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Fast thermal *cis–trans* isomerization of heterocyclic azo dyes in PMMA polymers

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ABSTRACT

A series of heterocyclic azo dyes were dispersed in poly(methyl methacrylate) (PMMA) matrix and the photochromic properties of the coloured films studied by UV–Vis spectroscopy. Visible irradiation of the coloured films lead to a fast decrease in the colour intensity due to the *trans–cis* photoisomerization reaction. When the light source was removed the spontaneous thermal *cis–trans* reverse isomerization occurred bringing the absorbance back to initial value with variable speed. Contrary to common azobenzenes that after photoisomerization with UV or visible light exhibit very slow thermal *cis–trans* back re-isomerization, that can last for hours or days, azo dyes bearing pyrrole, thiophene, thiazole or thiadiazole heterocycles display very fast switching between the two isomers (few seconds) even when dispersed in PMMA polymers.

1. Introduction

Aromatic azo compounds are a dominant class of synthetic dyes. Through the use of appropriate substituents a wide range of highly chemically stable molecules that displays intense and tuneable colours have been produced and exploited in materials science [1–4]. These compounds exist preferentially in the *trans* form but can be photochemically converted into the *cis* form, without any bond breaking, leading to a rearrangement of the electronic structure and therefore to a noticeable change in the absorption spectra [5].

The thermally more stable *trans* isomer of the unsubstituted azobenzene is planar allowing an extension of the π-electronic system between the two aromatic rings. It displays an high-intensity band (π–π^*) in the ultraviolet region (ca. 320 nm) and a weaker broad-band at 450 nm (n–π^* transition) that is responsible for the yellow colouration. When irradiated with UV light the *trans* isomer is converted into the *cis* that has an out-of-plane configuration of the aromatic groups attached to the azo group. In this species, the π–π^* band shifts to shorter wavelengths while there is an increase in the strength of the n–π^* transition at 450 nm. As a result the *trans–cis* photoisomerization leads to colour intensification [5].

Substitution at the *para* position with strongly donating groups such as dimethylamino, shifts the main absorption band into the visible spectrum causing an overlap with the n–π^* band and originating strong chromophoric systems. Since the *cis* isomer absorbs at lower wavelength (50–70 nm) the visible irradiation of a coloured solution of these dyes is accompanied by a noticeable decrease in the colour intensity [1].

Azobenzene belong to T-type photochromic systems, which means that when the irradiation source is removed the colour intensity increases again due to the spontaneous thermal *cis–trans* isomerization reaction that follows a first-order kinetic process (Fig. 1). So these molecular switches can be shifted between two different states by the simple application of an external light input, followed by a natural return to the starting point. Since the *trans–cis* isomerization is free from side reactions, the use of light as the external stimuli for these molecular switches allows an easy, clean, quick and remote control of the system using simple devices [6–8,3].

As the N=N isomerization is photochemically and thermally reversible, the UV–Vis irradiation of these dyes, at the maximum wavelength of the *trans* isomer, leads after some time to a photostationary state constituted by a mixture of *trans* and *cis* forms (Fig. 1). The ratio between the two isomers depends on the light intensity, on the rates of the isomerization reaction, the quantum yields of the photochemical reactions and on the extinction coefficients of each isomer. Considering a small absorption of the *cis* isomer at the maximum wavelength of the *trans* isomer, the percentage of the *cis* isomer present at the photostationary equilibrium can be estimated by the decrease in the absorbance at this wavelength. A 30% decrease in the absorbance indicates that nearly 30% of the *trans* isomer was converted to the *cis* [9].

Although the photoinduced *trans–cis* isomerization reaction is quite fast, depending essentially on the power of the light source, the thermal reconversion into the *trans* form is much more slower

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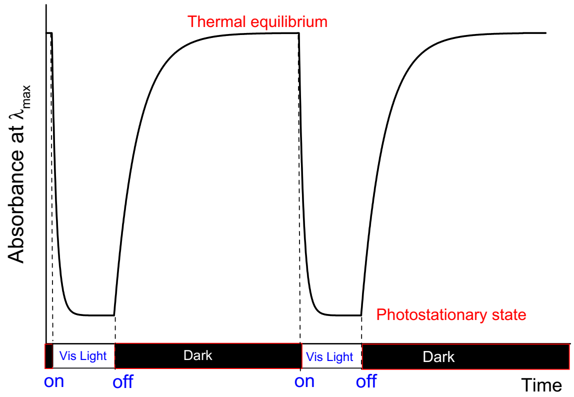

Fig. 1. Photochemical discoloration and thermal colouration processes.

being the rate determining step of the *trans*–*cis*–*trans* process. The main factor affecting the thermal relaxation rate of the *cis*-isomer and therefore the response time of these molecular switches is the molecular structure of the system [1,10–12].

The lifetime of the *cis* form of azo benzene derivatives, in solution, is usually very high, from several hours to a few days, although the introduction of electron donating or electron withdrawing groups in the azobenzene structure leads clearly to a faster thermal reconversion. This effect is enhanced when both electron donating and electron withdrawing groups are present in the 4 and 4′ positions (push/pull system). For example, the lifetime of the *cis* isomer of 4-nitro-4′-methoxyazobenzene in solution was found to be 22 min [1,5].

The introduction of hydroxyl groups in the azobenzene structure has a dramatic effect on the thermal stability of the *cis* isomer in particular in protic solvents like ethanol. For instance, the *cis* isomer of *p*-hydroxyazobenzene displays a thermal relaxation time of 31 min in toluene solution, but its lifetime in ethanol is just 0.2 s [13,14]. The increase of the thermal isomerization kinetic rate seems to be associated with the formation of hydrogen bonding between the azo group and/or the hydroxyl group and the solvent that favours a hydrazone-like electronic distribution with a simple N—N bond which facilitates the rotation to the more stable *trans* isomer [14]. This effect is particularly important in *ortho*-substituted azophenols that show very low *cis* relaxation times due to the formation of intramolecular hydrogen bonding between the OH and the azo group, even in apolar solvents like toluene. For example the lifetime of the *cis*-2-hydroxy-5-methylazobenzene in toluene is just 0.65 s [1].

Azobenzenes are robust molecules that can be easily incorporated into a wide variety of materials. The azo chromophores can be incorporated into polymers by covalent linking or they can be simply dispersed on the polymer matrix [15–17]. Both amorphous and liquid–crystalline systems have been extensively studied [18–22]. Recent applications tend to exploit the reversible geometrical and electronic modifications that occur during the switching between the two isomers (for example, the dipole moment changes from 0.5 D in the planar *trans* form, to 3 D in the *cis* isomer). The incorporation of azobenzene derivatives in polymers led, for example, to a series of new materials that exhibit birefringence properties [23–25]. When irradiated with polarised light a re-orientation of the azo groups occurs, leading to a change in the refractive index of the material. Similarly, the change in the shape of the azobenzene molecule during the photoisomerization has been used to create materials that show macroscopic mechanical deformations upon light irradiation [26–30].

Although this system is perfectly reversible and thousands of irradiation cycles can be consecutively perform without significant degradation, the lifetime of the *cis* form of azobenzene derivatives is usually very high (several hours/days) and therefore the return to the more stable *trans* isomer is normally incredibly slow [31]. Only through the introduction of specific substituents in the azobenzene structure, it is possible to obtain compounds exhibiting fast isomerization rates at room temperature. Therefore getting simple and fast molecular switches is still a challenge.

Most of the azo chromophores known belong to the azobenzene class which includes compounds with two phenyl rings linked through an azo-bridge. However, the studies on the optical switching of these compounds include usually only one compound per publication. There are few reports where a variety of azo compounds are studied in the same conditions and none of them include heterocyclic azo dyes [1,32–36]. These type of compounds have only recently been the subject of an extensive study [37–42]. Besides their classic applications as synthetic dyes and pigments, heteroaryl diazo chromophores containing five-membered aromatic heterocycles, exhibit second-order nonlinear optical (NLO) [43,44] as well as photochromic properties. We have shown that, donor–acceptor substituted azo dyes possessing heteroaromatic rings like pyrrole, thiophene, thiazole, benzothiazole and thiadiazole display photochromic properties in solution [9,44–47]. Visible irradiation of these dyes leads to a significant decrease in the colour intensity due to the *trans*–*cis* photoisomerization and after removal of the illumination a fast thermal process leading to the *trans* form is observed. The kinetic rate of the thermal back-reaction is dependent on the structure of the heterocycle but usually is in the range 0.01–1.6 s^{-1}. This means that a complete *trans*–*cis*–*trans* cycle can be performed in 1–100 s. In this paper we show that the switching between the two isomers of a series of heteroaromatic azo dyes dispersed in PMMA polymers can also be performed in few seconds, at room temperature, with a noticeable change in the colour intensity of the material.

2. Experimental

2.1. Preparation of the films

The heteroaromatic azo dyes presenting pyrrole, thiophene, thiazole, benzothiazole and thiadiazole rings were prepared according to published methods [44,48–52]. The poly(methyl methacrylate) used for this study (Alfa Aesar) has an average molecular weight of 550.000.

A mixture of poly(methyl methacrylate) (1.0 g) in CH_2Cl_2 (10 mL) was heated at 60 °C with occasional stirring with a grass rod for 20 min after which a transparent solution was obtained. A solution of the azo compound (1.0 mg) in CH_2Cl_2 (2.0 mL) was then added to the PMMA solution and after stirring for 2 min the polymer solution was transferred into a Petri dish and kept at room temperature for 6 days during which the solvent evaporated and a coloured transparent and detachable thin film of the polymer was formed. The round films (9 cm diameter) display a mass around 1.0 g with a 0.1% weight percentage of the dye. The films thickness were measured with a digital Vernier Caliper and found to be between 0.05 and 0.10 mm. Fig. 2 shows a PMMA thin film doped with heterocyclic azo dye **7**.

2.2. Photochromic measurements

The photochromic properties of the materials were studied by UV–Vis using a CARY 50 Varian spectrophotometer equipped with a 50 W Ozone free Xenon lamp (6255 Oriel Instruments). The light from the UV lamp was filtered using water (61945 Oriel Instruments) and a long-pass filter (Schott GG 420, $\lambda > 420$ nm) filters and then carried to the spectrophotometer holder at the right angle