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Catalysis of a β-elimination applying membranes with incorporated molecularly imprinted polymer particles

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Summary

Molecularly imprinted membranes are known to be applicable as recognition elements in separation, extraction and sensors, however, not as catalysts. In this paper, two different formats of molecularly imprinted membranes were generated and used as catalysts in a dehydrofluorination reaction. The first format was based on cellulose filter membranes which were coated with a polymer imprinted with a transition-state analogue of the chosen reaction. Alternatively, ground bulk polymers have been incorporated in polyvinyl alcohol (PVA) matrices on cellulose membranes. Both types of membranes were evaluated in membrane reactors. Either the substrate solution was pumped once only through the membrane, or the substrate solution was recirculated through the membrane. The coated membranes did not show any specific catalytic effect when comparing the molecularly imprinted with a non-imprinted control polymer membrane. Nevertheless, the PVA membranes containing the imprinted polymer particles showed specific catalytic effects, compared to PVA membranes with incorporated non-imprinted control polymer particles.

Introduction

Membranes are known to be applicable for many purposes in separation techniques [1, 2] or catalysis [3, 4]. Their major advantages are high throughput feasibility and the versatility of the technique regarding different analytes or reactions. Membranes are based on a variety of materials like cellulose, fiber glass, polymers or composites [5]. Particles of noble metals can be incorporated or attached in order to achieve a catalytic activity of the membrane [6, 7]. Nevertheless, it is difficult to generate membranes for selective recognition of only a single component. Antibodies or enzymes are known to provide the required specificity. However, like in HPLC the lack of durability of immobilised bioreceptors is the major bottleneck for the application of phases linked with biomolecules [8-10]. Therefore, molecular imprinting as a technique for fabricating artificial polymeric receptors with high specificity has been chosen to overcome these problems. Generally, in this imprinting

procedure appropriate functional monomers are added to a template, followed by their self-assembly based on covalent [11] or non-covalent [12] interactions. The actual polymerisation is executed in the presence of high amounts of crosslinker monomers and a porogen (solvent). After processing the polymer and extraction of the template, the imprints of the template molecules within the polymer network act as the template's antibody, if the template itself is considered as an antigen. Such molecularly imprinted polymers (MIPs) and can be applied for instance in affinity separation techniques [13, 14]. In case the template is a transition state analogue of a selected reaction, its polymer imprint is expected to work similarly to an active centre of an enzyme [15-28]. In the past years, a few groups have described the generation of molecularly imprinted polymer membranes, however nearly exclusively for analytical purposes, i.e., for separation, extraction or sensoring [29-49].

The production of molecularly imprinted membranes started in the 1990s based on the idea to use MIPs as highly specific phases for sensor applications. For this purpose, Piletsky et al. developed a membrane imprinted with the pesticide atrazine. They used methacrylic acid (MAA) as functional monomer, ethyleneglycol dimethacrylate (EGDMA) as crosslinker, azobis(isobutyronitrile) (AIBN) as initiator and dimethyl-formamide as porogen, and performed the polymerisation on a glass filter surface. The resulting membranes showed quantitative changes of electroresistance when sensoring atrazine in liquid samples in a range of 0.01 to 0.5 mg/mL [30, 31]. Sergeyeva et al. developed atrazine imprinted membranes with oligourethane as an additive between two glass slides. Using these membranes, atrazine could be detected down to 5 nmol/L [32, 33]. Kobayashi, Wang and others developed a phase inversion precipitation technique for the production of membranes imprinted, e.g., with theophylline [34-37]. They used poly(acrylonitrile-*co*-acrylic acid) in dimethylsulfoxide and casted the membranes by coagulation in the presence of water. With these membranes, it was possible to separate theophylline from its close derivative caffeine with a separation factor of $\alpha_{THO/CAF} = 52$ [35]. Furthermore, Yoshikawa et al. used tripeptides or tetrapeptides as anchor molecules immobilised in copolymers of acrylonitrile and styrene. This was done by a simple membrane casting process based on the evaporation of the solvent. By this means, membranes with even chiral recognition sites could be realised [38]. An alternative approach was presented by Mathew-Krotz et al. who produced film-like membranes imprinted with 9-ethyladenine on glass slides. Interestingly, the authors observed the highest transport through the membrane for the template itself or analogues like adenosine. Analytes structurally different to the template were more retarded and thus, could be separated from the adenine derivatives. The authors came to the conclusion that most probably the adenine components were selectively accelerated due to reversible complexations and exchanges between the adenine group and the imprints [39]. Kochkodan et al. described the generation of MIP coatings on polyvinylidene fluoride membranes to be used for microfiltration. High-permeabilities as well as mechanical and chemical stability were named as major advantages of the thin-layer MIP composite membranes [40]. A completely different topic was addressed when using membranes as vehicles for screening combinatorial libraries of MIP recipes [50]. When searching for publications demonstrating the use of molecularly imprinted membranes in catalytic approaches, only one reference could be found. However, this work shows only the combination of a catalyst and MIPs in one membrane, i.e., the use of a bifunctional polymer membrane exhibiting enantioselective permeabilities caused by an embedded

imprinted polymer as well as catalytic properties induced by the immobilised lipase [51].

Our paper describes for the first time catalytically active molecularly imprinted polymer membranes. Here, two ways of producing molecularly imprinted membranes are presented as well as their application as catalysts. The first attempt focused on the synthesis of catalytically active MIP films on membrane carriers which, however, did not show any specific catalytic effect compared to non-imprinted control polymer films on membranes. Similar to the approach of Lehmann et al. who used molecularly imprinted nanoparticles as separative phase in composite membranes [52, 53], our second approach aimed on the incorporation of MIP particles with catalytic properties in polyvinyl alcohol membranes.

The polymeric membranes were produced in order to be applied as catalysts for the dehydrofluorination of 4-fluoro-4-(p-nitrophenyl)-2-butanone. Therefore, N-benzyl-isopropylamine was chosen as template. N-benzylisopropylamine is a hybrid of a substrate analogue and a transition state analogue of the dehydrofluorination of 4-fluoro-4-(p-nitrophenyl)-2-butanone. First of all, this secondary amine is similar to the CH_2-bridge of the substrate 4-fluoro-4-(p-nitrophenyl)-2-butanone, but also allows strong interactions with an acidic monomer. And secondly it is comparable with a putative transition state of the butanone in the dehydrofluorination process due to the absence of a fluorine ligand.

Using MAA as functional monomer, specific molecular imprints of this transition state analogue can be generated with EGDMA as crosslinker (figure 1), as already shown in a few publications [22, 26].
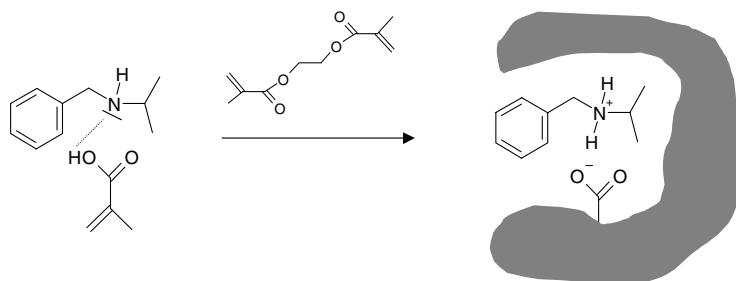
Figure 1. Generating an MIP imprinted with N-benzylisopropylamine as TSA of the dehydrofluorination of 4-fluoro-4-p-nitrophenyl-2-butanone

After polymerisation and extraction of the template, the resulting polymer allows the substrate to interact with the imprint and the carboxy functionality helps to accelerate the elimination of hydrofluoric acid from the butanone (figure 2).

Catalysis of this reaction by molecularly imprinted polymers (MIP) or imprinted proteins has already been shown, but it has been performed only in batch or fixed bed reactors [22-26]. In both discontinuous and continuous reactors product inhibition had been observed. Thus, a system was in demand to allow as well a continuous mode and reduction of product inhibition effects on the catalyst. Membranes allow a relatively high throughput of fluids and they are also known to act as separators or catalysts. However, the combination of catalytically active molecularly imprinted polymers and membranes has not been shown, yet.
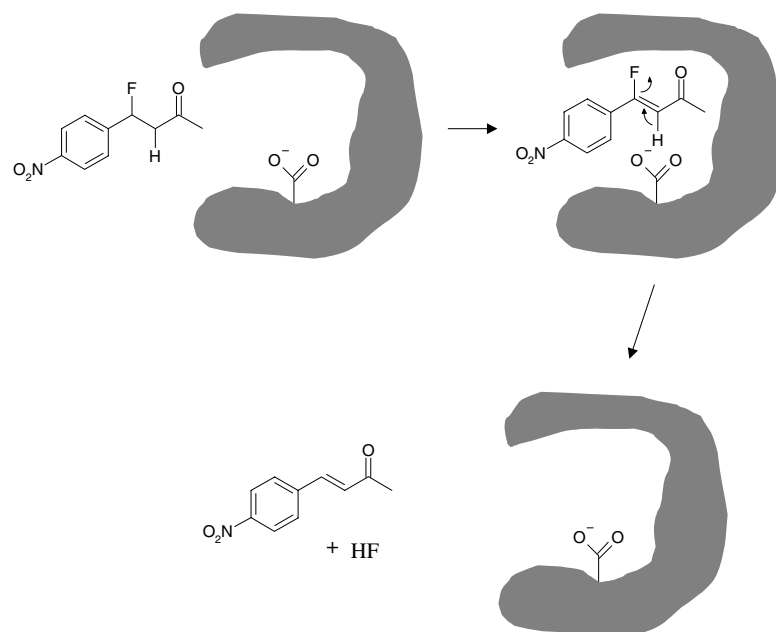
Figure 2. MIP-catalysed dehydrofluorination of 4-fluoro-4-p-nitrophenyl-2-butanone

Experimental

Materials

All solvents were from Fluka, all fine chemicals were obtained from Sigma.

Generating MIP particles to be incorporated in membranes

N-benzyl-isopropylamine was chosen as template. Based on a paper of Müller et al. [22] a molecularly imprinted polymer was generated by merging 233.2 mg N-benzylisopropylamine with 540 mg MAA, 4.95 g EGDMA and 40 mg AIBN in 2.5 mL CH_2Cl_2. The control polymer was generated in the same manner, but without the template. Polymerisation was carried out at room temperature applying UV radiation.

Resulting bulk polymers were ground utilizing a ball mill (Retsch, type S 100), wet sieved (mesh, 25 μm) with acetone, ultrasonicated and sedimented after 30 minutes (3 times), washed with methanol, dried (65°C) and extracted with methanol/acetic acid 7:1 (v/v), washed with methanol to remove the acid, dried and incorporated in the membranes.

Incorporating MIP particles in polyvinyl alcohol (PVA) membranes

2.6 g of a 5% (w/w) solution of vinyl alcohol was refluxed for 48 h at 90°C, cooled to room temperature and mixed with 0.295 g glutardialdehyde and 25 mg dry MIP or CP particles, respectively. The mixture was homogenised in an ultrasonication bath. A cellulose membrane wetted with 2 mol/L hydrochloric acid was covered with a film

of the vinyl alcohol mixture (thickness: 1 mm) and frozen for 30 minutes at –20°C and thawed at 0°C. The freezing/thawing process was repeated twice and finally, the membranes were rinsed with methanol/acetic acid (4:1) in order to remove the template.

Generating MIP coatings on supportive materials

Membranes were generated by wetting filter papers (MN 640, D = 65 mm, Macherey-Nagel) with 750 μl of the imprinting mixture already used for producing bulk polymers. Excess of the imprinting mixture was removed by 2 minutes centrifugating the wet filter papers on a membrane dish. Control membranes were produced by using the same mixture as for the MIP, but without the template. During polymerisation in an oven at 60°C or in a UV-reactor, the filter paper was sealed in a set of two petri dishes to avoid excessive evaporation of porogen or even monomers from the filter. After polymerisation, all membranes were individually inserted in a membrane reactor and rinsed with methanol/acetic acid (7:1) for removing remains of template and/or monomer. After a final cleaning step with methanol, the membranes were investigated in membrane reactors regarding their performance as catalysts for a dehydro-fluorination under aspects of chemical engineering, i.e., changing parameters like temperature, volume flow and substrate concentration.

Synthesis of substrate 4-fluoro-4-(p-nitrophenyl)-2-butanone

Nitrobenzaldehyd (4 g) was dissolved in 20 mL acetone and mixed with 500 μl of a 5.0 mol/L solution of NaOH. The mixture were stirred for 17 h and thermostated at 0°C. After this first step the remains of acetone were evaporated, the product redissolved in 80 mL ethyl acetate, washed twice with 80 mL saturated solution of NaCl, and dried with $MgSO_4$. After removal of ethyl acetate, the product was purified chromatographically applying silica 60 (0.063-0.2 mm, Merck) as stationary phase and hexane / ethyl acetate 8:2 (v/v) as mobile phase (control by TLC). The pure product (1.354 g) was dissolved in 10 mL CH_2Cl_2, cooled to –78°C (solid CO_2 in 2-propanol) and 1.234 g of diethylaminosulfur-trifluoride was added. The compounds were stirred overnight and the reaction was stopped when the mixture reached room temperature. A final purification of the 4-fluoro-4-(p-nitrophenyl)-2-butanone was carried out applying silica 60 and hexane / ethyl acetate 93:7 (v/v) (1 L) and 8:2 (v/v) (2 L) (TLC control) [22, 26].

*Investigating MIP membranes in membrane reactors*

Both types of membranes were used for investigating the catalytic effect on the dehydrofluorination of 4-fluoro-4-(p-nitrophenyl)-2-butanone. Therefore first of all, 11 mL of a solution of 0.05 mg/mL substrate in acetonitrile/water 1:1 was rinsed quickly through the reactor in order to replace the dead volume (1 mL/min). Afterwards, the membranes were rinsed with the same solution at a flow rate of 0.1 mL/min or 0.05 mL/min. The collected product samples were analysed by HPLC and UV-spectroscopy. The substrate stock solution to some extent already contained product. Thus, the actual substrate concentration had to be determined leading to a value of 0.032 mg/mL corresponding to 0.152 mmol/L. At a flow rate of 0.1 mL/min,

the contact time or length of stay of the substrate in the total volume of the membrane is around 6.6 min, when using a non-coated 0.2 mm thick membrane with a diameter of 65 mm. An additional polymer film on the membrane may lead to a doubled thickness of 0.4 mm, resulting in a contact time of 13.3 min. A wet PVA membrane with a thickness of approximately 1.2 mm allows every substrate molecule to stay for nearly 40 min in the membrane matrix at a flow rate of 0.1 ml/min.

Results

First attempts on generating molecularly imprinted catalytically active polymeric membranes were focused on coating filter membranes with a polymer. The paper membranes firstly were wetted with a monomer template mixture based on the MIP recipe already shown to be successful [26]. The excess of the imprinting composition was removed by centrifugation of the membrane on a plate. After polymerisation either in an oven or in an UV-reactor the membranes were rinsed with methanol/acetic acid (7:1) to remove the template and finally, the solution of the substrate 4-fluoro-4-(p-nitrophenyl)-2-butanone was pumped through. When comparing membranes covered with either MIP or a non-imprinted control polymer (CP) which was synthesised like the MIP but in the absence of the template, surprisingly no differences regarding substrate degradation could be observed. The question arose, whether a substantial coating has been established. Therefore, a blank filter paper membrane as well as a MIP coated membrane were investigated by scanning with an electron microscope. When comparing the two SEM results, neither a clear polymer coating could be observed on the MIP membrane, nor any differences of the blank and the coated membrane were noticed. Consequently, this approach was not focused any further.

However in a different attempt, MIP particles which already had been characterised in batch and fixed bed reactors [26] were incorporated in polyvinyl alcohol (PVA) membranes [52, 53]. PVA is a known material for the production of flexible and porous membranes [54-57]. The particles first of all were investigated microscopically, showing non-spheric ground fragments in a size range of 10 to 25 μm (figure 3, left) with macropores of about 50 nm in diameter (figure 3, right).
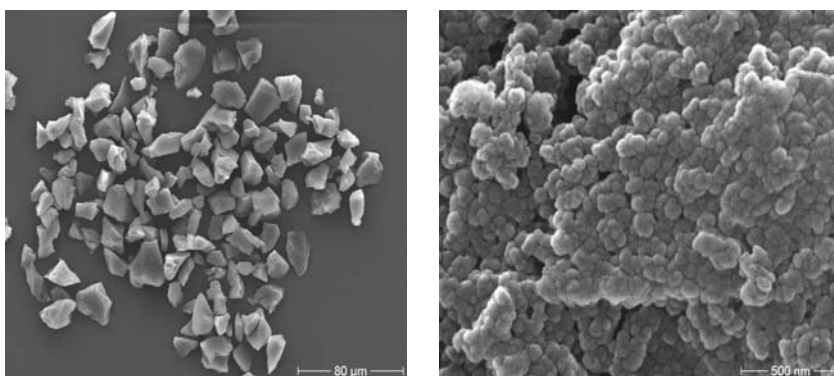
Figure 3. SEM of MIP particles to be incorporated into a PVA membrane and used as catalyst for a dehydrofluorination (scales: 80 μm (left), and 500 nm (right))

The results were found for both CP and MIP particles. For incorporating the particles into membranes, first of all vinyl alcohol and glutardialdehyde were mixed with MIP or CP particles, respectively. A cellulose membrane was used again as support material and, after activation with HCl, it was covered with a 1 mm thick film of this mixture. After polymerisation a repeated freezing/thawing process led to the desired PVA membranes. By this means, the MIP or CP particles were immobilised within the highly porous PVA membrane, as shown in figure 4.
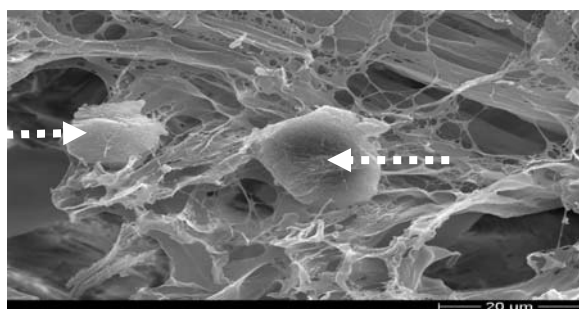

Figure 4. SEM of a PVA membrane with incorporated MIP particles (white arrows) to be used as catalyst for a dehydrofluorination (scale: 20 µm)

After a final extraction of remaining monomers and the template from the membrane using methanol/acetonitrile (4:1), the membrane was placed into a stainless steel membrane reactor for catalysing the dehydrofluorination in a continuous mode. In a first row of experiments, the substrate solution was passed at different volume flows (0.1 and 0.05 mL/min) at 55°C only once through the reactor, showing no measurable chemical reaction or catalysis effect. This may be explained by the relatively low capacity of the membrane in combination with relatively high flow rates resulting in contact times of the substrate with the bindings sites of the catalyst too short to allow any effect. In order to overcome this drawback, the substrate solution was circulated through the membrane. Based on this construction, obvious degradation of the substrate was observed when applying the PVA membranes containing MIP particles (figure 5) for 7 days at 55°C combined with a flow rate of 0.1 mL/min of the substrate solution.

The most drastic conversion occurred in the first 4 hours, explicable by the pseudo-first-order-rate law of the reaction [26]. Although the control membrane with incorporated CP particles also showed catalytic effects due to unspecific interaction, the MIP membrane performed better. Based on the assumption of a first order reaction, the following equation for the reaction rate was used for the determination of the rate constants: $\ln (n_0/n_i) = k \cdot t \cdot V_{membrane}/V_{solution}$ with $V_{membrane} = 3.3$ mL and $V_{solution} = 85$ mL (80 mL in the reservoir and 5 mL in the tubing).

Thus, at 55°C and at a flow rate of 0.1 mL/min rate constants for the MIP membrane of $k_{MIP} = 0.07$ min^{-1} ± 5% and for the CP membrane of $k_{CP} = 0.045$ min^{-1} ± 5% were calculated via linear regression of the values obtained in the first 4 hours (where a visable inhibition of the catalysts began to occur), resulting in a relative catalytic effect of $k_{MIP}/k_{CP} = 1.6 \pm 0.1$. This value is a little lower compared to the effects
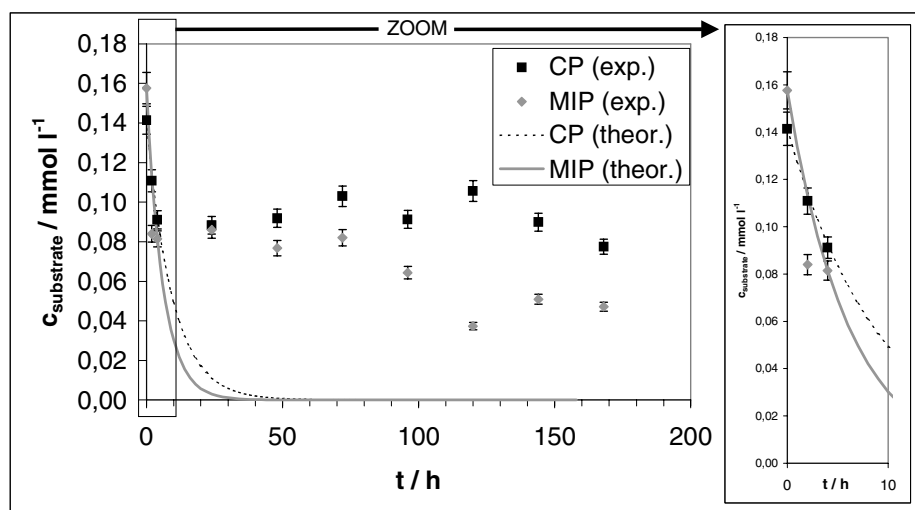
Figure 5. Dehydrofluorination reaction using PVA membranes with either incorporated MIPs (grey rhombuses) or CPs (black squares) (T: 55°C; flow: 0.1 mL/min) (experimental values). Substrate concentration versus time. The substrate was circulated through the membrane reactor. The theoretical curves were obtained with rate constants which have been determined based on the data points of the first four hours (see inlet on the right). After this period, product inhibition occurred in the experiments. The correlation coefficients for the experimental and theoretical curves in the first four hours are: r = 0.921 for the MIP, and r = 0.998 for the CP

obtained by Müller et al., Slade et al., Beach et al. and Ohya et al. [22-25] (table 1). And, it is lower than the value of $k_{MIP}/k_{CP} = 5.97$ which we obtained when using the same sort of MIP particles in batch reactors [26].

Using these newly determined rate constants, theoretical curves were calculated based on the pseudo-first-order rate law. These curves are also shown in figure 5. Especially in the insert (zoomed graph) it becomes obvious that the MIP membrane is catalytically more active than the CP membrane. In the MIP experiment at the beginning, a slightly higher substrate concentration was chosen compared to the CP investigation. However, the remaining substrate concentration at t = 4 h was clearly lower in case of the MIP-membrane compared to the CP-membrane (figure 5, insert on the right). After this first period of 4 hours, interestingly the runs of the experimental and the theoretical curves became different. This is simply explainable by the product inhibition of the MIP catalyst as well as of the non-specific CP. Nevertheless, the product inhibition observed for the catalysis with MIP particles suspended in batch reactors [26] could be reduced via this membrane set-up. Here, a substrate conversion of nearly 70% was obtained, in contrast to a value of approximately 55% for the same period in the suspension batch reactor.

When reducing the flow rate to 0.05 mL/min (at 55°C) the differences of MIP and CP membranes were less pronounced. When investigating the dehydrofluorination at a temperature of 30°C at a flow rate of 0.1 mL/min, preliminary results show a much lower relative catalytic effect, i.e. a k_{MIP}/k_{CP} value of around one. For calculating the actual activation energies more investigations at different temperatures are necessary and will be performed in the future.

Table 1. Dehydrofluorination of 4-fluoro-4-(p-nitrophenyl)-2-butanone catalysed by molecularly imprinted materials

TSA (template)	Imprinted Matrix	Solvent for substrate	Relative catalytic effect of the MIP	Reference
N-benzyl-isopropylamine	Polymer (MAA/EGDMA)	Acetonitrile	2.4	[22]
Benzylmalonic acid	Polymer (MMA/EGDMA)	Benzene	3.2	[23]
N-methyl-N-(4-nitrobenzyl)-δ-aminovaleric acid	Protein (BSA)	Ethyl acetate	3.3	[24]
N-(p-nitrobenzyl)-isopropylamine	Protein (β-lactoglobulin)	Acetonitrile	3.27	[25]
N-benzyl-isopropylamine	Polymer (MAA/EGDMA)	Acetonitrile / water (1:1)	5.97	[26]

Conclusion

For the first time, molecularly imprinted catalytically active polymer membranes are presented. These membranes are based on MIP particles incorporated in polyvinyl alcohol films on cellulose membranes. When comparing MIP and CP membranes at 55°C in combination with a modest flow rate of 0.1 mL/min of the substrate solution, a clear catalytic effect of $k_{MIP}/k_{CP} = 1.6$ was observed. However, this was obtained by applying a system allowing the substrate-product mixture to recirculate through the catalytic membrane. Passing the membrane only once, the substrate did not have enough time to interact sufficiently with the catalyst, i.e., a measurable degradation of the substrate was not observed. An investigation under aspects of chemical engineering, i.e., by varying temperature and flow rate of the substrate solution, led to the conclusion that, on the one hand, at reduced flow rates differences between MIP and CP are observed to a lesser extent. On the other hand at elevated temperatures the MIP membrane performed better than at lower temperatures, consistent with the Arrhenius rate law. Additionally, it was shown that the effect of product inhibition could be slightly reduced (figure 5) when relying on MIP membranes compared to suspended MIP particles used in batch reactors [26].

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Abbreviations

AIBN	Azobis(isobutyronitrile)
CP	Control Polymer
EGDMA	Ethyleneglycol dimethacrylate
exp.	experimental
MAA	Methacrylic Acid
MIP	Molecularly Imprinted Polymer
PVA	Polyvinyl Alcohol
theor.	theoretical
TLC	Thin Layer Chromatography
TSA	Transition State Analogue