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Water-assisted formation of novel molecularly imprinted polymer membranes with ordered porous structure

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Abstract

A functional polymer, poly(styrene-*stat*-acrylonitrile-*stat*-vinyl-2,4-diamino-1,3,5-triazine) (modified SAN, mSAN) with 13.6% triazine units, was synthesized. Using mSANs as the functional polymers and poly(styrene-*stat*-acrylonitriles) (SANs) as the matrix polymers, the molecularly imprinted polymer (MIP) membranes with (*S*)-5-benzylhydantoin (*S*-BZH) as template and the Blank membranes without *S*-BZH were prepared via the water-assisted method. Scanning electron microscopy (SEM) measurement revealed an ordered porous structure on the surface and a sponge-like porous structure in the cross-section of the MIP membranes. Further, the permeation experiments of the template *S*-BZH and its analogues in methanol solution were carried out with MIP as well as Blank membranes; the results provided evidence for imprint effect of the ordered porous membranes.

Keywords: Molecularly imprinted membrane; Water-assisted method; Ordered porous

1. Introduction

Molecular imprinting is a powerful method for preparation of materials with molecule-specific cavities that mimic the behavior of natural receptor binding sites [1]. Molecularly imprinted polymers (MIPs) have gained great attention in the field of analytical chemistry for the past decade [2–5]. However, MIP membranes for separation are still in their infancy [6]. In the previous works, two main preparation routes towards MIP membranes have been developed, the ‘‘traditional’’ *in situ* cross-linking polymerization and the ‘‘alternative’’ polymer solution phase inversion (PI), both in the presence of templates [7]. In the most studies, the recognition sites are distributed in the bulk polymer phase; the accessibility of the recognition sites is limited due to the pore structure of the membranes, which lead to the low membrane performance [8]. To solve the problem of high yield of recognition sites with porous morphology, many studies have been carried out, such as supramolecular self-assembly method [9], surface molecular imprinting method [10], and so on.

Here, we present a novel approach to prepare MIP membranes with ordered porous structure by the water-assisted method discovered by Francois and coworkers recently [11]. In this method, the highly ordered porous membranes are produced by evaporating polymer solution in volatile solvent under humid condition. These membranes have been fabricated from rod–coil block copolymers [12], polymers with ionic groups [13–15], amphiphilic copolymer [16–18] and star polymers [19–21], and so on. Recently, our group has also successfully prepared the ordered porous membranes from random poly(styrene-*co*-acrylonitrile) using THF as solvent via the water-assisted method [22].

This project’s strategy is to use the potential of porous membrane formation from polymer blends, here with SAN

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as the matrix and mSAN as the functional polymer (Fig. 1). Furthermore, via the water-assisted method the MIP membranes with controlled pore structure are prepared in the presence of template to increase the yield of the available imprinted sites and their accessibility, which subsequently leads to the improved membrane performance.

2. Experimental section

2.1. Materials

Poly(styrene-*stat*-acrylonitrile) (C.P.) (SAN) was purchased from PetroChina Lanzhou Petro and Chemical Company. The number-average molecular weight (M_n) and polydispersity index (PDI) of SAN were 3.1×10^4 and 1.91, respectively, determined by gel permeation chromatography (GPC) (Waters Co.) with polystyrene standard. The molar percent of acrylonitrile units was 25% by elemental analysis. The modified SAN (mSAN) with 13.6% triazine units was prepared according to the literature [23]. (*R*)-, (*S*)-5-Benzylhydantoin (*R*-BZH, *S*-BZH) and (5*S*)-3-phenyl-5-benzylhydantoin (*S*-PBZH) (structure, see Fig. 1) were prepared as described in the literature [24,25]. (*R*)- and (*S*)-β-Phenylalanine were purchased from Baosheng company (YangZhou, China, >98% ee). Tetrahydrofuran (THF) (Tianjin Chemical Reagent III Co.) was dried by distilling in the presence of sodium. Methanol was of chromatographic grade. Other chemicals were of analytical grade and were used as received without additional purification.

2.2. Treatment of silicate glass substrate

The silicate glass substrate was cleaned by pickling solution. The substrate was immersed in 500 mL 10% (v/v) dichlorodimethylsilene solution in toluene for 24 h at room temperature, then the substrate was washed with acetone and deionized distilled water, respectively. The substrate was kept in desiccator after drying for 8 h at 120 °C.

2.3. Preparation of MIP membrane

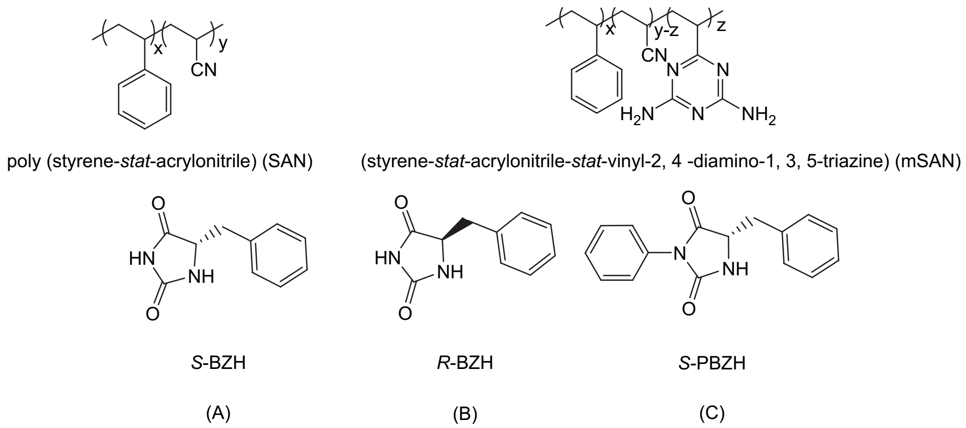
The membranes were fabricated as described in our previous work [22]. A typical preparation of the MIP membrane was carried out as follows. Thirteen milligrams of the template molecules *S*-BZH were dissolved in 3.0 mL of THF with 10 mg of mSAN. Then 190 mg of SAN was dissolved in the previous THF solution. The THF solution (0.2 mL) thus prepared was cast on a substrate, and the solvent was allowed to evaporate under 60% humidity at 25 °C for 24 h. The obtained membranes were dried in vacuum at ambient temperature for additional 24 h. After drying, the print molecule was removed from the resultant membranes by a known large volume of methanol until the print molecule could be hardly detected in methanol by UV analysis. In this study, most of the added print molecules were removed from the membrane. The thickness of the membrane thus obtained was approximately 80 μm. The print molecule was omitted for the preparation of Blank membranes by the same procedure.

2.4. Membrane morphology

The morphology of the membranes was investigated by environmental scanning electron microscope (ESEM; XL30, Philips). The cross-section was obtained by fracturing the membrane at liquid nitrogen temperature.

2.5. Pore analysis of MIP membranes

In the N_2 adsorption a sample of MIP membrane *ca*. 0.45 g was degassed at 50 °C for 8 h under vacuum. The adsorption and desorption isotherms were then recorded using a 200-point pressure table and 60 s equilibration time. The surface area was determined using the Brunauer–Emmett–Teller (BET) model, the *t*-plot using the Harkins–Jura average thickness equation and the pore distribution using the Barrett–Joyner–Halenda (BJH) model.



poly (styrene-*stat*-acrylonitrile) (SAN)

(styrene-*stat*-acrylonitrile-*stat*-vinyl-2, 4 -diamino-1, 3, 5-triazine) (mSAN)

S-BZH (A)

R-BZH (B)

S-PBZH (C)

Fig. 1. Chemical structures of matrix polymer, functional polymer and the analytes used in this study. A: (*S*)-5-benzylhydantoin (*S*-BZH), B: (*R*)-5-benzylhydantoin (*R*-BZH), C: (*S*)-3-phenyl-5-benzylhydantoin (*S*-PBZH).

2.6. Permeation experiment

Permeation experiments were carried out using the single-molecule type (the feed solution contained only *S*-BZH or only *R*-BZH, etc.). The membrane, with an effective area of 3.0 cm^2, was fixed tightly between two chambers of a permeation cell. The volume of each chamber was 40 mL. *S*-BZH (25 mL) of 250 μM or its analogues' solution in methanol was placed in the left-hand side chamber, while 25 mL methanol was placed in the right-hand side chamber. The permeation experiments were done at ambient temperature with stirring. The amounts of the substrate that permeated the membranes were determined by a UV system (Shimadzu 2010-PC, Japan).

3. Results and discussion

3.1. Preparation of S-BZH, R-BZH and S-PBZH

(5*R*)-5-Benzylhydantoin and (5*S*)-5-benzylhydantoin (*R*-BZH and *S*-BZH) were prepared as described in the literature [24]. (*R*)-β-Phenylalanine or (*S*)-β-phenylalanine (1.65 g, 10 mmol) and potassium cyanate (0.97 g, 12 mmol) were suspended in water (10 mL), and the mixture was kept at 70 °C with stirring for 30 min. Hydrochloric acid (10 mL) was added and the reaction mixture was refluxed for an additional 2 h. Cooling in an ice bath gave crystals which were filtered off and recrystallized from benzene–ethanol. (5*R*)-5-Benzylhydantoin: yield: 0.51 g (26.8%), m.p.179–181 °C. $[\alpha]_D^{25}$: −181° (ethanol). ^{1}H NMR (DMSO-d_6) δ: 3.01 (CH_2), 4.23 (C_5-H), 7.28 (Ar-H), 7.76 (N_1-H), 10.37 (N_3-H). (5*S*)-5-Benzylhydantoin: yield: 0.55 g (29.0%), m.p. 179–180.5 °C. $[\alpha]_D^{25}$: +181° (ethanol). ^{1}H NMR spectra were the same as those of (5*R*)-5-benzylhydantoin.

(5*S*)-3-phenyl-5-benzylhydantoin (*S*-PBZH) was prepared according to literature [25]. (*S*)-β-Phenylalanine (1.65 g, 10 mmol) was dissolved in 4 mL of water containing 0.68 g of potassium hydroxide. After solution was complete, phenylisocyanate (1.32 g, 11 mmol) was added to the rapidly stirred solution. After standing overnight, the diphenylurea was filtered off, and the filtrate was acidified to precipitate the phenylhydantoic acid. The phenylhydantoic acid was filtered off, dried for a short time in air, and cyclized by refluxing for 1 h with 2 mL of water and 2 mL of concentrated hydrochloric acid. The product crystallized on cooling was recrystallized from ethanol–water. The yield was 2.4 g (90%), m.p. 172–173 °C. ^{1}H NMR (DMSO-d_6) δ: 3.01, 3.31 (CH_2), 7.35 (Ar-H), 5.76 (N_1-H).

3.2. Blend compatibility study

The functional polymer mSAN prepared was analyzed by elemental analysis, and the mole content of triazine units was determined to be 13.6%. The compatibility of the solid

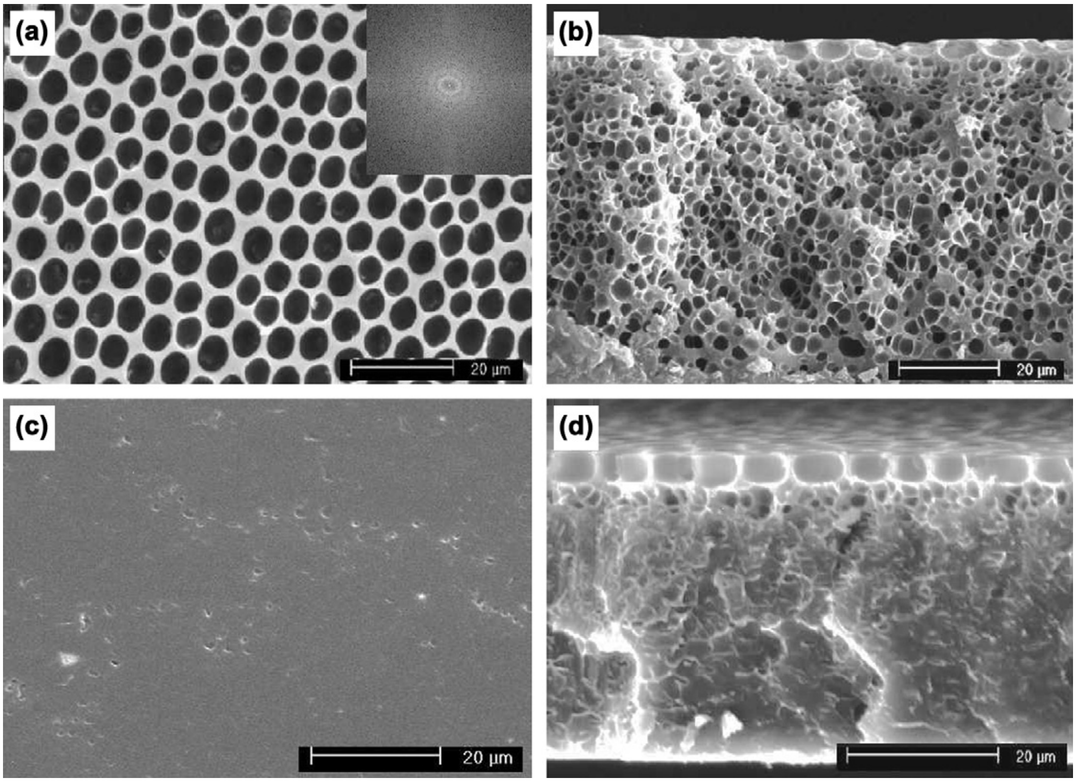


Fig. 2. SEM images of the membranes; a: the top surface of MIP membranes; b: the cross-section of the MIP membranes; c: the bottom surface of MIP membranes (the surface contacting the glass substrate during solidification); d: the cross-section of Blank membranes. The inset in Fig. 2a is Fourier transformation of the top surface SEM image of MIP membranes.

polymer blend was evidenced by the DSC data for the blend SAN–mSAN at a composition of 95/5 (w/w): A single T_g value at 106 °C was obtained. Under the same experimental condition, the polymers SAN and mSAN exhibited a T_g value of 110 and 148 °C, respectively.

3.3. Morphology characterization of MIP membrane

Fig. 2 showed the SEM images of the surface and the cross-section of the membranes. As shown in Fig. 2a, the ordered pores with average diameter of 5.33 μm were formed on the top surface, and a sponge-like structure appeared in the cross-section for the MIP membrane shown in Fig. 2b. The Fourier transform of the top surface image was given in the inset of Fig. 2a, which showed the ordered structure of the pores. The pore analysis of MIP membranes shows that the surface area is 1.20 m^2/g, the pore volume (between 17 and 1000 Å) 0.0017 mL/g, and the pore diameter (between 17 and 1000 Å) 16.87 Å. However, the bottom surface (the surface contacting the glass substrate during solidification) of the MIP membrane was solid and smooth as shown in Fig. 2c; and the sponge-like structures could not be observed in the cross-section of Blank membrane (Fig. 2d). Only one layer of pores was formed on the top surface, which was similar to previous work [26]. It had been proved that the water-assisted method to fabricate ordered porous membranes utilizes the water droplets as templates condensed water vapor by the cooling polymer solution surface caused by the solvent evaporation. Srinivasarao et al. [13] have reported the formation of porous membranes with three-dimensionally ordered structure by evaporating polystyrene with one carboxylic terminal group solution in the presence of moist air. Unlike their results, sponge-like structures were formed only in the MIP membrane. The results implied that the print molecule and/or the interaction between the print molecule and the functional polymer mSAN had an influence on the formation of sponge-like structures. The formation mechanism of inner morphology is not clear at this stage. Further studies are in progress.

3.4. Transport properties of MIP membrane

Fig. 3 showed the permeation experiment results of the membranes. As compared with the Blank membrane (Fig. 3b), a higher transport rate for the MIP membranes was obtained, which should be attributed to the porous structures of the MIP membranes. The ordered porous structures on the surface and the sponge-like porous structure in the cross-section are beneficial to the accessibility of recognition sites and mass transport for the analytes [8].

In permeation for *R*-BZH with the *S*-BZH-imprinted polymer membrane, the transport rate was lower than that for the template (Fig. 3a). Because *R*-BZH and *S*-BZH had the same chemical structure and molecule size, the difference of the transport rate may be due to the recognition sites complement in size and shape to template, i.e. so-called ‘‘imprinting effect’’, which led to the stronger interaction of imprinting cavity and the template. As compared with the transport rate of *S*-BZH and *S*-PBZH through the *S*-BZH-imprinted membrane, it was clearly found that *S*-PBZH was more difficult to transport through MIP membrane than *S*-BZH. In spite of size-sieving, the fact also should attribute to the weakened interaction of membrane with respect to the *S*-PBZH, since in its chemical structure 3-position H is substituted by phenyl group.

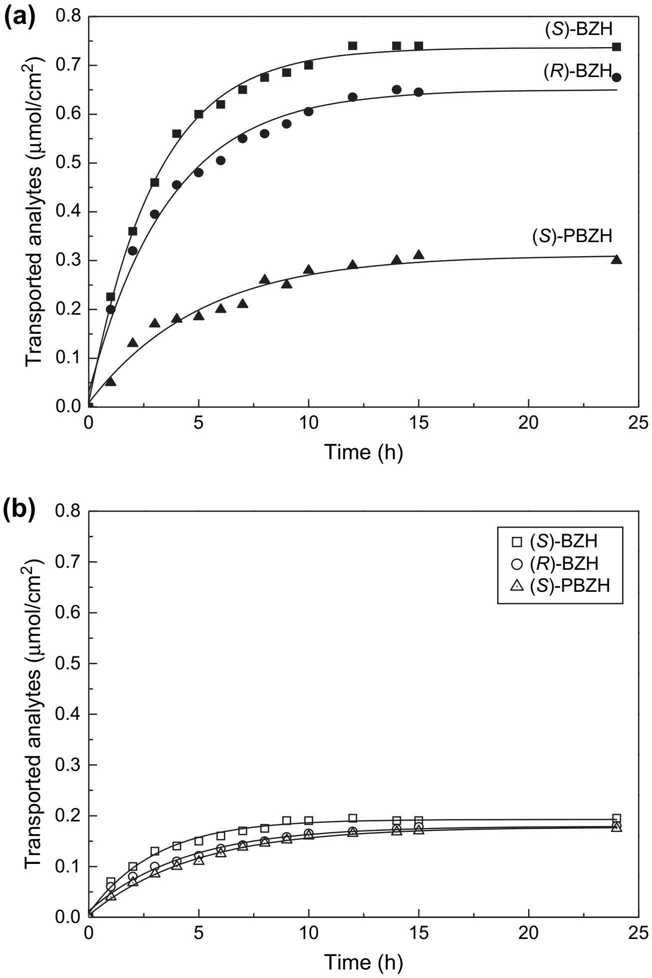


Fig. 3. Time–transport curves of (a) (*S*)-BZH-imprinted membranes and (b) Blank membranes in methanol. (■□) (*S*)-BZH, (●○) (*R*)-BZH and (▲△) (*S*)-PBZH. Permeation experiments were carried out in 250 μM solute concentration at ambient temperature.

Thus, the highest transport rate always was observed for the template molecule for the MIP membrane, which should be related to the interaction between print molecule and the triazine groups of the imprinted site on the membrane, via the specific three-point and/or multiple-point hydrogen bonds, which has been proved to be formed even using THF as solvent [27].

4. Conclusions

A novel approach to fabricate the MIP membranes with ordered porous structure by the water-assisted method was developed. SEM images showed the highly ordered pore structure and regular sponge-like structure on the MIP membrane surface and the cross-section, respectively. Furthermore, Permeation experiment results showed that the resultant MIP membranes recognized the template molecule effectively and transported it with efficient sorption manner to *S*-BZH. This kind of the novel MIP membrane with highly ordered porous structure could be used as highly efficient membrane adsorbents.

Acknowledgements

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