Preparation of Azobenzene-Containing Polymer Membranes That Function in Photoregulated Molecular Recognition

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ABSTRACT: Selective, stable, molecularly imprinted polymers having intrinsic photoresponsive properties were synthesized for the purpose of photoregulated binding of a predetermined ligand. Highly cross-linked, free-standing polymer membranes were synthesized from an optimized mixture of two cross-linkers—ethylene glycol dimethacrylate and tetraethylene glycol diacrylate. For synthesizing molecularly imprinted polymers, *p*-phenylazoacrylanilide (PhAAAn) was used as a new photoresponsive functional monomer. A study of the kinetics of photoisomerization of PhAAAn within the polymer membranes before and after treatment with various media showed the excellent functional stability of the membranes. Polymer membranes synthesized in the presence of the template dansylamide possess selective sites for recognizing dansylamide, and the affinity of these sites can be reversibly changed by illumination with ultraviolet or visible light.

Introduction

Molecular imprinting is an efficient method for mimicking the high selectivity of biological structures, such as antibodies, in molecular recognition. The essence of the method is formation of specific binding sites for a predetermined ligand. The preparation of molecularly imprinted polymers (MIPs) relies on the presence of a template (imprinting molecule) during polymerization. First, complexes between functional monomers and a template are formed in solution, and then these complexes are fixed by polymerization with a high degree of cross-linking. Subsequent removal of the template leaves cavities having size, shape, and arrangement of functional groups that are complementary to those of the desired ligand. Chemically and mechanically stable MIPs able to recognize specific substances can be used as the stationary phase in chromatography or solid-phase extractions, as sensitive elements in biomimetic sensors, and as artificial catalysts.[1−7] Usually MIPs are prepared as a polymer monolith, which can be crushed to small particles; preparation of molecularly imprinted polymer films or membranes has also been reported.[5−7]

Stimulus-sensitive materials, especially those with light-affected properties, have been the subject of numerous investigations.[8−12] Isomerization of photoresponsive chromophores incorporated into polymers leads to changes in their refractive index, dielectric constant, oxidation/reduction potential, and other physicochemical properties. Such polymers can be applied in various photonic devices, such as erasable optical memory media and photoswitches. Introduction of a photoresponsive monomer into stable, selective MIPs can lead to preparation of materials whose recognition ability can be regulated by illumination. A preparation of imprinted merocyanine copolymer membranes has been described.[13] To our knowledge, little progress has been made in developing photosensitive MIPs based on merocyanine, probably because merocyanine is not a very suitable monomer for preparation of reversibly photoregulated materials. That is, the rate of conversion of merocyanine to spiropyran varies depending on solvent polarity and on the presence of other compounds. For example, the rate constant for this process in benzene or toluene can be 1−2 orders higher that in DMSO or DMF.[14,15] Photoisomerization of merocyanine is accompanied by its fatigue and by the appearance of several degradation products. The number of alternating irradiation cycles sufficient to reduce the merocyanine absorbance to one-half its initial intensity (half-life cycle) was only four in nonpolar toluene, and addition of benzophenone induced a considerable acceleration of fatigue in both polar and nonpolar solvents.[16]

In contrast, the photoisomerization of azobenzene does not strongly depend on solvent polarity. For example, the quantum yield for cis-to-trans photoisomerization of azobenzene in various solvents was about 0.4 in all solvents examined.[17] There is no known evidence for emission from the excited states of azobenzene in either its cis or trans form, so the photochemical process is entirely efficient.[9] Photoisomerization of azobenzene residues within the recognition sites of imprinted polymers would lead to changes in distribution of electron density within these sites and in their geometrical parameters and, consequently, their recognition ability. However, photoinduced isomerization would influence the process of dansylamide recognition only when the energy of isomerization is comparable to or higher than that of the interaction of dansylamide with azobenzene residues in the recognition sites. Otherwise, photoregulation of the recognition would be

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impossible. The energy difference between the ground state of the trans or "*E*" form and the cis or "*Z*" form of azobenzene is about 50 kJ mol^{-1}.[8] This value corresponds to an association constant of 10^8-10^9 M^{-1} and is comparable to or greater than published data on the affinity of known MIP binding sites.[18] The distance between the 4 and 4′ positions is about 9.0 Å in *trans*-azobenzene and 5.5 Å in *cis*-azobenzene, and the dipole moment increases from 0.5 to 3.1 D on going from the trans to cis isomers. These data show the potential for preparing photoregulated MIPs based on azobenzene and formed the basis for our investigations.

Several methods can be used to prepare various forms of photoresponsive materials (for example, mono-, bi-, or multilayer structures such as Langmuir−Blodgett films, vesicles, or polymer membranes), which can be broadly classed into two approaches: (1) noncovalent modification (doping) of conventional materials, e.g., formation of poly(vinyl chloride) membranes in the presence of an azobenzene derivative, and (2) synthesis of polymers containing a covalently attached chromophore. Doping procedures are much simpler than making covalently bound derivatives, but depending on the solvent composition and other working conditions, doped membranes demonstrate rather limited stability and reproducibility. Therefore, polymers with pendant photoresponsive chromophores are usually much more attractive. Thus, the aim of the current work was to prepare molecularly imprinted polymer membranes containing an azobenzene chromophore and study the possibilities for regulating their properties by light.

Experimental Section

Materials. Dansylamide (DA), dansyl-L-leucine (DL), *N*,*N*-dimethyl-1-naphthylamine (DMN), 4-phenylazoaniline (4-aminoazobenzene), tetraethylene glycol diacrylate (TEGDA), and acryloyl chloride were purchased from TCI (Tokyo, Japan). Ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), 2,2′-azobis (4-methoxy-2,4-dimethylvaleronitrile) (ABMDV), and acetonitrile (HPLC grade) were obtained from Wako (Osaka, Japan).

Synthesis of *p*-Phenylazoacrylanilide. *p*-Phenylazoacrylanilide (PhAAAn) was prepared by condensation of acryloyl chloride with 4-phenylazoaniline, as described earlier.[19]

Polymerization. Polymerizability of PhAAAn was investigated in mixtures in which one-half the volume consisted of acetonitrile and the other half of mixtures of monomers. These mixtures contained from 1 to 10 mol % of PhAAAn and 90 to 99 mol % of the cross-linking agent TEGDA. After degassing by sonication for 1 min in a bath-type ultrasonicator and adding ABMDV as a free radical initiator, the polymerization mixtures in screw-capped glass reaction vials were purged with nitrogen for 1 min. Polymerization was carried out at 35 °C overnight. The resulting polymers were crushed into vials and washed with several portions of acetonitrile until PhAAAn could no longer be detected in the washing solutions. The quantity of unreacted PhAAAn in the washing solutions was determined spectrophotometrically at 353 nm. After washing, the polymer samples were dried until their weights were constant. The quantity of TEGDA included in the polymer was determined by subtracting the incorporated quantity of PhAAAn from the constant weight of the polymer sample. The copolymerization reactivity ratios for PhAAAn and TEGDA were calculated according to method 6 of Tüdós et al.[20]

For preparation of imprinted polymers, DA as the template, PhAAAn as the functional monomer, and EGDMA and TEGDA as the cross-linkers were dissolved in acetonitrile in a screw-capped glass reaction vial. After degassing, adding ABMDV, and purging with nitrogen as described above, the polymerization mixtures were poured between two glass plates. Polymerization was carried out at 35 °C overnight. The thickness of the membranes was determined by spacers and was about 80 μm. The resulting membranes were washed several times with acetonitrile until DA could no longer be detected in the supernatant. Control (nonimprinted) polymers were synthesized under the same conditions but in the absence of the template.

Spectroscopic Measurements. A membrane (9 mm × 25 mm) was inserted into a screw-capped quartz cell (optical path length 1 cm), which had four transparent sides and contained 3 mL of acetonitrile. The mechanical properties of the prepared membranes allow them to stand upright inside the cell. UV−vis spectra were obtained at 25 °C in a V-530 spectrophotometer (Jasco, Tokyo, Japan). Isomerization was induced by irradiation with a UI-501C mercury lamp (500 W, Ushio, Osaka, Japan). The UV light was isolated using a UV-D35 band-pass filter (Toshiba, Tokyo, Japan). The visible light was obtained with a Y-43 cutoff filter (Toshiba). To reduce the intensity of irradiation, a TND-30% filter (Toshiba) was used. For photoisomerization and its monitoring, both the beam of illuminating light from the mercury lamp and the light beam of the spectrophotometer were perpendicular to the plane of the tested membrane.

For monitoring of DA adsorption by membranes in rebinding experiments, after the removal of template DA by intensive washing with acetonitrile, a piece of membrane was inserted into a screw-capped spectrophotometric quartz cell containing 3 mL of 10 μM DA solution in acetonitrile. The solution concentration of DA was measured at 251 nm with the light beam of the spectrophotometer parallel to the plane of the tested membrane. The samples were first incubated in the dark; after equilibration was achieved, the cell was exposed to UV irradiation; and after the next equilibration, the cell was exposed to visible light irradiation.

FTIR spectra were measured on an FT/IR-620 spectrometer (Jasco, Tokyo, Japan) at room temperature. The samples were prepared as KBr pellets.

Results and Discussion

To develop materials possessing photoresponsive properties, we synthesized a polymerizable derivative of azobenzene, *p*-phenylazoacrylanilide (PhAAAn), by condensation of acryloyl chloride with 4-phenylazoaniline. The progress of synthesis and purification of the monomer was monitored by thin-layer chromatography. The molecular mass and composition of PhAAAn were confirmed by FTIR, mass spectrometry, and elemental analysis; we also studied its photochromic properties.[19]

For the formation of defined recognition sites within MIPs, the structural integrity of the monomer−template assemblies must be preserved during polymerization to allow the functional groups of the polymer to be fixed in space in a stable arrangement that is complementary to the template. This is achieved by using a high degree of cross-linking. Usually the amount of cross-linker in the polymerization mixture must be more than 50% of the total quantity of monomer used for synthesis of MIPs. However, a polymer matrix must not only contain the binding sites in a stable form, but also be porous enough for easy access by the template (or other analytes) to these sites. Porosity is achieved by carrying out the polymerization in the presence of a solvent (a porogen).[1−4,21] Therefore, we started by investigating the polymerizability of PhAAAn in mixtures with various concentrations of PhAAAn and the cross-linking agent TEGDA. The copolymerization diagram and the values of $r_{PhAAAn} = 0.84$ and $r_{TEGDA} = 0.99$ showed a similar level of reactivity of both PhAAAn and TEGDA, which means that the compounds do not tend to form homopolymer blocks. The product $r_{PhAAAn} \cdot r_{TEGDA} = 0.84$ confirms that the copolymerization behavior is close to the ideal type that leads to a truly random copolymer,

Table 1. Dependence of Photoisomerization Rate Constant on PhAAAn Concentration within Polymer Membranes and on Monomer/Solvent (M/S) Ratio during Polymerization

PhAAAn, mol % and (M/S ratio, v/v)	trans-to-cis rate constant, s^{-1}	cis-to-trans rate constant, s^{-1}
0.05 (5/5)	0.052	0.032
0.1 (5/5)	0.039	0.022
0.2 (5/5)	0.026	0.018
0.1 (6/4)	0.033	0.019
0.1 (7/3)	0.029	0.018

whose composition depends primarily on monomer concentration in the polymerization mixture. These properties of the monomers create favorable conditions for the formation of specific recognition sites within MIPs.

Conventional MIPs are hard and fragile. However, free-standing MIP membranes require a combination of some flexibility, necessary for their handling, and hardness, to ensure stability of their recognition sites. We explored several cross-linking agents and their mixtures for use in preparing PhAAAn-containing membranes. EGDMA or TEGDA, used as the only cross-linker, led to formation of fragile, brittle membranes. However, mechanically stable, but flexible, membranes were obtained when EGDMA and TEGDA were mixed at molar ratios from 5:5 (stress to breakage 22.9 MPa; strain to breakage 4.7%) to 3:7 (stress to breakage 24.1 MPa; strain to breakage 10.2%).

The high level of cross-linking of the synthesized polymers was confirmed by FTIR spectrometry. Whereas the spectrum of monomeric TEGDA has IR bands near 1200 and 1280 cm^{-1} (typical of the acrylate C=C group) as well as bands at 987 (=CH wag) and 811 cm^{-1} ($=CH_2$ twist),[22] these bands are barely evident in the FTIR spectra of the polymers based on this cross-linker. This means that the quantity of unreacted double bonds is very low. Therefore, our polymers are indeed highly cross-linked.

Upon UV irradiation of these membranes, PhAAAn undergoes trans-to-cis isomerization. Upon visible light irradiation, cis-to-trans isomerization occurs. Correspondingly, the shapes, intensities, and positions of the absorption bands change. The UV−vis spectra of PhAAAn (trans configuration) show an intense band centered at around 350 nm and a weak one at around 440 nm. These correspond to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the azobenzene chromophore. When the content of PhAAAn in the membranes was more than 0.3 mol %, its absorbance at around 350 nm was too strong for accurate measurement (>1.5 o.u.). Therefore, we studied the process of photoisomerization first with membranes having relatively low PhAAAn content.

The photoisomerization kinetics of PhAAAn within the membranes was studied at 25 °C in acetonitrile by monitoring the absorbance at 353 nm (λ_{max} for the trans isomer). Kinetic data were fitted to the equation $\ln [(A_0 - A_{ps})/(A_t - A_{ps})] = kt$, where A_0, A_t, and A_{ps} are the absorbance at times *0* and *t* and at the photostationary state, respectively.[23,24] Both processes (trans-to-cis and cis-to-trans photoisomerization) obeyed first-order kinetics. The photoisomerization kinetics of PhAAAn within the membranes depended on the concentration of this monomer (Table 1). The dependence of the cis-to-trans photoisomerization on the PhAAAn concentration was less pronounced than that of the trans-to-cis photoisomerization. The process was reversible (Figure 1) at all PhAAAn concentrations tested.

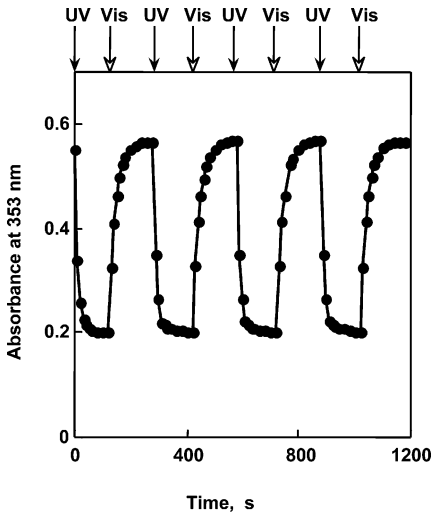


Figure 1. Reversibility of photoisomerization of PhAAAn within a membrane containing 0.1 mol % PhAAAn.

The above results were obtained with membranes that were polymerized in a mixture consisting of 50 vol % of monomer mixture (including cross-linkers and functional monomers) and 50 vol % of solvent. A high level of cross-linking ensures good chemical and mechanical properties of the membranes. On the other hand, the rather high concentration of solvent, which plays the role of a pore-forming agent (porogen), results in the formation of membranes with porous structure. However, the monomer-to-solvent ratio can be changed over a rather wide range and is one of the ways to regulate the membrane's properties. Therefore, we also prepared membranes in polymerization mixtures having 6:4 and 7:3 monomer-to-solvent ratios (and 0.1 mol % PhAAAn) and investigated them (Table 1). An increase in this ratio results in small decreases in the photoisomerization rate. Again, the relative effect on the trans-to-cis photoisomerization was more pronounced than that on the cis-to-trans photoisomerization, and complete reversibility of the process was observed for all the membranes tested. When we compared a solution of monomeric PhAAAn with polymer membranes containing nearly the same quantity of PhAAAn, their rates of photoisomerization were similar as well (data not shown). These data suggest that the free volume within the synthesized membranes is probably large enough for virtually unrestricted azobenzene photoisomerization. This feature can be considered an important advantage of our cross-linked porous polymer membranes, compared with condensed LB films and membranes prepared by spin coating or casting from polymer solution.[8−10]

To investigate the chemical stability of the synthesized photoresponsive membranes, we compared the rates of photoisomerization of PhAAAn within the membranes in acetonitrile before and after incubating for 2 h in solvents of various polarities and in acidic and alkaline aqueous solutions. After the incubations, the membranes were washed several times in acetonitrile (or in water and then in acetonitrile). The essentially identical rate constants we obtained clearly indicate the excellent functional stability of the synthesized membranes (Table 2).

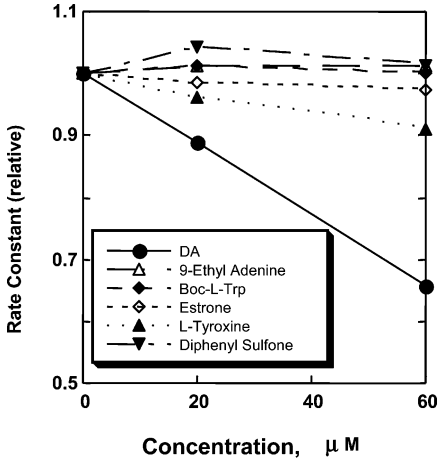


Figure 2. Effect of various compounds on the rate of trans-to-cis photoisomerization of 20 μM PhAAAn in acetonitrile.

Table 2. Photoisomerization Rate Constants of PhAAAn within Polymer Membranes in Acetonitrile before and after Treatment with Various Media

treatment	trans-to-cis rate constant, s^{-1}	cis-to-trans rate constant, s^{-1}
before	0.025	0.018
Milli Q water	0.026	0.019
1 M HCl	0.028	0.019
1 M NaOH	0.026	0.018
methanol	0.025	0.019
heptane	0.027	0.019

Interactions between functional monomers and a template molecule should be strong enough to form complexes in solution, which can then be stabilized during the polymerization process. A reliable method for preliminary screening of suitable pairs of a functional monomer and a template can be very useful for efficient synthesis of highly selective MIPs. We expected that any interactions in solution between our functional monomer PhAAAn and other compounds would affect the photoisomerization of PhAAAn. Thus, investigation of the photoisomerization kinetics of PhAAAn in the presence of other compounds would allow selecting a good template for this functional monomer. Compounds having a rather rigid core structure and a few functional groups can usually serve as a good template. We tested several cyclic and heterocyclic compounds, including steroids, aromatic amino acids, and nucleic acid bases. The most pronounced decrease in the rate of trans-to-cis photoisomerization of PhAAAn was observed in the presence of DA (Figure 2), which probably forms a combination of hydrogen bonds and stacking interactions with PhAAAn. Therefore, DA was chosen as a template for the synthesis of MIP membranes. DA has the added advantage that it can be easily monitored by UV−vis and fluorescence spectrometry. It is widely used as a probe of the binding sites of enzymes,[25] for monitoring polymerization reactions,[26,27] and in the development of bio- and chemosensors.[28,29]

For preparation of MIP membranes, the polymerization mixture consisted of 0.05 mmol DA as a template, 0−0.2 mmol PhAAAn as a functional monomer, and EGDMA and TEGDA (both 1.5 mmol) as cross-linkers, dissolved in acetonitrile (monomer-to-solvent ratio 1:1). At the maximum PhAAAn:DA ratio, the concentration of PhAAAn in these membranes was about 6 mol %, which is much higher than in the membranes we studied earlier (Table 1). At this concentration the absorbance at about 350 nm, which was monitored in the previous experiments, was too strong. Therefore, to study the process of PhAAAn photoisomerization within these membranes, we monitored the absorbance at 440 nm, which corresponds to a peak for the cis isomer. The spectra recorded after different irradiation times showed the presence of an isosbestic point at 412 nm (Figure 3), which confirms that only two absorbing species, namely, the trans and cis isomers, were present in the membranes. Under the same conditions of light irradiation as in the previous experiments (Table 1), the photoisomerization rate within these membranes containing a much higher quantity of PhAAAn was slower (for example, the rate constants are about 0.006 and 0.002 for cis-to-trans and trans-to-cis photoisomerization, respectively). However, photoisomerization continued to be reversible.

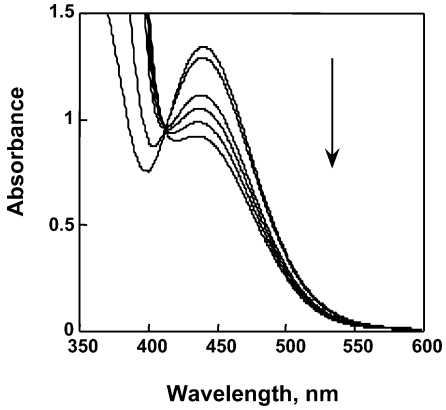


Figure 3. Absorbance spectra of a membrane containing 6 mol % PhAAAn. Spectra were recorded before irradiation and after 0.5, 2, 3, 5, and 20 min of irradiation by visible light (curves from top to bottom, respectively).

After synthesizing the imprinted membranes and washing out DA, we investigated the ability of these membranes to adsorb DA. For this purpose, a piece of membrane was incubated at room temperature in a spectrophotometric quartz cell containing 3 mL of 10 μM DA in acetonitrile. When incubated in the dark, imprinted membranes that were prepared at PhAAAn-to-DA ratios of 2:1 and 4:1 adsorbed DA from solution (Figure 4). Imprinted membranes prepared at a PhAAAn-to-DA ratio of 4:1 adsorbed much more DA than control membranes or imprinted membranes prepared at lower PhAAAn-to-DA ratios. This finding can be explained if some cooperativity between two or more molecules of PhAAAn is necessary for formation of complexes with the template molecule in solution, then during polymerization, and finally in the rebinding experiments. After incubation in the dark, the cell containing the membrane and DA solution was irradiated with UV light (Figure 4). For imprinted membrane prepared at a PhAAAn-to-DA ratio of 4:1, UV irradiation caused previously adsorbed DA to be released. Subsequent exposure of this cell to visible light caused the concentration of DA in solution (and, consequently, in the imprinted membrane as well) to return to nearly the same level as before UV irradiation. The kinetics of this process completely coincided with the kinetics of photoisomerization of the same membranes. Neither UV nor visible irradiation changed the amount of DA adsorbed by control membranes or by imprinted membranes prepared at PhAAAn-to-DA ratios of 2:1 or 1:1. Probably at these ratios there is not enough PhAAAn for formation of efficient recognition sites, and their photoizomer-

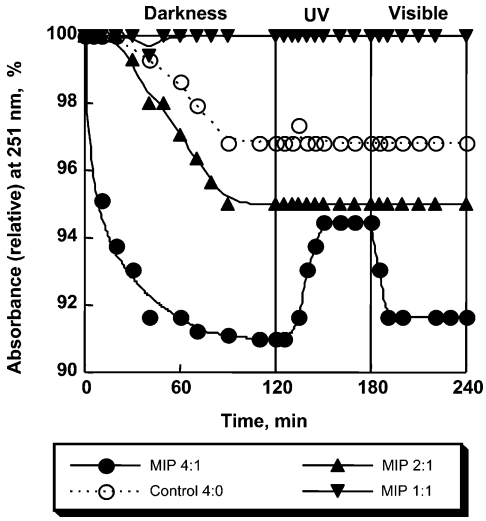
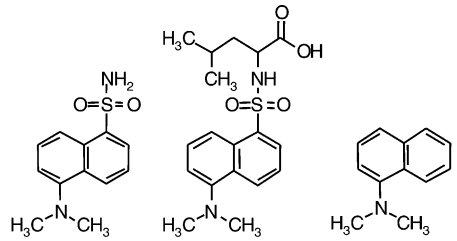


Figure 4. Binding of DA by polymer membranes synthesized with PhAAAn-to-DA ratios of 1:1 to 4:1. DA concentration was 10 μM.

Chart 1. Structures of Dansylamide (DA), Dansyl-l-leucine (DL), and *N*,*N*-dimethyl-1-naphthylamine (DMN)



ization cannot influence interactions with DA. Assuming that the amount of DA adsorbed by the control membrane represents nonspecific adsorption and that the difference between imprinted and control membranes represents specific adsorption, we can say that more than one-half of the specifically adsorbed DA can be reversibly released and then readsorbed by changing the wavelength of light used to irradiate the sample.

The level of DA adsorbed by our imprinted membranes is much higher than the reported levels of photoinduced effects seen in other azobenzene-containing materials. For example, photoinduced changes in gas flow through a glass membrane modified with an azobenzene derivative were only 1−2%.[30] In another work, transmittance by a system containing only the trans isomer of derivatized azobenzene (98%) was very close to the transmittance of a cis/trans mixture (100%).[31]

Compounds having structures similar to that of the template—dansyl-L-leucine (DL) and *N*,*N*-dimethylnaphthylamine (DMN) (Chart 1)—were tested to study the selectivity of imprinted membranes prepared with a PhAAAn-to-DA ratio of 4:1. Probably because of its larger size and modified structure, DL did not interact with the recognition sites: DL adsorption by the membranes was very low and not affected by UV or visible irradiation (Figure 5). DMN, which is similar to the template DA but smaller, is adsorbed by the DA-imprinted membranes (Figure 5). The difference in

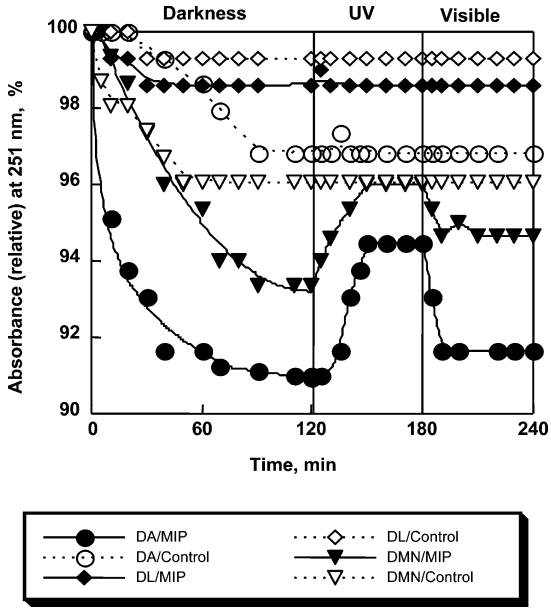


Figure 5. Binding of DA by DA-imprinted and control polymer membranes and binding of DL and DMN by DA-imprinted polymer membranes. The polymers were prepared with a PhAAAn-to-DA ratio of 4:1. The concentration of all tested compounds was 10 μM.

DMN adsorption between control and DA-imprinted membranes is much smaller than that for DA adsorption. The level of DMN adsorption was reduced by UV and increased by visible light. However, the relative extent of these changes was clearly smaller than for adsorption and release of DA. The observed level of selectivity of our membranes is higher than that of tryptophan-imprinted merocyanine copolymer membranes.[13] Those membranes interacted with phenylalanine, which is smaller than the template, and with a larger substrate, *N*-(3-carboxypropionyl)-L-phenylalanine-*p*-nitroanilide, at levels similar to that of the template.

To estimate the saturation capacity and the association constant for DA binding to the MIP membrane, we incubated the imprinted membranes (prepared at a PhAAAn-to-DA ratio of 4:1) with various concentrations of DA (4−100 μM). Scatchard plots were constructed by plotting the ratio of bound-to-free DA against the bound DA concentration. Linear least-squares fitting to the Scatchard plot provided the values of the association constant $K_{ass} = 4.1\ 10^4\ M^{-1}$ and the saturation capacity $N = 0.37\ \mu mol\ g^{-1}$ of polymer. The free energy change for DA binding (-26.3 kJ mol^{-1}) is smaller than for photoisomerization of free azobenzene. These data are in accordance with our expectations and with obtained results showing that photoinduced isomerization of PhAAAn within DA-imprinted membranes is accompanied by photoregulated adsorption and desorption of DA.

In summary, the present report describes the preparation of imprinted, photosensitive membranes by using PhAAAn as a photoresponsive functional monomer, DA as a template, and mixtures of EGDMA and TEGDA as cross-linkers. The affinity of DA-specific recognition sites within these MIP membranes can be reversibly changed by illumination with UV or visible light. Such photoresponsive molecularly imprinted materials should prove to be important for the development of environmentally 'friendly', wasteless technologies for separa-

tion, extraction, and assays of various chemical and biological compounds.

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