Development of Molecularly Imprinted Polymer Films for L-Proline Detection

M. L. Homer, S.P.-S. Yen, M. A. Ryan, A. Ksendzov
Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive
Pasadena CA 91109

Polymers can be made to be selective to specific molecules by imprinting them with molecular recognition sites; these sites select molecules based on size, morphology and chemical functionality. As the film takes up target molecules in the imprinted sites, the electrical characteristics will change in the film. Monitoring the selective film for changes in one or more electrical characteristics (conductivity, impedance and capacitance) allows for detection of the target molecule. In this report we present data on a molecularly imprinted polymer (MIP) which was imprinted for the amino acid L-Proline. The MIP was synthesized from methacrylic acid (MAA) using L-Proline as the template. The MIP was tested using both current versus voltage measurements and impedence measurements, as well as IR spectroscopy.

To synthesize the molecularly imprinted polymer membrane using L-proline as a template, we adapted procedures from a combination of approaches. [1, 2] Before polymerization, the MAA was passed through a MEHQ inhibitor remover column and then the L-proline was dissolved in the MAA. Dimethylformamide, azobis (isobutyronitrile) and a distilled a trifunctional monomer were added and the mixture was degassed by bubbling N_2. The mixture was polymerized at 353 K for 16 hours. The polymer was strongly cross-linked and the template molecule was removed from the polymer by washing the frit/membrane with an acetic acid/methanol solution (15% v/v) three times for 1 hour each wash. A final wash was done in acetone and the membrane was stored in distilled water. A control polymer was synthesized in the same manner, but without the L-Proline present.

Both the MIP membrane and the control membrane were placed in electrochemical cells with a platinum electrode on either side of the membrane. Impedance measurements were taken at 1kHz with a 5 mV amplitude, and the membranes were tested for their ability to detect L-Proline. In addition, the films were tested for response to addition of an electrolytic solution (1 µL additions of 50 mM KCl solution).

Figure 1a shows that the control polymer (not imprinted) has a negligible change in capacitance when L-proline is added to the solution. Similarly, tests where KCl is added to the solution do not change the capacitance of the membrane. Figure 1b shows that the MIP membrane responded with a change in capacitance of 4.8%. The addition of L-proline gave a solution of 6.5x10-6 moles/L L-proline. The lower limit of sensitivity was not reached.

In this effort, we fabricated and tested a non-conducting sensing membrane for the amino acid L-Proline, based on a molecularly imprinted polymer (MIP). The MIP was synthesized from methacrylic acid (MAA) using L-Proline as the template. Subsequently, the membrane was tested using both current versus voltage measurements and impedence measurements. Although we we did not reach the lower limit of sensitivity in these measurements, we anticipate that by measuring the capacitance changes of the membrane we should be able to measure concentrations down to at least 100s of nanomoles/L.

[1] Ye et al. *Macromoleucles*, **33**, 8239 (2000).
[2] Piletsky et al. *Biosensors and Bioelectronics*, **10**, 959 (1995).

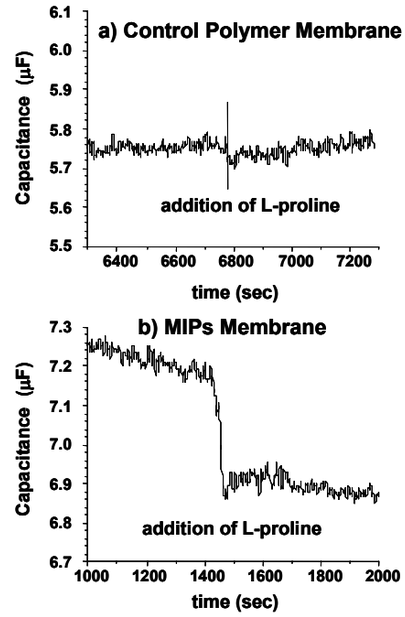

Figure 1. MIP response to L-Proline. *a) The control membrane shows no response to the addition of 6.5x10^{-6} M L-Proline, The MIP membrane responds to addition of 6.5x10^{-6} M L-Proline, while the control membrane does not.*