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Photochromism of dihydroazulene-based polymeric thin films

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HIGHLIGHTS

- Dihydroazulene (DHA) derivatives have been incorporated into polymer matrices for the first time.
- The photochromic behavior of polymeric films doped with DHAs was characterized.
- The photoactivity of DHA and the thermal back reaction of vinylheptafulvene (VHF) were maintained in the polymeric films.

ABSTRACT

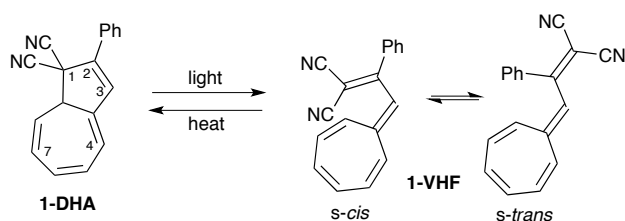
We report on the preparation of polymeric thin films doped with six dihydroazulene derivatives whose photochromic properties were previously screened in organic solution studies. Spectroscopic investigations into the photochromic behavior of the polymeric matrices have given important insights on the stability and the photophysical properties of the photoswitches impregnated into polymers.

KEYWORDS: Dihydroazulene, photochromism, photoswitch, energy storage, polymeric film, materials.

1. Introduction

The field of light-responsive photochromic materials has been widely investigated in the past few decades for the design of advanced materials with a broad variety of applications, from the well-known ophthalmic lenses or photochromic eye-glasses, to cosmetics or novelty products, which all take advantage of the color change induced by light exposure.¹ Indeed, the most used photochromes are colorless/pale yellow in their stable form and turn intensely colored upon light irradiation. In some cases (such as for T-type switches), a thermally driven back reaction (TBR) reverts the colored species to the colorless low energy parent molecule; in others (P-type), the original form is recovered only by irradiation with light at a different wavelength. Among the different classes of molecular switches, dithienylethenes, spiropyrans and azobenzenes are considered the most promising for organic photochromic materials, and the properties and applications achieved in the past decades have been reviewed several times.²

In the context of T-type molecular switches, the dihydroazulene/vinylheptafulvene (DHA/VHF) pair, discovered by J. Daub in 1984,³ is a less explored class of photo/thermochromes (Scheme 1). The effect on the photophysical properties of the system by functionalization at positions 2, 3, 4 and 7 of the DHA scaffold has been broadly investigated in Nielsen's group since 2007, in solution studies.⁴



Scheme 1. The DHA/VHF T-type photoswitch with the numbering of the *core* structure.

Single-molecule break-junction studies involving these DHA derivatives have been performed⁵ and, more recently, photoresponsive liquid crystalline materials based on neat photoactive DHA derivatives and in a nematic host have been reported for the first time.⁶ Given the energy conversion involved during the forward and back isomerizations, the photochromism of this class of molecules has been lately probed for energy storage applications.⁷ One challenge in this regard is to achieve both sufficiently high energy storage capacity and control of the energy-releasing back reaction. By various functionalizations, we have so far found that the energy storage capacity (in MJ kg⁻¹) can be increased up to fourfold relative to the **1-DHA/1-VHF** couple, but these improvements were unfortunately accompanied by undesirable sigmatropic rearrangements and degradation upon irradiation.⁷

Detailed studies on the photochromic behavior of this class of molecules in solid matrices, more suitable for real applications, are still lacking. It was thus decided to investigate the photochemical properties of some carefully selected DHA molecules embedded into polymers. This study provides useful insights for the design of new DHA derivatives valid for incorporation into optically switchable materials. Indeed, in the development of fast responsive materials, fast switching may be desirable for some applications, while for other applications (i.e. solar energy storage) slow switching is preferred. In relation to the latter challenge, recently we reported a series of singly substituted monocyano- dihydroazulenes, prepared in one-step from the parent dihydroazulene (DHA) **1** or the 2,3-diphenyldihydroazulene **2** (Figure 1), showing that substitution of one nitrile at C-1 of the original scaffold with another group has dramatic consequences on the photochemical properties of the molecules in solution, expanding the lifetimes of the VHF form from milliseconds to days.⁸ Conveniently, this change also resulted in a doubling of the energy storage capacity

(value of ca. 0.2 MJ kg⁻¹) relative to **1-DHA/1-VHF** (ca. 0.1 MJ kg⁻¹), but reversible “slow” switching without degradation is still a necessary issue to be overcome for such structural modifications. In any case, the energy storage capacities of these simple derivatives are similar to those of *cis/trans* azobenzenes,⁹ but one particular advantage of the DHA/VHF system is the T-type photochromism, which in azobenzenes is not always observed since the back isomerization must be photoinduced as well. On the other hand, a photoswitch with high potential for energy storage is the norbornadiene/quadracyclane couple, which in fact has had the storage calculated at ca. 0.7 MJ kg⁻¹. While the quantum yield of photoisomerization of **1-DHA** is 55%,¹⁰ it is, however, only 9% for norbornadiene (characterized by undesirable, poor overlap with the solar spectrum).¹¹

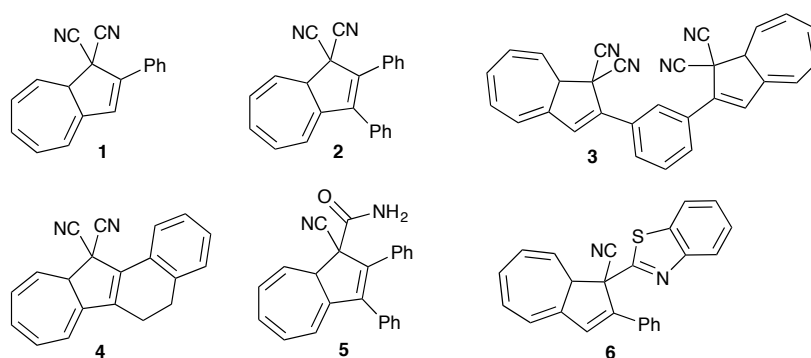


Figure 1: The DHAs **1-6** investigated in PMMA

The selection of dihydroazulenes **1-6**, whose syntheses have been already reported elsewhere,^{8,12-15} was made on the basis of structural features. Compounds **1-2** are considered reference compounds, that is, parent systems on which the scaffold is based, and compound **3** is the first derivative containing two DHA units which influence the photoactivity of one another (exhibiting stepwise ring openings in solution).¹⁴ Compounds **4-6** were selected for the short half-lives exhibited by the corresponding VHF in solution, which was achieved either by locking the VHF in its

reactive *s-cis* conformation by an ethylene bridge (**4**)¹⁵ or by replacement of one cyano group with a primary amide (**5**)⁸ or with a benzothiazole ring (**6**).⁸

We report herein *a*) the preparation of photoresponsive polymeric films through the doping of DHA derivatives into the matrix, and *b*) the photophysical characterization of the obtained materials. PMMA was selected as matrix because it is a readily available, cheap and inert polymer in which organic photochromes (e.g. spiropyrans, chromenes, etc.) have shown good solubility and maintain photochromic properties, despite a drastic reduction in the interconversion rate.¹⁶ Polycarbonate (PC) was also tested as matrix, since it is a standard polymeric material used in photochrome-based applications such as ophthalmics.²

2. Materials and methods

2.1 Materials

Poly(methylmethacrylate) (PMMA, molecular weight of 120,000 g/mol, $T_g = 105$ °C¹⁷), poly(bisphenol A carbonate) (PC, $T_g = 146$ °C¹⁸) were purchased from Sigma-Aldrich. The syntheses of the DHA dyes were described elsewhere.^{8, 12-15} The solvents (CH₂Cl₂ and CHCl₃) for the film preparation were provided by Scharlab and were used as received.

2.2 Methods

Preparation of the photochromic polymer films

To prevent photodegradation of the photochromes, the film preparations were carried out in the dark. 115-120 mg of PMMA (or PC) and 0.5-5 mg (specified in the text) of DHA (0.4-4 wt.%) photochromic dye were dissolved in 5 mL of degassed CHCl₃ or CH₂Cl₂. The solution was stirred until all PMMA was completely dissolved. Once a homogeneous solution was obtained, the liquid was transferred on a glass Petri plate

(6 cm in diameter) and the solvent was evaporated in the dark at room temperature over 12 hours, yielding the clear photochromic film which was kept in the glass Petri plate during the measurements.

Study of the photochromism

To induce the photoisomerization, the films were irradiated with a low pressure 6 W Hg lamp at 365 nm at a distance and a period of time depending on the type of experiment (photostationary state and non-photostationary state conditions, see below). The UV-Vis spectra of the unactivated (DHA) and photoactivated (VHF) form of the film were recorded with UV-Vis spectrophotometers (Agilent Cary 4000 and Cary 60) before and immediately after stopping the irradiation with the Hg lamp, respectively. A glass Petri dish without the photochromic polymeric material was used as reference. The coloring and fading processes were monitored by recording the absorption spectra of the films under UV irradiation and in the dark (after irradiation), over time. Thermal back isomerization kinetics were obtained by plotting the absorbance, at the corresponding absorption maxima, of the VHF isomer (and in some cases of the DHA) over time.

The fading kinetics curves of the films were measured after irradiation times shorter or longer than the amount of time required for the system to reach the photostationary state, here referring to a situation where the rates of the light-induced forward reaction and the thermal back reaction are identical. In non-steady state measurements (Cary 4000 spectrophotometer, 5 minutes of UV irradiation at 1 cm of distance) the absorption spectra of the VHF form were recorded from immediately after stopping the UV irradiation. The absorbance at $t = 0$ (A_0) was extrapolated from the fitting function of the obtained decay curve. In photostationary state measurements (Cary 60 spectrophotometer, between 10-40 min of irradiation at 6.5 cm distance, depending on

the photochromic system), while detecting, the film was irradiated for the time required to reach a steady state, observable by the fact that the absorbance does not change over time. This value is the maximum absorbance achievable with the specific film (dye, concentration, thickness) and irradiation conditions (power density). Once the steady state was reached the irradiation was stopped ($t = 0$) and the film absorption spectra were recorded overtime. The absorbance at $t = 0$ (A_0) was directly obtained from the measurement (steady state absorbance).

The fading kinetics reported below have been normalized by fixing the absorbance A_0 at 1. When possible, a multiexponential function was used to fit the data using OriginPro 8 software. The values $t_{1/2}$ and $t_{3/4}$ were determined as the times required for the VHF isomer to reduce its absorbance (i.e. concentration) to its half ($t_{1/2}$) or quarter ($t_{3/4}$) of the value (A_0) at the moment the irradiation is stopped.

3. Results and discussion

The optical properties in solution of the dihydroazulene derivatives selected for this study have been previously reported and are inserted in the text during the discussion of the results on the polymeric films.

3.1 Optical properties of the DHA-based PMMA films

The parent DHA **1** was the first investigated dye, since it is known to be soluble and stable in a variety of organic solvents and present good fatigue resistance under an aerial atmosphere. The **1-DHA@PMMA** film obtained resulted in having a pale-yellow color, corresponding to the stable DHA form homogeneously dissolved in PMMA (Figure 2a). Without exposure to light, the DHA mainly absorbed in the UV region ($\lambda_{\text{max}} = 358$ nm) with a tail reaching $\lambda > 400$ nm (Figure 2b). Subsequent exposure of **1-DHA@PMMA** to UV radiation for 5 minutes produced a strongly red-

colored film (**1-VHF@PMMA**), which gradually faded to the initial color when the irradiation was stopped. The color change upon irradiation was accompanied by the decrease of the absorption band in the UV region ($\lambda_{\text{max}} = 358 \text{ nm}$) and the appearance of a broad band at $\lambda_{\text{max}} = 470 \text{ nm}$, attributable to the VHF form, which slowly reverted back to DHA in the dark. The restoration of the initial color (and DHA spectrum, Figure 2b) confirms that the photochromism of DHA was maintained once embedded in the solid matrix.

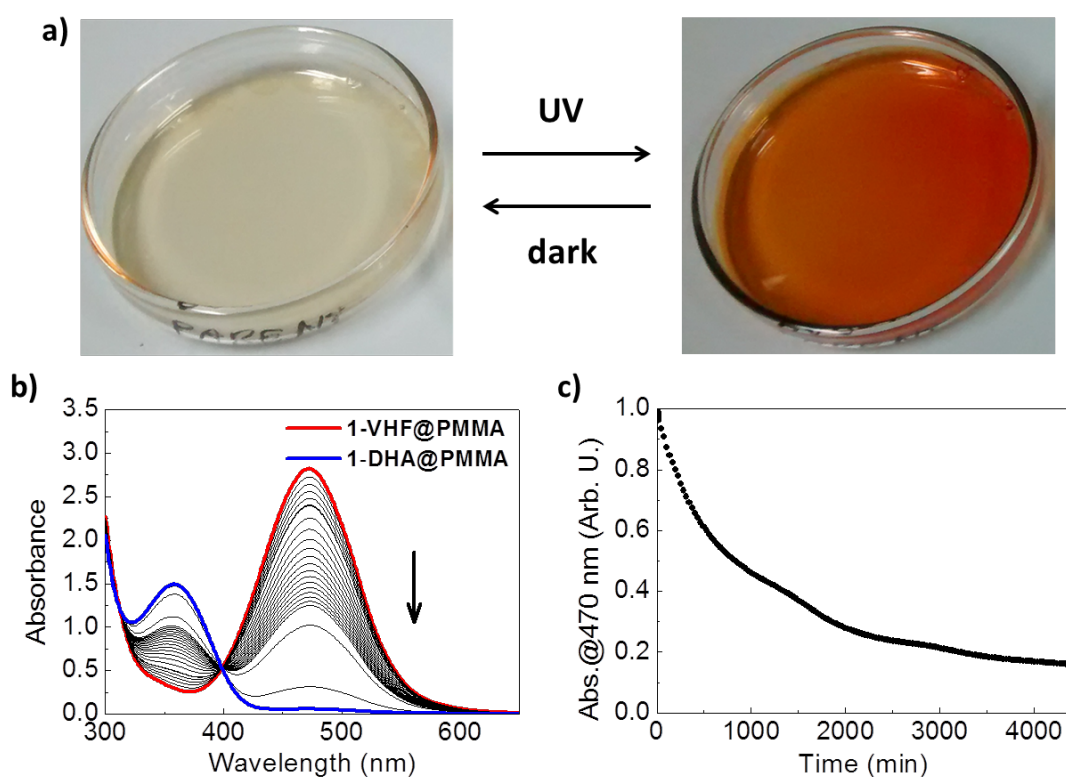


Figure 2: a) Non-irradiated (left, **1-DHA@PMMA**) and irradiated (right, **1-VHF@PMMA**) **1@PMMA** film (0.88 wt.%); b) absorption spectra of the **1@PMMA** before (blue), immediately after stopping the irradiation (red) and at different delays after stopping the irradiation (black); c) fading kinetics (@ 470 nm) of **1@PMMA** obtained after reaching the photostationary state.

The room temperature kinetics of the thermal fading was monitored by measuring the absorbance decrease of **1-VHF@PMMA** over time, in the dark (Figures 2b and S1). It was found that a) the isomerization kinetics had to be fitted with a biexponential function ($k_1 = 7.0 \times 10^{-4} \text{ min}^{-1}$; $k_2 = 4.3 \times 10^{-3} \text{ min}^{-1}$), rather than following a first order

192 decay as, instead, has been observed in homogenous organic solutions;¹² and b) the
193 back isomerization of **1-VHF@PMMA** was as far slower ($t_{1/2} = 735$ min, $t_{3/4} = 1745$
194 min) than what is reported in acetonitrile solutions ($t_{1/2} = 218$ min).¹² Both features are
195 the result of the matrix effect exerted by the polymer on the dye. The much higher
196 rigidity of the medium PMMA in comparison with a solution reduces the mobility of
197 the photochromic molecules impeding the significant structural changes involved
198 during the isomerization processes, in particular the VHF *s-cis* to *s-trans*
199 isomerization (Scheme 1), which it is partly responsible for prolonging the ring-
200 closure in solution. On the other hand, the inhomogeneity of the material makes the
201 photochromic molecules fading with different rates, causing a multifunctional decay.
202 The inhomogeneity of the material also affects the photoinduced isomerization. The 5
203 minutes of irradiation used to color the **1@PMMA** film from **1-DHA@PMMA** to **1-**
204 **VHF@PMMA** is far less than the amount of time required by the system to reach a
205 photostationary state, at which it is assured that photochromic molecules from
206 different environments (more or less rigid) are photoisomerized to the VHF form. At
207 lower irradiation times, mainly molecules with softer environments are isomerized
208 and therefore the fading process is recorded only for those molecules isomerizing
209 faster, giving a kinetics profile not representative of the film. To better evaluate the
210 fading rate of **1-VHF@PMMA**, the thermal isomerization was studied after reaching
211 the photostationary state (PS), which required an irradiation of 25 min using similar
212 power density (Figure S2). Though the decay curve could not be fitted to any
213 multiexponential function due to thermal fluctuations during the long measurements,
214 it could be noted that the fading resulted in significantly slower decays ($t_{1/2}^{PS} = 825$
215 min, $t_{3/4}^{PS} = 2535$ min) than observed without reaching the steady state and after 3
216 days the DHA form was still not completely recovered (Figure 2c).

217 Interestingly, the fading of **1-VHF@PMMA** was faster than in the non-polar
218 solvent cyclohexane solutions ($t_{1/2} = 2333$ min),¹² signaling that although it is not
219 possible to insert a polymeric matrix into a classical polarity solvents scale, the
220 PMMA environment is more polar than pure cyclohexane and it is stabilizing the
221 polar transition state better than cyclohexane, despite the rigidity of the matrix.¹⁹

222 In order to demonstrate that the photochromism in solid matrices can be
223 extended to other DHA derivatives, PMMA films with compounds **2-6** were prepared
224 and studied through absorption spectroscopy. In the dark, PMMA films prepared from
225 DHAs **2, 3, 4, 5** and **6** were colorless or slightly yellow, indicating that in this polymer
226 the photochromic molecules were stabilized into the corresponding DHA form
227 (Figures 3 and S3). Reversible and significant color changes were observed upon UV
228 irradiation of both **3-DHA@PMMA** (slightly yellow to red) and **6-DHA@PMMA**
229 (colorless to orange) films (Figure 3) and a broad absorption band in the visible region
230 ($\lambda_{\text{max}} = 470\text{-}474$ nm) emerges (Figures S4a and S5a).

231 The analysis of the thermal fading (multiexponential functions) studied after 5
232 minutes of irradiation or after reaching the photostationary state (50 and 30 min for
233 **3@PMMA** and **6@PMMA**, respectively) showed in both cases that **3@PMMA**
234 (Figures 3a and S4b) faded slower ($t_{1/2}^{\text{PS}} = 4252$ min, $t_{3/4}^{\text{PS}} = 11716$ min) than the
235 parent **1@PMMA** ($t_{1/2}^{\text{PS}} = 825$ min, $t_{3/4}^{\text{PS}} = 2535$ min), while **6@PMMA** (Figures 3b
236 and S5b) resulted in significantly faster decays ($t_{1/2}^{\text{PS}} = 25$ min, $t_{3/4}^{\text{PS}} > 75$ min). The
237 thermal isomerization rates are thus significantly dependent on the type of the
238 embedded DHA, although different from the fading rate order observed in acetonitrile
239 solution (in solution **6** > **3** > **1**; **1**: $t_{1/2}\text{-CH}_3\text{CN} = 218$ min;¹² **3**: $t_{1/2}\text{-CH}_3\text{CN} = 160\text{-}140$
240 min;¹⁴ **6**: $t_{1/2}\text{-CH}_3\text{CN} = 1.7$ min⁸). For compounds **1** and **6**, the relative half-lives in
241 PMMA are consistent with those observed in acetonitrile (**6** > **1**), while compound **3**

in PMMA showed a much slower fading rate, maybe ascribable to the presence of two photochromic DHA units, **whose reciprocal** influence might be different in solid and liquid media.¹⁴ Hence, the functionalization of the DHA scaffold allows a fine control of photochromic properties of the dye, not only in standard liquid solution but also in solid matrices, making these DHA-based films suitable for applications where different time responses and color changes are required.

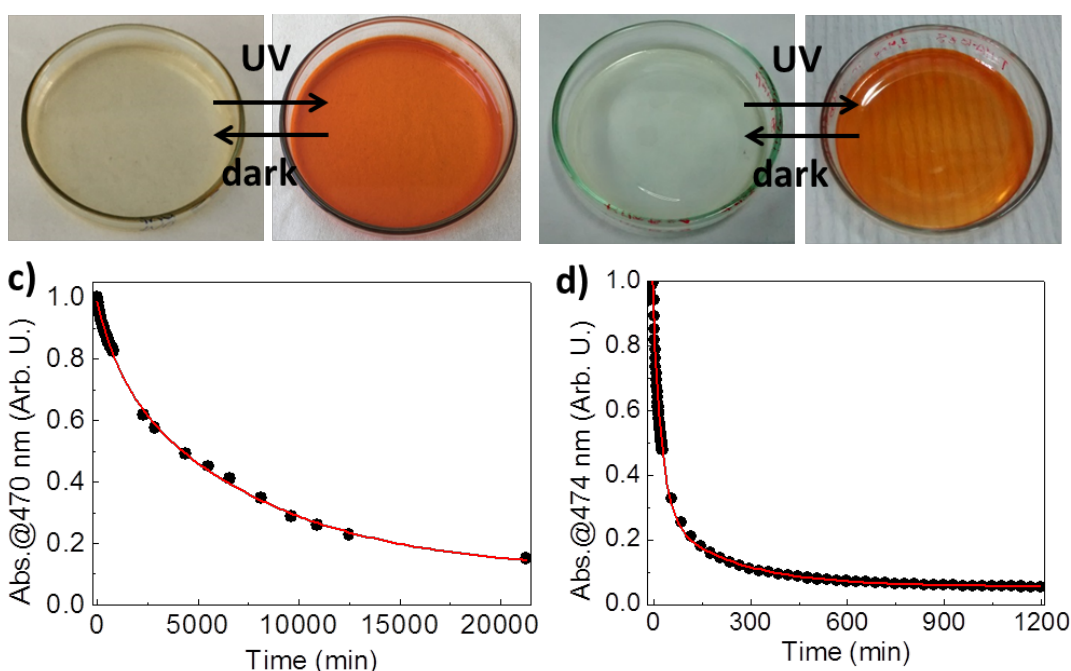


Figure 3: Non-irradiated (left) and irradiated (right) *a*) **3@PMMA** (0.86 wt.%) and *b*) **6@PMMA** film (1.13 wt.%); fading kinetics of *c*) **3@PMMA** (@470 nm) and *d*) **6@PMMA** (@474 nm) obtained after reaching the photostationary state.

On the other hand, PMMA films with DHAs **2**, **4** and **5** did not show significant color changes (Figure S3), similar to the behavior in solution, and very weak absorption bands in the visible region were formed upon UV irradiation even with more than twice the amount of photochromic dye loaded into the matrix (Figures S6 and S7). Moreover, after a few cycles the activity of the films was completely lost, showing quite considerable fatigue. The little absorbance loss measured for

2@PMMA at 485 nm during the UV irradiation to reach photostationary state (5 min) revealed that photodegradation of **2-VHF** occurred (Figure 4a) if longer irradiation times were employed. The study of the fading (Figure 4b), monitored at 485 nm after reaching the steady state, revealed that **2@PMMA** was the fastest fading film ($t_{1/2}^{PS} = 1.97$ min and $t_{3/4}^{PS} = 4.59$ min) among those studied in this work. For comparison, the fading times of the same dyes observed in the organic solvents in which they possess good solubility are given: **2**: $t_{1/2_CH_3CN} = 0.23$ min;¹³ $t_{1/2_cyclohexane} = 20$ min;⁸ **4**: $t_{1/2_cyclohexane} = 0.9$ s;¹⁵ **5**: $t_{1/2_CH_2Cl_2} = 69$ ms.⁸

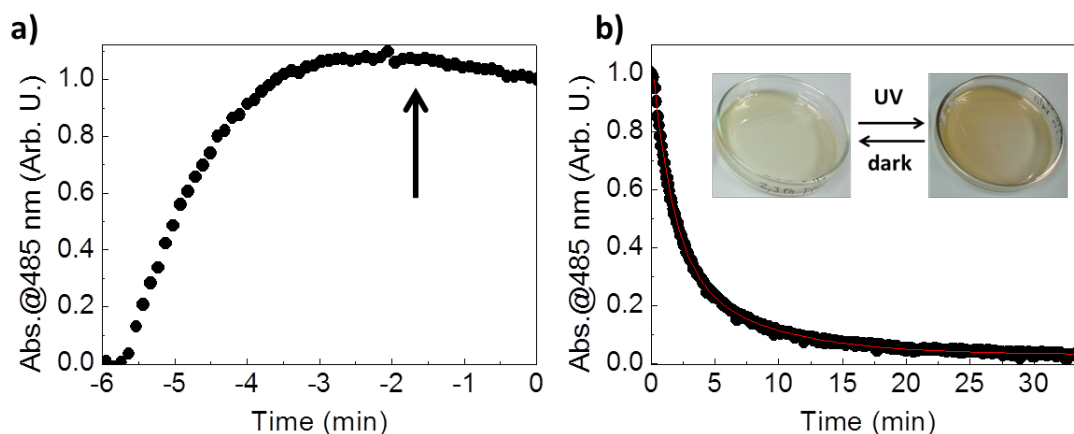


Figure 4: a) Increase and decrease of the absorbance (@485 nm) of the **2@PMMA** (2.54 wt.%) upon UV irradiation to reach the photostationary state (5 min). The negative values for the time axis are used to differentiate the photoactivation from the fading process; b) fading kinetics of **2@PMMA** film (@485 nm).

4@PMMA and **5@PMMA** films did not show degradation during the photoactivation to the corresponding VHF forms (Figure S8). For both films, once the irradiation was halted, the absorbance in the visible region dropped in less than 3 minutes ($t_{1/2}^{PS} = 0.3$ and 2.7 min; $t_{3/4}^{PS} = 3.1$ and 27 min, respectively). However, after this period the absorbance reached a steady value, quite different from the one recorded before irradiation, even after keeping the film in the dark for 120 min, and showing a residual absorbance at λ_{max} of 0.16 and 0.22, respectively. This behavior

was even more evident when the kinetics of the **4@PMMA** and **5@PMMA** films were followed at their respective absorption maxima in the UV region (Figure S8). The initial absorbance of the DHA isomers could not be reestablished after one light/heat cycle and the dramatic drop of concentration of DHA isomers accounts for the loss of the photochromic activity.

For the best performing films (**3@PMMA** and **6@PMMA**) preliminary studies of their fatigue resistance were carried out. After subsequent activation/deactivation cycles (reaching the photostationary state) the films did not show, in the dark, any loss of initial transparency, indicating that no irreversible colored species are formed upon prolonged irradiations (Figure S10). On the other hand, the absorption of the activated films (measured at the respective λ_{max}) decreased from 1.66 to 1.32 for **3@PMMA** (2 activations) and from 0.80 to 0.44 for **6@PMMA** (4 activations). The partial decrease of the color intensity could be ascribed to possible irreversible reactions of the photoexcited photochromic molecules with molecular oxygen permeating in the polymer matrix. The use of radical scavengers and antioxidant should enhance the fatigue resistance.

3.2 Optical properties of the DHA-based PC film

In order to investigate how the matrix rigidity affects the fading kinetics of DHA dyes, a polycarbonate (PC) ($T_g = 146\text{ }^\circ\text{C}$)¹⁸ film of **1** was prepared. Similarly to what was observed in PMMA, under UV exposure the film turned from slightly yellow (mainly DHA form) to dark orange (VHF), confirming that the photochromism was maintained (Figure 5). The fading process of **1-VHF@PC** monitored at $\lambda_{\text{max}} = 475$, after reaching the photostationary state, was significantly slowed down ($t_{1/2}^{\text{PS}} = 1334\text{ min}$, $t_{3/4}^{\text{PS}} = 3659\text{ min}$) in respect to what was measured for **1-VHF@PMMA**. The slower thermal isomerization can be ascribed to the higher

rigidity of PC in respect to PMMA, which decreases the intramolecular flexibility of the photochromic molecules embedded in the matrix. This behavior is analogous to what is reported for commercial spirooxazine photochromes, which in PC show a slower fading than in PMMA.¹⁶

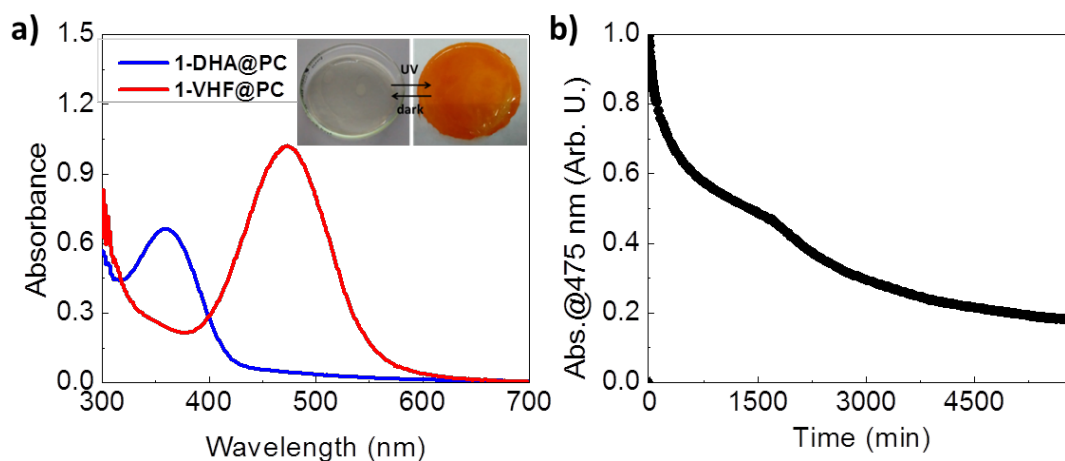


Figure 5: a) Absorption spectra of **1@PC** in its DHA or VHF form Inset: **1@PC** (0.27 wt.%) in the dark and irradiated forms; b) Decay of **1-VHF@PC** recorded at VHF absorption maximum (@475 nm).

4. Conclusions

Our studies have shown that photoisomerization of DHA into VHF and the thermal back reaction of VHF into DHA are both maintained when the system is embedded in solid matrices. For the reference compounds **1-2**, the VHF to DHA decays were slowed down in PMMA matrix relative to in a polar solvent like acetonitrile, but were actually faster in the polar PMMA matrix than in less polar solvent like cyclohexane. The medium still affects the ring-closure like solvent does. Hence, the behavior in the polymeric films is influenced by the characteristics of the PMMA matrix, both in terms of polarity, for stabilizing the transition state, and in terms of rigidity, which is possibly influencing the VHF *s-cis* to *s-trans* conformational equilibrium in favor of the *s-cis* conformer, essential for the ring-closure.

In addition, multifunctional decays were obtained in the PMMA matrix due to the inhomogeneity of the material, which affects both the direct photoactivation and the fading processes.

The half-lives of various VHF s were found to follow the same relative sequence in the PMMA matrix as in acetonitrile solution, only compound **3**, containing two DHA units, had a much slower fading rate in PMMA than in acetonitrile. For the most promising films (**3@PMMA** and **6@PMMA**), preliminary studies of the fatigue resistance were carried out and showed that partial loss of color of the photoactivated films was induced by prolonged irradiation. This photoinstability could be improved by adding antioxidant or radical scavengers. Photochromism was also maintained in a polycarbonate film, but the conversions were slowed down in this more rigid material. Thus, both structural variations of the photochromes and intrinsic characteristics of the matrices (i.e. polarity and rigidity) conveniently allow for tuning the switching properties of the materials.

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