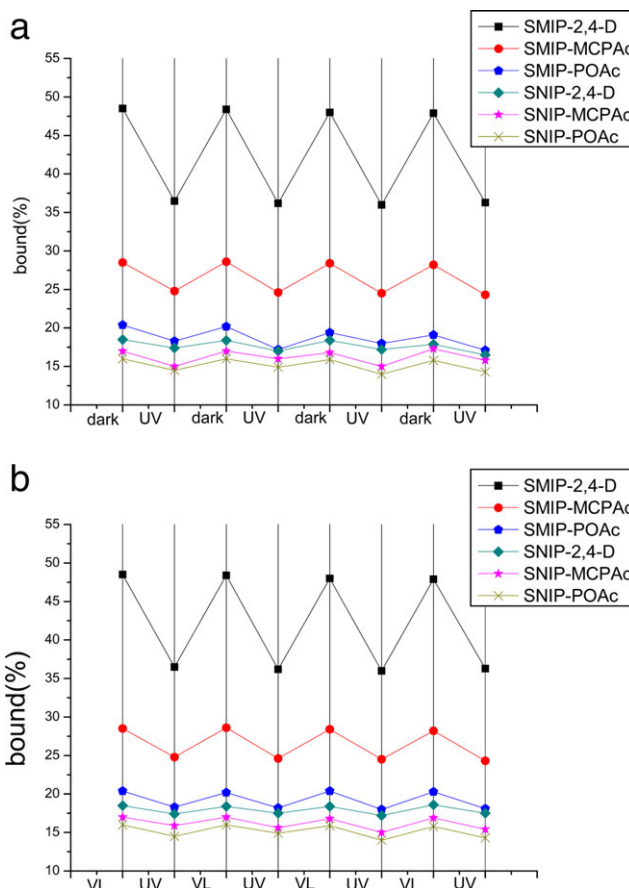


Figure 7. Photoregulated release and uptake of 2,4-D and its analogues MCPAc, POAc by the SMIP and SNIP microspheres under photoswitching conditions: a, irradiation with 365 nm UV light and dark; b, irradiation with 365 nm UV light and 440 nm visible light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the binding sites in the SMIP microspheres possessed a specific affinity for the template 2,4-D.

In order to further test the adsorption performance for targets between SMIP and SNIP under the photoresponsive. The adsorption performance of SNIP was also detected on the same condition. And the result was showed in the same Figure 7. It could be seen that the SNIP was able to photoregulated release and uptake of 2,4-D, but the extent was significantly lower than that of 2,4-D under the similar experimental conditions.

Based on the above results, it can be concluded that the 2,4-D-SMIP microspheres indeed show obvious photoresponsive template binding properties and the affinity of the binding sites in the SMIP microspheres toward the template molecular can be easily tuned by the simple photoswitching.

CONCLUSIONS

In this work, the photoresponsive SMIP microspheres with template binding properties were prepared via silica surface polymerization. The resulting photoresponsive SMIP microspheres showed obvious molecular imprinting effects toward the

template, fast template binding kinetics, and a high selectivity over structurally related compounds. They have exhibited obvious photoresponsive binding properties toward the template molecule. Because of the excellent performance of the SMIP, we foresee that such spherical photoresponsive SMIP particles have tremendous potentials in many applications.

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