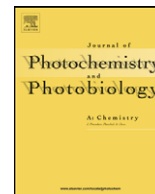




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## Effect of the chemical environment on the light-induced degradation of a photochromic dye in ormosil thin films

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### ABSTRACT

The naphthopyran (NP) derivative (3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran) exhibits photochromism in solution or embedded in solid matrices. The molecule suffers a progressive photodegradation upon prolonged irradiation with UV-light, which depends strongly on the solvent or the embedding matrix. The photodegradation of the dye molecules in THF or benzene solutions is much faster than that of the molecules embedded in solid matrices (polymer or ormosil).

The organic functional groups incorporated in the network of the ormosil matrix play an important role in the photostability of the dye, as they determine the chemical environment of the dye molecules in the matrix. In this way, the dye embedded in matrices whose inner pore surface is functionalized with phenyl groups exhibits a photostability nine times higher than in unmodified matrices, being their degradation half-life ( $t_{1/2(\text{deg})}$ ) 181 h and 21 h, respectively. The photostability of the photochromic dye in the ormosil matrices was also measured as a function of the dye loading, showing higher stability as the amount of dye is increased. The photostability of the dye in photochromic materials is an important issue in sight of the possible applications of these materials, as the performance of the devices involves repeated exposure to UV radiation.

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### 1. Introduction

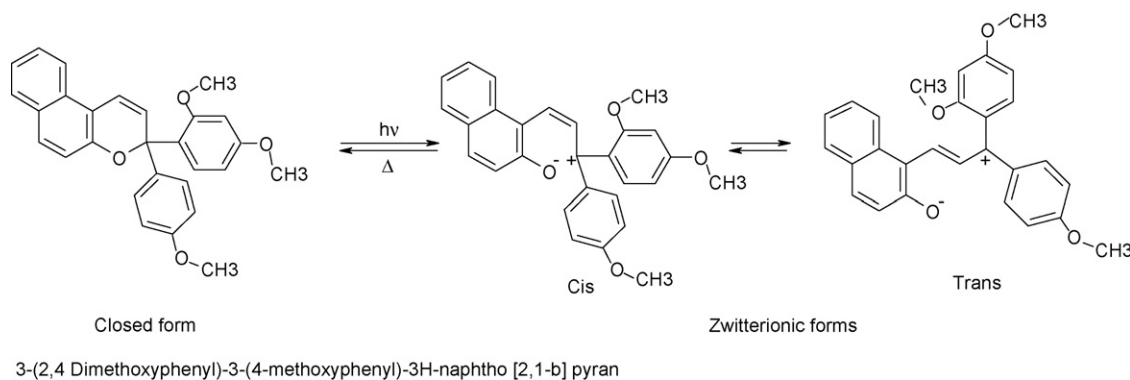
Naphthopyran (NP) compounds are known to exhibit photochromism since the first report of Becker et al. in the early 1960's [1]. The industrial interest on these materials started in the early 1990's, and was directed to the preparation of photochromic ophthalmic lenses [2]. Nowadays, these photochromic compounds are also used in architecture, automotive industry, cosmetics, textiles, decoration, etc. [3–6]. The reversible cleavage of the C(sp<sup>3</sup>)–O spiro bond of the colourless form leads to a deeply coloured open form or photomerocyanine, generally in different stereoisomers [7]. The system reverts thermally to its original colourless form, as shown in Fig. 1.

The most important photochromic properties of these materials, the absorption spectra and the kinetics of the bleaching process, can be controlled by various factors, such as chemical substitutions on the NP molecules [7], the temperature and the properties of the environment, in which the photochromic molecules are dissolved [8,9] or embedded [10–14]. In a previous work, we have demonstrated the feasibility of introducing photochromic naphthopyran derivatives into ormosil matrices prepared by the sol–gel method

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[15]. This method, being a low temperature process, allows the preparation of hybrid organic–inorganic ormosil matrices and the doping of these matrices with optically active organic molecules [16–19]. The properties of the photochromic molecules dispersed in solid matrices depend strongly on the pore environment, where the molecules are located. Moreover, the size and shape of the pores containing the dye molecules have an important effect on the spectral and kinetic behaviour of the photochromic system, as it may provoke steric inhibitions during molecule opening–closing process [20–25]. The loss of photochromic properties upon prolonged exposure to UV-light, commonly referred to as fatigue, limits the use of photochromic molecules in outdoors application or in environments with strong UV radiation. The first studies on the photodegradation of photochromic compounds with UV-light were carried out by Gautron on spiropyran derivatives in the 1960's [26]. Salemi-Delvaux et al. [27] and Balliet [28] investigated the stability of photochromic naphthopyran derivatives in solvents and polymer networks, respectively. The photodegradation of some photochromic molecules in the indolinspiropyran and indolinspiropoxazine series was studied, in solvent solution [29–32] and in the solid-state [33]. In a recent work we have studied the photostability of a photochromic naphthopyran dye in different sol–gel prepared ormosil coatings [34]. The photostability of the photochromic molecules upon prolonged irradiation with UV-light depend also on the temperature to which the photodegradation of



**Fig. 1.** Chemical structure of the naphthopyran dye and different stereoisomers of the open form (merocyanines).

the samples is carried out. Temperature favours the side-reactions between the coloured open form of the photochromic dye and the matrix pore surface, responsible for the degradation of the dye.

The main objective of the present work is to study the photostability of the photochromic naphthopyran molecules embedded in functionalized ormosil matrices as a function of the composition of the matrix and the photochromic dye loading. A comparison will be done with the stability of the dye dispersed in a polymeric matrix (pHEMA) and in solvents (THF or benzene). Different amount of the phenyl groups will be used for the preparation of the ormosil matrices and the optimization of the photostability of the embedded dye molecules. The photostability of the photochromic molecules in ormosil matrices is a key issue for the preparation of materials for industrial applications.

## 2. Experimental

### 2.1. Materials

Tetracetoxyasilane (TAS) and phenyl triethoxysilane (PhTES) were from ABCR. 2-Hydroxyethyl methacrylate (HEMA), 2,6-dichloro-4-(2,4,6-triphenyl-*N*-pyridino)-phenolate [ $E_T(33)$ ], benzene and tetrahydrofuran (THF) were purchased from Aldrich Chemicals.  $\alpha,\alpha'$ Azoisobutyronitrile (AIBN) was from Fluka and Ethanol from Merck. Double-distilled water was used for all preparations. The photochromic dye used for the preparation of samples, 3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3H-naphtho[2,1-b]pyran, was generously donated by PPG Industries Inc. The chemical structure of the dye is given in Fig. 1.

### 2.2. Preparation of coatings

Samples were prepared from mixtures of tetracetoxyasilane and phenyl triethoxysilane in the appropriate ratio (from Ph/Si = 0.0 to 0.9). The amount of water to hydrolyzing group was kept 1:1 in all samples. The reaction was self-catalyzed by the slow release of acetic acid from the TAS during hydrolysis. The sols were allowed to hydrolyze for 24 h under stirring at 25 °C. The photochromic dye was added as a THF solution, after the hydrolysis of the sol, to obtain the required photochromic-dye:Si molar ratios. THF was used as solvent due to the possibility to obtain highly concentrated solutions and good miscibility with the coating sol. The samples were named after the organic substituents used for preparation followed by the Ph/Si molar ratio in the matrix.

The deposition of the films was carried out after the addition of the dye using the spin-coating technique. A sol volume of 0.1 mL was used for the preparation of each film with the sample-holder spinning at 2000 rpm. The films were cured for 24 h at 100 °C.

The polymer matrix was prepared from a mixture of 2-hydroxyethyl methacrylate and  $\alpha,\alpha'$ azoisobutyronitrile in a HEMA:AIBN molar ratio of 100:1. The photochromic dye was added as a THF solution in a HEMA:dye molar ratio of 800:1. The sample was cured for 7 days at 50 °C forming a polymer network of poly(hydroxyethyl methacrylate). The concentration of the dye in the THF and benzene solutions was adjusted to  $7.6 \times 10^{-3}$  M.

### 2.3. Characterization

The photochromic samples were irradiated with a 365 nm, 100 W, B-100AP UV lamp from UVP, giving a UV-light intensity on the sample of 8.9 mW/cm<sup>2</sup>. The absorption spectra of the resulting samples, as well as the kinetics of the bleaching were measured in a Varian Cary 50 Bio UV-vis spectrophotometer. The absorption spectra were measured between 300 nm and 800 nm, and are given as  $\Delta Abs (A_{a,i} - A_{b,i})$ , where  $A_{a,i}$  and  $A_{b,i}$  are the absorption after and before irradiation, respectively. The decay of the photochromic effect was monitored vs. time at the wavelength of the maximum absorption of each sample in the visible, at 25 °C. The kinetic constants were calculated from the bleaching curves using a bi-exponential decay equation.  $t_{1/2(bleach)}$  is defined as the time required by the sample to reach  $\Delta Abs_{max}/2$  during the thermal bleaching. The thickness of the films was measured with a surface roughness measuring system SurfTest SV-3000H4. The photodegradation of the photochromic molecules was measured following the absorbance of the samples during prolonged irradiation with UV-light.  $t_{1/2(deg)}$  is defined as the time needed for the degradation of half of the photochromic molecules.

The polarity of the pore environment in the different ormosils matrices was measured by the polarity probe  $E_T(33)$  [35] since the most commonly used  $E_T(30)$  is not stable in acetic acid [36]. The  $E_T(33)$  polarity value can be calculated via equation:

$$E_T(33) (\text{kcal mol}^{-1}) = \frac{28,591}{\lambda_{max}} (\text{nm})$$

where  $\lambda_{max}$  is the wavelength of the maximum absorption of this dye in the different matrices. The  $E_T(30)$  value can be calculated by the following equation [37]:

$$E_T(30) (\text{kcal mol}^{-1}) = 0.979 E_T(33) - 7.461.$$

## 3. Result and discussion

The photochromic properties of the naphthopyran dye, such as the absorption spectra and the kinetics of the bleaching process, were measured in solution and embedded in pHEMA and ormosil matrices. The photochromic effect was progressively lost when the samples were exposed to prolonged UV radiation. The photodegra-

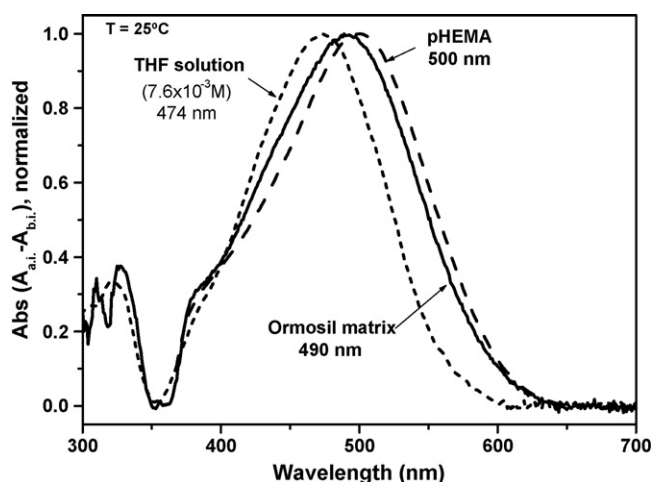


Fig. 2. UV-vis spectra of the photochromic naphthopyran dye in a THF solution, embedded in pHEMA and in Ph-modified ormosil matrix.

dation or fatigue of the photochromic dye embedded in ormosil matrices was measured as a function of the composition of the matrix (amount of the phenyl groups) and the dye loading. The photodegradation of the photochromic molecules was also measured in solvents (THF or benzene) and dispersed in a polymeric matrix for comparison with the ormosil samples.

### 3.1. Photochromic properties

The photochromic samples prepared consist of a transparent thin-film deposited on a glass slide substrate. The films acquire a reversible deep red coloration upon irradiation with UV-light. The absorption spectra of the irradiated naphthopyran molecules in a Ph-modified ormosil matrix are shown in Fig. 2 together with those of the molecules in a polymer (pHEMA) matrix and in a THF solution. The absorption band of the dye molecules embedded in a Ph-modified ormosil matrix shows a significant shift to higher wavelengths, as compared to the absorption band of the molecules in a THF solution. This behaviour can be due to the higher polarity of the Ph-modified ormosil matrix ( $E_T(30) = 43.6$ ) [20] as compared with that of the THF ( $E_T(30) = 37.4$ ) [38]. The absorption band of the dye dispersed in the polymeric matrix shows an even larger bathochromic shift as compared to that of the dye embedded in a Ph-modified ormosil matrix. This behaviour can be due to the intramolecular rearrangement of the dye molecules embedded in the different matrices [39], that affect the formation of the *cis*- and *trans*-isomers of the coloured merocyanine (Fig. 1). The  $\lambda_{\max}$  of the *trans*-isomers, which are generated by the rotation of the *cis*-isomers [40], shows a slight shift to the UV with respect to that of the *cis*-isomer [41]. The spectroscopic data of the photochromic molecules in solvent solutions and in the different solid matrices are summarized in Table 1.

Upon cessation of the irradiation, the coloured molecules undergo a slow thermal bleaching at dark, recovering their orig-

**Table 1**  
Spectroscopic and dynamic data of the naphthopyran molecules in THF and benzene solutions, and embedded in solid matrices

Photochromic molecules in:	$\lambda_{\max}$ (nm)	$k_1 \times 10^3$ (s <sup>-1</sup> )	$k_2 \times 10^3$ (s <sup>-1</sup> )	$t_{1/2(\text{bleach})}$ (s)
THF solution	474	1.86	–	750.1
Benzene solution	478	2.95	–	483.6
Ph-modified matrix	490	22.20	0.86	316.4
Polymeric matrix	500	38.02	7.4	51.3

Measured at 25°C.

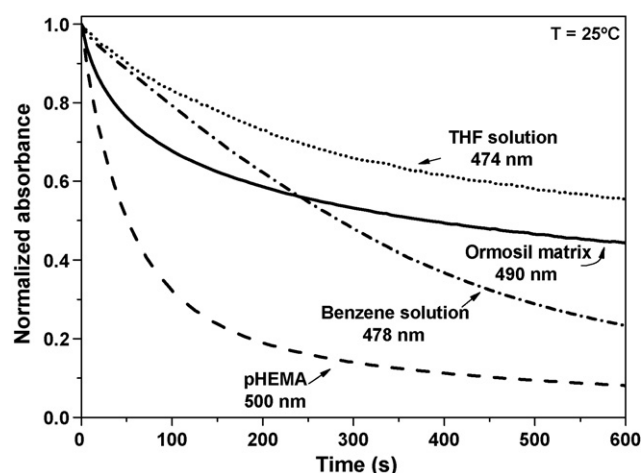


Fig. 3. Thermal bleaching of the naphthopyran dye molecules in solvents (THF, Benzene) and embedded in solid matrices (pHEMA, Ph-modified ormosil).

inal whiteness. Fig. 3 shows the kinetics of the thermal bleaching of the photochromic molecules in THF and benzene solutions, and in the solid matrices. The kinetics of this bleaching process follows a bi-exponential decay in the solid matrices and a single exponential decay in the solvent solutions. The kinetics data of the different samples are summarized in Table 1. The bleaching kinetic is faster in a benzene solution ( $t_{1/2(\text{bleach})} = 483.6$  s) than in a THF solution ( $t_{1/2(\text{bleach})} = 750.1$  s), due to the lower polarity of the benzene ( $E_T(30) = 34.3$ ) as compared with that of the THF ( $E_T(30) = 37.4$ ) [36]. A more polar solvent stabilizes the coloured merocyanine (open form) resulting in a slower bleaching process. In solid matrices, the photochromic molecules show faster bleaching than in solution, due to the steric interactions between the molecules and the pore surface of the matrices, which limits the opening mechanism of the dye. The bleaching kinetics of the photochromic molecules was found to be much slower in phenyl modified ormosil matrices than in the polymer matrix (pHEMA), due to the larger pore size observed in phenyl modified silica network [39] that leads to a decrease of the above mentioned steric interactions.

### 3.2. Photostability

The photodegradation of the photochromic naphthopyran molecules upon prolonged exposition to UV-light was measured in solvents (THF and benzene) and in solid matrices. The absorbance of the photochromic samples was monitored vs. time, while irradiating the samples with a UV lamp, to follow the photodegradation of the photochromic molecules.

The photodegradation, leading to the formation of benzophenones,  $\beta$ -phenylcinnamaldehydes and other minor photoproducts [27,42,43], is much faster in solution than in solid matrices (Fig. 4), due to the higher mobility of the dye molecules. The photochromic dye in a THF solution undergo a faster photodegradation than in a benzene solution, due to the higher polarity of THF [36], that result in a stabilization of the open coloured form of the dye molecules, promoting the photodegradation of the naphthopyran dye. No important differences were observed in the photostability of the dye molecules in the polymeric and ormosil matrices. However, in polymeric matrices, the photostability of the naphthopyrans is limited by the low stability of the matrix itself upon UV irradiation [44,45]. The usage of ormosil matrices is, therefore, a good choice for the entrapment of photochromic molecules due to the good photostability of both, the photochromic molecules and the matrices.

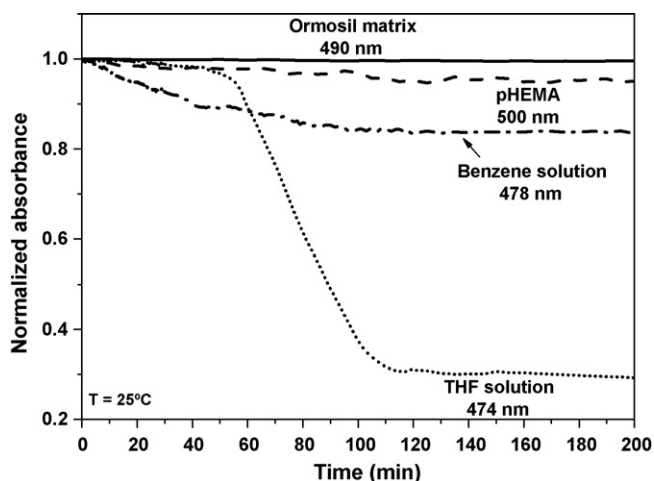


Fig. 4. Photodegradation of a naphthopyran molecule in THF and benzene solutions and embedded in pHEMA and Ph-modified ormosil matrices.

### 3.3. Photostability of the dye in ormosil matrices

The photostability of the dye molecules embedded in ormosil matrices was found to depend strongly on the amount of the organic functional groups in the ormosil matrix and the photochromic dye loading in the matrix.

#### 3.3.1. Organic functional groups

The nature and amount of the organic functional groups in the matrix have an important effect on the photodegradation of the naphthopyran dye [34]. The introduction of organic groups (R) into the sol-gel matrix results in a decrease of the relative amount of silanol groups in the inner pore surface where the photochromic molecules are allocated and therefore, in a decrease of the pore surface polarity. The polarity of the pore environment in Ph-modified matrices was measured, using the  $E_T(33)$  polarity probe, as a function of the Ph groups loading in the matrix, giving  $70.7 \text{ kcal mol}^{-1}$  for an unmodified matrix and about  $51.4 \text{ kcal mol}^{-1}$  for a matrix prepared with Ph/Si ratio of 0.9. This values correspond to the most commonly used  $E_T(30)$  polarity values of  $61.8 \text{ kcal mol}^{-1}$  and  $42.8 \text{ kcal mol}^{-1}$ , respectively. In order to correlate the photodegradation of the dye with the composition of the matrix, the time required for the UV-light to produce the photodegradation of 20% of the molecules embedded in the film (20% drop in the intensity of the absorbance peak) was measured as a function of the amount of R-groups in the silica matrix. Increasing the R/Si molar ratio in the matrix results in a progressive increase of the time required for the degradation, reaching a saturation value around Ph/Si=0.3, as shown in Fig. 5 for Ph-modified ormosil samples. This effect is due to the fact that the zwitterionic forms of the open coloured merocyanine (Fig. 1) molecules are stabilized in more polar environments, favouring its interaction with the OH

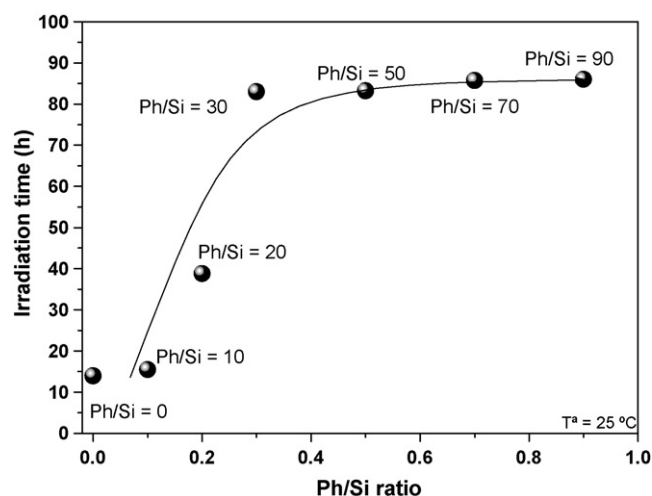


Fig. 5. Time of irradiation with UV-light required for a loss of 20% of the photochromic molecules embedded in Ph-modified matrices with different Ph/Si molar ratio.

groups in the pore surface via hydrogen bonding or ionic interactions [25] that promote the degradation of the photochromic molecules [34].

The photodegradation of the dye molecules in the ormosil matrices could be reduced by a factor of 9 in Ph-modified matrix as compared to an unmodified silica matrix. This effect can be observed by the  $t_{1/2(\text{deg})}$  of the degradation of the photochromic molecules in unmodified matrices and Ph-modified samples, being 21 h and 181 h, respectively. Table 2 shows the photostability of the photochromic dye in samples prepared with different amount of the Ph-groups, expressed as  $t_{1/2(\text{deg})}$ , the time required for half of the molecules to be degraded by irradiation with UV-light. The degradation half-time have been calculated taking into account the thickness and the intensity of the absorption band of the samples during irradiation with UV-light.

#### 3.3.2. Photodegradation as a function of the amount of dye embedded in the matrix

The dye loading in the matrix has an important effect on photodegradation of the photochromic films. Fig. 6 shows the photodegradation of the naphthopyran dye embedded in a Ph-modified matrix as a function of the dye/Si molar ratio. Increasing the relative amount of dye in the ormosil matrix resulted in an increase of the photostability of the photochromic molecules, as it diminished the interaction of the dye with the pore surface (hydrogen bonding or ionic interactions). Large amounts of dye in the pores can also lead to the screening of the UV-light, responsible for its degradation, by the dye molecules themselves [46,47].

The ability to obtain photochromic films with high dye loadings is of a great importance from the point of view of possible applications, as it allows obtaining films that develop a deep coloration

Table 2

Spectroscopic properties and degradation half-time of the naphthopyran molecules upon prolonged exposition to UV-light in different ormosil matrices

Ph/Si molar ratio	Matrix				
	$\lambda_{\text{max}}$ (nm)	$\Delta\text{Abs}$ ( $A_{\text{a.i.}} - A_{\text{b.i.}}$ )	Thickness, $e$ ( $\mu\text{m}$ )	$\Delta\text{Abs}/e$	$t_{1/2(\text{deg})}$ (h)
0.0	546	0.023	0.30	0.077	21
0.1	507	0.043	0.60	0.072	33
0.3	492	0.064	0.90	0.071	187
0.5	490	0.091	1.20	0.076	181
0.7	490	0.131	1.80	0.073	187
0.9	490	0.179	2.50	0.072	183

Measured at 25 °C.

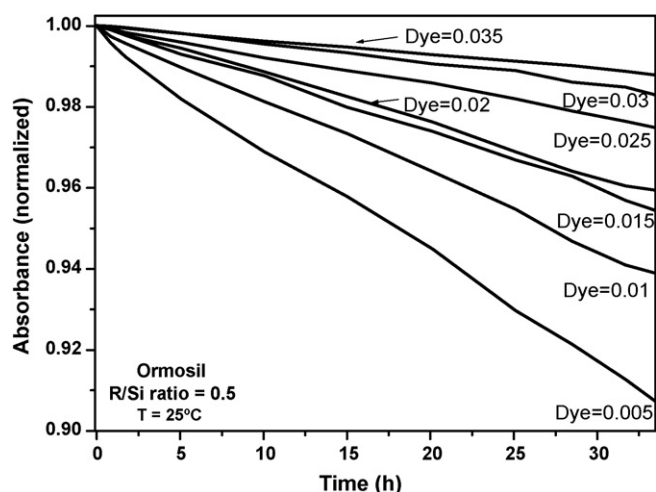


Fig. 6. Effect of the dye loading on the photodegradation of the photochromic naphthopyran molecules embedded in Ph-modified matrix.

upon irradiation with UV-light, enhancing at the same time the photostability of the dye.

#### 4. Conclusions

The photostability of a photochromic naphthopyran derivative embedded in ormosil matrices upon irradiation with UV-light was found to depend strongly on the composition of the embedding matrix. The amount of the organic functional groups (R-groups) in the pore surface has an important effect on the photostability of the NP molecules. The introduction of R-groups in the inner pore surface of the matrix allows controlling the chemical environment and polarity of the pore cage, due to the decrease of OH groups in the pore surface, and hence the stability of the molecules upon prolonged exposition to UV-light. It was found that a decrease of the polarity of the embedding matrix results in a progressive increase of the photostability of the NP molecules. In this way, the photostability of the photochromic molecules in the ormosil matrices could be improved by a factor of 9 in matrices prepared with Ph-groups as compared to the photostability of the dye in unmodified matrices ( $t_{1/2(\text{deg})}$  values of 181 h and 21 h, respectively). The degradation of the photochromic dye in ormosil matrices was also measured as a function of the amount of dye in the matrix, showing a much slower degradation at higher dye loadings.

The photostability of the dye molecules was also measured in solvents (THF and benzene) and dispersed in a solid polymeric matrix. The rate of photodegradation of the photochromic molecules is substantially reduced in polymeric and ormosil matrices, as compared with the molecules in solution, due to the reduced mobility of the molecules in solid matrices. The polarity of the environment, in solution and in solid matrices, plays an important role in determining both, the kinetics of the thermal bleaching and the photostability of the photochromic molecules upon prolonged exposition to UV-light.

Sol-gel ormosil matrices are a good choice for the entrapment of the photochromic dye molecules due to the slower photodegradation of the dye in a solid matrix and the higher photostability of the matrix itself upon prolonged exposition to UV-light, as compared with polymer matrices.

The ability to control the photostability as well as the photochromic properties of naphthopyran molecules in ormosil matrices, by tailoring the chemical environment where the dye molecules will be located, opens a new way for the design of materials with defined properties.

#### Acknowledgements

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