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Preparation of Molecular Imprinted Copolymer Membrane for Uracil Recognition

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Abstract: Uracil molecular imprinted membrane was prepared by phase inversion technique with [P(AN-co-MAA)] copolymer. SEM photograph shows that the resultant membrane has a typical ultrafiltration structure with Water Volume Flux of $3.7\times10^{-5}m^3/m^2\cdot s$, and uracil substrate permeation experiment shows that the resultant membrane can bind uracil into its structure, and shows a binding equilibrium.

Keywords: Molecular imprinting, membrane, phase inversion.

Molecular imprinting is an effective method to create selective recognition sites in synthetic polymers[1]. Molecular imprinted polymers (MIPs) as tailor made polymer materials are practically applied in the separation of chiral compounds[2] and amino acid derivatives[3] and in drug assays[4]. The process of molecular imprinting mainly contains that functional monomer and print molecule (template) is pre-arranged by reversible covalent binding or noncovalent interactions (*i.e.* ionic, hydrophobic, hydrogen bonding, *etc.*), after polymerization, the template molecule is removed from the polymer, and the template site which has memory of the template molecule in both shape and functionality is created in polymer[1,4].

However, these imprinted materials are mainly used as stationary phase gels in chromatography, little is known about membrane with imprinting functionality. Recently, H.Y. Wang, T. Kobayashi and co-workers prepared theophylline molecular imprinted copolymer membranes using a new phase inversion precipitation technique[5-8]. Presently, we prepared uracil molecular imprinting in poly(acrylonitrile-co-methacrylic acid) membrane using this process. As shown in **Scheme 1**, the template site was created during precipitation procedure. Here, we report our preliminary results of investigation on uracil recognition behaviors of molecular imprinted membrane.

Experimental

Membrane material poly(acrylonitrile-co-methacrylic acid) [P(AN-co-MAA), **Scheme 2**] was synthesized with acrylonitrile (AN) and methacrylic acid (MAA) monomers (mole

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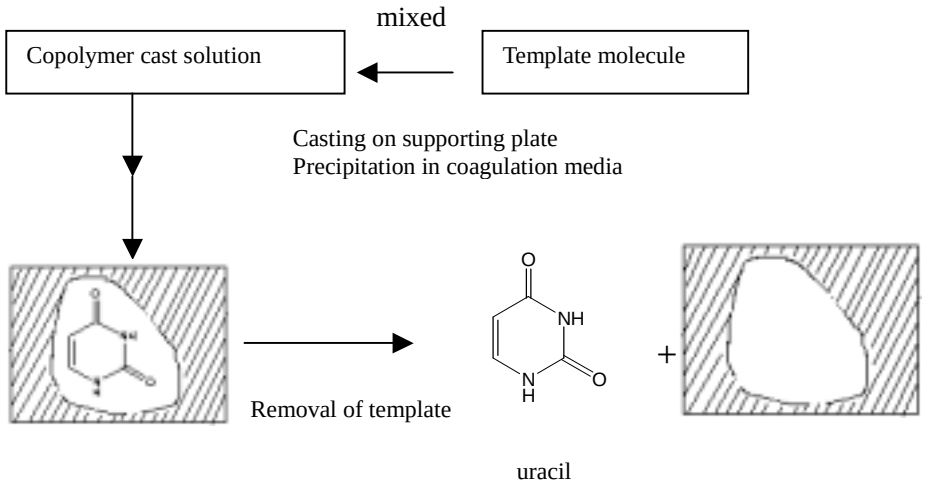
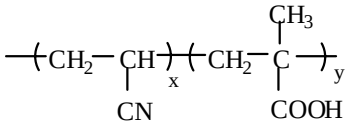
Scheme 1 Process of uracil molecular imprinting in membrane

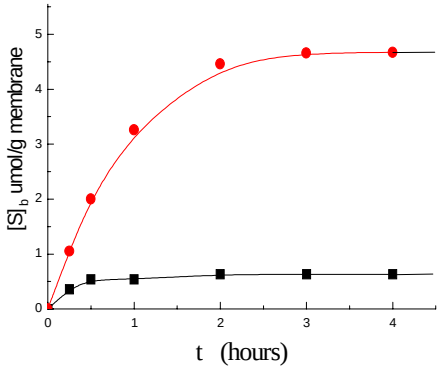


Scheme 2 Structure of copolymer



P(AN-co-MAA)

Figure 1 Plots of the amounts of uracil taken in uracil molecular imprinted (●) and unimprinted (■) membrane at various time



ratio AN:MAA=95:5) by radical polymerization, using dimethylsulfoxide (DMSO) as solvent, and azobis(isobutyronitrile) (AIBN) as initiator. Here AN is membrane formation segment and MAA is functional segment (**Scheme 1**) which can bind uracil with hydrogen bond. Uracil molecular imprinted membrane was prepared with the cast solution containing P(AN-co-MAA) (10wt%) and uracil (1.1wt%), according procedure shown in **Scheme 1**. As previously reported[9], the resultant membrane was washed with 0.1wt% acetic acid aqueous solution and large quantity of water to remove uracil and solvent from the membrane[4].

The study of uracil imprinted membrane was observed using Scanning Electron Microscope (JSM-5600). To estimate the characters of the resultant membrane, water volume flux (F) and molecule rejection (R) were tested by ultrafiltration set of dead end[5]. The substrate permeation experiment of uracil solution was also carried out to study the

substrate uptake in the resultant membrane. The concentration of uracil in feed and permeation solution was measured using UV-Vis (Shimazu, UV-2401) at 258 nm.

Results and Discussion

1. SEM photograph of cross-section of the membrane shows that the membrane has an asymmetric porous structure with a dense layer and supporting layer formed with many pores in micrometer order, which is typical for ultafiltration membrane[10]. The membrane is characterized with the water volume flux of $3.7\times10^{-5}m^3/m^2\cdot s$, and rejection of 93% and 18.8% for bovine serum alrumin (M=68,000) and polyethylene glycol (M=1,540) , respectively.

2. Substrate permeation experiment was carried out. **Figure 1** shows plots of the amounts of uracil uptaken in membrane $[S]_b$ (μmol/g membrane) , *versus* permeation time.

The values of $[S]_b$ increase with the increase of permeation time, and then become constant at about 4.69 and 0.63 μmol/g membrane, respectively. For the membranes prepared from the cast solution with and without uracil, we noticed that for uracil imprinted membrane, the value of $[S]_b$ (4.69 μmol/g membrane) is far larger than the value of $[S]_b$ (0.63 μmol/g membrane) for the unimprinted membrane. This means that the molecular imprinted membrane recorded the shape of uracil molecule in it, and uracil could be rebound into the recognition site when it was permeated through the membrane. Further study on the uracil molecular imprinted membrane is being carried out, and the detail will be reported elsewhere.

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