

ABSTRACT

A molecular imprinting procedure based on hydrogen bonding interactions between the template butoxycarbonyl-D-phenylalanine (Boc-D-PhA) and the functional monomer methacrylic acid (MAA) was used to synthesize a porous molecularly imprinted polymer (MIP) in the pores of polypropylene (PP) microfiltration and poly(ethylene terephthalate) (PET) track-etched membranes for the separation of enantiomeric mixture (Boc-DL-PhA) in solution via permselective transport through these composite membranes under diffusion (dialysis) and electro dialysis conditions. Bulk porous MIP and non-imprinted polymer (NIP; for control experiments) monoliths were synthesized to optimize the synthesis conditions and their pore morphology. Pre-modification of the entire pore surface of the PET track etched and PP microfiltration membrane by UV-initiated grafting with polyethylene glycol (400) monomethacrylate (PEGMA) was done using an already established method including the adsorption of the photoinitiator, benzophenone (BP). Subsequently these membranes were functionalized by filling the pores with porous MIP and NIP monoliths from MAA and ethyleneglycol dimethacrylate (EDMA) (*poly(MAA-co-EDMA)*) and compared with the membranes which had been functionalized without pre-modification step.

Characterization had been done mainly by degree of grafting (DG), scanning electron microscopy (SEM), gas adsorption isotherm method (BET), and adsorption experiments in combination with chiral high performance liquid chromatography. Diffusion (dialysis) and electro dialysis experiments were conducted using these enantioselective membranes to separate Boc-DL-PhA racemic mixture. In case of bulk monoliths, MIP *poly(MAA-co-EDMA)* monoliths have shown higher binding capacity and enantioselectivity for the imprint molecule (Boc-D-PhA) in the racemic mixture of Boc-D/L-PhA in acetonitrile (AN) as solvent. However, the enantioselectivity was slightly decreased with the increase in the equilibration time. The MIP *poly(MAA-co-EDMA)* monolith PP and PET composite membranes have

shown higher binding capacity than their respective NIP composite membranes. The pre-modified MIP composite membranes have shown better enantioselectivity than the unmodified MIP composite PP membranes.

The effect of pre-modification on the interaction of macroporous substrates (membranes) with mainly micro- and mesoporous polymer monoliths has also been studied. DG values after composite membrane preparation under identical conditions were not influenced by the pre-modification. However, from SEM images it was very clearly seen that the pre-modification step prevents the formation of voids at the monolith-membrane pore interface. Larger specific surface area and pore volume values for composite membranes prepared after pre-modification fully support the SEM results. Especially large differences in pore structure between the two different composite membranes were found in the mesopore range. Hence, with the pre-modification step, it is possible to prepare porous composite membranes where the trans-membrane transport is exclusively controlled by the pore and surface structure of a functional polymeric monolith, for example made from a molecularly imprinted polymer (MIP).

The effective diffusion rate of PEGs or a racemic mixture of template (Boc-D-PhA) and its counterpart (Boc-L-PhA) through the composite membranes was a function of imprinting and degree of pre-modification. The MIP *poly(MAA-co-EDMA)* monolith PET composite membranes pre-modified with 25 g/L of *PEGMA* had shown larger effective diffusion coefficient values than the NIP *poly(MAA-co-EDMA)* monolith PET composite membranes and the further increase in the DG values of pre-modification resulted in a significant decrease in effective diffusion coefficient values. The larger values of effective diffusion coefficient for the diffusion of PEGs in water and racemic mixture in AN through MIP composite membranes indicated that the imprinting leads to connected pores within the composite structure which are responsible for this increased flux. In contrast, during the diffusion of single enantiomer in AN/H₂O system, these membranes behaved like a “gate”: only for the

amino acid used as template, no flux was detected while the other enantiomer diffused through the membrane. This effect is presumably due to an increase of membrane swelling as a consequence of binding of the template to imprinted sites which resulted in the blocking of the pathways for the transport of the molecules.

The process of electro dialysis had facilitated the transport of template molecules (Boc-D-PhA) through the *poly(MAA-co-EDMA)* PET composite membranes pre-modified with *poly(PEGMA)*, while there was no significant transport of the template molecules through these composite membranes during the diffusion process. However, both MIP and NIP composite membranes did not show any enantioselective transport during the process of diffusion or electro dialysis when using racemates. The nature of the solvent and its pH are very much important for the binding and selective transport of molecules through the imprinted polymer materials. The influence of solute concentration onto enantioselectivity (high for low concentrations) and onto flux through the membrane (high for high concentrations) are contradictory with respect to enantio-selective transport in the diffusion experiments performed in AN. And electro dialysis was only possible in an aqueous solvent where enantio-selectivity was not detectable.