Chinese Chemical Letters Vol. 14, No. 9, pp 979– 982, 2003 979
http://www.imm.ac.cn/journal/ccl.html

Preparation and Selectivity of Molecularly Imprinted Polymer Coating on the Micro Pore Membrane of Polytetrafluoroethylene

Hong Sheng GUO[1,2], Yu Mei JIA[1], Xi Wen HE[1]*

[1] State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Department of Chemistry, Nankai University, Tianjin 300071
[2] The College of Pharmaceuticals and Biotechnology, Tianjin University, Tianjin 300072

Abstract: In order to obtain mechanically stable membrane for practical application, the imprinted polymer was synthesized in the pores of polyfluoromembrane, the binding and transport ability of the membrane were studied.

Keywords: Molecular imprinting, trimethoprim, membrane of polytetrafluoroethylene.

Molecular imprinting technique is a technology that allows for the creation of molecular recognition sites in synthetic polymers *via* the use of templates. Imprinted materials have been used in various applications, including stationary phase for chromatography [1], recognition elements in sensors [2], or solid phase extraction [3].

The development of artificial/synthetic membrane that rivals biological membranes in selectivity is an important current goal in bioorganic, pharmaceutical and environmental chemistry. As widely recognized, for effective performance, imprinted polymers should be highly cross-linked for retaining the shape of the selective cavities of the imprinted polymeric membranes after the removal of the template. However, the highly cross-linked imprinted polymeric membranes are very fragile. This character restricts their practical use. The present paper reports on mechanically stable imprinted polymeric membrane. The imprinted polymer was synthesized in the pores of polyfluoromembrane, the binding and transport experiment showed that this membrane can selectively bind and transport the template molecule, trimethoprim, among the sulfa-bacteriophage.

Experimental

Trimethoprim imprinted membrane

Porous poly (tetrafluoroethylene) membrane was soaked into polymerization mixture containing 0.0145 g (0.05 mmol) trimethoprim TMP (template molecule), 0.0172 g (0.2 mmol) methacrylic acid (MAA functional monomer), 0.06768 g (0.2 mmol) tris (hydroxymethyl)propane trimethacrylate (TRIM cross linker), 0.15 mL acetonitrile

* E-mail:xiwenhe@nankai.edu.cn

(porogen) and 0.5 mg 2,2'-azobisisobutyronitrile (AIBN) for 20 minutes, then the membrane was placed between two glass plates, and polymerized for 6 hours under UV irradiation at 365 nm. After that glass plates were separated and the imprinted membrane was washed with methanol/acetic acid 9:1 (v/v) for 24 hours to remove the template molecule and kept in acetonitrile at room temperature. The average pore size of the membrane is 8.3 nm, the specific surface area is 13.9 m^2/g obtained from gas adsorption instrument.

Non-imprinted control membrane P (NIM) was prepared in the same way but without the addition of the TMP.

Binding experiments

20.0 mg of P (TIM) or P(NIM) were placed in a conical flask and mixed with 2.0 mL acetonitrile solution of the substrates in a known concentration. The conical flask was oscillated in a oscillator at room temperature for 16 h. The concentration of free substrates in the solution was determined using a spectrophotometer at appropriate wavelengths; the amount of substrates bounds to membrane was calculated by subtracting the concentration of free substrate from the initial substrate concentration.

Membrane transport experiments

Membranes were mounted in a diffusion cell consisting of two stirred chambers of 15 mL volume. A solution of 0.5 mmol/L analytes in acetonitrile was placed in the feeding chamber, and pure solvents in the receiving chamber. The amount of the transported analytes in receiving chamber was monitored by UV absorption measurements. All transport experiments were carried out at room temperature.

Results and Discussion

Substrate selectivity of P(TIM)

The selectivity of P (TIM) was carried out with a series of substrates TMP, sulfanilamide, and cefalexin as substrates. The amounts of binding to P (TIM) and P(NIM) were determined by the equilibrium binding method. **Table 1** shows that P (TIM) has the highest selectivity to the template molecule. This indicated that the binding ability was introduced into the polymer membrane by the molecular imprinting technology.

Membrane transportation studies

Transport studies with MIP membranes can provide a deeper understanding of the relationship between the shape of the template cavities and the arrangement of the functional groups of functional monomer in these cavities. As to the selective transport of the molecular imprinted membrane, two different mechanisms for selective transport should be regarded[4]. 1. The non-specific analytes (non-template) did not transplant or its rate of transport was slower due to the preferential sorption of the template together with the better transport path matched with size and shape of the template. 2. The permeation of the template molecules was retarded owing to affinity binding (the

interaction between the functional groups in cavities and the template was relatively strong than the non-template molecules). The transport rate of the template molecule and the similar structure molecules depend on above mechanism that has dominant effect.

Figure 1 The schematic of the structure of the substrates

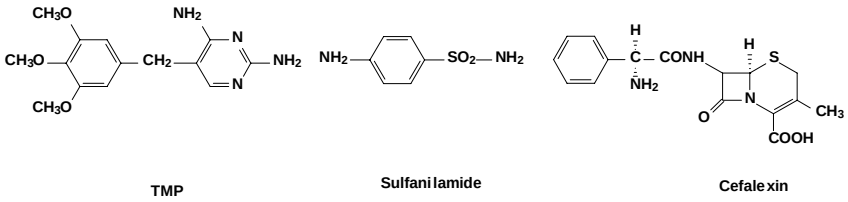
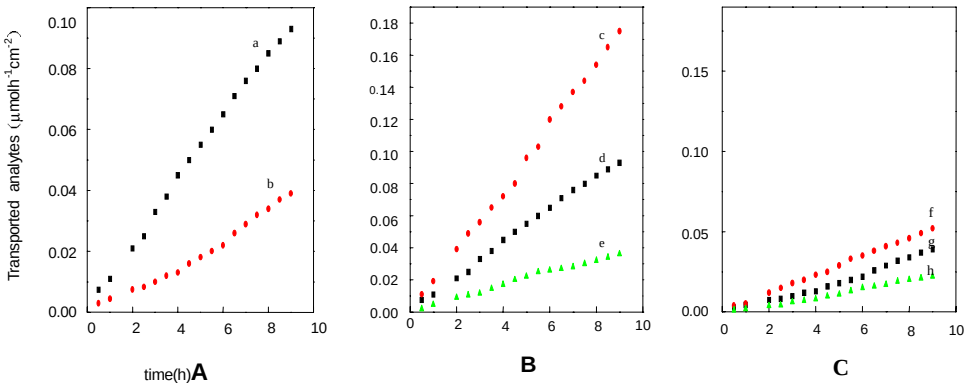


Table 1 The amount of substrates bound to P (TIM) and P (NIM) under equilibrium binding conditions (unit:μmol/g)

	Substrates bound to P (TIM)	Substrates bound to P (NIM)
TMP	0.552	0.257
Cefalexin	0.163	0.175
Sulfanilamide	0.118	0.108

[Initial concentration of substrates] = 2.00mmol/L, V = 2.0mL, t = 25° C, absorption time = 12h

Figure 2 The plot of the transport experiments of the membrane



A TMP imprinted membrane and non-imprinted membrane. (a: imprinted membrane; b: non-imprinted membrane)
B TMP imprinted membrane. (d:TMP; c:sulfanilamide; e:cefalexin)
C Non-imprinted membrane. (g:TMP; f:sulfanilamide; h:cefalexin)

The transport properties of imprinted polymer membrane were investigated using TMP, sulfanilamide and cefalexin as analytes. **Figure 2B** shows the time recording of the transport of the different analytes across the imprinted polymeric membrane and **Figure 2C** shows those across the corresponding control membrane.

As shown in **Figure 2C**, the transport rate of all the analytes across the non-imprint membrane differs only slightly and the transport rate of the analytes are much slower

compared with the imprinted polymer membrane. The different transport results of imprinted and non-imprinted membrane can be inherited from different polymer morphology between polymerization with or without template molecule. The presence of template molecule during polymerization makes the membrane to have different structure, porosity and swelling. The different sizes of micro pores in imprinted and non-imprinted membrane may lead to differences in transport of analyte of different molecular size.

Conclusion

The molecularly imprinted polymeric membrane supporting by the porous poly (tetrafluoroethylene) membrane possesses high selectivity and affinity to template molecule, and its flexibility makes it easy to deal in the practical use.

Acknowledgments

The authors thank the National Natural Science Foundation of China (No. 29975014), Tianjin Natural Science Foundation (No. 003602211) and the Doctoral Foundation of Educational Ministry, China (No. 20020055002) for financial support.

References

1. L. I. Andersson., A., Paprica Arvidsson D., *Chromatographia*, **1997**, *34*, 303.
2. D. Kriz , K.,Mosbach , *Anal. Chim. Acta*, **1995**, *300*, 71.
3. B.Sellergren , *Anal. Chem*., **1994,** *66* (9), 1578.
4. H.S. Guo, X.W. He, *Fresenius Journal of Analytical Chemistry*, **2000**,*368* (8), 763.

Received 12 September, 2002