SPECIAL ISSUE ARTICLE

A surface molecularly imprinted polymer as chiral stationary phase for chiral separation of 1,1′-binaphthalene-2-naphthol racemates

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Abstract

Acrylamide (AM) was copolymerized with ethylene glycol dimethacrylate (EGDMA) in the presence of (R)-1,1′-binaphthalene-2-naphthol (BINOL) as the template molecules on the surface of silica gel by a free radical polymerization to produce a chiral stationary phase based on the surface molecularly imprinted polymer (SMIP-CSP). The SMIP-CSP showed a much better separation factor ($\alpha = 4.28$) than the CSP based on the molecularly imprinted polymer (MIP-CSP) without coating on the silica gel ($\alpha = 1.96$) during the chiral separation of BINOL enantiomers by high-performance liquid chromatography. The influence of the pretreatment temperature and the content of the template molecule ((R)-BINOL) of the SMIP-CSP, and the mobile phase composition on the separation of the racemic BINOL were systematically investigated.

KEYWORDS
1,1′- binaphthalene-2-naphthol, chiral stationary phase, high performance liquid chromatography, in situ crosslinking polymerization, surface molecularly imprinted polymers

1 | INTRODUCTION

An axially chiral compound, such as (R)-1,1′-binaphthalene-2-naphthol (BINOL), plays an important role and has been widely utilized in metal-catalyzed or organo-catalyzed asymmetric reactions, and it also serves as a chiral host for the enantiomeric separation of racemic mixtures of "guest" compounds or as chiral reagents during the optical purity studies of the enantiomers by ^{1}H NMR. Furthermore, they have been extensively utilized in asymmetric catalytic synthesis, inclusion resolution, molecular recognition, and new material design.[1-7] For these reasons, the chiral separation of axial chiral compounds has been an attractive field.[8]

Huang et al.[9] reported a method of using a chiral dehydroabietic amine as a chiral resolution reagent for separating racemic BINOL, and explored the influences of the concentration, reaction time, and dosage on the chiral separation of BINOL. Lv et al.[10] synthesized a chiral selector, (8S,9R)-(−)-N-benzylcinchonidium chloride, for the chiral separation of a BINOL racemate. Zhang et al.[11] reported CSPs (Lux Amylose-2) based on starch derivatives for separating BINOL and its derivatives by high-performance liquid chromatography (HPLC) with a separation factor of 1.32. Zhan et al.[12] employed polysaccharide-based CSPs (Chiralcel OD-H) for chiral separating a BINOL racemate with a separation factor of 1.46. Ma et al.[13] reported the chiral separation of a BINOL racemate by utilizing an immobilized Chiralpak IC column with a separation factor of 1.48. Gao and colleagues[14] prepared a molecularly imprinted polymer monolith to realize the chiral separation of binaphthol enantiomers by the method of capillary electrochromatography. The influence of several parameters on the column permeability was investigated. The results showed that baseline separation was obtained with a resolution of the binaphthol enantiomers that reached 1.8. Liu et al.[15] reported that they observed the chiral separation of a series of C2-asymmetric bi-naphthyl compounds on the molecularly imprinted polymers using 1,1′-bi-2-naphthol as template and postulated that the specific hydrogen bonding interactions seemed to be the key factor to achieve the chiral separation.

Molecularly imprinted polymers (MIPs) possess a significant amount of 3D structure cavities which afford it a specific molecularly recognition ability.[16] Molecularly imprinted technology (MIT) has been widely studied and applied in molecular recognition and preferential adsorption due to this high selectivity for the template molecules. However, this method also had some disadvantages, such as a slow mass transfer, i.e., time-consuming, and has a poor chiral recognition. These are caused by the fact that most of the imprinted holes in the MIPs are distributed inside the material and this results in the lower adsorption and is distributed inside the material and this results in the lower adsorption and desorption rates during the separation procedure by HPLC. The surface molecularly imprinted technology (SMIT)[17-19] shows unique advantages in comparison to the MIT, since most of the imprinted holes are established on the surface of the support materials; therefore, SMIP can allow the faster mass transfer, more accessible sites, and a more effective separation capacity for template molecules than MIP.

In 1986, Okamoto et al. reported CSPs based on surface-coated silica gel particles with chiral selectors,[20] and they have now been widely used in various fields.[21-25] Inspired by this, an MIP coated silica gel (SMIP-CSP) was prepared in this study by the in situ copolymerization of AM with ethylene glycol dimethacrylate (EGDMA) in the presence of (R)-BINOL as the template on the surface of the silica gel, and the resulting materials were employed as the CSPs for the chiral separation of racemic BINOL by HPLC. The influence of the pretreatment temperature, the content of the template molecule of the SMIP-CSPs, and the mobile phase on the separation of the racemic BINOL were systematically investigated.

# 2 | MATERIALS AND METHODS

2.1 | Chemicals and reagents

Silica gel (diameter about 7 μm, pore diameter about 100 nm) as a support medium for preparation of the surface molecularly imprinted microspheres was purchased from the Japan Daicel (Tokyo, Japan). BINOL was purchased from Sichuan Tiancai Fine Chemical (Sichuan, China). EGDMA and acrylamide (AM) were purchased from Aladdin (Shanghai, China) and distilled before use. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Tianjin Chemical Reagent Factory (Tianjin, China) and recrystallized from ethanol before use. Acetonitrile, chloroform, methanol, and acetone were purchased from Kermel (Tianjin, China). All chemical reagents were of analytical or HPLC grade.

2.2 | Equipment

All the chromatography measurements were performed by the HPLC system (Jasco, Japan), UV (UV-2070 Plus), chiral detector (CD-2095 Plus), pump (PU-2089 Plus), column thermostat (CO-2060 Plus), and intelligent sampler (AS-2055 Plus). The morphology of the materials was measured using a scanning electron microscope (SEM) (JSM-6480, Hitachi, Japan).

2.3 | Preparation of SMIP-CSPs

All the reactions proceeded under N_2 atmosphere, as a simple experimental procedure (Scheme 1), (R)-BINOL (0.25 mmol, 71.6 mg) as the template molecule, and AM (0.50 mmol, 35.6 mg) as the functional monomer were dissolved in acetonitrile (3.0 mL). A 0.8 g silica gel sample was placed in a thick-wall eggplant flask. In order to evenly coat the precursor on the surface of the silica gel, 0.5 mL of the precursor solution was gradually dropped into the flask. The flask was then stroked on a cork mat to evenly coat the precursor on the surface of silica gel, then the coated silica gel was dried using rotary evaporators. After drying in a vacuum, EGDMA (1.59 mmol, 280 μL), as the crosslink agent, solution in acetonitrile/chloroform (1/2, v/v, 3 ml), were mixed with the coated silica gel, followed by the addition of AIBN (0.049 mmol, 8 mg) as the initiator. The flask containing the complex of BINOL and AM was placed in a water bath
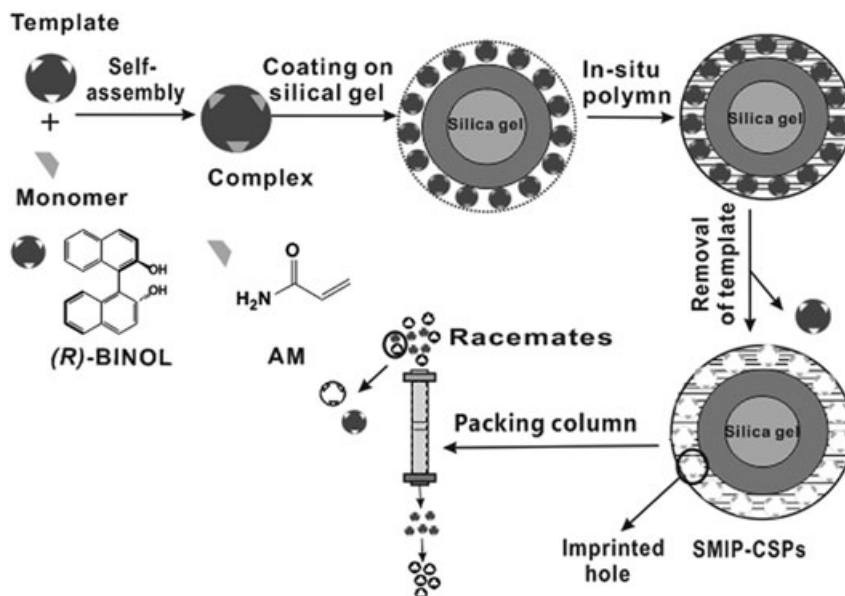
SCHEME 1 Illustration for preparation of SMIP-CSPs

at 60°C. After a 12 h polymerization, the resulting coated silica gel particles were dried for 24 h and washed with a mixed solvent of methanol/acetic acid (9/1, *v*/v) to completely remove the template and residues. After drying in a vacuum, the resulting particles were sieved through stainless steel sieves. The silica gel is a microsphere with a porous structure. After the crosslinking reaction, the coated thin film of the precursor solution (the mixture of the template molecule and functional monomer) on the surface of the microbores in the silica gel formed a crosslinked polymer with net structure and tightly wrapped the silica gel.

As the control, The MIPs were prepared by the bulk polymerization and directly used as the CSP for chiral separation by HPLC.

2.4 | Preparation of the HPLC column

The sieved particles with sizes between 30 μm and 50 μm were collected. A 0.8 g sample of SMIP-CSP was packed on the stainless-steel HPLC column (250 × 2.0 mm) using the conventional slurry method in which the liquid paraffin was used as a dispersing agent. The residual template and residues in the column were completely washed out with acetonitrile as the mobile-phase until a stable baseline was obtained by HPLC.

2.5 | Chromatographic analysis

Evaluation of the chiral separation ability of the prepared column was done using the HPLC system. The detecting wavelength of the UV and CD detectors was 254 nm. The flow rate was 0.06 mL/min. The pure or mixture of acetonitrile with chloroform or acetic acid was used as the mobile phase. The sample size of the racemic BINOL solution (6 mg/mL) was 20 μL. All the HPLC experiments were carried out at 25°C. The results of the chromatographic analysis are summarized in Table 1.

The retention factor (k) was calculated using equation 1, and it determined the retention behavior of the analyte.

$$k = (t_1 - t_0)/t_0 \tag{1}$$

where t_1 is the retention time of the analyte, and t_0 is the elution time of the void marker, acetone.

The separation factor was calculated using equation 2

$$\alpha = k_2/k_1 = (t_2 - t_0)/(t_1 - t_0) \tag{2}$$

where k_1 and k_2 are the retention factors of (S)-BINOL and (R)-BINOL, respectively.

The resolution was calculated using equation 3

$$Rs = 2(t_2 - t_1)/w_1 + w_2 \tag{3}$$

where t_1 and t_2 are the retention times of (S)-BINOL and (R)-BINOL, and w_1 and w_2 are the baseline peak widths of (S)-BINOL and (R)-BINOL, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Scanning electron micrograph (SEM)

The SEM images of the original silica gel particles, the resulting SMIP-CSPs, and the MIP-CSPs are shown in Figure 1. The rough surface of the SMIP-CSPs (Figure 1B) indicates the successful coating of the polymer layer on the silica gel particles. The SMIP-CSPs are of spherical

TABLE 1 Chiral separation of racemic BINOL on the SMIP-CSPs by HPLC

CSPs	Type of CSP	Monomer	Supporting materials	T/M[a](mol/mol)	T[b](°C)	α [c]	Rs[d]
1	SMIP-CSP	AM	Silica gel	1/2	0	1.00	-
2	SMIP-CSP	AM	Silica gel	1/2	10	2.86	0.84
3	SMIP-CSP	AM	Silica gel	1/2	20	4.13	1.22
4	SMIP-CSP	AM	Silica gel	1/2	30	3.41	1.03
5	SMIP-CSP	AM	Silica gel	1/1	20	2.14	0.42
6	SMIP-CSP	AM	Silica gel	1/3	20	3.17	0.90
7	SMIP-CSP	AM	Silica gel	1/4	20	2.68	0.75
8	MIP-CSP	AM	non[c]	1/2	20	1.96	0.38

[a]The molar ratio of (R)-BINOL to AM in the SMIP-CSPs;

[b]The pretreatment temperature of the mixture of (R)-BINOL/AM before coating;

[c,d]Separation factor and resolution for racemic BINOL on the SMIP-CSPs by HPLC, respectively (mobile phase: acetonitrile, flow rate: 0.06 mL/min, at 25°C).
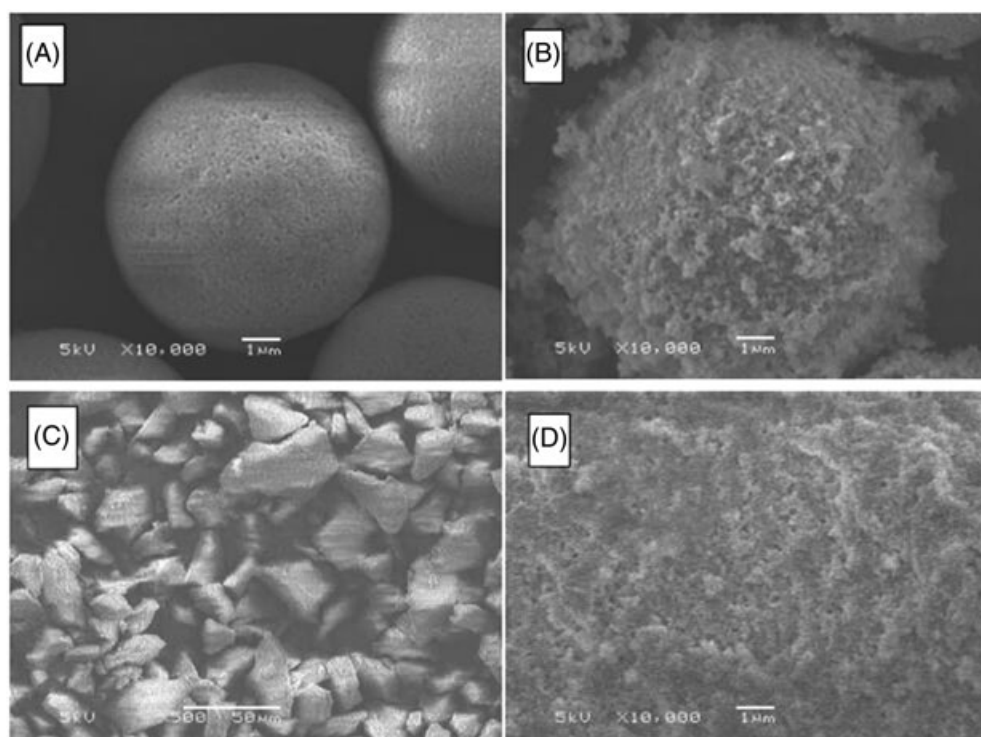
FIGURE 1 SEM images of silica-gel particles A, and the SMIP-CSPs B, and MIP-CSPs C and D

morphology, which indicates that the prepared SMIP-CSPs maintained the unity and dispersity of the silica gel particles after the coating and polymerization. In the case of the MIP-CSPs (Figure 1A), the particles showed an irregular shape with a larger particle size (Figure 1C,D).

3.2 | Effect of pretreatment temperature on separation of the racemic BINOL

In order to prepare an efficient SMIP-CSPs for chiral separation, an efficient combination between the template molecule and the monomer before the copolymerization is necessary to form imprinted holes with a high and stable recognition ability in the resulting materials. Hence, the precursor solution of AM and (R)-BINOL in CH₃CN was pretreated at different temperatures to investigate the effect of the pretreatment temperature on the separation ability of the resulting SMIP-CSPs (Table 1, Figure 2).

Interestingly, the pretreatment and coating temperature of the precursor solution showed a clear influence on the chiral recognition ability of the corresponding CSPs. For instance, CSP 1 pretreated at 0°C did not show any chiral separation for the racemic BINOL, while CSP 3 pretreated at 20°C
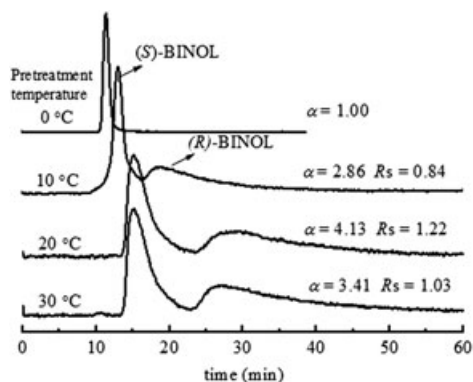
FIGURE 2 Effect of pretreatment temperatures on chiral separation of racemic BINOL

showed the best chiral recognition for the racemic BINOL (α = 4.13, Rs = 1.22) of all the CSPs (Table 1). Both the CSPs pretreated at 10°C (CSP 2, α = 2.86, Rs = 0.84) and pretreated at 30°C (CSP 4, α = 3.41, Rs = 1.03) showed lower chiral recognition abilities than CSP 3 pretreated at 20°C (Table 1).

After coating the precursor solution on the silica gel, along with the solvent evaporation, the complex manner of BINOL and AM might be influenced by the adjacent molecules due to the $-NH_2/-OH$ or $-NH_2/-NH_2$ hydrogen bonding between them. Since hydrogen bonding is very sensitive to the environmental temperature, the temperature in this process should have a clear effect on the complex nature of BINOL and AM in the CSPs. There is the possibility that the hydrogen bonds between the adjacent amide groups of AM might be strong at a low temperature (0°C), which might weaken the intermolecular hydrogen bonding between the amide groups in AM (monomer) and the phenolic hydroxy groups of (R)-BINOL (template) so as to reduce the template effect of the (R)-BINOL on the resulting SMIP-CSPs. By increasing the pretreatment temperature, the hydrogen bonding interaction between AM and the (R)-BINOL template became more effective, resulting in the higher forming efficiency of the regular imprinted holes in the resulting SMIP-CSPs. The best combination between the monomer and the template was realized with the pretreatment at 20°C, which produced the SMIP-CSPs with the highest chiral recognition ability for the racemic BINOL (CSP 3). By further increasing the pretreatment temperature, the combination between the monomer and the template became weaker and unstable; this reduced the regularity of the imprinted holes in the resulting SMIP-CSPs and decreased the chiral separation ability. As a conclusion, the pretreatment temperature clearly affected the chiral recognition abilities of the SMIP-CSPs, and 20°C was the most suitable pretreatment temperature for preparing the SMIP-CSPs for chiral separation of the racemic BINOL.

3.3 | Influence of the (R)-BINOL content on separation of the racemic BINOL

To investigate the influence of the molar ratio of the template/monomer (T/M) on the chiral separation ability of the CSP, SMIP-CSPs with different molar ratios of (R)-BINOL/ AM (T/M) were prepared. The results are summarized in Table 1. CSP 3 with T/M = 1/2 showed the highest separation factor (α = 4.13) and resolution (Rs = 1.22), while the separation factors and resolutions of CSP 5 (T/M = 1/1), CSP 6 (T/M = 1/3), and CSP 7 (T/M = 1/4) were much lower than those of CSP 3 (Table 1).

When the T/M ratio was higher than 1/2, an insufficient amount of the monomer should cause the irregular imprinted holes in the corresponding SMIP-CSPs to reduce the selectivity of the CSP (for instance, CSP 5 with TM = 1/1) for the racemic BINOL. At the lower T/M ratio, such as 1/3 in CSP 6 and 1/4 in CSP 7, the higher excess of monomer caused an insufficient amount of imprinted holes, which reduced the separation capacity of the imprinted polymers. Therefore, 1/2 was the most suitable T/M ratio for preparing the best CSP for the chiral separation of the racemic BINOL.

3.4 | Influence of surface coating on separation of racemic BINOL

To investigate the influence of the surface coating on the separation of the racemic BINOL, i.e., to compare the chiral separation ability of SMIP-CSPs and MIP-CSPs, the MIPs were prepared as a control and directly utilized as the CSP for separation of the racemic BINOL (CSP8, Table 1). In comparison to the surface coated SMIP-CSP (α = 4.28,
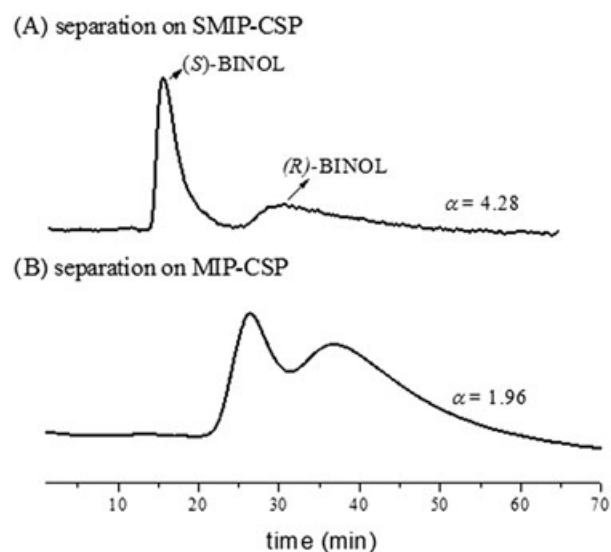

FIGURE 3 Chiral separation of racemic BINOL on A, SMIP-CSPs (CSP 3 in Table 1) and B, MIP-CSPs (CSP 8 in Table 1) by HPLC. Mobile phase: Acetonitrile/chloroform (9/1, *v*/v), flow rate: 0.06 mL/ min, [(R, S)-BINOL] = 0.6 mg / mL, sample size: 20 μL

TABLE 2 Effect of mobile phase on chiral separation of racemic BINOL

	Retention time		Capacity factor			
Mobile phase	t1(min)	t2(min)	k1	k2	α	RS
Acetonitrile	15.12	29.46	0.43	1.79	4.13	1.22
Acetonitrile / chloroform(90/10)	15.28	31.13	0.46	1.98	4.28	1.29
Acetonitrile / chloroform (85/15)	14.40	23.14	0.50	1.42	2.82	0.99
Acetonitrile / acetic acid (94/6)	11.51	14.99	0.23	0.60	2.62	0.93

Rs = 1.29), the chiral separation ability of the MIP-CSP for the racemic BINOL was rather low (CSP 8, (α = 1.96)) (Table 1, Figure 3). In addition, the separation on SMIP-CSPs had a shorter retention time than that on MIP-CSPs, i.e., the peak of (S)-BINOL appeared earlier in the separation on SMIP-CSPs (t_1 = 15.2 min by CSP 3) than that on MIP-CSPs (t_1 = 23.2 min by CSP 8) in HPLC (Figure 3). The higher chiral separation efficiency and the shorter retention time on the SMIP-CSPs than those on the MIP-CSPs was thought to be due to difference from the inside distributed imprinted holes in the MIP-CSPs; most imprinted holes distributed on the surface of silica gel in SMIP-CSPs, and the multipore structure of the silica gel afforded the SMIP-CSPs with higher specific surface area and more active binding sites than the MIP-CSPs. The surface distributed imprinted holes also resulted in the faster adsorption and desorption speed of the analyte on the CSP during the separation. Therefore, the separation on the SMIP-CSPs had a shorter retention time than that on the MIP-CSPs.

In summary, the SMIP-CSPs prepared by coating the MIP on silica gel showed a higher chiral separation ability and efficiency than the MIP-CSPs for the chiral separation of racemic BINOL by HPLC.

3.5 | Influence of mobile phase composition on separation of the racemic BINOL

Since the chemical structure of BINOL contains both hydrophobic naphthyl groups and hydrophilic hydroxyl groups, to optimize the chromatography condition, four kinds of mobile phases including acetonitrile and its mixtures with chloroform or acetic acid were used in the separation of BINOL on the SMIP-CSPs by HPLC (Table 2). When pure acetonitrile was utilized as the mobile phase, the separation factor reached 4.13 and the resolution reached 1.22 (Table 2). By adding 10 vol. % of chloroform to the acetonitrile, the separation factor and resolution further increased to 4.28 from 4.13 and 1.29 from 1.22, respectively. In addition, the capacity factors also increased (k_1: from 0.43 to 0.46, k_2: from 1.79 to 1.98) by adding 10 vol. % chloroform to the acetonitrile. However, with a further increase in the content of chloroform in the acetonitrile to 15 vol. %, the separation factor and resolution decreased

to 2.82 and 0.99, respectively (Table 2). These results indicated that a suitable content of hydrophobic chloroform was beneficial for the separation. This might be caused by the fact that adding hydrophobic chloroform improved the interaction between the phenolic hydroxy groups in BINOL and the amide groups in the imprinted holes so as to improve the chiral separation ability.

In addition, to check the influence of the hydrophilic molecule in the mobile phase on the chiral separation of BINOL, a mixture of acetonitrile containing 6 vol. % hydrophilic acetic acid was utilized as the mobile phase. As shown in Table 2, adding acetic acid to the mobile phase clearly decreased the separation factor, resolution, capacity factors, and shortened the retention time. These could be caused by the disturbed interaction between the $-COOH$ of acetic acid with $-NH_2$ in the imprinted holes and weakened interaction between BINOL with $-NH2$ in the imprinted holes. This reduced the chiral recognition ability of the CSP and shortened the retention time. In summary, the mixture of acetonitrile/chloroform (9/1 v/v) was a suitable mobile phase for the chiral separation of BINOL by HPLC.

4 | CONCLUSION

In summary, The SMIP-CSPs were successfully prepared by the in situ copolymerization of AM and EGDMA in the presence of (R)-BINOL as the template molecules on the surface of the silica gel. The pretreatment temperature and the molar ratio of the template ((R)-BINOL)/monomer (AM) in the precursor solution of (R)-BINOL and AM was found to clearly influence the chiral separation ability of the resulting SMIP-CSPs. Efficient SMIP-CSPs could be prepared under the following conditions: the pretreatment temperature of the precursor was 20°C, and the molar ratio of the template/monomer in the precursor was 1/2 mol/mol.

The resulting SMIP-CSPs showed a better chiral separation ability and shorter retention time (α = 4.28, Rs = 1.29, t_1 = 15.2) for the chiral separation of the racemic BINOL than the MIP-CSPs (α = 1.96, Rs = 0.38, t_1 = 23.2). The surface-distributed imprinted holes and the high specific area of SMIP-CSPs increased the chiral

separation ability and efficiency for the racemic BINOL during the separation by HPLC. In addition, the suitable mobile phase for the separation of racemic BINOL on SMIP-CSPs by HPLC was acetonitrile/chloroform (9/1 v/v). This study provides an alternative method for preparing new types of CSPs and developing new chiral separation techniques.

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