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PAPER

Diarylethene-based photochromic polyurethanes for multistate optical memories[†]

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Photochromic polyurethanes (PPUs) are synthesised by reaction between a diarylethene end-capped with hydroxyl groups and an aliphatic diisocyanate. *In situ* polymerisation provides amorphous films with remarkable optical properties. The possibility to vary the amount and the chemical structure of the photochromic monomer without affecting the reactivity of the polymerization allows one to tune in a wide range the optical properties of these films. In addition, different diarylethenes can be mixed together to give copolymers which may find application as photochromic layers for multistate optical memories. A setup for a non-destructive readout based on Raman signal is proposed.

Introduction

Functional materials are attractive for the development of smart optical devices. Among them, photochromic materials play an important role as they reversibly change the color by using suitable optical stimuli.^{1–3} Based on this change in color, such materials have been used for more than 30 years in photochromatic lenses, filters and inks.^{4,5} Moreover, many other applications based on photochromism, such as optical memories,^{6–15} optical switches,^{16–21} holographic elements,^{22–28} and tunable masks^{29–32} have been studied. Some of them exploit the change of physico-chemical properties other than color, for example refractive index,^{33–38} vibrational spectra,^{6,10,39,40} and luminescence.^{41–47}

What is usually required for the development of reliable optical devices based on photochromic materials is a large change of their response that is related to the chemical structure of the chromophore and is proportional to its content, combined with a good optical quality. It is well-known that increasing the content of active molecules in a polymer matrix, the material transparency worsens due to the scattering contribution coming from aggregation, thus preventing its practical use. In order to solve this issue, backbone photochromic polymers^{48–53} and side-chain photochromic polymers^{54–57} have been proposed. By following this approach it is possible to achieve a content of photochromic moiety up to 100% according to the polymerization process and the monomer structure.

In comparison to the photochromic polymers where the dye is just dispersed in the polymer matrix, the development of mainchain and side-chain photochromic polymers is more demanding, as the photochromic monomers have to be suitably synthesised according to the chemistry of the specific polymerization reaction. The possible complexity of the synthetic work is certainly a limitation of this method.

On the other hand, photochromic dyes embedded in a polymer matrix suffer from a limited optical contrast between the two states, as their content is relatively low to guarantee homogeneity.

With this background, a good option comes from the chemistry of polyurethanes (PUs), which is known to be extremely versatile: the basic reaction between a diisocyanate and a dialcohol yields a wide choice of polymer materials whose properties strongly depend on the molecular structure of the reactants (*i.e.* hard and soft moieties), on the addition of additives (such as cross-linkers, chain-extenders, water) and on polymerization conditions.⁵⁸ Moreover, the same reaction can be easily carried out *in situ* to produce polyurethane coatings.

Based on these approaches we developed diarylethene-based photochromic PU films (PPUs) with controlled thickness and very good optical properties. The optical contrast can be easily varied by changing the stoichiometric ratio between the photochromic molecule and a polyol, which is used to impart to the polymer good mechanical properties. Moreover, the color of the polyurethane can be easily tuned by polymerizing hydroxyl end-capped diarylethenes (DTE) which differ in the π -conjugation, thus shifting the absorption band of the closed form. By

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copolymerization of different diarylethene derivatives, multiaddressing photochromic materials were obtained.

Experimental

Chemicals and reagents: all reactions were carried out under a dry, oxygen-free argon atmosphere. Reagent-grade solvents were distilled over potassium benzophenone ketyl, under argon and stored over A3 molecular sieves. Unless otherwise specified, all reagents and catalysts were commercial (Aldrich).

1,2-Bis-(5-chloro-2-methyl-3-thienyl)perfluorocyclopentene was prepared according to the procedure reported in ref. 59.

1,2-Bis-(5-formyl-2-methyl-3-thienyl)perfluorocyclopentene (1) was synthesized following the same procedure described in ref. 37 starting from the 1,2-bis-(2-methyl-3-thienyl)perfluorocyclopentene. As an alternative, the procedure described in ref. 60 provides the same compound 1 from 1,2-bis-(5-chloro-2-methyl-3-thienyl) perfluorocyclopentene. ¹H NMR (CDCl₃): δ = 9.84 (d, *J* = 1.49 Hz, 2H, -CHO), 7.71 (s, 2H, Th-H), 2.04 (s, 6H, -CH₃).

1,2-Bis-(5-hydroxymethyl-2-methyl-3-thienyl)perfluorocyclopentene (**DTE-1**, ¹H NMR (CDCl₃): $\delta = 6.93$ (s, 2H, Th–H), 4.75 (d, J = 3.36 Hz, 4H, –CH₂), 1.90 (s, 6H, –CH₃)) and 1,2-bis-(5-*p*-hydroxymethylphenyl-2-methyl-3-thienyl)perfluorocyclopentene (**DTE-2**, ¹H NMR (CDCl₃): $\delta = 7.54$ (d, J = 8.2 Hz, 4H, –Ph), 7.38 (d, J = 8.2 Hz, Ph), 7.28 (s, 2H, Th–H), 4.71 (s, 4H, –CH₂), 1.97 (s, 6H, –CH₃)) were synthesized according to the ref. 61 and 59 respectively.

Polymerization

The general procedure to synthesise the diarylethene-based photochromic polyurethanes consists of the reaction between DTEs and 4,4'-diisocyanate dicyclohexylmethane ($H_{12}MDI$) in butyl acetate (urethane grade).

Polycaprolactone diol (average $M_n \approx 530 \text{ g mol}^{-1}$) and triol (average $M_n \approx 300 \text{ g mol}^{-1}$, 12% mol on total amount of dialohols) were also added. The relative quantity between the DTEs and other alcohols was varied, maintaining the overall stoichiometry with the diisocyanate. The reaction was catalyzed by the organometallic compound dibutyltin dilaurate (DBTL) and 1,4-diazabicyclo[2.2.2] octane (DABCO).

Once all the reactants were mixed, the batch was directly processed by spin coating (LAURELL WS-400 B-6NPP Lite) to form films through an *in situ* polymerization. The prepolymer obtained by solvent evaporation was placed in an oven at 80 $^{\circ}$ C to complete the drying process. Polymerization was then completed at 130 $^{\circ}$ C for about eight hours.

Apparatus

Raman spectra were recorded using a Nicolet NXR9650 FT-Raman (Nd-YVO4 laser at 1064 nm) with the thermoelectric cooled InGaAs detector. The resolution was set on 4 cm⁻¹ and 1024 scans were acquired.

IR spectra were recorded on films deposited on the ZnSe substrate using a Nicolet NEXUS FTIR interferometer (DTGS detector). The resolution was 1 cm^{-1} and 128 sample scans were acquired.

A Jasco 570V spectrometer was used to collect the UV-vis spectra on both solution and solid samples. The spectra of films were obtained using a bare glass slide as reference.

DSC was carried out by using a DSC SEIKO 6300, in nitrogen. For any sample, subsequent heating (from -120 °C to 140 °C, scan rate: 20 °C min⁻¹), cooling (+140 °C to -150 °C, scan rate 10 °C min⁻¹) and re-heating (-150 °C to 350 °C, scan rate: 20 °C min⁻¹) thermograms were registered.

Polymer and films

Basically, the procedure to produce the PU films consists of mixing the two components, i.e. a solution containing the diisocyanate and the other one containing the dialcohol, with the catalysts and possible additives. Among the wide choice of commercially available diisocyanates, we selected the 4,4'-diisocyanate dicyclohexylmethane (H₁₂MDI) due to its good resistance to UV irradiation. Polycaprolactone diol and triol were used in order to provide a solution with a suitable viscosity and to give the processed material good mechanical properties. Once the two main components are mixed, the polymerization starts and the solution becomes more and more viscous depending on the quantity of solvent and on the time passed after mixing. The polymerization batch was deposited on a glass substrate by spin coating. The polymerization was monitored by infrared spectroscopy (Fig. 1), that is by analyzing the change in intensity of the peculiar normal modes of vibration of the isocyanate and urethane groups.

It is well-evident that the isocyanate stretching band at 2260 cm^{-1} progressively fades during the heating process until it completely disappears and, at the same time, the bands of the urethane group increase (amide II at 1528 cm^{-1} , C–O stretching at 1231 cm^{-1} , C=O stretching at 1737 cm^{-1}) and change shape. The polymerization turned out to complete in eight hours.

Due to the addition of polycaprolactone triol, macromolecular chains result in cross-linking. It follows that the polyurethane is totally insoluble and, accordingly, no solution technique can be used to characterise (*i.e.* molecular weight) and process the material after polymerization.

Differential Scanning Calorimetry (DSC) was carried out to study the occurrence of thermal transitions and provide information on solid phases in the polyurethane. The films appear to be amorphous with a glass transition temperature at 25 °C and no melting, whereas degradation takes place over 300 °C (Fig. 2). Since photochromic dyes usually find applications as



Fig. 1 FTIR spectra of PU films on ZnSe (t1) just before the thermal treatment (blue line), (t2) after 20' of thermal treatment at 80 °C (green line), (t3) at after 8 h at 130 °C (red line).



Fig. 2 DSC curve of a PU film with the amount of polycaprolactone triol of 12% mol with respect to polycaprolactone diol (see the Experimental part).

optical devices, amorphous materials are preferred to avoid scattering phenomena which may be caused by crystalline domains.

The procedure allows one to conveniently vary the thickness of the coating (which is a relevant parameter as the thicker the film the higher the optical density) by acting on the spinning parameters and on the viscosity of the solution. As regards the latter, it depends on (i) the relative amount of the polyol, (ii) the amount of solvent (*i.e.* butyl acetate) and (iii) the time passed from the deposition of the reactants to the spinning, $t_{\rm P}$. In addition, the thickness of a spin coated film (*h*) follows the power law $h \propto \omega^{-0.5}$, where ω is the rotation speed. The thickness of the films which have been obtained by systematically varying the rotation speed and $t_{\rm P}$ are reported in Fig. 3.

Surface quality and thickness homogeneity of the films were evaluated by spectral reflectance, registering a fringe pattern in the near infrared region. For an ideal thin film, it is known that the amplitude of the fringes depends on the difference in the refractive indices between the film and the substrate. As a matter of fact, it also depends on the homogeneity and surface roughness. In the case herein studied, the amplitude of the fringes is large and almost constant with the wavelength, thus testifying to the high quality of the PU films (see the ESI[†]).

The method to develop PU coatings turned out to be very effective in producing amorphous films with a well determined thickness and good optical properties.

Diarylethene-based photochromic polyurethanes

By keeping constant the stoichiometry between isocyanate groups and hydroxyl groups, a diarylethene end-capped with hydroxyl was added and the content of polycaprolactone diol



Fig. 3 Thickness of PU films as a function of the rotation speed and of the waiting time $t_{\rm P}$.



Scheme 1 Reagents and conditions: (i) t-BuLi, -30 °C, DMF, THF; (ii) NaBH₄, 0 °C, THF; (iii) Pd(PPh₃)₄, Na₂CO₃, 4-(hydroxymethyl)phenyl boronic acid, DME-H₂O, reflux.

consequently decreased. In particular, two dithienylethenes were considered (*e.g.* **DTE-1** and **DTE-2**), which were synthesised starting from the 1,2-bis-(2-methyl-5-chloro-3-thienyl)per-fluorocyclopentene, according to Scheme 1.

Hydroxymethylthienyl and hydroxymethylphenyl were chosen instead of hydroxythienyl and phenol, respectively, as aliphatic alcohols are more reactive than aromatic ones with isocyanates.58 The two photochromic monomers differ mainly in conjugation length. Phenyl, affecting the extension of the π -conjugation, modifies remarkably the spectroscopic features (in particular UV-vis and Raman spectra). As a consequence, the two diarylethenes show a different color in the closed form, that is pink and blue for DTE-1 and DTE-2, respectively. The electronic effect of the -OH group is negligible since the functionality is spaced from the aromatic rings by a methylene: a weak inductive effect is generated by the higher electronegativity of the oxygen while no mesomeric effect results as there is not any interaction between the oxygen lone pairs and the π -electrons of the aromatic rings. The absorption maxima of the DTE derivatives as monomers in chloroform solution are reported in Table 1.

Both the diarylethene derivatives have been used to produce photochromic polyurethane coatings (PPUs).

In principle, the amount of the photochromic chromophore can be up to 1 : 1 mol : mol with respect to the isocyanate, but in order to impart proper viscosity to the solution and good optical and mechanical properties to the films it is convenient to reduce it and a portion of polycaprolactone diol was added anyway. The concentration of the photochromic species can be also expressed as a total weight percentage, which is the common run in this field.

As a representative example, herein we report the results on films with 18 wt% of photochromic alcohol, which corresponds to an equivalent molar ratio with respect to the isocyanate moles of 29.7% for **DTE-1** and 22.6% for **DTE-2**. Actually, good PPU films with a content of photochromic dye up to 50 wt% have been obtained.⁶²

The photochromism of the chromophore was retained after polymerization: upon irradiation with UV light (254 nm), the colorless polyurethane film obtained with the **DTE-1** in the open form (**PPU-1**) turns pink (Fig. 4). The conversion between the coloured and uncoloured forms is fully reversible.

The UV-vis spectra recorded at different irradiation times (Fig. 4a) are characterised by a strong change in absorption with a clear isosbestic point at 313 nm.

Table 1 Absorption maxima of the DTE monomers in chloroformsolution and the corresponding PPU films. For the closed form, the molarextinction coefficient (ε) is also reported

	$\lambda_{\rm max}$ open/nm		$\lambda_{max} \operatorname{PSS}^{a}/\operatorname{nm}$ and $\varepsilon/\operatorname{M}^{-1}\operatorname{cm}^{-1}$			
Molecule	Sol. (CHCl ₃)	Film PU	Sol. (CHCl ₃)		Film PU	
DTE-1			517	5700	521	5000
DTE-2	283	288	590	11 000	592	9500
^a PSS: pho	tostationary state	a				

A very slight shift of the absorption band of the coloured form occurs when **DTE-1** is part of the main chain of **PPU-1** (see Table 1), thus indicating that the structure of the chromophore is almost unperturbed by the polymer chains and solvatochromism is negligible.

Since the polyurethane coating is not soluble due to the crosslinking, solution techniques which are currently used to determine the conversion at the photostationary state (PSS) cannot be applied. Nevertheless, a good method consists of the comparison of the absorption coefficients at the PSS of the DTE monomer in solution and PPU as a film.

Regarding the latter, the linear fitting of the absorbance A of films of different thicknesses gives the absorption coefficient of the PSS e:

$$A = eD \tag{1}$$

where D is the film thickness.

The absorption coefficient e can be related to the molar absorption coefficient ε as follows:

$$\varepsilon = \frac{100eM_{\rm Ph}}{{\rm wt}^0\!\!\circ\!\rho} \tag{2}$$

where $M_{\rm Ph}$ is the molar mass of the photochromic monomer, wt% its concentration in the film, and ρ the density of the film.

Before discussing our specific case, it is worth reminding that there are fundamental differences when photochromism of diarylethene in solution and in the solid state is compared. In solution, the fast interconversion between the parallel and antiparallel conformers of the uncoloured form allows large conversions to be reached at the photostationary state (PSS) under UV illumination. Generally, the lack of mobility of the chromophores in the solid state limits the maximum conversion to a lower value, which depends on the content of the photoactive conformer. Processing from solutions containing the closed form allows this issue to be solved as the photo-induced ring opening of the solid state material affords only the photoactive C_2 species.

According to the method discussed above (*i.e.* eqn 1 and 2), PPU films with thicknesses ranging from 0.5 to 4.0 microns have been produced, and photoconversion under UV illumination was measured by means of UV-vis spectroscopy, until reaching the photostationary state. Results for **PPU-1** are reported in Table 1 and compared with **DTE-1** in chloroform solution.

The similarity between the two values indicates a large photoconversion at the PSS even in the solid state (assuming no solvatochromic effects on the intensity of the bands). As the photochromic monomer has been polymerised starting from its open form, two possible hypotheses can explain this result: (i) the free volume of the polyurethane is large enough to enable isomerization of the two conformers in the open form, or (ii) insertion of the dithienylethene units in the growing



Fig. 4 (a) UV-vis spectra of PPU-1 upon different UV light exposures (254 nm); (b) IR spectra of the coloured (pink line) and uncoloured forms (black line); (c) Raman spectra of the same two states.

The IR spectra of PPU-1 in its coloured and uncoloured states (Fig. 4b) are normalized to the CH stretching bands (2800-3100 cm⁻¹), since they do not show any change in intensity upon photoisomerization. By looking at the fingerprint region (1600-800 cm⁻¹), the spectra are dominated by the bands ascribed to the vibration of the perfluorocyclopentene ring⁴⁰ and by the bands of the urethane group. The differences between the coloured and uncoloured forms are small. This result is not surprising as in this diarylethene there is not any polar group directly linked to the π backbone of the molecule which can be affected by the increment in conjugation that occurs by photoisomerization, thus enhancing the IR intensity.¹⁰ Nevertheless, focusing the attention to the spectral region between 970 and 990 cm⁻¹, some modifications of the spectral features come from the photochromic process. The band at 985 cm⁻¹ in the open form, which is related to the normal mode of vibration involving the bending/stretching of the perfluorinated ring with a weak coupling with the other part of the molecule, moves to 969 cm⁻¹. This shift results from the fact that in the closed form, which is characterised by a more rigid structure, a strong coupling with the methyl groups in α position of the thienyl rings takes place.⁶³ Such bands could be conveniently used to measure the degree of conversion of the photochromic moiety upon irradiation.

As regards the Raman spectra, larger changes have been expected if compared to IR spectra, since the Raman intensity is strongly dependent on the extension of the π -conjugation.⁶⁴ In the open form, the Raman spectrum is dominated by the CH stretching bands, but the overall intensity of the spectrum is weak (Fig. 4c). In the closed form a few new bands appear, in particular a sharp intense band at 1540 cm⁻¹ which is assigned to the

cooperative in-phase stretching of the CC double bonds of the conjugated structure.

The same methods were used to characterise the polyurethane films containing **DTE-2** monomer unit (**PPU-2**) and the spectra are reported in Fig. 5. Upon irradiation with UV light at 366 nm, the uncoloured film turns into a deep blue, with a band in the visible region at 592 nm (Fig. 5a). If compared with **PPU-1**, the red-shift of **PPU-2** is obviously due to the presence of the phenyl group which enhances the conjugation, especially in the closed form. The isosbestic point is also apparent at 313 nm. Also for **PPU-2**, similar values of the absorption coefficients both for **DTE-2** in solution and the corresponding polymer in the solid state (see Table 1) indicate large photoconversion at the PSS.

Similar features between the two forms result from the infrared spectroscopy, as there is not any IR active groups which can be enhanced by the conjugation change which occurs upon photoisomerization (Fig. 5b). Focusing the attention to the region 970-990 cm⁻¹, we still find the shift of the peak at 988 cm⁻¹ to 977 cm⁻¹, going from the open to the closed form. An interesting difference in the IR spectrum is the shoulder that appears at 1496 cm⁻¹ in the closed form, which is related to the cooperative stretching of the CC double bonds that acquires a little bit of intensity from the extension of π -conjugation and also varies its position in wavenumbers, as usually occurs for conjugated molecules.⁶⁴ A very large Raman intensity for this normal mode is then expected in the coloured state. By looking at the Raman spectra in the region 1000-1800 cm⁻¹, a strong enhancement of the Raman intensity really occurs in the coloured form (Fig. 5c). This enhancement is a known feature of diarylethenes,⁶⁵ as the photocyclization leads to an increase of π -conjugation which turns into an overall increment of the intensity of the Raman spectrum. Actually, the band at 1496 cm⁻¹ is one of the two most



Fig. 5 (a) UV-vis spectra of PPU-2 upon different UV light exposures (366 nm); (b) IR spectra of the coloured (blue line) and uncoloured forms (black line); (c) Raman spectra of the same two states.



Fig. 6 Normalized absorbance during fading illumination at 532 nm of a 3.45×10^{-5} M, 2 ml CHCl₃ solution of **DTE-2** (solid line) and **PPU-2** film of 8 microns, 18 wt% of **DTE-2** content (dashed line).

intense bands of the Raman spectrum, as just predicted. The other one (1514 cm^{-1}) is due to a different combination of conjugated CC stretching normal modes.

Finally, a photochromic polyurethane coating and the homologous monomer in solution in their coloured form were irradiated at 532 nm with the same nominal power to mol of chromophores in order to analyse how the conversion rate is affected by the aggregation state of matter. The number of molecules considered during irradiation corresponds to (i) the total amount of chromophore in solution, the liquid state allowing the mixing of the medium during light exposure, (ii) to the concentration of the chromophore multiplied by the illuminated volume in the solid state (*e.g.* a circle with a diameter of 3 mm illuminated with light beam of uniform intensity).

The rate of change in absorbance with time is almost the same for the polyurethane in the solid state and the photochromic monomer dissolved in chloroform (Fig. 6), thus confirming that the photochromic monomeric units linked in the polyurethane chain have molecular mobility large enough to effectively switch by means of light irradiation. To sum up, we have shown how a versatile polymerization route is effective in producing photochromic high quality optical films where the film thickness can be varied by acting on the solution properties (*i.e.* viscosity) and on the processing parameters (*i.e.* rotation speed), and photochromism can be conveniently tuned by using different hydroxyl end-capped diarylethenes. No strong differences in photochromism resulted from the diarylethene monomer in solution to the photochromic polyurethane, thus indicating that the polymer material in the solid state provides to the photochromic moiety a free volume large enough to enable photoisomerization.

A multistate photochromic polyurethane

By following the same synthetic procedure different DTE derivatives can be mixed together thus affording the opportunity of a fine tuning of the photochromism and of the spectroscopic features to give a multiple switch. Indeed, if the UV-vis absorption spectra of two diarylethene moieties are different enough, it is possible to address four different states, namely open–open (o–o), open–closed (o–c), closed–open (c–o), and closed–closed (c–c). **DTE-1** and **DTE-2** fulfil this basic requirement and they have been copolymerized to form a multi-addressable switch (**PPU-1/2**), as reported in Fig. 7.

Two different copolymers have been synthesised, with a weight ratio of **DTE-2** : **DTE-1** equal to 1 : 2 (**PPU-1/2-a**) and 1 : 5 (**PPU-1/2-b**), which corresponds to a molar ratio of 2.1 : 5.6 and 1 : 7, respectively. Polycaprolactone was added to reach the overall stoichiometry –NCO : –OH of 1 : 1. The optical quality, as well as the thickness, was similar to that obtained by polymerizing only one DTE derivative.

Starting from the o-o state (where the first term represents the state of the **DTE-1** moiety and the second term is the state of **DTE-2**), the c-c state was obtained by exposing the film to UV light (254 nm). Upon irradiation with visible light (wavelength longer than 650 nm) the c-c state converted into the c-o state.



Fig. 7 Scheme of the four states from PPU-1/2; on the right the superimposition of the UV-vis spectra of the open and closed forms of the single component PPU-1 and PPU-2.



Fig. 8 UV-vis spectra of the four states in the **PPU-1/2-a** film, using a bare glass substrate as a reference (o–o: black line; c–o: pink line; o–c: blue line; c–c: purple line). Inset: pictures of the film in the four different states.

The o-c state was reached upon irradiation of the o-o state with UV light at 366 nm. Illuminating the c-c, c-o, and o-c states with visible light in the range 500–600 nm, the o-o state was restored. The UV-vis spectra of **PPU-1/2-a** in its four states are reported in Fig. 8. The analysis of the spectra shows that the four states are clearly different, with the c-o and o-c characterised by the absorption of the single component **PPU** and the c-c state with a structured band. The shape of this band can be easily tailored by changing the illumination conditions, *i.e.* changing the relative conversion of the two photochromic moieties.

By looking at the IR spectra (Fig. 9a), the differences between the states are limited, as previously discussed for the single component films (see Fig. 4b and 5b). By the way, the region between 900 and 1000 cm⁻¹ which is sensitive to the structure of the photochromic unit offers the possibility to distinguish the four states anyway. Moreover, as noticed in the UV-vis analysis, the bands of 969 and 977 cm⁻¹ which are ascribed to the closed forms of **DTE-1** and **DTE-2**, respectively, are more or less equivalent. This means that the intensity of the normal mode for the blue form is probably larger than the intensity of the pink form. The changes are small in intensity, due to the weakness of the considered bands.

Completely different are the features of the Raman spectra of the polyurethane films containing both the diarylethene derivatives, **PPU-1/2-a** (Fig. 9b).

Herein, the changes are not balanced. When the **DTE-2** moiety is in the closed form, it dominates the Raman spectrum and the differences between the two states which differ from the isomeric form of the **DTE-1**, namely o–c and c–c, are really small. Just a shoulder at approximately 1545 cm⁻¹ can be detected. This is clearly due to the larger π -conjugation change that occurs upon photoirradiation in the case of the blue moiety if compared to the pink one. Moreover, the differences in Raman spectra between the o–o and o–c states are limited just to the weak band that appears at 1545 cm⁻¹.

A new set of films have been obtained with a ratio between the two diarylethenes of 1 : 5, keeping the total concentration of the photochromic alcohol equal to 18% (**PPU-1/2-b**). The optical quality was good, as expected. The characterization has been carried out as described before for **PPU-1/2-a**, and four states can be addressed again.

The large excess of **DTE-1** if compared to the other diarylethene is well-evident by the UV-vis spectra (Fig. 10a), especially for the c–c state. Indeed, the band in the visible region is clearly asymmetric with the same absorption maximum of the film which contains only the pink unit (**PPU-1**), but slightly broader.

While IR spectra will not be discussed further, since the differences between the open and closed forms are small, Raman spectroscopy shows that the four states can be actually distinguished, being characterised by strong changes in intensity (Fig. 10b).

The Raman spectrum of the o-o state is characterised by very weak intensities over the entire range, both the diarylethene moieties being in the non-conjugated open form. An intermediate situation occurs when only one diarylethene is converted into the closed form, so that just a strong signal results from the conjugated coloured form of a single diarylethene (*i.e.* the band at 1540 cm⁻¹ for the c-o state and the two bands at 1514 and 1496 cm⁻¹ for the c-o state). The large excess of **DTE-1** in the **PPU-1**/**2-b** allowed to make well evident the feature of its closed form, thus making up for the weak absolute intensity of the band due to the limited π -conjugation.

Raman based readout: a setup proposal

According to the results obtained with a 5 : 1 ratio between the two photochromic moieties, the four states are clearly distinguishable in the Raman spectrum. It is then possible to conceptually develop a "safe" readout system based on Raman signal, if no absorption of the excitation line source occurs (for example 1064 nm, as in the FT-Raman). The idea is to design a reliable system which does not require the registration of the whole



Fig. 9 (a) FTIR spectra of the four states of PPU-1/2-a in the region $950-1000 \text{ cm}^{-1}$; (b) Raman spectra of the same four states (o-o: black line; c-o: pink line; o-c: blue line; c-c: purple line).



Fig. 10 (a) UV-vis spectra of the four states in the **PPU-1/2-b** film, using a bare glass substrate as a reference; (b) Raman spectra of the four states of **PPU-1/2-b** in the region 1700–1000 cm⁻¹ (o–o: black line; c–o: pink line; o–c: blue line; c–c: purple line).



Fig. 11 Scheme of the simple readout process based on the Raman signal.

Raman spectrum that may be experimentally complex (Fig. 11). The setup would consist of a shortpass multilayer filter with a sharp transition at 1270.2 nm. Indeed, this wavelength corresponds to a Raman shift of 1525 cm⁻¹ which is in between the intense bands of the two photochromic moieties (1514 and 1540 cm⁻¹). The reflected signal ($\lambda < 1270.2$ nm) consists mainly of the Raman scattering of the **DTE-2** moiety, whereas the transmitted one will consist mainly of **DTE-1**.

The two signals will be detected by using two photodiodes and the four states are determined by a comparison of the two signals according to Table 2.

 Table 2
 Detection of the four memory states according to the signals read by the two photodiodes

State	Photodiode 1 signal	Photodiode 2 signal		
00	No	No		
OC	No	Yes		
CO	Yes	No		
CC	Yes	Yes		

It is worth noting that the readout is simply based on the presence or absence of signals to the photodiodes and not on the intensity. This approach can be further improved by designing photochromic molecules with larger separation of the intense Raman bands in order to relax the constrain of the filter.

Conclusions

Photochromic polyurethane films which are characterised by good optical quality and effective light-triggered switching have been produced by a catalyzed in situ polymerization between 1,2dithienvlethenes end-capped with hydroxyl groups and 4,4'-diisocyanate dicyclohexylmethane. The method is very versatile, as it allowed the content of the photochromic moiety to be varied over a wide range. A fine tuning of the spectroscopic features has been obtained by conveniently changing the molecular structure of the diarylethene derivative, that is the π -conjugation, or by copolymerizing different diarylethenes and varying the molar ratio. Following this last approach, a multistate switching system has been developed by using two diarylethene derivatives with the absorption bands of the closed forms different enough to address and distinguish four states by UV-vis light. Moreover, the correct relative content between the two photochromic moieties allowed Raman spectroscopy to be used to distinguish the four states. With a proper choice of the excitation line, far from the absorption band of the material, this method can be used as a non-destructive readout in rewritable optical memories. A simple scheme based on a band pass multilayer filter is proposed.

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