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Singlet oxygen generation using PDMS occluded dyes

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Abstract

Several dyes that generate singlet molecular oxygen ($^1O_2$) were occluded in polydimethylsiloxane (PDMS). For the homogeneous dyes, this occlusion forms an easy way of heterogenization, whereas it improves the performance of dyes that are heterogenized already in molecular sieves. These systems were investigated for the singlet oxygenation of test substrates, such as 2,3-dimethyl-2-butene and 1-methyl-1-cyclohexene. The PDMS elastomer was selected for its transparent, hydrophobic and permeability characteristics. The elastomer is ‘wrapped’ around the sensitizing system and hence shields the dyes from polar components, such as water, and balances the sorption of solvents and reagents. This results in an enhanced oxygenate yield for water sensitive dyes. Finally, a new porphyrin, 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin, was synthesized and chemically anchored to PDMS, resulting in a highly active heterogeneous singlet oxygen generating system.

Keywords: PDMS; Singlet molecular oxygen; Porphyrins; Dye heterogenization

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1. Introduction

Photo-oxidative reactions are among others the principal processes that lead to the degradation of plastics and the destruction of biological substances in the combined action of light and molecular oxygen. Moreover, photo-oxidation brings important contributions to synthesis, more specifically in the field of natural product synthesis [1].

The reactive intermediate in many of these processes has been characterized as singlet molecular oxygen O_2 ($^1\Delta_g$). This active form of molecular oxygen is the lowest excited state. It is mostly obtained via an energy transfer from an excited sensitizer molecule, having a triplet state, to the triplet or ground state of molecular oxygen. Since photosensitization is still the most applied method for $^1O_2$ generation and because of the availability of elaborate research reports, photosensitization remains the reference system for singlet oxygenation [1,2].

During the energy transfer from sensitizer to molecular oxygen, superoxide $O_2{}^-$ is sometimes formed instead of singlet molecular oxygen, with the simultaneous formation of a radical cation on the sensitizer. The very reactive $O_2{}^-$ is responsible for aselective reactions and contributes to many degradation processes of organic compounds. While superoxide can be of interest in degradation reactions, it is most surely not for selective oxygenation reactions where singlet molecular oxygen is the desired oxidant [1,3].

The potential of many selective $^1O_2$-sensitizers has initiated research in the field of sensitizer immobilization. Table 1 gives an overview of some relevant literature in this field. Most immobilized sensitizers are characterized by some loss in singlet oxygen quantum yield. Although many immobilization procedures have been published or patented, immobilized systems were implemented in only a few practical industrial applications [2–5]. Polymer linked Bengal Rose was the only commercialized system, marketed under the trade name of ‘Sensitox’ by Hydron Laboratories Inc. This can be related to the poor photo-oxidative stability of many of these dyes upon prolonged irradiation. Nowadays, some new sensitizers such as porphyrin derivatives are being explored [6]. These structures show an enhanced photostability compared to the more conventional dyes, such as methylene blue and Bengal Rose.

In the current paper, PDMS membranes are used to occlude the dye systems. The specific properties of PDMS, like light transparency, hydrophobicity and a very high chemical and thermal resistance, comprehend its potentials

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Table 1
Literature overview of immobilized sensitizers[a]

Sensitizer	Immobilization	References
Bengal Rose	Amberlite IRA-400	[20,21]
Eosine	Amberlite IRA-400	[20,21]
Methylene blue	Amberlite IRC-200	[20,21]
Bengal Rose	Silica gel	[22]
Polymer linked Bengal Rose	Polymer linked styrene-divinylbenzene beads	[4,23]
Methylene blue	Silica gel	[24]
Bengal Rose	Glass plate	[25]
$Ru(bpy)_3{}^{2+}$	Zeolite Y	[13]
Sensitizers[b]	Polysiloxane	[5]
Bengal Rose	Copolymers[c]	[26]
Thionine	Li-Y, Na-Y, Rb-Y, Cs-Y	[7]
TPFPP[d]	Biphase system (two liquids)	[27]

[a] http://www.rcdc.nd.edu/compilations/Qy/IntroQy.htm.

[b] Sensitizers: Zn- and Mg-phthalocyanine, Zn-tetraphenylporphyrin, Bengal Rose, acridine orange, methylene blue, rhodamine B, fluoresein.

[c] Copolymers: poly(sodium styrenesulfonate-styrene-vinylbenzylchloride) and poly(sodium styrenesulfonate-2-vinylnaphtalene-vinylbenzylchloride).

[d] TPFPP = 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin.

as a useful tool in photochemical generation of singlet oxygen.

2. Experimental

2.1. Synthesis and sensitizer immobilization

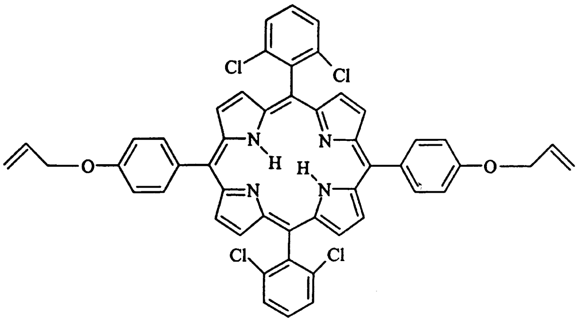
Cationic sensitizers, like thionine, can be exchanged for the Na^+ ions of a zeolite Y. An aqueous solution containing 2 mg of thionine (Aldrich) is mixed with 600 mg of zeolite Y (Uetikon) for 3 h. The purple zeolite is subsequently filtered, washed thoroughly and submitted to a Soxhlet extraction for 24 h. Finally, it is dried at 60°C yielding a blue thionine-Y zeolite [7].

In an alternative approach, occlusion of bulky complexes inside zeolite cavities was realized via the in situ synthesis. In 1991, Parton et al. described the synthesis of metallo-phthalocyanines inside the cages of zeolite Y [8]. The main advantage of this procedure is that it allows the preparation of phthalocyanine (Pc) with high purity. Due to the monomeric dispersion of Pc in the zeolite cages, the molecules are highly stabilized. The sodium ions of the Na-Y zeolite are first replaced with Zn^{2+}, using 1 l of a 0.5 M $Zn(OAc)_2$ (ACROS) aqueous solution in which 5 g of Na-Y is refluxed. The dried Zn-Y zeolite is mixed with 2.5 g of 1,2-dicyanobenzene (DCB, Aldrich). The solid mixture is heated for 24 h at 120°C under nitrogen, inducing a solid state migration of DCB inside the zeolite towards the Zn^{2+} cations. DCB chelates with the zinc cations and the $Zn(DCB)_4$ complexes thus formed subsequently react to yield the desired zinc–phthalocyanine (ZnPc) complex. The tetramerization is actually a redox reaction, which requires traces of water. To purify the ZnPc-Y zeolite, the reaction mixture is Soxhlet extracted with acetone for 3 days or until disappearance of the color in the extraction solution.

5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrin is prepared using a standard procedure: 0.057 mol 2,6-dichlorobenzaldehyde (Aldrich) is added to a mixture of acetic acid (70 ml, ACROS) and nitrobenzene (30 ml, ACROS). After complete dissolution, a slight excess of pyrrole (0.059 mol, Aldrich) is added to the solution. The reaction mixture is protected against light and stirred at 388 K for 1 h. After cooling the solution, the porphyrin is separated by filtration and purified on a silica column with CH_2Cl_2 (Biosolve Ltd.) as the carrier solvent [9].

Metal insertion in tetraphenylporphyrins (TPPs) is achieved as follows: 0.5 g of the porphyrin is dissolved in 300 ml dimethylformamide (DMF, Aldrich). 3 ml collidine (ACROS) and 1 g of a metal chloride are added to the solution. The mixture is refluxed in the dark under nitrogen atmosphere till completeness of the insertion (UV–VIS verification). Finally, the reaction is poured into an ice-cooled NaCl solution (300 ml). The porphyrin is separated, washed with water and vacuum dried at 303 K.

The novel porphyrin, 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin, is synthesized according to following procedure: a solution of 5-(2,6-dichlorophenyl)-dipyrromethane (0.5 g, 1.72 mmol) and 4-allyloxybenzaldehyde (0.278 g, 1.72 mmol, Aldrich) in dichloromethane (172 ml) is deoxygenated by purging with argon for 15 min. Boron trifluoride etherate (0.024 g, 0.17 mmol, ACROS) is added and the solution is stirred under argon, protected from light, for 1 h. *p*-Chloranil (0.845 g, 3.43 mmol, ACROS) is added and the mixture is refluxed for 1 h. The solvent is removed and the residue is purified over silica gel (hexane/CH_2Cl_2 = 3/2); the yield is 0.17 g or 23%. The porphyrin is characterized with ^1H NMR ($CDCl_3$, 400 MHz, δ): 8.88 (d, $^3J = 4.8$ Hz, 4H), 8.64 (d, $^3J = 4.8$ Hz, 4H), 8.12 (d, $^3J = 8.6$ Hz, 4H), 7.78 (dd, $J = 0.9 \times 8.9$ Hz, 4H), 7.67 (dd, $J = 8.9 \times 8.9$ Hz, 2H), 7.28 (d, $^3J = 8.6$ Hz, 4H), 6.25 (m, 2H), 5.60 (dd, $J = 1.5 \times 17.3$ Hz, 2H), 5.42 (dd, $J = 1.4 \times 10.6$ Hz, 2H), 4.81 (d, $J = 5.4$ Hz, 4H), −2.59 (s, 2H, NH); electrospray-MS shows a $(M+1)$ ion of 863.1.



5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin

The synthetic procedure for PDMS membranes consists of mixing the prepolymer (General Electric, RTV 615A) with the cross-linker (General Electric, RTV 615B) in a 10:1 ratio in a suitable solvent (CH_2Cl_2 or toluene (Biosolve Ltd.), 80 vol.%). Prepolymerization takes place for 1 h at 60°C before adding the sensitizer. For thionine and ZnPc, a saturated dye solution is prepared first, by ultrasonic treatment in toluene for 1 h, followed by filtration. The saturated dye solution is then mixed with the prepolymerized PDMS solution. For the zeolite–dye systems, a similar procedure is used to disperse the zeolite. For the porphyrins, a prepolymerization of only 45 min is used, followed by 1 h stirring at room temperature. After casting the solution in a petri dish and overnight evaporation of the solvent, the mixture is finally cured under vacuum at elevated temperatures (between 60 and 150°C).

To immobilize the 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin, it is first mixed in CH_2Cl_2 with part of the cross-linker in presence of extra Pt catalyst (NX 6276, Nünchritz Chemiewerk) for at least 1 h. After this linkage, the rest of the cross-linker (in an excess of 10% compared to the prepolymer) is added together with the prepolymer.

2.2. Spectroscopic characterization

UV–VIS spectra are recorded on a Perklin Elmer Lambda 12 spectrophotometer. Membranes are fixed outside the sample holder, while an unfilled PDMS membrane is used as the reference. Spectra in solution are recorded using a quartz cell with 10 mm free path length.

The diffuse reflectance spectra are recorded on a UV–VIS–NIR Varian Cary 5 spectrophotometer with a certified reflectance standard (Labsphere, SRS-99-010) as reference.

X-band ESR spectra are recorded with a Bruker ESP-300 apparatus at room temperature. ESR spectra of the photoinduced 4-oxo-TEMPO radical are obtained from samples (150 μl) injected into a flat ESR quartz cell or by adding a piece of membrane in a flat ESR quartz cell. They are illuminated directly inside the microwave cavity with a Schott KL-1500 cold light source. 4-oxo-TEMPO was purchased from ACROS and used without further purification.

2.3. Reaction set-up

Photo-oxidations are done in small closed glass reactors (7.5 ml) at room temperature and irradiated with a cold light source KL-1500 (Schott). Reaction mixtures of 1-methyl-1-cyclohexene (Aldrich) and 2,3-dimethyl-2-butene (ACROS) oxidation are analyzed on a GC equipped with a 50 m CP-Sil 5 column and a FID. Mixtures containing enyl hydroperoxides are reduced with an excess triphenylphosphine (PPh_3, Merck) prior to GC analysis. The reduction is complete after a few minutes. Products are identified with GC–MS on a MD 800 mass spectrometer (Fisons).

3. Results and discussion

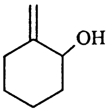
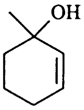
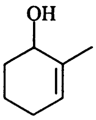
3.1. Reaction mechanisms

To monitor the different oxygenation reactions performed, the diagnostic substrate 1-methyl-1-cyclohexene was selected, because it clearly marks the different reaction types [10]. Table 2 shows the outcome of the oxygenation of 1-methyl-1-cyclohexene after reduction of the samples with triphenylphosphine and as obtained in typical oxidation reactions like autoxidation and singlet oxidation.

$$ROOH + PPh_3 \rightarrow ROH + OPPh_3$$

From Table 2, it can be deduced easily that the allylic alcohol selectivities of entries 1 and 2 are completely different from those of a photosensitization (entry 3). For the first entry, a kind of peroxygen rebound [11,12] is assumed or a radical initiated system with a fast combination of the radical formed and molecular oxygen. The second entry yields a typical radical initiated oxidation as is expected for a Haber–Weiss-type decomposition of hydrogen peroxide (35% in water, ACROS). In both cases, the relative amount of 1-methyl-cyclohex-2-en-1-ol (AA2) is low, while for the Bengal Rose sensitized reaction (entry 3) AA2 (or its correspondent enylhydroperoxide) is the most abundant product. Photosensitization with Bengal Rose has been

Table 2
Reference oxygenation reactions with 1-methyl-1-cyclohexene

Entry	Reaction type	Selectivity (%)		
		AA1 	AA2 	AA3 
1	LDH-Mn_4, O_2[a]	56	2.5	42
2	Fe(II/III), H_2O_2[b]	39	7	54
3	Photosensitization[c]	31	50	19

[a] 5 mg of LDH-Mn_4 [28], 10 ml of 1-methyl-1-cyclohexene at 65°C, oxygen atmosphere.

[b] Traces of $FeSO_4 \cdot 7H_2O$ in 1,4-dioxane, 2.5 mmol 1-methyl-1-cyclohexene and 2.5 mmol H_2O_2 (35% in H_2O) at RT.

[c] Bengal Rose (15 mM), O_2, 24 h irradiation, 2 mmol 1-methyl-1-cyclohexene in 2 ml of ethanol, RT.

a well-established method for the generation of singlet molecular oxygen and is a clean way to produce singlet molecular oxygen. The difference in relative amounts of AA2 can easily be explained via the ongoing mechanisms: singlet molecular oxygen adds to an olefin with a shift of the double bond and attacks the more substituted position. Hence, AA2 is the expected product. For radical-type reactions, hydrogen abstraction takes place first, followed by an oxygen attack (fast recombination between radical and diradical). Since there are no abstractable hydrogen atoms present on the carbon atom of the cyclohexenyl group on which the methyl group is positioned, it is impossible to have a radical oxygenation that leads to the direct formation of a hydroperoxide on the same carbon atom as the methyl group, unless via a double bond shift. So, hardly any presence of AA2 is expected for radical initiated or intermediated reactions.

The photosensitization of 1-methyl-1-cyclohexene with an allylic alcohol distribution after sample reduction of about 3:5:2 corresponds perfectly to the ones reported in literature [13]. This typical allylic alcohol distribution of 1-methyl-1-cyclohexene will be applied throughout this work to verify whether singlet molecular oxygen is the dominant system or whether other reaction types are at work.

3.2. Thionine

When a dry, blue colored (λ_{max} at 605 nm) thionine-Y zeolite is contacted in air, it changes fast into purple (λ_{max} at 557 nm) (Fig. 1). This change depends on humidity and is related to the presence of monomeric (blue) or non-monomeric (purple) thionine agglomerates. Zeolites, fairly hydrophilic systems, easily adsorb water from the surrounding and thus induce a rearrangement of thionine from a monomeric into a dimeric or oligomeric form (Fig. 1). In order to stabilize monomeric thionine in a zeolite Y, the system should be shielded from any traces of water. Here, the hydrophobic properties of PDMS may offer a way out [14].

In order to evaluate thionine-Y occluded in PDMS, attempts were made to occlude thionine itself in the PDMS network. Due to the completely different chemical properties of both components, the ionic thionine easily agglomerates in the hydrophobic polymer. Hence, a good dispersion could not be achieved and a maximum absorption at 557 nm, typical for non-monomeric agglomerated thionine, was observed (Fig. 2a). Moreover, when thionine–PDMS was placed in ethanol, the dye rapidly leached out from the PDMS into the solvent phase.

The incorporation of thionine-Y in the PDMS elastomer is achieved via two similar procedures. The difference consists in different membrane curing temperatures. The so-called ‘cold’ synthesis never exceeded a temperature of 60°C, while for the ‘warm’ synthesis a curing temperature of about 110°C was reached in the vacuum oven (see Fig. 2b).

The ‘cold’ synthesis procedure had the disadvantage not to remove enough water from the zeolite, thus leading to a purple thionine-Y in PDMS. The more aggressive approach with elevated curing temperatures removed most water from the zeolite and yielded the blue colored, monomeric thionine-Y system. Increasing the curing temperature up to about 150°C resulted in a new absorption at 703 nm. This is attributed to protonated thionine molecules. These excessive high temperatures are not desired, since the generated protonation reactions decrease the amount of the monomerically dispersed thionine molecules aimed at.

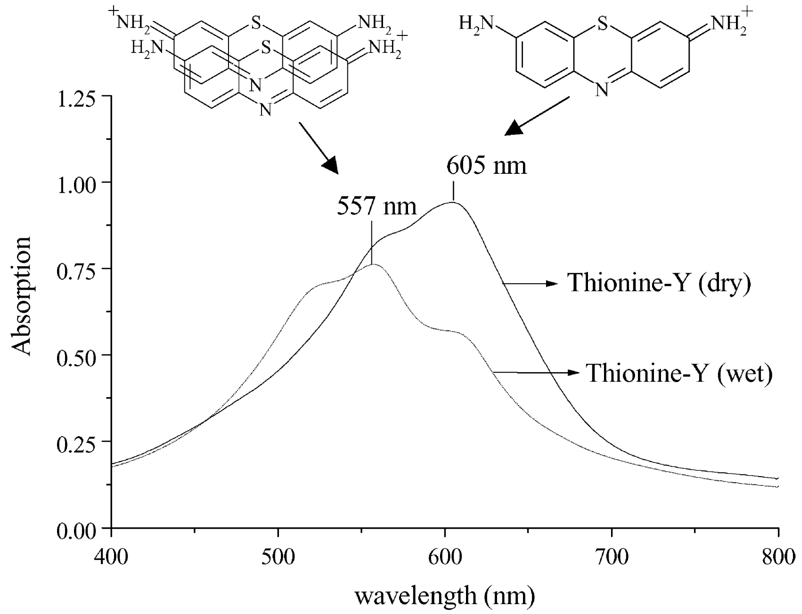
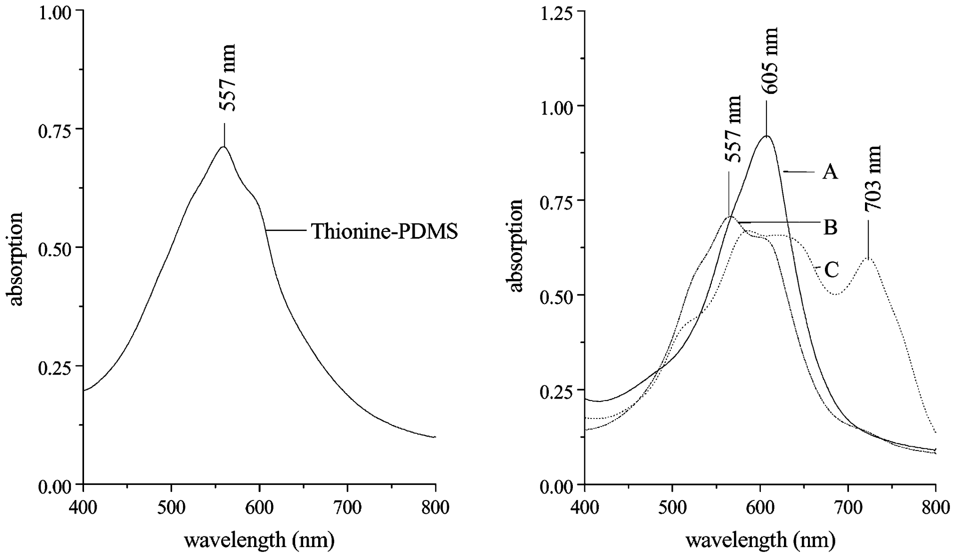


Fig. 1. DR spectra of dry and wet thionine-Y.



(a) (b)

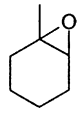
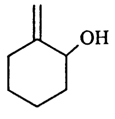
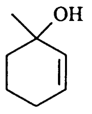
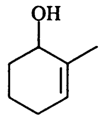
Fig. 2. (a) UV–VIS measurement of thionine in PDMS occluded and (b) UV–VIS DRS of thionine-Y in PDMS (2.5 wt.%): (A) 'warm' synthesis (110°C), (B) 'cold' synthesis (60°C) and (C) synthesis at 150°C.

The difference between dry and wet thionine-Y occluded in PDMS for singlet molecular oxygen formation is clearly shown with ESR. Two equal pieces were taken of a membrane from the cold synthesis procedure of thionine-Y–PDMS. One of those pieces was activated, i.e. carefully dried at 110°C under reduced pressure, resulting in the blue colored PDMS–thionine-Y. Both membranes were equilibrated in an oxygen saturated 0.1 M 4-oxo-TEMPO ethanol solution. The membrane pieces were put in a flat ESR cell and directly irradiated in the microwave cavity. 4-oxo-TEMPO easily reacts with the generated singlet molecular oxygen to form the stable radical 4-oxo-TEMPO (Fig. 3), which can be monitored with ESR [15–17]. In Fig. 3c, the 4-oxo-TEMPO formation and hence the singlet molecular oxygen formation is represented for both the dry and wet thionine-Y–PDMS systems. Leaving the induction period aside, the ratio of the singlet oxygen yields (ϕ) can be calculated from the slopes of the curves. This results in $\phi_{\mathrm{dry}}/\phi_{\mathrm{wet}} = 1.7$ which clearly shows the different activity of the monomeric and non-monomeric thionine for the formation of singlet molecular oxygen.

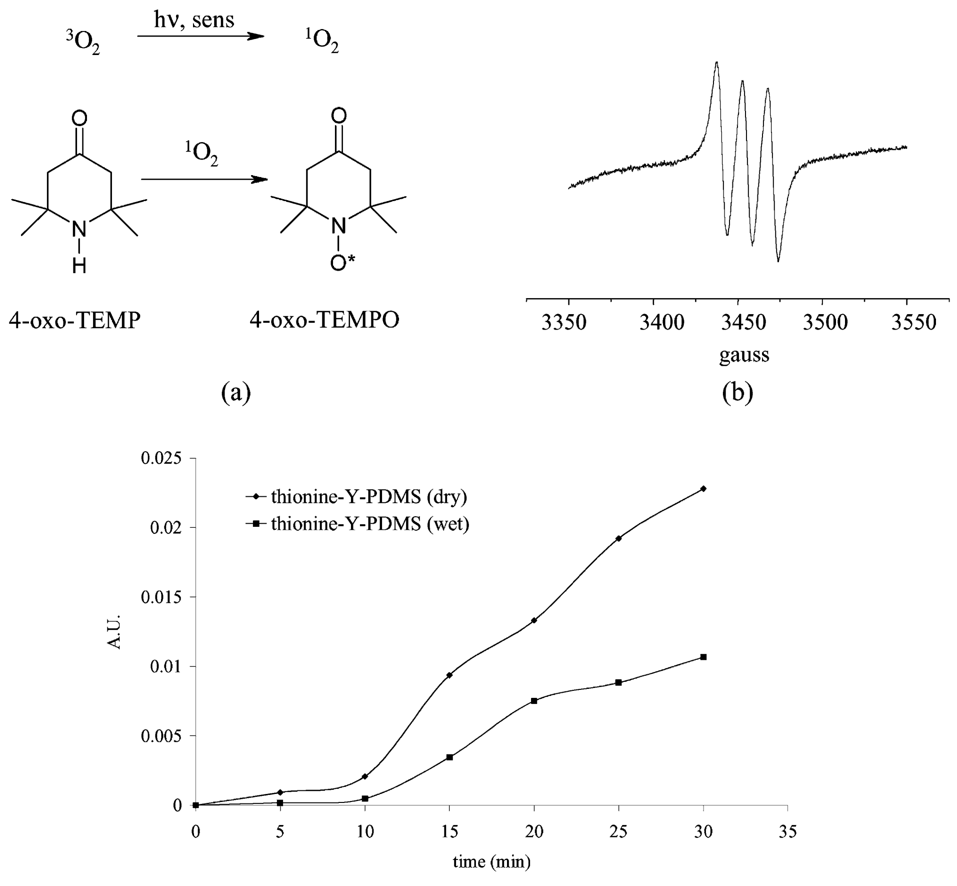
Table 3 summarizes the photo-oxidative properties of the thionine systems. For the three non-occluded systems, the solution becomes slightly gray upon reaction time, pointing to some leaching and oxidative destruction of the sensitizer. This phenomenon is not observed for the PDMS occluded thionine-Y.

The only moderate increase in TON that is observed for the dry thionine-Y system versus the wet system is due to residual water present in ethanol. This results in a dimerization or oligomerization of the thionine molecules in the dry zeolite system and hence becomes identical after a while to the wet thionine-Y. In contrast to this observation, there is a clearly increased TON for the thionine-Y in PDMS. Here, the hydrophobic elastomer excludes all traces of water and accumulates the olefin, thus increasing reaction possibilities.

Table 3
Oxidation of 1-methyl-1-cyclohexene with thionine sensitized systems[a]

System	TON	Yield (%)		Selectivity (%)		
			AA	AA1 	AA2 	AA3 
Thionine	120	0.4	12	34	52	14
Thionine-Y-wet	205	0.3	1.0	34	50	16
Thionine-Y-dry	300	0.3	1.6	34	51	15
Thionine-Y–PDMS-dry	1200	0.3	7.3	28	54	18

[a] Reaction conditions: 2.5 mmol 1-methyl-1-cyclohexene, 2 ml of ethanol, 24 h of irradiation (KL-1500 cold light source of Schott), 2.5 mmol thionine (homogeneous) or 0.16 μmol thionine (heterogeneous). TON = turn over number: amount of allylic alcohols (AA) formed (mol) per mole of catalyst.



(a) (b)

(c)

Fig. 3. (a) Formation of singlet molecular oxygen via photosensitization, $^1O_2$ being trapped with 4-oxo-TEMPO; (b) ESR signal of the formed 4-oxo-TEMPO; (c) ESR signals of 4-oxo-TEMPO in time of reaction with wet and dry thionine-Y–PDMS.

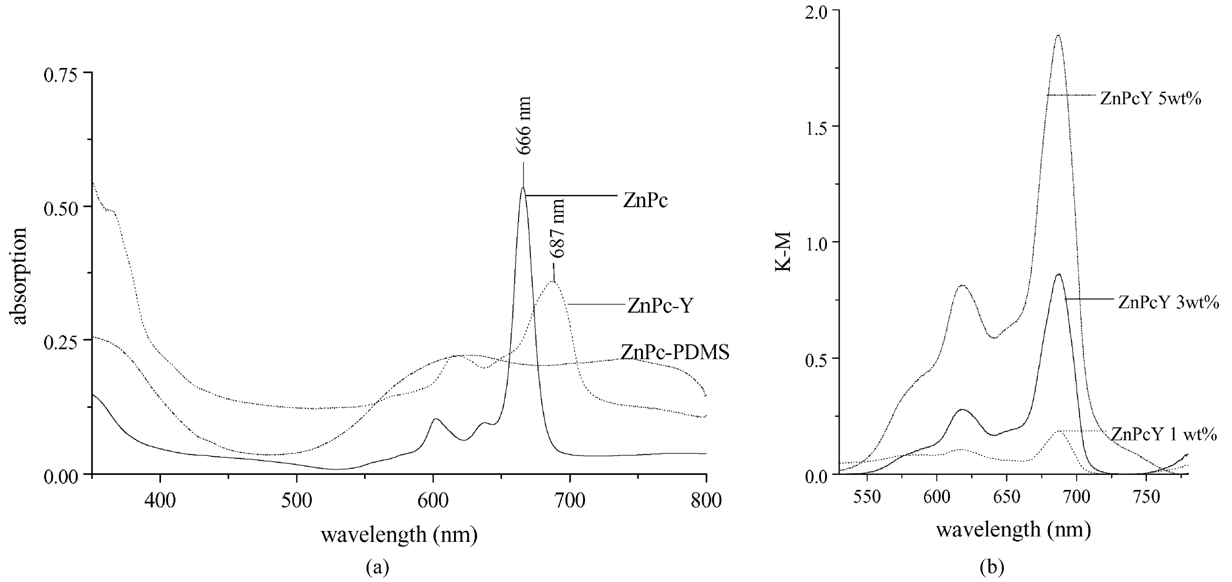
Indeed, the active but briefly living singlet molecular oxygen and substrate are now in close proximity.

3.3. Phthalocyanines

In Fig. 4, UV–VIS spectra of zinc–phthalocyanines systems are presented. For well dissolved ZnPc, the typical absorption bands are located at 666 nm (Q(0, 0)-band) and at 609 nm (Q(0, 1)-band). A totally different spectrum is obtained for ZnPc occluded in PDMS: a broad band, without any distinctive maxima, is observed between 500 and 800 nm. This points to the existence of strongly aggregated ZnPc in PDMS. This is not surprising given the different chemical nature of ZnPc and the elastomer. A similar behavior in PDMS was observed for other ionic dyes,like Bengal Rose and the above-mentioned thionine. When these dye–PDMS systems are brought in a solvent in which the complex dissolves, the complex will leach from the polymer. For ZnPc-Y, absorption bands are slightly broader compared to the homogeneous system, due to the loss of motional freedom. The shift of the absorption maximum to 687 nm represents the different chemical environment in which the Pc is located.

Photo-oxidations of 1-methyl-1-cyclohexene with ZnPc systems are represented in Table 4. First of all, the homogeneous ZnPc is subjected to photo-degradation. As reflected in the high TONs, the zeolitic systems are stable and do not show leaching or photo-degradation. The incorporation of more ZnPc-Y in the polymer does not result in a corresponding increase of the yield: going from 1 to 3 wt.% ZnPc-Y in PDMS (Table 4) only doubles the allylic alcohol yield. The effect is even more significant when going from 3 to 5 wt.% of ZnPc-Y. This anomaly can be rationalized as follows: with increasing amounts of zeolite in PDMS, the system reflects more and more light. As a consequence, only the outer layer of the polymer is activated by light and the underlying sensitizers are not efficiently excited. Moreover, with increasing amounts of zeolite, PDMS becomes denser [18], thus decreasing both swelling and diffusion. In spite of the high chain flexibility of PDMS, mass transfer limitations can become important. Possibly, more optimized and hence thinner membranes may solve these drawbacks.

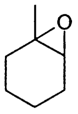
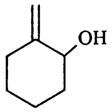
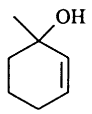
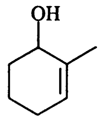
Table 5 represents the photo-oxidation of 2,3-dimethyl-2-butene, as well as some solvent effects. As can be seen, the nature of the solvent is an important parameter in photo-oxygenation. Solvent effects are expected to play



(a) (b)

Fig. 4. (a) UV–VIS spectra of dissolved ZnPc and ZnPc–PDMS and DR spectrum of ZnPc-Y; (b) DR spectra of different ZnPc-Y loading in PDMS.

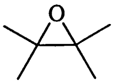
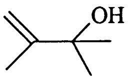
Table 4
Photosensitized oxidation of 1-methyl-1-cyclohexene with ZnPc[a]

System	TON	Yield (%)		Selectivity (%)		
			AA	AA1 	AA2 	AA3 
ZnPc	100	0.3	13	39	46	15
ZnPc-Y	430	0.3	18	37	48	15
ZnPc-Y–PDMS (5 wt.%)	305	0.3	11.8	37	48	15
ZnPc-Y–PDMS (3 wt.%)	440	0.3	10.5	35	49	16
ZnPc-Y–PDMS (1 wt.%)	750	0.3	5.9	36	49	15

[a] Reaction conditions: ZnPc (2.5 μmol homogeneous, 0.84 μmol as ZnPc-Y, or 50 mg of PDMS; membrane thickness is 750 ± 20 nm), 2.0 mmol 1-methyl-1-cyclohexene, 2 ml of ethanol, irradiation for 12 h. Yields are calculated on a substrate basis.

a role at different levels: on the interaction between singlet molecular oxygen and the substrate molecule, on the quantum yield of singlet oxygen formation [19] and on the lifetime of the reactive species. For instance, the lifetime of singlet molecular oxygen ($^1\Delta_g$) in hexane is about three times longer than in ethanol. In all these reactions, a certain amount of epoxide is formed, due to a non-catalyzed side reaction. In DMF, ZnPc is optimally dispersed and

Table 5
Photosensitized oxidation of 2,3-dimethyl-2-butene with ZnPc[a]

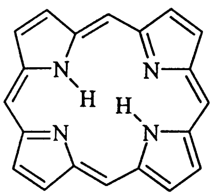
Entry	System	TON	Yield (%)	
			Epoxide 	AA 
1	ZnPc in DMF	360	5.8	30
2	ZnPc–PDMS in ethanol	120	5.4	6.6
3	ZnPc-Y in hexane	150	5.6	9.5
4	ZnPc-Y in ethanol	300	5.4	25
5	ZnPc-Y–PDMS in hexane	120	nd	12
6	ZnPc-Y–PDMS in ethanol	420	5.9	36

[a] Reaction conditions: 2.5 μmol ZnPc (ZnPc-Y–PDMS, 3 wt.%), 2.5 mmol 2,3-dimethyl-2-butene, 2 ml solvent, irradiation for 24 h. Yields calculated on a substrate basis; nd: not detected.

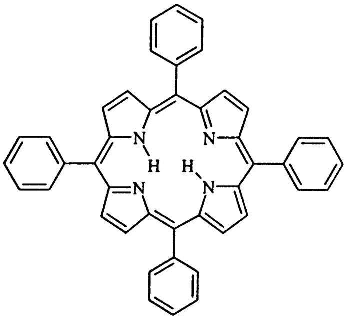
thus shows a high activity (entry 1). ZnPc–PDMS (entry 2) shows a poor activity, as expected from a badly dispersed system (Fig. 4a). Moreover, this agglomerated system is unstable and photo-deactivates. Immobilization of the sensitizer in the zeolite cages — with only one Pc complex per cage — renders a far more stable heterogeneous system, as shown already above for the 1-methyl-1-cyclohexene oxygenation (Table 4). Entries 3–6 compare the immobilized ZnPc-Y and ZnPc-Y–PDMS in solvents with strongly different polarity. The zeolitic system preferentially sorbs the more polar components. Ethanol can be regarded as a ‘cleaning agent’: the formed products in the zeolite pores are removed by ethanol, but not by hexane. For the PDMS system, analogous sorption aspects are important. In hexane, solvent and substrate compete for sorption in the elastomer, thus reducing the substrate concentration. The highest singlet oxygenation yield is obtained for ZnPc-Y–PDMS in ethanol: the more hydrophobic substrate is accumulated in the elastomer hence increasing reaction possibility. Nevertheless, sufficient ethanol remains in the membrane to ‘clean’ the catalyst. These effects result in an even more active system than the homogeneous one, which is also subject to some photo-degradation.

3.4. Porphyrins

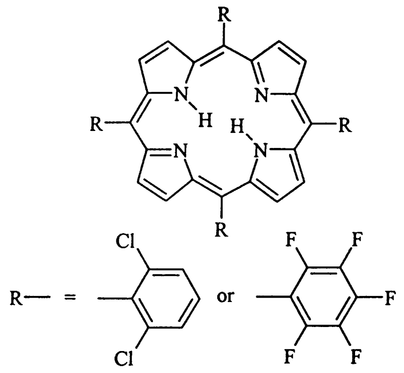
Porphin structures lack photo-stability and are easily bleached under photo-oxidative conditions, due to stacking [6]. Upon light activation, this can lead to energy transfers between the stacked molecules, causing the formation of radical anion–cation pairs. The formed radicals rapidly react with the diradical molecular oxygen. The stability problem of porphin structures was partially overcome by adding large groups at the meso-positions (positions 5, 10, 15, and 20). For instance, the phenyl groups in 5,10,15,20-tetraphenylporphyrin result in a structure that is no longer totally flat and thus less susceptible to stacking. Further reduction of oxidative degradation is obtained by placing electron-withdrawing groups on the phenyl ring, such as fluoro- or chloro-groups. Almost any porphyrin can be applied as photosensitizer. However, the singlet oxygen yield strongly depends on the metal present in the porphyrin structure.



Porphin



5,10,15,20-tetraphenylporphyrin



5,10,15,20-tetrakispentafluorophenyl- or 2,6-dichlorophenyl-porphyrin

A number of porphyrinic sensitizers were occluded in PDMS and their singlet oxygen generating properties are compared in Table 6. 2H-porphyrin structures are well dispersed in PDMS, given their comparable hydrophobic

Table 6
Porphyrin sensitized reaction of 1-methyl-1-cyclohexene[a]

Dye occluded in PDMS	Epoxide yield (%)	AA yield (%)	TON
2H-tetraphenylporphyrin (0.1 wt.%)	0.3	49	11400
Zn-tetraphenylporphyrin (0.1 wt.%)	0.3	39	10600
Co-tetraphenylporphyrin (0.1 wt.%)	0.5	2.2	570
Tetrakis(2,6-dichloro)phenylporphyrin (0.033 wt.%)[b]	0.5	70	54700

[a] Reaction conditions: 2 mmol of 1-methyl-1-cyclohexene, 2 ml of ethanol, ~50 mg of PDMS, oxygen saturated. Irradiation time: 24 h. Yields are calculated on substrate basis.

[b] 1.25 mmol of 1-methyl-1-cyclohexene and 1.5 ml of ethane and other conditions same as in Footnote ‘a’.

properties. All but one have the typical allylic alcohol distribution (35:50:15) for singlet oxygenation; but Co-TPP shows a more radical-like oxygenation (allylic alcohol distribution of 66:12:22). This is expected since Co-TPP has been reported to have a singlet oxygen yield of less than 0.1%, in perfect match with our observations [19]. Even though the TPP–PDMS systems show a high oxidative activity, the sensitizers tend to leach slightly. While leaching in EtOH is very low for TPP, it is more pronounced for the metalloporphyrins, but completely absent for the tetrakis(2,6-dichlorophenyl)porphyrin. This is probably due to the chloro-atoms on the phenyl groups that induce a higher steric retention.

Other approaches to fully solve the leaching problem, is by rendering the sensitizer bulkier, by shortening the polymer chains or by anchoring the sensitizer chemically to the polymer. Even though the latter option bears the risk that absorbed energy may be dissipated over the polymer and thus lead to a poor singlet oxygen generating system, this was tested for a derivatized porphyrin system. Chemical anchoring of a molecule to PDMS can best be achieved via the same mechanism as the curing of PDMS: vinyl groups, present on both our newly designed porphyrin and on the PDMS prepolymer, can be linked with the cross-linker's hydride groups via a Pt-catalyzed hydrosilylation [5]. To assure a successful linking of our porphyrin, it was prepolymerized with a part of the cross-linker before adding the PDMS prepolymer.

Fig. 5 shows the UV–VIS spectra of dissolved 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin and of 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)-porphyrin anchored to PDMS. No important changes were noted in the spectra with the exception of a minor shift, indicating the slightly different chemical environments of the porphyrin. However, the chromophoric core of the porphyrin remains unaltered.

In Table 7, the photo-oxidations with 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin are summarized, showing that the newly synthesized porphyrin do generate singlet molecular oxygen, both under dissolved conditions and under anchored conditions. Both components remain stable during the photo-oxidation and no leaching of anchored porphyrin was observed. To verify the true heterogenity and stability of the PDMS bound sensitizer recycle experiments were set-up. Since no significant changes are observed in the singlet oxygenation yield, the system's stability and heterogenity are demonstrated. Here again, solvent effects play an important role, as can be seen for EtOH and CH_2Cl_2. The much higher activity in CH_2Cl_2 is related to the higher lifetime of singlet oxygen in dichloromethane in one respect, and the stronger swelling of PDMS in another. Table 7 further illustrates some dye concentration effects. For the different dye loadings in PDMS (entries 2 and 4), the highest yields are obtained for the highest loading (entry 4), but its TON is lower. This indicates that not all sensitizing molecules are optimally used. When applying less membrane (entry 5), higher TONs are again realized. These results indicate that the supply of one of the two reagents is rate limiting.

Most of the occluded and well-dispersed porphyrins in PDMS yield high to very high turnover numbers, clearly demonstrating their very interesting properties as heterogeneous systems for singlet molecular oxygen formation from ground state oxygen. It should be emphasized that none of the presented systems have been optimized completely. First of all, higher activities can possibly be obtained by making the polymer films thinner since diffusion inside the polymer might govern transport. If higher dye concentrations are

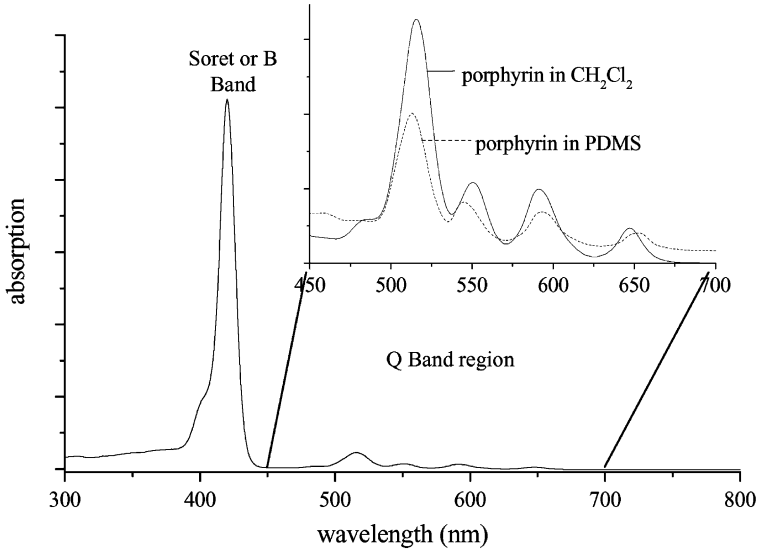
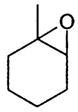


Fig. 5. UV–VIS spectra of 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin. The insert shows a magnification of the 450–700 nm range of the porphyrin dissolved in CH_2Cl_2 and chemically anchored to PDMS.

Table 7
Photo-oxidation of 1-methyl-1-cyclohexene with 5,15-(2,6)-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin[a]

Entry	System	TON	Yield (%)	
				AA
1	Dissolved in CH_2Cl_2	28100	0.6	36
2	In PDMS in CH_2Cl_2 (0.04 wt.%)	38700	0.3	45
	First recycle	37800	0.2	44
	Second recycle	39400	0.2	46
3	In PDMS in ethanol (0.04 wt.%)	14700	0.3	19
4	In PDMS in CH_2Cl_2 (0.1 wt.%)[b]	18000	0.4	52
5	In PDMS in CH_2Cl_2 (0.1 wt.%)	30600	0.2	35

[a] Reaction conditions: 2 mmol of 1-methyl-1-cyclohexene in 2 ml solvent; about 26 pmol of 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin; oxygen saturated, irradiation time 12 h with cold light source KL1500 of Schott.

[b] 65 pmol of 5,15-(2,6-dichlorophenyl)-10,20-(4-allyloxyphenyl)porphyrin and other conditions same as in Footnote ‘a’.

desired, attention should be paid to dye agglomeration. This problem is best overcome via chemical anchoring, which is more demanding on the level of preparation.

4. Conclusions

Thanks to its transparent, hydrophobic and highly permeable nature, occlusion of dyes in PDMS is an interesting tool to heterogenize dyes and/or to improve their performance in photo-oxidations.

Aggregate formation during membrane synthesis or leaching under reaction conditions did not allow successful occlusion of charged dyes in PDMS. Uncharged dyes or zeolite resident species could be incorporated and often showed strongly increased activities with unchanged selectivities as compared with homogeneous reactions. Indeed, the new catalyst environment created by PDMS repelled water and hence increased catalyst stability. Furthermore, it prevented the dyes from leaching and realized a selective and favorable substrate sorption. In other cases, catalytic membranes performed better than the homogeneous reference reactions due to a more adequate solvent choice, made possible by the occlusion. When embedding more bulky or covalently linked porphyrins, even solvents that would normally cause catalyst leaching could be used to increase activities.

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References

[1] A.A. Frimer, Singlet O_2, Vols. I–IV, Boca Raton, 1985.
[2] E.C. Blossey, D.C. Neckers, A.L. Thayer, A.P. Schaap, Polymer-based sensitizers for photooxidations, J. Am. Chem. Soc. 95 (1973) 5820.
[3] A.M. Braun, M.-T. Maurette, E. Oliveros, Technologie Photochemique, Presses Polytechniques Romandes, Lausanne, 1986.
[4] D.C. Neckers, E.C. Blossey, A.P. Schaap, Polymer-bound photosensitizing catalysts, US Patent 4315998 (1982).
[5] S.F. Yates, M.L. Good, I.M. Brubaker, Polysiloxane bound photosensitizer for producing singlet oxygen, US Patent 4921589 (1988).
[6] H. Quast, T. Dietz, A. Witzel, Tetra(2,6-dichlorophenyl)porphyrin, a superior sensitizer for the singlet-oxygen ene reaction (Schenck reaction), Liebigs Ann., 1995, p. 1495.
[7] R.J. Robbins, V. Ramamurthy, Generation and reactivity of singlet oxygen within zeolites: remarkable control of hydroperoxidation of alkenes., J. Chem. Soc., Chem. Commun. (1997) 1071.
[8] R.F. Parton, L. Uytterhoeven, P.A. Jacobs, Iron-phthalocyanines encaged in zeolite Y and VPI-5 molecular sieve as catalysts for the oxyfunctionalization of *n*-alkanes, in: M. Guisnet, J. Barrault, C. Bouchoule, D. Duprze, G. Pérot, R. Maurel, C. Montassier (Eds.), Stud. Surf. Sci. Catal., 59, Heterogeneous Catalysis and Fine Chemicals II, 1991, p. 395.
[9] P. Neys, Immobilization of metallo-porphyrins and -phthalocyanines on hydrophobic support materials, Dissertationes de Agricultura 376, Fac. Landb. & Toeg. Biol. Wet., Leuven, 1998.
[10] F.M.P.R. van Laar, D.E. De Vos, F. Pierard, A. Kirsch-De Mesmaeker, L. Fiermans, P.A. Jacobs, Generation of singlet molecular oxygen from H_2O_2 with molybdate-exchanged layered double hydroxides: effects of catalyst composition and reaction conditions, J. Catal. 197 (2001) 139.
[11] J.E. Bond, S.M. Gorun, R.T. Stibrany, W.G. Schriver, T.H. Vanderspurt, in: D.H.R. Barton, et al. (Eds.), The Activation of Dioxygen and Homogeneous Catalytic Oxidation, Plenum Press, New York, 1993, p. 199.
[12] R.T. Stibrany, S.M. Gorun, Angew. Chem. Int. Ed. Engl. 28 (1990) 1156.
[13] T.L. Pettit, M.A. Fox, Photoassisted oxygenation of olefins: an exchanged zeolite as heterogeneous photosensitizer, J. Phys. Chem. 90 (1986) 1353.
[14] I.F.J. Vankelecom, D. Depré, S. De Beukelaer, J.B. Uytterhoeven, Influence of zeolites in PMDS membranes: pervaporation of water/alcohol mixtures, J. Phys. Chem. 90 (1995) 13193.

[15] J. Moan, E. Wold, Detection of singlet oxygen production by ESR, Nature 279 (1979) 450.

[16] Y. Lion, E. Gandin, A. Van de Vorst, On the production of nitroxide radicals by singlet oxygen reaction: an EPR study, Photochem. Photobiol. 31 (1980) 305.

[17] E. Delaey, F. van Laar, D. De Vos, A. Kamuhabwa, P. Jacobs, P. de Witte, A comparative study of the photosensitizing characteristics of some cyanine dyes, J. Photochem. Photobiol. B: Biol. 55 (2000) 27.

[18] I.F.J. Vankelecom, E. Scheppers, R. Heus, J.B. Uytterhoeven, Parameters influencing zeolite incorporation in PDMS membranes, J. Phys. Chem. 98 (1994) 12390.

[19] R.W. Redmond, J.N. Gamlin, A compilation of singlet oxygen yields from biologically relevant molecules, Photochem. Photobiol. 70 (1999) 391.

[20] J.R. Williams, G. Orton, L.R. Unger, Preparation of singlet oxygen by heterogeneous photosensitization, Tetrahedron Lett. 46 (1973) 4603.

[21] J.R. Williams, Photosensitization of oxygen to the singlet excited state using ion exchange resin to which is attached a dye and photooxidative waste water treatment, US Patents US4104204 (1978).

[22] S. Tamagaki, C.E. Liesner, D.C. Neckers, Polymer-based sensitizers for photochemical reactions silica gel as a support, J. Org. Chem. 45 (1980) 1573.

[23] A.P. Schaap, D.C. Thayer, A.C. Blossey, D.C. Neckers, Polymer-based sensitizers for photooxidations: II, J. Am. Chem. Soc. 97 (1975) 3741.

[24] D. Brkic’, P. Forzatti, I. Pasquon, Homogeneous and heterogeneous photo-oxygenation of 2,3-dimethyl-2-butene, J. Mol. Catal. 3 (1977/1978) 173.

[25] W.R. Midden, S.Y. Wang, Singlet oxygen generation for solution kinetics: clean and simple, J. Am. Chem. Soc. 105 (1983) 4129.

[26] M. Nowakowska, E. Sustar, J.E. Guillet, Studies of the antenna effect of polymer molecules 25. Photozymes with Rose Bengal chromophores, Photochem. Photobiol. A: Chem. 80 (1994) 369.

[27] S.G. DiMagno, P.H. Dussault, J.E. Schultz, Fluorous biphasic singlet oxygenation with a perfluoroalkylated photosensitizer, J. Am. Chem. Soc. 118 (1996) 5312.

[28] D. Vanoppen, Autoxidation of cyclohexane, cyclohexene and cumene in the presence of zeolites and other solid catalysts, Dissertationes de Agricultura 335, Fac. Landb. & Toeg. Biol. Wet., Leuven, 1997.