# Surface Functionalization of Porous Polypropylene Membranes with Molecularly Imprinted Polymers by Photograft Copolymerization in Water

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ABSTRACT: In the presence of a template, desmetryn, commercial porous polypropylene membranes were photografted, using benzophenone as photoinitiator, with the functional monomer 2-acrylamido-2-methylpropanesulfonic acid and the cross-linker *N,N′*-methylenebis(acrylamide) in water. The influence of the polymerization conditions on membrane properties was studied by solute sorption analyses and membrane permeability measurements as well as electron spectroscopy for chemical analysis, FTIR spectroscopy, BET analysis, and scanning electron microscopy. It was found that molecularly imprinted polymer (MIP) membranes can be obtained which possess group affinity for the template and other triazine herbicides. Remarkably, the MIP membrane affinity for the template in buffer solution can be improved by the presence of salt during photograft copolymerization. This work presents the first successful example for molecular imprinting by in situ polymerization in water and on the surface of a commercially available synthetic polymer. The novel MIP membranes can be used in a fast preconcentration step, solid-phase extraction, by a simple microfiltration for the determination of herbicides in water. The possibility to introduce specific binding sites into porous membranes by surface imprinting polymerization without reducing their high permeabilities opens a general way to design new high-performance affinity membranes.

## Introduction

Molecular imprinting is a straightforward method for the synthesis of materials with receptor properties similar to that of natural receptors, such as polyclonal antibodies.[1−4] Recently, several attempts were made using the imprinting approach to develop new stable affinity membranes for separation and sensor technology.[5−12] Those membranes can be classified in barrier separation and affinity sorption types.[13] While for the former types facilitated or "selective gate" transport mechanisms for the permeation through the barrier layer of the membrane have been proposed, the latter ones typically behave similar to adsorption chromatography materials. However, only moderate success was achieved thus far, because comparatively high selectivities for the template molecules were shaded by ineffective performance, especially due to small fluxes.[10−13]

Surface functionalization of porous membranes by grafting is one possible solution of this problem. Depending on pore size, the resulting materials may be novel affinity membranes (e.g., for solid-phase extraction, SPE[14]), but potentially pore-filling composite membranes with entirely novel separation properties could be achieved as well.[13] The first preparation of a molecularly imprinted polymer (MIP) membrane by a surface modification was accomplished with laboratory-made membranes from a special photoreactive polymer [poly(acrylonitrile-*co*-(diethylamino)dithiocarbamoylmethylstyrene)]: UV-initiated graft copolymerization of acrylic acid and *N,N*-methylenebis(acrylamide) (MBA) in the presence of theophylline yielded membranes with theophylline specificity.[10] Shortcomings were the complicated procedure due to the use of a special polymer for membrane formation, the very long reaction times for MIP functionalization (24 h), and the strongly asymmetric pore morphology with large macrovoids and very low permeability. Such a structure is poorly suited for affinity membrane separations.

The aim of this work was the development of a general method for molecular imprinting the surface of a stable synthetic polymer, which can also be used for functionalization of optimized porous membranes with MIPs (see Scheme 1). Another important aspect was developing a MIP synthesis using aqueous environment, so that ultimately affinity separations can be achieved for templates from water solutions. 2-(Isopropylamino)-4-(methylamino)-6-methylthio-1,3,5-triazine (desmetryn), one of the *s*-triazine herbicides, was chosen as a template. Microfiltration (MF) membranes made of polypropylene were used as matrix. Surface photograft copolymerization in the presence of template should introduce specific binding sites into the porous membrane without damaging its pore structure and thus preserving its transport properties. A benzophenone coating as photoinitiator, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) as functional monomer, and MBA as cross-linker were found to be suited for MIP membrane synthesis. Surface functionalization with MIP was also characterized with polymer surface analytics. The affinity of the synthetic "receptor" sites was evaluated in filtration experiments revealing a group specificity for special *s*-triazines compared with tri-

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**Scheme 1. MIP Synthesis via Surface Photografting onto Porous Polymer Membranes**

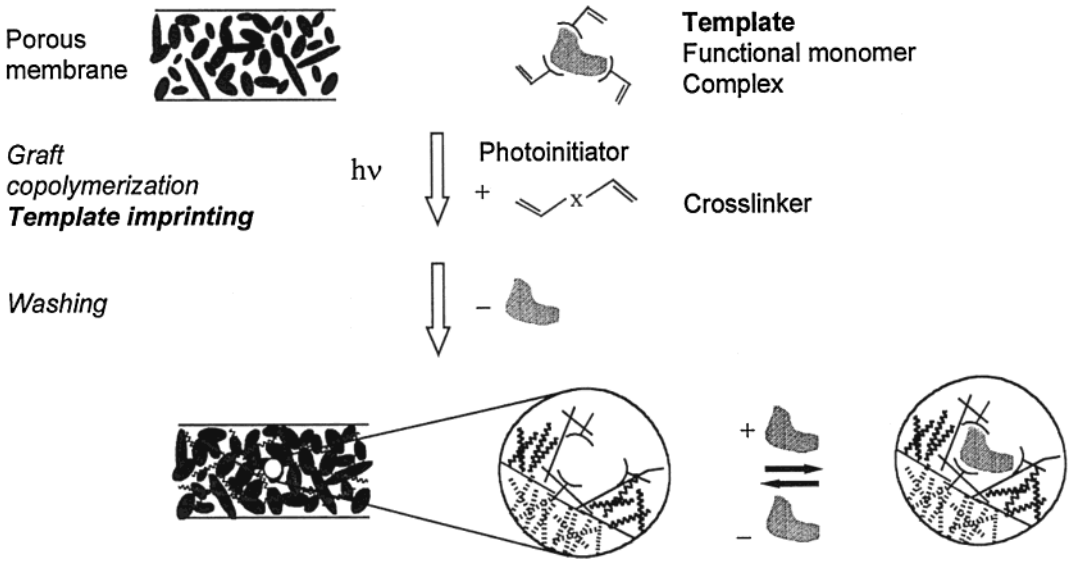


**Table 1. Surface Photografting Functionalization of Polypropylene Membranes[a]**

| | DG ($\mu$g/cm$^2$) | BET surface $A$ (m$^2$/g)/ hysteresis (−)[b] | ESCA C/O/N/S (%) | $J/p$ (L/(m$^2$ h bar)) |
|---|---|---|---|---|
| PP | | 17.5/0.96 | 100/0/0/0 | 12 000 |
| MIP1 | 780 ± 90 | 19.5/1.14 | 69.1/14.8/15.1/1.0 | 7800 |
| blank1 | 390 ± 50 | 21.9/0.97 | n.d. | 9700 |
| blank1a | 720 ± 60 | 21.4/1.00 | 69.6/15.9/13.7/0.8 | 8800 |

[a] BP coating; 10 mM desmetryn for MIP, no desmetryn for blank, in monomer solution: 50 mM AMPS, 100 mM MBA in water, saturated with BP, pH 1.5; UV irradiation at room temperature: 10 min for MIP 1 and blank 1; 20 min for blank 1a; degree of graft copolymerization (DG), specific surface area from BET, surface composition from ESCA, and water permeabilities ($J/p$). [b] Ratio between experimental surface area data for adsorption and desorption.

azinones, with an additional impact of the substitution pattern. Furthermore, MIP synthesis in the presence of salt improved the membrane performance in buffers. Finally, the application potential of the novel MIP composite membranes for a fast SPE of herbicides from dilute water solutions was demonstrated.

## Materials and Methods

Polypropylene (PP) membranes were purchased from Akzo Nobel (Accurel PP 2E HF, nominal pore size from sieving, $d_p$ = 0.2 $\mu$m; membrane thickness, $d_m$ = 150 $\mu$m). 2-Acrylamido-2-methylpropansulfonic acid (AMPS), benzophenone (BP), and *N*,*N*′-methylenebis(acrylamide) (MBA) from Merck, desmetryn, metribuzin, terbutryn, and terbuthylazine from Riedel-de Haen, and terbumeton from Sigma were used as received without further purification. All other chemicals and solvents (HPLC grade) were obtained from commercial sources and used as received.

**Potentiometric Titration**. A 20 mL aliquot of 5 mM desmetryn solution in 0.1 mM NaOH was titrated by a solution of 50 mM AMPS in water. The pH of the solution, monitored with a digital pH-meter, was plotted against the aliquots of acid added, and the quantity of groups ionized was calculated from the inflection points of the curve.

**MIP Membrane Preparation**. Circular PP membrane samples ($A$ = 46 cm$^2$) were extracted with methanol, weighted, and placed in a 100 mM solution of BP in methanol for 30 min. Next, the membranes with the pores still wetted by this solution were immersed in 20 mL of monomer mixture (see Tables 1−3) in Petri dishes. UV irradiation was done on a pilot-scale UV curing system equipped with two 4000 W mercury lamps (Beltron GmbH, Germany) for 10 cycles (1 cycle = 1 min); the used UV intensity (one lamp at 50% power, glass filter), measured with a photoelement having its sensitivity peak at 334 nm, was 220 mW/cm$^2$. Thereafter, the membranes were washed intensively with methanol, 50 mM HCl, water, and again with methanol. After drying, the membranes were weighted again, and the degree of graft copolymerization (DG) was calculated from the weight differences. Membrane samples for the tests in the filtration cells were cut to 25 mm diameter.

**Table 2. Influence of PP Surface Functionalization onto Desmetryn Uptake by the Membranes[a]**

| | DG ($\mu$g/cm$^2$) | desmetryn sorption (nmol/cm$^2$) | (%) |
|---|---|---|---|
| PP | | 6.3 | 48 |
| MIP1 | 860 | 12.1 | 92 |
| blank1 | 390 | 7.0 | 53 |
| blank1a | 795 | 7.5 | 57 |

[a] For synthesis details cf. Table 1; for sorption data cf. Experimental Section.

**Table 3. Influence of Buffer and pH onto Photografting Functionalization of PP Membranes[a]**

| | desmetryn $c$ (mM) | salt (50 mM) | pH | DG ($\mu$g/cm$^2$)[b] |
|---|---|---|---|---|
| MIP1 | 10 | | 1.5 | 780 ± 90 |
| blank1 | | | 1.5 | 390 ± 50 |
| MIP2 | 10 | NaCl | 1.5 | 790 ± 70 |
| blank2 | | NaCl | 1.5 | 400 ± 30 |
| MIP3 | 10 | phosphate[c] | 2.1 | 880 ± 50 |
| blank3 | | phosphate[c] | 2.1 | 340 |
| MIP4 | 10 | phosphate[c] | 5.6 | 1100 |
| blank4 | | phosphate[c] | 5.6 | 560 |

[a] BP coating; monomer solution: 50 mM AMPS, 100 mM MBA in water, saturated with BP; UV irradiation at room temperature: 10 min. [b] Mean values; standard deviations were calculated for data where 4−12 independent preparations had been done. [c] Sodium phosphate buffers.

**MIP Membrane Characterization.** The membrane functionalization was characterized measuring attenuated total reflection (ATR) spectra using a Fourier transform infrared

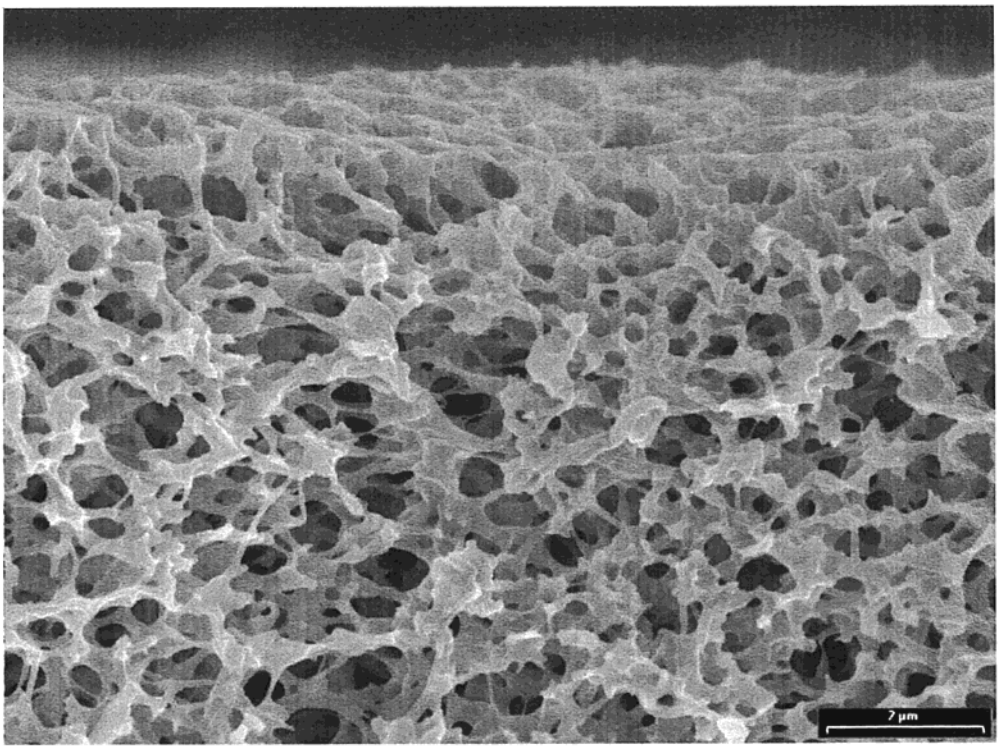


**Figure 1.** Scanning electron microscopy cross-section detail of a PP microfiltration membrane.

(FTIR) spectrophotometer (FTIR-8201 PC, Shimadzu). Scanning electron microscopy (SEM) was performed using a JEOL FE-SEM JSM 6400-F with membrane specimen after breaking in liquid nitrogen and magnetron-sputter coating. Photoelectron spectra for chemical analysis (ESCA) were measured with a Specs SAGE 100 instrument operated with Mg Kα radiation (250 W) at 12 500 V. Determinations of specific surface area were performed using an ASAP 2000 instrument (Micrometrics) based on the nitrogen BET method (maximum experimental error <1%). Water permeability measurements were performed in a UF cell ($d$ = 25 mm, model 8050, Amicon Corp.) using different hydrostatic pressures as driving force.

**Analysis of MIP Membrane Performance**. Sorption of the herbicide by the membrane from water solution was measured in filtration experiments using a syringe connected to a filter holder from stainless steel ($d$ = 25 mm, Schleicher & Schuell). A 10 mL aliquot of herbicide solutions with spiked concentrations of about $10^{-5}$ M was filtered through the membranes, typically at a rate of 10 mL/min. The filtrate was extracted with 10 mL of chloroform. The herbicide concentrations in feed and permeate solutions, both after the chloroform extraction, were determined using a gas chromatograph (column HP5MS, Hewlet Packard GC system HP 6890 with mass selective detector HP 5973). The variations for repeated analyses of standard and feed samples with the complete procedure were ≤5%.

## Results and Discussion

**MIP Synthesis by Surface Photograft Copolymerization.** The most established procedure for MIP synthesis via the noncovalent approach is radical polymerization of the template/functional monomer complex in the presence of a cross-linker monomer.[1,2] For low molecular weight templates, the contribution of binding to charged functional groups in appropriate orientation in the MIP cavity is the most efficient prerequisite for obtaining high ligand specificity.[1] Because of the sensitivity of electrostatic interactions to solvent polarity, and thus a limited stability of the template/functional monomer complex in water, polymerization had to be performed in relatively hydrophobic solvents. No or very low affinities of MIPs to the template resulted from previous syntheses in water systems. In general, the synthesis of MIPs for molecular recognition in aqueous media is still one of the major challenges in this field, which limits seriously the practical applications. For an attempted improved complex stability in water, strong ionic bonds or/and hydrophobic interactions should be chosen for the polymer design.

Taking into account the basic nature of desmetryn, a *s*-triazine with two alkyl amino groups as substituents (p$K_a$ = 3.93), a strong acid, AMPS, had been selected as functional monomer, in combination with a hydrophilic, but relatively rigid, cross-linker monomer, MBA. Commercial PP membranes with spongelike fibril-nodule pores were the preferred matrix for surface functionalizations. This selection was based on the chemical and mechanical stability of the polymer, the high membrane permeability (for nitrogen: 1300 $m^3/(m^2\ h\ bar)$) and the SEM characterization indicating a relatively even pore size distribution over the cross section (see Figure 1). The moderate specific surface area of about 20 $m^2/g$ is a typical value for MF membranes. These membranes were photofunctionalized without pore degradation using a procedure similar to the one described earlier:[15,16] With a surface coating of BP as photoinitiator and the membrane polymer as co-initiator, UV irradiation ($\lambda_{exc}$ > 300 nm) created starter radicals for a graft copolymerization on the PP surface, and thus the modification was restricted to a thin film and did not block the membrane pores (cf. Scheme 1).

During screening experiments, the UV irradiation time (10−50 min) as well as the concentrations of functional monomer (AMPS: 10−250 mM) and cross-linker (MBA: 0−300 mM) had been varied at a desmetryn concentration of 10 mM. The composition giving MIP membranes with highest affinity to desmetryn (cf.

below) contained AMPS and desmetryn in a molar ratio of 5:1 (pH = 1.5), and an optimum cross-linker concentration was found at 100 mM MBA. Functionalizations with desmetryn (MIP) and without (blank) were done (see Table 1).

Interestingly, in the presence of template always higher degrees of modification were observed. This suggests a higher probability for the monomers to be grafted to the membrane surface if they are organized in the complex with the template (cf. Scheme 1). To take into account an eventual effect of total DG onto membrane properties, additional blanks (blank 1a) were synthesized by using longer UV irradiation. No changes of pore morphology could be identified by SEM analyses. For both MIP and blank membranes, similar ATR-FTIR spectra were obtained, clearly indicating the functionalization of PP with a grafted AMPS-*co*-MBA polymer (data not shown). Opposite to PP, the functionalized membranes were easily wetted by water.

ESCA data reveal that both MIP and blank membranes have about the same outer surface chemical composition (cf. Table 1). From sulfur data, AMPS grafting can be verified, but the surface exposed composition is lower than expected from the polymerization stoichiometry. From oxygen data, PP surface coverage of about 75% can be estimated for the ESCA sampling depth. In conclusion, a several nanometer thin film of grafted AMPS-*co*-MBA polymer covers the PP membranes. In qualitative agreement with that, the average dry MIP layer thickness (for DG = 780 $\mu$g/cm$^2$), relative to the PP membrane specific surface area (cf. Table 1), estimated assuming a graft copolymer density of 1 g/cm$^3$ is about 10 nm.

The BET analyses revealed no detectable effects of membrane micropore filling with grafted polymer in the dry state (cf. Table 1). Even a slight increase of specific surface area was observed for blank and MIP membranes compared to PP. However, the adsorption/desorption hystereses were significantly higher for the MIP membranes. This could be an indication for the typical microporosity in cross-linked polymers, and this effect is usually specifically increased for MIPs synthesized by cross-linking polymerization ("microcavities" for MIP receptor sites).[1,13]

Potentiometric titration experiments indicated that only the two aliphatic nitrogens of desmetryn are protonated under the conditions in the polymerization mixture. With that information and the optimum stoichiometry found in the grafting experiments, the structure of the template/functional monomer complex was estimated using the HyperChem 3.0 software. The AM1 procedure was used which is a semiempirical SCF method for chemical calculations (an improved MNDO approach) and charged molecules in a vacuum. The other functional groups of the template interact with AMPS and, presumably, MBA via hydrogen bonds and hydrophobic interactions (cf. ref 17). Possible structures of this complex as well as the oligo-AMPS fixed on the surface, obtained by heterogeneous grafting of imprinted polymer onto PP and subsequent desmetryn removal, are presented in Figure 2. This illustration could suggest that the MIP contains a hydrophilic binding site core surrounded by a hydrophobic shell, similar to natural receptors and enzymes.

The specific orientation of the functional monomers around the template molecule in the complex must be preserved during the polymerization step. In absence

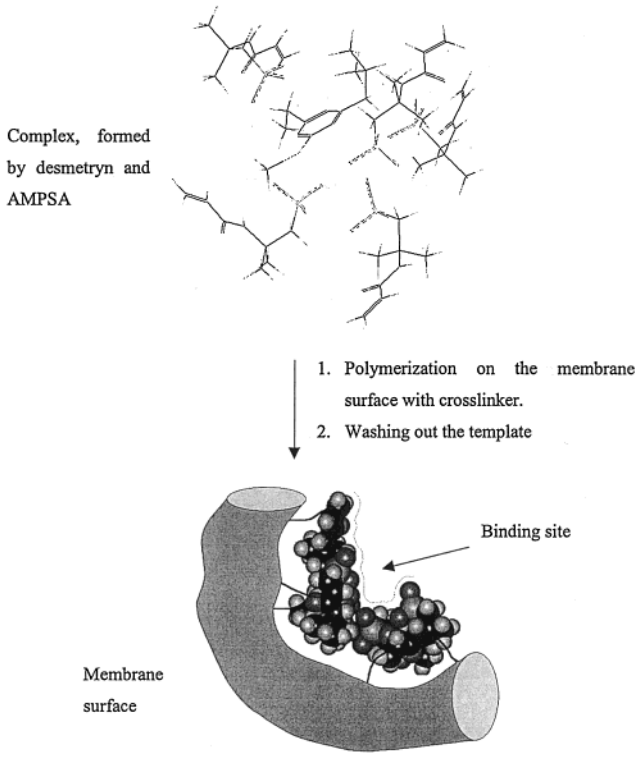


**Figure 2.** Model for synthesis of a MIP desmetryn receptor via surface photografting of an AMPS polymer: (a) solution complex of desmetryn and AMPS, (b) surface grafted AMPS complex after desmetryn removal.

of a cross-linker, membranes with very low desmetryn binding capacity and without specificity, compared with blanks, were obtained (data not shown).

**MIP Membrane Filtration Performance.** Some reductions of water permeabilities with increasing DG were observed (cf. Table 1). Nevertheless, the data indicate relatively low impact of the functionalization on membrane porosity in the swollen state (dry MIP layer thickness had been estimated to be 10 nm; cf. above). The same PP membranes with grafted, non-cross-linked poly(acrylic acid) or other anionic polyacrylates at the same DG had water permeabilities of less than 100 L/(m$^2$ h bar).[16] Hence, relatively small effects of extended chain conformation (pore blocking) due to charge repulsion were observed with PP-grafted-P(AMPS-*co*-MBA) membranes, indicating that the chemically cross-linked MIP layer is rather compact.

**MIP Membrane Template Affinity and Specificity.** The conditions of a fast solid-phase extraction were applied to characterize membrane/solute affinity. Desmetryn binding to the functionalized membranes was estimated in filtration experiments using solutions with $10^{-5}$ M herbicide in water. In all cases MIP membranes demonstrated higher herbicide sorption in comparison with blank ones; the effect of DG alone was rather small (see Table 2).

The membrane specificity for the template was also analyzed in filtration experiments using several different triazines, the *s*-triazines desmetryn, terbutryn, terbumeton, and terbuthylazine, and the triazinone metribuzin; the oil/water distribution coefficients for these test solutes[18,19] are also given (see Figure 3). In all tests a solute concentration of $10^{-5}$ M in water was applied. For unmodified PP membranes, 48% uptake for desmetryn and 100% for terbuthylazine and terbutryn were observed (not shown). Hence, similar to reversed

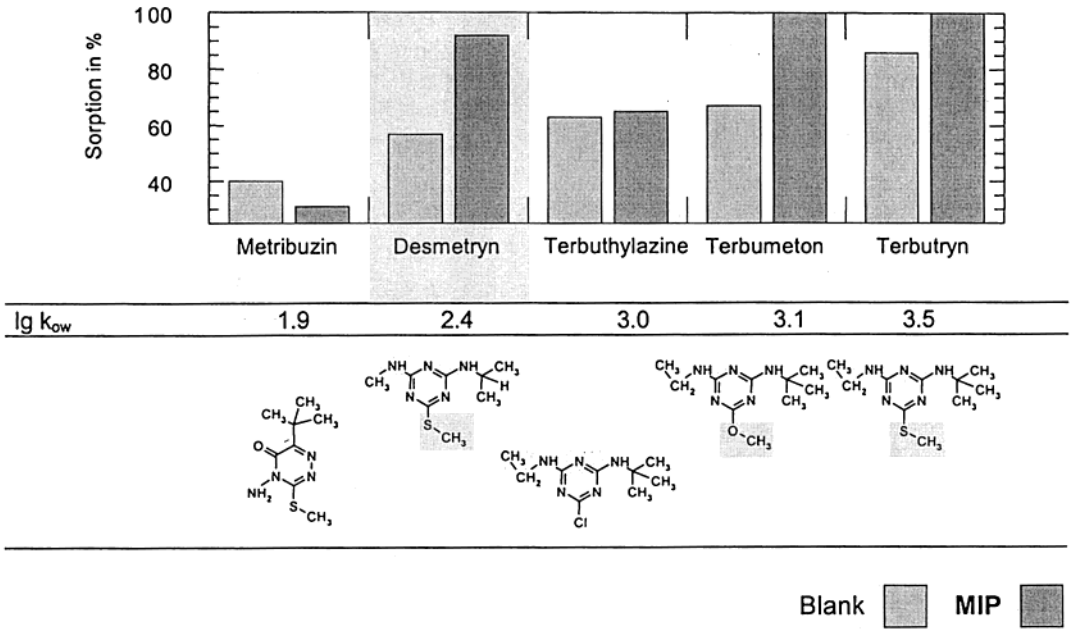


**Figure 3.** Herbicide sorption for MIP and Blank membranes ($d_m = 150\ \mu$m, 3.5 cm$^2$; cf. Tables 1 and 2) in filtration experiments with 10 mL of $10^{-5}$ M herbicide solution in water at a flow rate of 10 mL/min.

phase chromatography media, sorption onto the unmodified hydrophobic PP from the aqueous solutions is driven by hydrophobic interactions. For the blank membranes there is also a correlation of herbicide sorption with solute hydrophobicity, giving the highest uptake for terbutryn (log $k_{ow} = 3.48$). However, in comparison to PP, the functionalization with grafted P(AMPS-*co*-MBA) strongly rendered the sorption capacity of the membrane via hydrophilization and introduction of cation-exchange groups. The uptakes for terbuthylazine and terbutryn were 63% and 86% (cf. Figure 3), respectively; thus hydrophobic interactions were reduced. For the MIP membrane much higher affinities for desmetryn (log $k_{ow} = 2.38$) and two of the three other *s*-triazines were observed in comparison with the blank membrane (cf. Figure 3). At the same time, very low sorption of metribuzin (log $k_{ow} = 1.9$) was observed for the MIP membrane. Moreover, it is remarkable that two *s*-triazines with almost the same oil/water distribution coefficients, terbumeton (log $k_{ow} = 3.1$) and terbuthylazine (log $k_{ow} = 3.04$), show much different sorption by the MIP membrane. While terbuthylazine has a chloro substituent besides the two alkylamino groups, the three other triazines have either a methoxy or methylthio group in that position (cf. Figure 3). In conclusion, the orientation of the polymer functional groups in the imprinted "receptor" site is suited for specific binding of several triazines. This "receptor" site, however, cannot recognize molecules with different orientation of their functional groups, such as the 1,2,4-triazineone metribuzin. A group specificity for particular *s*-triazines is imparted by desmetryn imprinting, as shown by the only nonspecific binding of terbuthylazine. Hence, additional substituent effects, presumably via different polarity, are important for the ligand "fit" in the artificial receptor site (cf. Figure 2).

The fluxes applied for this membrane ($J = 120$ L/(m$^2$ h)) are by far the highest up to now achieved for imprinted membranes, where fluxes usually had values below 5 L/(m$^2$ h).[9,13] Note that the membrane permeabilities (cf. Table 1) would allow even much higher fluxes. This is important for the practical application

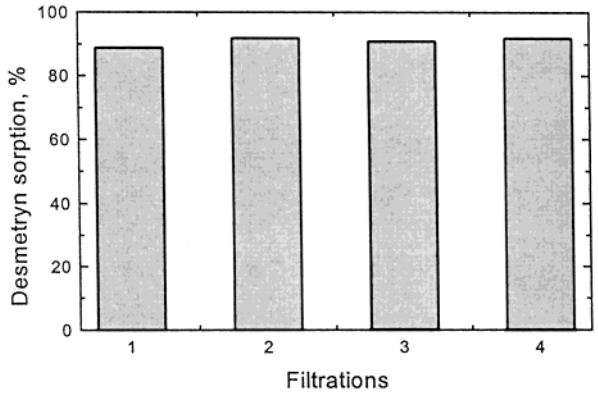


**Figure 4.** Repeated use of a MIP membrane for herbicide sorption: 10 mL of $10^{-5}$ M desmetryn solution was filtered through the membrane at a flow rate of 10 mL/min; the membrane was regenerated by filtration of 10 mL of 50 mM HCl and 10 mL of water.

of MIP membranes which was limited before particularly because of their insufficient transport performance.

MIP membranes can be used repetitively using simple regeneration procedure by washing with 50 mM HCl and water (see Figure 4).

The binding capacity of the MIP1 membrane was determined in filtration experiments using saturation with 1 mM desmetryn. The value determined was 27.3 $\mu$g/cm$^2$ (0.128 $\mu$mol/cm$^2$) which corresponds to 41% of the theoretical value, calculated from the degree of modification and the stoichiometry of the template/functional monomer complex (cf. Figure 2). Up to now, this is the highest level of specific modification, achieved with imprinting polymerization, because the number of binding sites involved in selective interaction between analyte and imprint is typically less than 1% and can rise to 35% of the theoretical maximum.[20] This provides additional evidence for having achieved surface imprinting yielding a relatively thin layer (cf. above) covering the accessible specific surface of the membrane.

Triazine specific MIP membranes could be used for herbicide preconcentration (SPE) in environmental

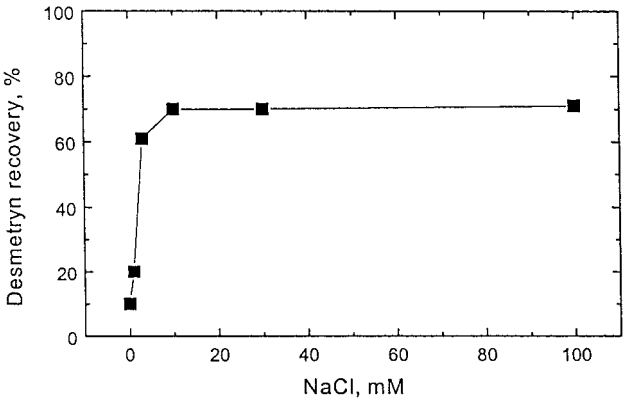


**Figure 5.** Recovery of sorbed desmetryn from a MIP membrane depending on sodium chloride concentration: Sorption was done as in Figure 4; subsequent elution was performed by filtration of 10 mL of sodium chloride solution.

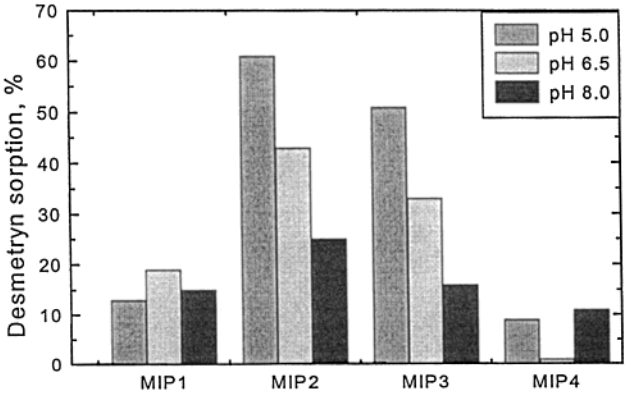


**Figure 6.** Influence of the buffer pH on desmetryn sorption during fast filtration for various MIP membranes (cf. Table 3): 10 mL of $10^{-5}$ M desmetryn solution in 50 mM sodium phosphate buffer was filtered through the membranes at a flow rate of 10 mL/min.

analyses. However, such ion-exchange membranes, with respect to their binding sites, are sensitive to salt. High ionic strength disrupts ionic bonds and causes very low binding of herbicide to MIP in buffers, as it can be also concluded from the data for herbicide recovery from the MIP with salt solutions (see Figure 5). Even a concentration such small as 3 mM NaCl decreases herbicide binding three times compared with water.

**Improving MIP Membrane Specific Sorption Capacity in the Presence of Salt.** The loss of membrane affinity to herbicide in the presence of salt can be also phenomenologically explained by a distance change between the functional groups due to changed charge repulsion either directly in the active site or by distortion of the swollen cross-linked polyacrylamide network. To avoid that, the distance between sulfonic acid groups in the template/functional monomer complex should be the same in the reaction mixture during polymerization and in the resulting MIP when it is exposed to a salt solution. To prepare a MIP with such a correct structure of the binding sites, membranes were functionalized in buffers at different pH (see Table 3). And indeed, those MIP membranes work much better in buffer solution than membranes prepared in water (see Figure 6). All blank membranes for the various syntheses tested under the different buffer conditions showed very low desmetryn sorption ($\leq$10%).

It is important to note that the pH plays also an important role in ligand recognition properties. Thus, membrane MIP4, prepared at pH 5.6, had a very low binding ability for desmetryn, even although the degree of modification for this membrane was the highest (DG = 1100 $\mu$g/cm$^2$; cf. Table 3). Again, it is evident that not only the quantity of the functional groups grafted to the membrane surface but also their orientation is important for the herbicide recognition. In the polymerization mixture with pH 5.6, the excess of sodium ions competes with desmetryn for binding with AMPS and therefore disturbs the formation of the template/functional monomer complex. This leads to a more random orientation of the sulfonic acid groups on the membrane surface. The highest desmetryn binding was observed for the membrane MIP2 prepared at pH 1.5 and tested in acidic buffer with pH 5.0 (cf. Figure 6). However, for the improved membranes MIP 2 and MIP 3, the effect of pH in the range of pH 5.0 to pH 8.0 onto sorption efficiency was rather large. This may be due to deprotonation of the analyte, but it could also indicate that the MIP layer is indeed susceptible to swelling effects with impact onto binding specificity.

**MIP Application Potential.** The membrane stability was studied by repeating measurements of herbicide binding for 3 weeks. During this time membranes, stored in dry state, showed no change in sorption capacity for desmetryn.

Membranes MIP2 and MIP1 were tested as solid-phase extraction preconcentration media for recovering of triazine herbicides from dilute solutions with a concentration of $2 \times 10^{-9}$ M. Preliminary results for these membranes were a 200-fold sample enrichment and herbicide recoveries between 64% and 90%, depending on the triazine structure.

## Conclusions

Polypropylene membranes were functionalized via photograft copolymerization in water with an imprinted polymer, specific for desmetryn. The synthesized MIP membranes possess a group specificity for triazine herbicides in water.

Photoinitiation directly on the surface of the support polymer, PP, along with the cross-linking nature of the polymerization ensure the limitation of functionalization to a relatively thin and compact, moderately swollen layer. This is the precondition for high permeability and relatively large specific surface area of the synthesized porous MIP composite membranes. However, improving of MIP membrane performance should be also possible, by further optimizing polymer composition and grafting procedure. The remarkable performance of water-synthesized MIP, even in buffer solutions, and the achieved triazine binding specificities in aqueous systems are directly linked to the covalent fixation of the MIP receptor sites by grafting to a rigid polymer surface. This seems to be a main precondition for the function of MIP receptors in an otherwise water-swollen, flexible AMPS-*co*-MBA polymer.

This work will have immediate practical significance relaying on the needs in (SPE) preconcentration systems for polar herbicides in environmental analysis.[21] The method proposed can be adapted to other systems, e.g., membranes and films as well as to other templates (cf. Scheme 1). Preliminary experiments indicate that different support materials, with larger specific surface area, can be easily applied when they can act as hydrogen donor co-initiator for the benzophenone photoinitiator. Therefore, work is in progress to use surface

imprinting by photograft cross-linking copolymerization as a general procedure for development of a new generation of affinity membranes for separation, purification, and environmental analysis.

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