

# Energy Transfer and Photoactivity of Photozymes Included in Polyacrylate Hydrogels

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**ABSTRACT:** Two photozymes poly(vinylnaphthalene/sodium styrenesulfonate) (PZ1) and poly(vinylnaphthalene/sodium styrenesulfonate/*N,N'*-dimethyl methacryloyloxethyl propanesulfonate) (PZ2) were synthesized and used for the modification of hydrogels. The hydrogels were composed of acrylamide and 2-acrylamido-2-methylpropanesulfonic acid monomers, and modified with sodium bentonite (NB). The fluorescence properties and photoactivity of the photozymes were examined. Both photozymes demonstrated high self-assembly in both aqueous solutions and hydrogel matrices, which is of great importance for the antenna effect. For the NB-reinforced hydrogel, strong

energy transfer from the excited chromophores to the NB was observed and assigned to the high surface conductivity of clay. PZ2 exhibited higher photocatalytic activity for the methylene blue (MB) photodegradation than PZ1. This is most likely due to the better self-assembly and thus enhanced antenna effect of the zwitterionic PZ2. MB absorbed by the hydrogel from aqueous solution was efficiently decomposed in a photozyme-catalyzed photochemical process. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** photozyme; zwitterionic; photoactivity; hydrogel; antenna-effect

## INTRODUCTION

During the last years, smart hydrogel materials have found numerous applications, especially in the medical field.<sup>1</sup> The main feature that makes hydrogels so interesting for the integration in biological systems is their high water content and high responsiveness to external stimuli. Although most interest has been shown in the application for drug delivery, there are potentials for further applications based on the variety of properties that these materials exhibit. Because of their high water content (up to 90 wt %), hydrogels are characterized by a high biocompatibility and low

inflammatory response, which make them very promising smart biomaterials with a tunable switching on–off behavior.<sup>2</sup> Moreover, hydrogels are widely used in the field of water purification by using their high ability to absorb organic compounds, e.g., dyes, from aqueous solutions.<sup>3,4</sup> The addition of photoactive components to the hydrogels enables the catalytic photodegradation of absorbed dyes which is of great environmental interest.<sup>5</sup> In this view, the modification of hydrogels by photozymes opens perspectives for new and promising applications.

Photozymes are amphiphilic water-soluble copolymers that consist of two units. One unit is hydrophobic and contains pendant chromophores, and the other one is hydrophilic. Photozymes in aqueous media are able to form nanosized pseudomicelles with hydrophobic cores due to their self-assembling ability.<sup>6,7</sup> Such copolymers possess very interesting and promising light-emitting properties due to the formation of excimer complexes, and have received a great attention due to their potential as light-harvesting materials.<sup>8</sup> They can be utilized to efficiently transform the solar light into chemical energy via

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the antenna effect and produce a singlet oxygen after splitting water molecules followed by a tailored photochemical transformation of the molecules solubilized in the hydrophobic pocket.<sup>7,9</sup> These are similar processes to those utilized by nature in the photosynthesis. From that point of view, the investigation of the photochemical properties of copolymers with pendant groups such as poly(vinylnaphthalene) attracts great attention.<sup>10,11</sup> Moreover, the self-assembly of such copolymers in aqueous solutions plays an extremely important role in their photoluminescence properties.<sup>12</sup> Several works have shown the possibility of modified hydrogels possessing a side-chain chromophore, which was found to be very effective for energy transfer from the incorporated fluorescent moieties toward a hosted fluorophore, supporting its photodegradation.<sup>13,14</sup> However, the inherent photo-physical and photochemical properties can be altered because the photosensitizers are constrained within the environment of a polymeric matrix, and therefore, the photoactivity of the resulting material cannot be directly extrapolated from the known behavior in a solution. Although the hydrogel materials as well as photozymes are of a great practical and scientific interest and widely investigated, there are no reports studying the photoluminescence properties of photozymes incorporated in hydrogel matrices, despite the practical importance of such systems.

Because of the high water content, hydrogels are usually very weak materials, so considerable efforts are made to improve the hydrogels' mechanical performance. The related research follows basically two ways: creation of novel-type crosslinked structures (double networks, hybrid or interpenetrating networks, etc.) and incorporation of water swellable or dispersible nanofillers (e.g., layered silicates).<sup>15</sup> The latter approach, e.g., the reinforcement of hydrogels via the incorporation of water swellable sodium bentonite (NB) was found to be very effective.<sup>16</sup>

This work reports studies on the integration of two photozymes poly(vinyl naphthalene-*co*-sodium styrene sulfonate) (PZ1) and poly(vinyl naphthalene-*co*-sodium styrene sulfonate-*co*-*N,N'*-dimethyl methacryloyloxyethyl propane sulfonate) (PZ2) in the polymer hydrogels consisting of acrylamide (AAM) and 2-acryloylamido-2-methylpropanesulfonic acid (AMPASA) comonomers, as well as in their NB-reinforced versions, and on the spectral fluorescence properties and photocatalytic activity of these materials for their dye removal ability.

## EXPERIMENTAL

### Materials

The sodium styrene sulfonate (SSS, Fluka), 2-vinyl naphthalene (VN, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), and *N,N'*-dimethyl methacryloyloxyethyl propane sulfonate (DMAPS, Merck,

Darmstadt, Germany) were used as monomers for the photozyme synthesis, as well as the initiator of radical copolymerization dibenzoyl peroxide (Merck) were used without additional purification. The solvents [dimethyl sulfoxide (DMSO) and acetone] were supplied by Sigma-Aldrich and were of analytical grade. The AAM and AMPASA monomers, as well as the methylene-bisacrylamide (MbAAM) crosslinker, purchased from Sigma-Aldrich, were used as received. Potassium persulfate ( $K_2S_2O_8$ ) was obtained from Merck and used as polymerization initiator for the preparation of the hydrogels. The pristine sodium bentonite (EXM 757 type, abbreviated further on by NB), which belongs to the family of natural montmorillonites, was supplied by Süd Chemie AG (Munich, Germany). Its cation exchange capacity and interlayer spacing were about 80 mequ/100 g and 1.24 nm, respectively.

### Synthesis of photozymes

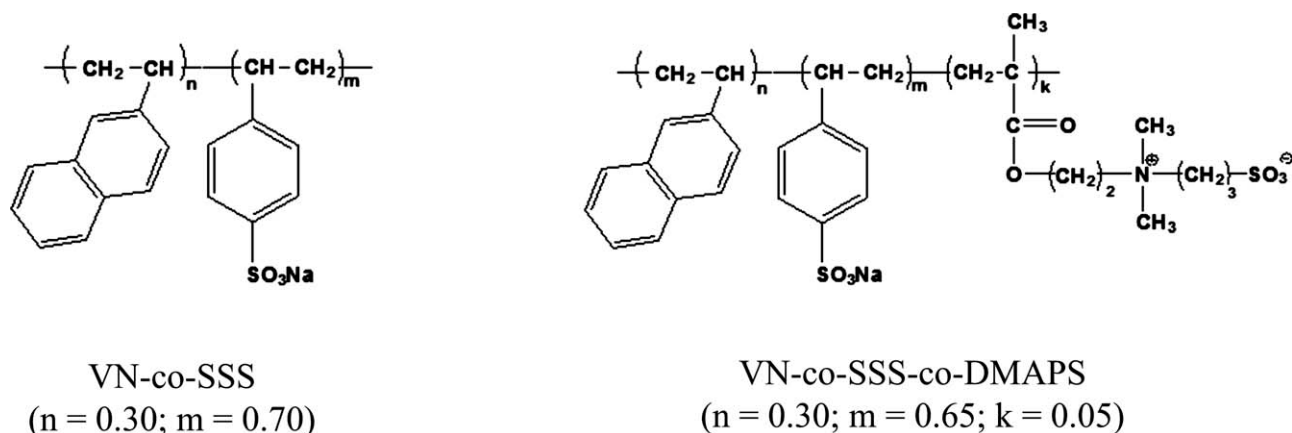
Poly(VN-*co*-SSS) (code PZ1) and poly(VN-*co*-SSS-*co*-DMAPS) (code PZ2) photozymes were synthesized by a random free radical copolymerization in DMSO at 80°C in nitrogen atmosphere for 12 h, using dibenzoyl peroxide as an initiator (1 wt % relative to the comonomers). The total comonomer concentration was 20 vol % and the initial comonomer mole ratios (VN/SSS and VN/SSS/DMAPS) were 0.30/0.70 and 0.30/0.65/0.05, respectively. The copolymerization conversion achieved for the reaction time was determined gravimetrically and was assessed as 0.92 for PZ1 and 0.96 for PZ2. Once the copolymerization was complete, the copolymers obtained were precipitated in acetone, dissolved in distilled water, and dialyzed against water for a week to remove the nonpolymerized comonomers and initiator. Then the photozymes obtained were freeze dried. Their chemical structure is shown in Figure 1.

### Characterization of photozymes

The composition of the synthesized PZ was determined by elemental (C, H, and S) analysis (Vario EL III Element Analyzer, Elementar Analysensysteme GmbH, Germany).

Molecular weight characteristics were determined by size exclusion chromatography (Waters chromatograph) with two columns (PigeMixer) 30 × 7.5 mm. The calibration was performed with PEG-standards. The probe volume was 30 μL with concentrations between 0.15 and 0.24 mg mL<sup>-1</sup>. The temperature was 45°C. As eluent water was used, the eluent rate was 1 mL min<sup>-1</sup>.

Fourier transform infrared (FTIR) spectroscopic measurements were performed on a Nicolet 510



**Figure 1** Chemical structure and composition of the synthesized photozymes: PZ1 (left) and PZ2 (right).

spectrometer (Madison, WI). The photozymes were dried *in vacuo* for 2 days, then the powdered samples were mixed with KBr and pressed into disks. FTIR spectra were recorded in the transmission mode at  $4 \text{ cm}^{-1}$  spectral resolution in the wavenumber range  $4000\text{--}500 \text{ cm}^{-1}$ .

### Preparation of hydrogels

All hydrogels were synthesized as previously described.<sup>16</sup> Briefly, 1 g of AMPSA, 1 g of AAm, and 0.005 g of MbAAM were dissolved in 6 g of bidistilled water at continuous stirring. When a transparent solution was obtained, 0.0025 g of  $\text{K}_2\text{S}_2\text{O}_8$  was added last. These hydrogels were entitled H gels. For the NB-modified hydrogels (H-NB gels), 0.08 g of NB was first dispersed in water, and all monomers and initiator were added to the prepared nanoparticle slurry. The concentration of solids in water was 40 wt %. For photozyme-modified hydrogels, photozymes were dissolved in water before the addition of all other components in the concentration of 1 wt % considering the total amount of monomers. After the reactive mixtures were prepared, they were poured into Petri dishes and heated for 8 h at  $60^\circ\text{C}$ . After the synthesis, the gels were dried for 24 h at  $50^\circ\text{C}$  under vacuum to constant weight. The dry specimens were then submerged in distilled water for 2 weeks at room temperature to remove soluble components, and the sol fraction was calculated as described elsewhere<sup>16</sup> and was assessed as 10–12% for all hydrogels.

### Swelling behavior of hydrogels

The swelling degree ( $Q$ ,  $g_{\text{H}_2\text{O}}/g_{\text{polymer}}$ ) of the hydrogels was calculated by the following equation:

$$Q = \frac{m_s - m_d}{m_d}$$

where  $m_s$  and  $m_d$  are the weights of the swollen and dry samples, respectively. The swelling behavior of the gels was investigated at  $25^\circ\text{C}$  in distilled water by measurement of their weight at regular time intervals. The mean values of  $Q$  were deduced from three parallel measurements, and the standard deviation was assessed.

### Fluorescence properties

The photoactivity of the PZ in aqueous solutions and in hydrogels was tested by fluorescence spectroscopy. The absorption spectra were recorded with a compact UV-vis spectrometer (CHEM2000, Ocean Optics, Ostfildern, Germany) using a 1-cm quartz cuvette. The steady-state fluorescence and fluorescence excitation spectra were recorded with a fluorometer (Jobin-Yvon, Longjumeau, France; Fluoromax-2, 1-cm quartz cuvette) equipped with a  $1200\text{-mm}^{-1}$  excitation grating (blaze 300 nm), a  $1200\text{-mm}^{-1}$  emission grating (blaze 300 nm), a Xe arc lamp for excitation (150 W Xe OFR), and a photomultiplier for detection (Hamamatsu R-928P, Hamamatsu, Japan).

### Photoefficiency

The photocatalytic efficiency of the PZ in the solutions and within the photo-modified hydrogels was tested using a model cationic dye, methylene blue (MB). A 0.1 wt % of PZ or cubic (ca.  $1 \text{ cm}^3$ ) sample of each hydrogel was submerged in 10 mL of  $10^{-5} \text{ mol L}^{-1}$  methylene blue aqueous solution. The samples were then irradiated for 5, 15, 25, 35, 45, and 55 min. The UV irradiation was performed with a UVASPOT 400/T (Dr. Höhnle AG, Gräfelfing/München, Germany) equipment with a Hg-metal-halogen irradiator (Dr. Höhnle 400F, Power: 380 W) in a distance of 378 mm from the samples. After each step of the irradiation, UV spectra of the MB solutions

**TABLE I**  
**Elemental Analysis and Molecular Weight Characteristics (Number Molecular Weight,  $M_n$ , and Polydispersity Index,  $M_w/M_n$ ) of the Synthesized Photozymes**

Photozyme	Theoretical			Experimental			$M_n$ (kDa)	$M_w/M_n$
	%C	%H	%S	%C	%H	%S		
PZ1	57.92	4.30	11.75	58.01 ± 0.10	4.09 ± 0.05	11.77 ± 0.08	6.17	2.44
PZ2	57.76	4.58	11.53	57.89 ± 0.10	4.39 ± 0.05	11.56 ± 0.08	5.32	2.34

were acquired with a UV-2101/3101PC scanning spectrophotometer (Shimadzu Europa GmbH, Duisburg, Germany). Parallel to that, identical hydrogel samples were kept nonirradiated (in darkness) for the same periods of time to get the degree of uptake of MB by the hydrogels. To assess the degree of MB decomposition under UV irradiation without photozymes, the pure  $10^{-5}M$  methylene blue aqueous solution was placed in the irradiation chamber together with the other samples. For the determination of the degree of pollutant decomposition, a concentration calibration curve was acquired for the MB solutions at different concentrations. The data for the calibration were collected for the characteristic absorption peak of methylene blue at 660 nm. The decomposition of MB was presented as the relative concentration  $C/C_0$ , where  $C$  is the current concentration at the time of irradiation, and  $C_0$  is the initial concentration of MB ( $10^{-5}M$ ).

The concentration of photozymes in the swollen gels was calculated considering their feed rate in the reactive mixtures at the synthesis of hydrogels and the data of their water content. Parallel to that, the actual photozyme concentration in swollen gels was estimated from the data of UV-vis spectroscopy using calibration curves acquired for the several concentrations of the photozymes aqueous solutions.

## RESULTS AND DISCUSSION

### Characterization of the photozymes

The results of the elemental analysis of the photozymes synthesized are presented in Table I. These experimental data are in agreement with our expectations in relation to the feed ratios of the polymerization. The molecular weight characteristics of photozymes (number molecular weight,  $M_n$ , and polydispersity index,  $M_w/M_n$ ) are given in Table I and are comparable for both photozymes. Their structure was investigated by FTIR spectroscopy. The FTIR spectra of PZ1 and PZ2 (Fig. 2) were very similar due to the close chemical composition. For the PZ2, the new band at  $1726\text{ cm}^{-1}$  was observed and was attributed to the stretching vibrations of C=O ester groups of the DMAPS units.

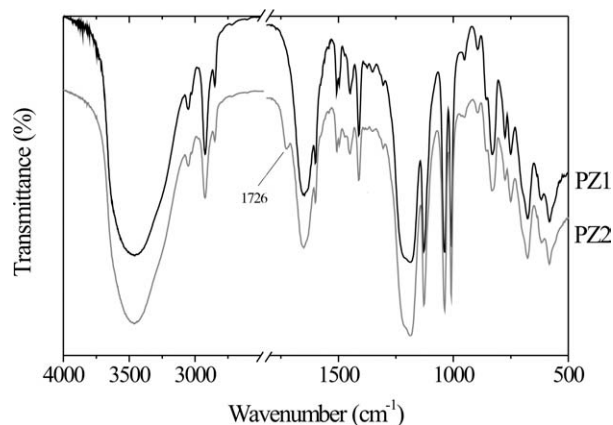
The investigation of self-assembling ability of the photozymes by dynamic light scattering<sup>17</sup> and z-

potential measurements<sup>18</sup> showed that the photozyme containing zwitterionic groups (PZ2) demonstrates high self-organization and forms more stable nanomicelles with higher values of z-potential ( $\sim -80\text{ mV}$ ) than the photozyme without DMAPS units ( $\sim -65\text{ mV}$ ).

### Swelling of hydrogels

One of the most important parameters of hydrogel systems is their water uptake. When modified by photozymes, this parameter has significant importance since it determines the concentration of photozymes in the volume of the swollen gels, and accordingly, the photoactivity of the modified hydrogels. Our detailed investigations on water uptake for these hydrogels are presented elsewhere.<sup>16</sup>

All synthesized hydrogels demonstrated high swelling degree ( $Q$ , Table II). Unexpectedly, we found that the modification with photozymes reduces the swelling degree of gels in water. The incorporation of PZ1 in the H-gels decreases  $Q$  from 194 to  $180\text{ g g}^{-1}$  for H-PZ1 and to  $166\text{ g g}^{-1}$  for H-PZ2 gels (Table II). This fact can be attributed to the strong interactions between the polar groups of the photozymes and those of the hydrogels. Although these interactions are not as strong as covalent bonds, they prevent the photozymes from being completely washed away from the gel and may increase its apparent crosslink density. The hydrophobic nature of the chromophoric groups of the photozyme macromolecules should also be taken



**Figure 2** FTIR spectra of the synthesized photozymes.



**TABLE II**  
**Swelling Degree ( $Q$ ) of Hydrogels and Concentration of the Photozymes (Theoretical, Calculated from the Swelling Data, and Experimental, Determined from UV-Absorbance Spectra) and the Relative Contribution of the Excimer Band at 400 nm ( $A_{400}$ ) into the Total Area of the Emission Spectra ( $A_{\text{total}}$ )**

Sample code	$Q$ (g g <sup>-1</sup> )	Concentration of PZ (ppm)		$A_{400}/A_{\text{total}}$ (%)
		Theoretical (from swelling data)	Experimental (from UV-absorption data)	
PZ1 solution	–		70	29.8
PZ2 solution	–		74	35.6
H	193.7 ± 3.2		–	–
H-PZ1	180.0 ± 4.2	70	27	25.4
H-PZ2	165.9 ± 3.9	74	29	29.9
H-NB	109.3 ± 1.1		–	–
H-NB-PZ1	106.2 ± 3.1	93	–	–
H-NB-PZ2	104.1 ± 3.7	95	19	32.1

Data are collected from deconvoluted Gaussian bands of emission spectra ( $\lambda_{\text{ex}} = 280$  nm).

into account, as it could also affect the swelling degree. Moreover, when modified with the zwitterionic photozyme (PZ2), the more pronounced reduction of the swelling degree can be explained by the higher self-assembling ability of PZ2 due to the presence of the zwitterionic units reducing its solubility in water.<sup>19</sup> Moreover, the sulfonic units of AMPSA in the hydrogel matrix may strongly interact with the ammonium cations of DMAPS in PZ2. This leads to the formation of intermolecular complexes<sup>20</sup> enhancing the interaction of PZ2 with the hydrogel matrix.

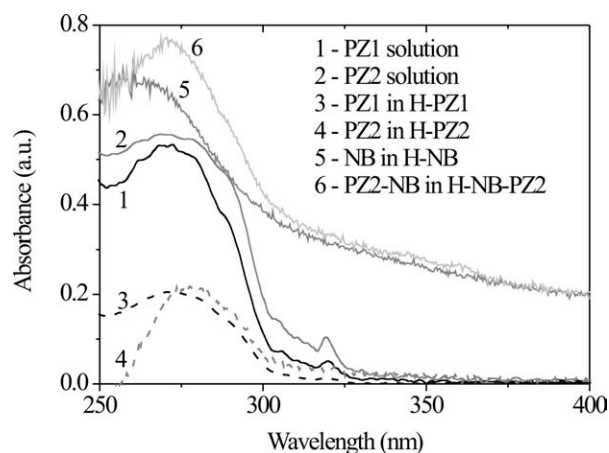
For the hydrogels reinforced by sodium bentonite (H-NB gels), a significant decrease of the swelling degree was observed. Such an effect of clay modification on the swelling behavior has also been observed by other investigators<sup>20,21</sup> and was explained by additional crosslinks formed by the clay-platelets. The results of our investigations on how sodium bentonite influences the mechanical properties of gels have been presented and discussed in detail.<sup>16</sup> It is interesting that for the clay-reinforced samples, the decrease of the swelling degree due to the modification with photozymes (H-NB-PZ1 and H-NB-PZ2 gels) was also observed. This tendency resembles the swelling behavior of PZ-modified H-gels; however, in the case of NB-reinforcement, the effect of the PZ on the swelling behavior was not so pronounced. Obviously, the interactions of the gel matrix with the PZ become weaker because the mineral clay platelets interact preferably with a hydrogel matrix via ionic forces enhancing the mean crosslink density,<sup>21,22</sup> which results in a negligible effect of the PZ on the swelling degree.

### UV-vis absorption

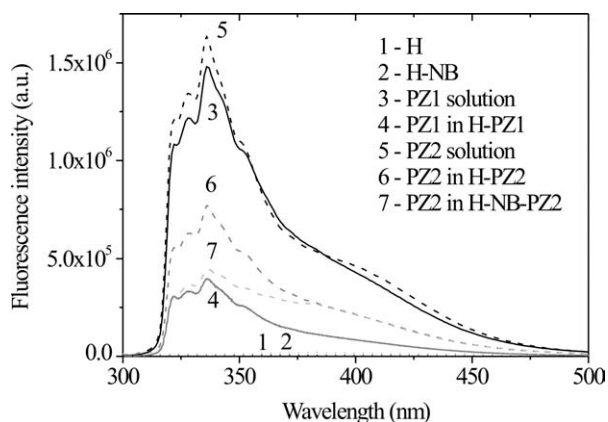
To compare the photozyme photoactivity within the modified hydrogels with that of their aqueous solutions, absorption spectra were acquired before the fluorescence studies for a 70-parts per million (ppm)

aqueous solution of PZ1 and a 74-ppm aqueous solution of PZ2. The concentrations of these solutions were taken similar to those in the hydrogels, calculated according to the feed rate of PZ at synthesis of gels and the swelling degree of hydrogels. The related data are given in Table II.

The absorbance of photozymes within the hydrogels was computed as the difference between the absorbance of a photo-modified hydrogel (H-PZ1 or H-PZ2) and the absorbance of the virgin gel (H). Figure 3 demonstrates the UV-vis absorption spectra of PZ1 and PZ2 in the solutions and within the H and H-NB gels. The UV-vis spectra of the aqueous solutions of PZ1 and PZ2 are very similar because of the similar structure of the chromophore moieties. The main absorption peak is located at 270 nm and is typical for the naphthalene chromophore. When PZ2 is introduced in the hydrogel (Fig. 3, curve 4), a shifting of the main absorbance peak to 280 nm can be observed suggesting a strong interaction between the naphthalene chromophores being aggregated.<sup>12</sup>



**Figure 3** UV-vis absorption spectra of PZ1 (1) and PZ2 (2) in the solutions and within the H-hydrogels (3 and 4), NB in the H-NB gel (5), and additional effect of PZ2 and NB in the H-NB-PZ2 hydrogel (6).



**Figure 4** Emission spectra of the pure hydrogels (1 and 2), PZ1 and PZ2 in their aqueous solutions (3 and 5), and within the hydrogels (4, 6, and 7);  $\lambda_{\text{ex}} = 280$  nm.

As PZ2 exhibited a very high degree of self-assembly in water,<sup>19</sup> the effect of NB on the spectral properties was studied for the H-NB-PZ2 hydrogel. For the nano-reinforced gel matrix (H-NB), a strong UV absorption was observed in a broad wavelength range with an intensity maximum at 250 nm and a long tail in the spectral region of 300–800 nm (Fig. 3, curve 5). Such an effect could occur due to the strong scattering of absorbed light by the inorganic nanoparticles of NB dispersed within the hydrogel matrix.<sup>16</sup> For the H-NB-PZ2 hydrogel, the simultaneous use of NB and PZ2 for hydrogel modification affects the absorption of UV light (curve 6) showing an increase of peak intensity at 270 nm compared to the H-PZ2 and H-NB gels (curves 4 and 5, respectively).

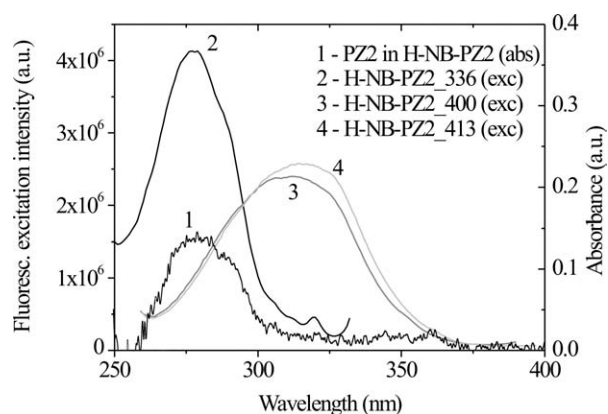
Although the concentrations of photozymes in aqueous solutions were nominally similar to those of the PZ-modified gels, their absorption spectra clearly demonstrate that the concentrations of the photozymes in the gels are lower. This indicates their partial washing out of the gel with sol-fraction (measured as 12%) during the purification process, which is due to the absence of covalent bonding between the gel matrix and the photozyme. Therefore, the actual concentrations of the photozymes within the gels were determined from their UV spectra and were estimated to be 27 ppm for the PZ1 in the H-PZ1 gel, and 29 and 19 ppm for the PZ2 within the H-PZ2 and H-NB-PZ2 hydrogels, respectively. These data are presented in Table II and indicated as experimental concentrations.

### Fluorescence studies

Steady-state fluorescence emission spectra were acquired at the excitation wavelength  $\lambda_{\text{ex}} = 280$  nm, in the region where isolated naphthalene chromophores absorb light. The results are presented in Figure 4. As expected, neither hydrogel matrices (H and

H-NB, curves 1 and 2, respectively) show any emission of light. For PZ-containing systems, the main emission band is located at 336 nm (Fig. 4, curves 3–7) and corresponds to the naphthalene monomer emission.<sup>11</sup> However, an intense band at longer wavelength (peak maximum at  $\sim 400$  nm) is observed, which indicates the formation of the low-energy excimer suggesting a strong aggregation of the hydrophobic naphthalene moieties.<sup>6,9,13</sup> To estimate the contribution of the excimer emission into the total spectra, the emission spectra were additionally deconvoluted into Gaussian bands.<sup>23</sup> The results of the relative areas of the excimer band at 400 nm are presented in Table II. The contribution of excimer emission into the total spectra is higher for all PZ2-containing samples, indicating its better self-assembling ability due to the DMAPS units in the structure of the photozyme. At the same time, for PZ-modified hydrogels, these values are lower compared to the corresponding solutions. This indicates some confinement effect of the hydrogel matrix on the free motion of naphthalene groups hindering their self-assembly and, accordingly, excimer formation. However, the obtained results demonstrate that the aggregation of the photozymes chromophore groups is not destroyed by the hydrogels matrix, which is of great importance for the photocatalytic properties.

It is also interesting to note that for the H-NB-PZ2 hydrogel, the relative value of excimer emission is higher than that of the H-PZ2 gel and is comparable to that of the solution, despite the much lower concentration of the PZ2 (see Table II). An interpretation of these phenomena is quite difficult because of many factors influencing such complex systems; therefore, the excitation spectra for the H-NB-PZ2 hydrogel were recorded at the emission wavelengths near the naphthalene and its excimer emission (at 336, 400, and 413 nm, Fig. 5). Note that for the PZ2

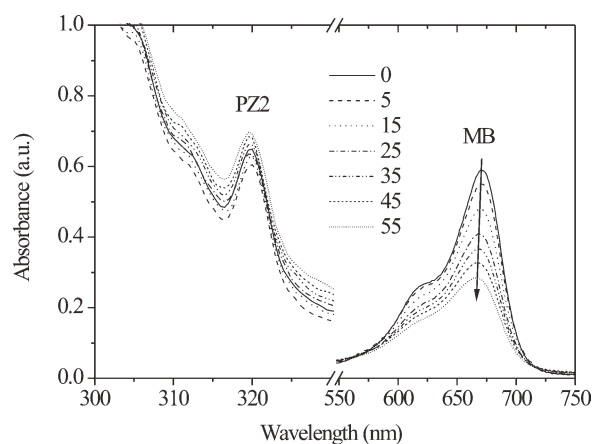


**Figure 5** UV-vis absorption spectra (1) and fluorescence excitation spectra (2–4) of the H-NB-PZ2 hydrogel at the different emission wavelengths (are depicted in the legend).

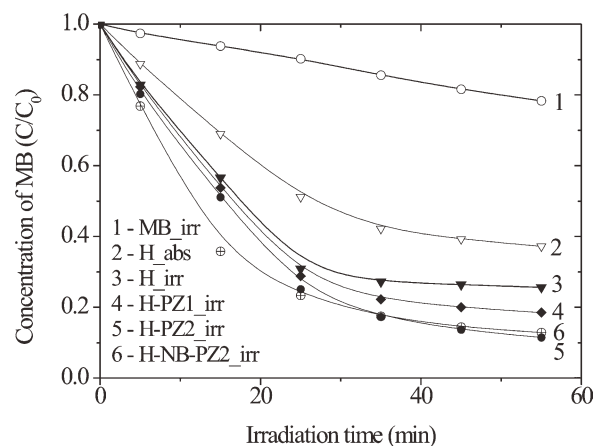
incorporated in H-NB gel, no correlations were detected for its absorption (Fig. 5, curve 1), and the excitation spectra recorded at  $\lambda_{em} = 400$  and 413 nm (curves 3 and 4). This indicates that there are various emitting species, and their concentration may be very small to be clearly detected by UV-vis spectroscopy. Moreover, the much smaller intensity of these peaks compared to that of naphthalene (Fig. 5, curve 2) indicates that the transfer of excitation energy to these species is significant but not complete. It can significantly influence the light emission of PZ2 incorporated into the H-NB hydrogel and impair it because of the strong energy exchange between NB and the chromophores of the photozyme due to the high surface conductivity of the clay.<sup>24</sup> It is also possible that protonation of SiOH groups of NB by the acidic groups of AMPSA changes the charge of the clay-layers resulting in some deformation of the octahedral structure of the clay sheets.<sup>25</sup> The latter may significantly affect the fluorescence behavior of this complex system.

### Photocatalytic properties

The typical UV-absorbance curves of the PZ2-MB solution on UV irradiation are shown in Figure 6. As can be seen, MB shows one main peak at 670 nm with a shoulder at 610 nm which is due to the dye dimmer formation.<sup>26</sup> After 55 min of irradiation, the intensity of the maximum absorption peak decreased due to the degradation of MB and slightly blue-shifted due to the formation of the demethylated dyes.<sup>27</sup> As was determined, the MB dye on photodegradation undergoes different photochemical reactions, and several decomposition products are formed. This can also be a reason for the slight increase of the PZ2 peak intensity at 320 nm. A similar tendency was observed for both photozymes in



**Figure 6** Absorbance spectra of the PZ2 solutions (0.1 wt %) in  $10^{-5}$  mol L<sup>-1</sup> MB solution depending on time of UV-illumination (indicated in the legend).



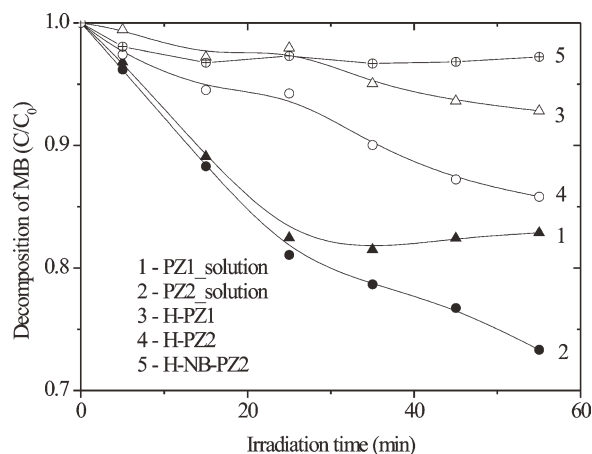
**Figure 7** Decrease of the relative concentration depending on time of irradiation of the MB aqueous solution due to the UV irradiation alone (1) and due to the absorption by the H-hydrogel without irradiation (2) and additional effect of the absorption and irradiation of hydrogels (3–6).

all tested media: in their solutions and in the hydrogels, and the Beer-Lambert law was used to determine molar concentrations of the decomposed MB.

The decomposition of MB ( $C/C_0$ ) alone on UV illumination amounts to 20% (Fig. 7, curve 1). In the presence of the H-gel, for nonirradiated samples, the dye concentration decreased by three times (curve 2), which was due to the strong absorption capacity of the hydrogel. On UV irradiation of PZ-containing hydrogels (curves 4–6), a stronger decrease of the MB concentration can be seen, indicating a combined effect of absorption by the gels and decomposition due to the UV light. It is interesting to note that the modification of the hydrogel with NB increases the MB absorption during the first 20 min (curve 6) in comparison to the H-PZ2 gel. This can be traced back to the additional adsorption of dye by the clay surface. The ability of bentonites to adsorb contaminants from water is well known and widely used in the water purification area for a long time.<sup>28,29</sup>

To investigate the photocatalytic effect of photozymes alone on the MB decomposition in solution and in the different hydrogel matrices, we subtracted the concentration decrease of MB due to the hydrogel absorption and its own decomposition at UV irradiation. Figure 8 presents the subtracted curves of MB decomposition under UV irradiation caused only by PZ1 and PZ2 in different media: in their 0.1-wt % aqueous solutions and in the H and H-NB hydrogels (the concentrations of PZ in the hydrogels are given in Table II). PZ2 demonstrates higher photoefficiency than PZ1 in both their solutions (curves 2 and 1, respectively) and being incorporated in the H-gel (curves 4 and 3, respectively). As the concentrations of both PZ either in their





**Figure 8** Decomposition of MB on irradiation due to the PZ1 and PZ2 in their aqueous solutions (1–2) and in the H and H-NB gels (3–5).

solutions or in H-gels were taken similar, this effect should be attributed to the better photocatalytic properties of the zwitterionic photozyme. It is also very important that this tendency was not affected by the hydrogel matrix and was still found to be very high.

In the presence of the H-NB-PZ2 gel, the decomposition of MB due to the PZ2 was very low (Fig. 8, curve 5). Such a behavior is in good accordance with the fluorescence properties of this system, indicating weak excitation and strong energy dissipation by the NB distributed in the hydrogel matrix.

It is interesting to note that the photodecomposition of MB in the presence of PZ-modified hydrogels during the first 30 min of UV-irradiation is very weak and stays almost constant, which is different from the corresponding solutions. A possible explanation for this phenomenon is the aggregation of cationic dye with the anionic hydrogel network rendering some stabilizing effect on the MB dimer formation with an increase of the dye concentration.<sup>30</sup> After 30 min of illumination, the photodecomposition of MB by H-PZ gels becomes dominant, and the concentration of the dye decreases. However, for NB-modified gels, the decrease of MB concentration almost stopped, possibly due to the additional strong aggregation of MB with clay sheets.

## CONCLUSIONS

Although no covalent bonding between the gel matrix and the photozymes occurred, the photozymes were fixed within the gels, which was confirmed by UV-vis and fluorescence spectroscopies. The small concentration of zwitterionic units (5 mol %) in the chemical structure of PZ2 enhanced the aggregation of the vinyl naphthalene chromophores in water media, and this effect was not hindered by the

hydrogel matrix. It was argued that the enhanced photocatalytic behavior of PZ2 originates from its stronger antenna-effect caused by a better self-assembly in water, which was also true for the hydrogels.

The observed high uptake of MB from aqueous solutions allows the trapping of dye molecules by the hydrophobic pockets of the photozymes. Such effects play an important role in the energy transfer from the excited naphthalene moieties to the entrapped MB molecules whereby accelerating the photochemical decomposition of the latter. The absorption of MB by the NB reinforced gel was much stronger than for the nonreinforced one, which is due to the strong additional binding to the clay-sheets. This can prevent the entrapment of the dye molecules by the chromophoric pockets of the photozymes within the gels reducing their photocatalytic activity.

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