Synthesis and Evaluation of a Molecularly Imprinted Polyurethane–Poly(HEMA) Semi-Interpenetrating Polymer Networks as Membrane

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ABSTRACT: Semi-interpenetrating polymer networks based on polyurethane and poly(2-hydroxy ethyl methacrylate) [poly(HEMA)] has been synthesized with memory towards cholesterol, which is induced by molecular imprinting. It is found that the polymer possesses the mechanical integrity of a typical membrane together with the molecular recognition ability. The polymer has been evaluated for its ability to differentiate the print molecule by studying its interaction with cholesterol and testosterone. The novel approach discussed here seems to an interesting approach to synthesise molecularly imprinted polymers as membranes. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 19–22, 1998

Key words: molecularly imprinted polymer; semi-interpenetrating polymer networks

INTRODUCTION

Molecular imprinting has received considerable attention in recent years as a simple and elegant method for creating memory sites of template molecules in crosslinked polymers.[1,2] The procedure of molecular imprinting is based on the prearrangement of print (template) molecules and functional monomers prior to polymerization. After the polymerization, the print molecules are removed, and the resultant polymer contains specific sites, which can bind the print molecules with a remarkable degree of selectivity.[1] The wide applicability of molecular imprinting is reflected in its uses as diverse as the preparation of chiral chromatographic phases, antibody–receptor mimics, artificial enzymes, and adsorbents for biomolecules.[1,3–7]

Molecularly imprinted polymers are highly crosslinked, rigid matrices that can be powdered and are normally insoluble in most solvents.[1] Though these systems can be used as adsorbents for molecules of interest, the feasibility of using them as membranes that could be used in permselective separation, affinity separation, and as sensor's membranes are highly restricted. As far as we know, molecularly imprinted polymers (MIPs) have not been prepared in the form of flexible films. This article describes a simple approach to design a molecularly imprinted semi-interpenetrating polymer (semi-IPN) in the form of a film and discusses its preliminary evaluation as membrane.

EXPERIMENTAL

2-hydroxy ethyl methacrylate (HEMA), testosterone, and cholesterol were obtained from Sigma Chemicals, St. Louis, MO. HEMA was used after removing the stabilizer. Ethylene glycol dimeth-

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acrylate (EGDMA) procured from Emerck, AG, Germany, was used without further purification. Polyurethane used in this study was based on polytetra methylene glycol (PTMEG; molecular weight, 1000), methylene bis(p-cyclohexyl isocyanate) (H_{12}MDI), and 1,4-butane diol. The polymer was synthesized as reported elsewhere.[8] The polymer with a weight percentage of hard segment content of 23%, having a molecular weight of 123,000 (weight-average), was used for the study.

A Nicolet (Nicolet Inc, Madison, WI) model Impact 410 Fourier transform infrared (FTIR) spectrophotometer and horizontal attenuated total reflection (ATR) accessory (Nicolet Inc) were used for recording the ATR IR spectra of the samples. The number of scans were 50.

A Hitachi model S-2400 scanning electron microscope was used to visualize the surface features of the samples. A thin layer of gold was coated prior to the observation.

A Waters (Waters Assoc Inc, Milford, CT) high-pressure liquid chromatography (HPLC) system consisting of a model 510 solvent delivery pump, a Rheodyne model 7725 I injector, and a model 486 tunable absorbance detector was used for the chromatographic analysis. A μ-Bondapack C 18 column in conjunction with methanol as mobile phase at a flow rate of 1 mL/min was used for the separation. The column effluents were detected at 206 nm (for cholesterol) and 241 nm (for testosterone).

A Universal Testing machine (Instron Co, UK) was used for the mechanical properties of the polymers as per ASTM D 882.

Synthesis of the Molecularly Imprinted Membrane

1 g of polyurethane was dissolved in chloroform. 0.5 g of HEMA and 2 g of EGDMA were added to the polyurethane solution. 400 mg of cholesterol (print molecule) was also added to this solution. The solution was stirred at room temperature (30°C) to get a clear solution and then transferred to polyethylene container. The container with the solution was exposed for a period of 20–30 min to evaporate the chloroform. The mixture then appeared as a soft gel. The container was filled with nitrogen, closed, and then subjected to gamma irradiation to initiate the polymerization of the monomers from a ^{60}Co source [Panoramic batch irradiator (BARC) Bombay, India] to total dose of 0.25 mrad at a rate of 0.1 mrad per hour. After the irradiation process, the polymer was extracted with methanol and then with hexane to remove the print molecule. The complete removal of cholesterol (print molecule) was ensured prior to the use of the polymer for further studies. In a similar fashion, polyurethane–poly(HEMA) semi-IPN polymer was also prepared without adding cholesterol to serve as control.

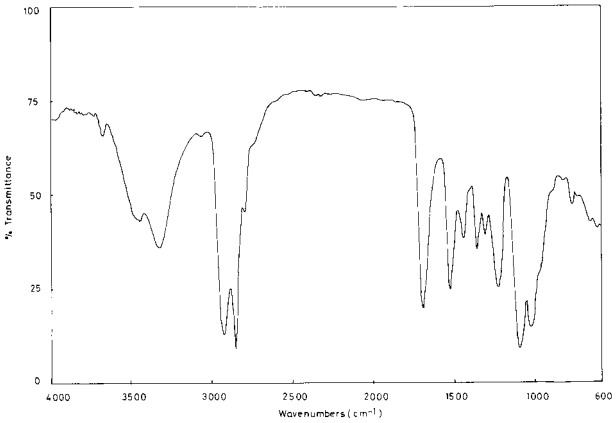

Figure 1 FT–ATR infrared spectra of MIP–IPN.

Sorption Studies Using the Polymers

The polymer strips (3×2 cm^2) having a thickness of 0.2 mm were placed in methanolic solution of cholesterol and testosterone for a period of 1 h. The polymers strips were taken out and then extracted with hexane. The extracts were analyzed chromatographically to estimate the quantity of cholesterol and testosterone. All the estimations were performed in triplicate.

RESULTS AND DISCUSSION

Figure 1 shows the ATR IR spectrum of the molecularly imprinted semi-interpenetrating polymer networks. (MIP–IPN). The spectrum shows all the features of polyurethane based on PTMEG, H_{12}MDI, and 1,4-butanediol.[9] The additional feature of the spectrum is the presence of a relatively strong peak centred around 3500 cm^{-1}, which could be assigned to the —OH group of poly(HEMA). Other major peaks associated with C=O and C—O—C stretching modes cannot be differentiated since these peaks are merged with absorption peaks of polyurethane (PU).

The equilibrium water uptake of the MIP–IPN is nominally higher (2.3%) than the PU used in this study (0.49%). It is well known that the extent of water uptake of MIPs derived from hydro-

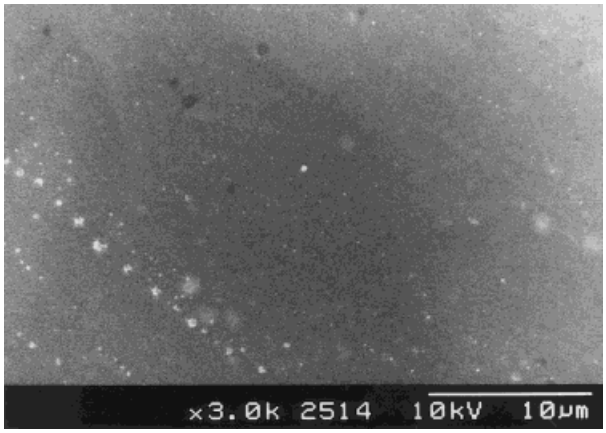

Figure 2 Scanning electron micrograph of polyurethane.

philic monomers such as HEMA is several fold less than the respective homopolymers since the MIPs are extensively crosslinked. The equilibrium water uptake, though less compared to the water uptake of a typical hydrophilic polymer, is higher that of the PU. This variation in the water uptake could be due to the presence of poly(HEMA) species in the PU matrix.

Figures 2 and 3 depict the scanning electron micrographs of PU and MIP–IPN. The surface of PU is nearly smooth, while the texture of the MIP–IPN is distinctively altered further, reflecting the formation of a different matrix.

Table I summarizes the mechanical properties of the polymers. The ultimate stress and strain of the MIP–IPN is less than PU. The highly crosslinked HEMA species in the matrix could prevent stretch-induced ordering in PU, which is a prominent factor contributing to the ultimate stress–strain parameters of PU.[10]

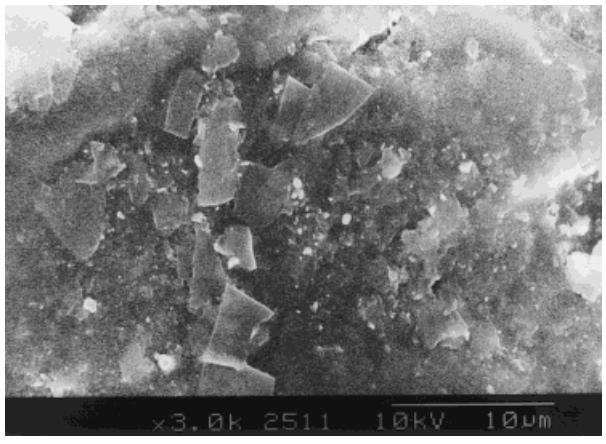

Figure 3 Scanning electron micrograph of MIP–IPN.

Table I Mechanical Parameters of the Polymers

Polymer	Stress (MPa)	Strain (%)
MIP–PIN	19.6 ± 4	346 ± 8
Semi-PIN (control)	19.8 ± 3	356 ± 3
Polyurethane	35.0 ± 7	620 ± 16

Table II shows the uptake of cholesterol by PU control semi-IPN and MIP–IPN. The cholesterol absorption is more in MIP–IPN. It is less in control semi-IPN. Comparatively higher uptake of cholesterol by MIP–IPN compared to PU and control semi-IPN indicates that the increased absorption is due to the molecular imprinting, which leads to the creation of recognition sites in the polymer towards cholesterol. PU absorbs relatively higher quantity of cholesterol compared to the control semi-IPN. PU of the type used here is hydrophobic, and it is well known that these polymers absorb lipophilic components, such as fatty acid esters and cholesterol.[11,12] The extent of absorption is normally increases with the soft segment content of the PU. The PU used in this study contains a higher amount of soft segment content and as a result of this, an increased amount of cholesterol absorption can be expected. The reduced absorption of cholesterol by the control semi-IPN could assigned to the increased polarity of the material acquired as a result of the interpenetration of poly(HEMA) chains.

Table III shows the testosterone absorption of the polymers under the similar experimental conditions. Testosterone is taken as a molecule of similar structure and shape of cholesterol. Normally, this molecule is used to evaluate the selectivity of MIP imprinted for cholesterol.

The affinity of MIP imprinted for cholesterol towards testosterone or similar molecules should be negligibily small. In other words, the extent of absorption of such molecules should be very small.

Table II Extent of Absorption of Cholesterol by the Polymers

Polymer	Amount of Cholesterol Absorbed by 100 mg of the Polymers (mg)
MIP–PIN	5.52 ± 0.06
Semi-PIN (control)	0.72 ± 0.05
Polyurethane	2.61 ± 0.04

The data summarized in Table III, in fact, agree well with this view. Interestingly the testosterone absorption by the MIP–IPN is less than PU, and it is nearly equal to the quantity absorbed by the control semi-IPN. This parameter clearly suggests that imprinting imparts affinity sites to only the print molecules which is, of course, well known. The increased absorption of testosterone by PU compared to control semi-IPN and MIP–IPN again can be assigned to the hydrophobicity of the PU. More absorption of testosterone can be expected since testosterone is also a hydrophobic molecule. The absorption of testosterone by the control semi-IPN and MIP–IPN can be due to presence of the hydrophobic polyurethane chains in the respective matrices.

MIPs are well known for their reusability.[1] The MIP–IPN after equilibrating with the cholesterol solution is extracted with hexane and subsequently used for further absorption studies. The quantity of cholesterol absorbed in each cycle is depicted in Table IV. The data apparently suggest that binding ability of the polymer is unaffected by the extensive extraction process reflecting the reusability of the polymer.

The data discussed here demonstrate the feasibility of synthesizing MIP in the form of a semi-IPN with the morphology of a typical membrane. Synthetic polymeric membranes with such imparted affinity may be useful in the selective separation of molecules of interest. The mechanical data show that polymer has the required flexibility and strength of commonly used membranes. The method suggested here appears to be a simple approach to create selectivity in membranes towards the separation of structurally close molecules.

Table III Uptake of Testosterone by the Polymers

Polymer	Amount of Testosterone Absorbed by 100 mg of the Polymers (mg)
MIP–PIN	0.57 ± 0.03
Semi-PIN (control)	0.62 ± 0.04
Polyurethane	1.87 ± 0.07

Table IV The Effect of Extraction on Absorption Capacity of MIP–PIN

Extraction Cycle	Extent of Uptake of Cholesterol by 100 mg
0	5.52 ± 0.06
1	5.48 ± 0.07
2	5.46 ± 0.06
3	5.56 ± 0.04

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