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Photochromic cooligomers from pyridazinespirodihydroindolizine and styrene

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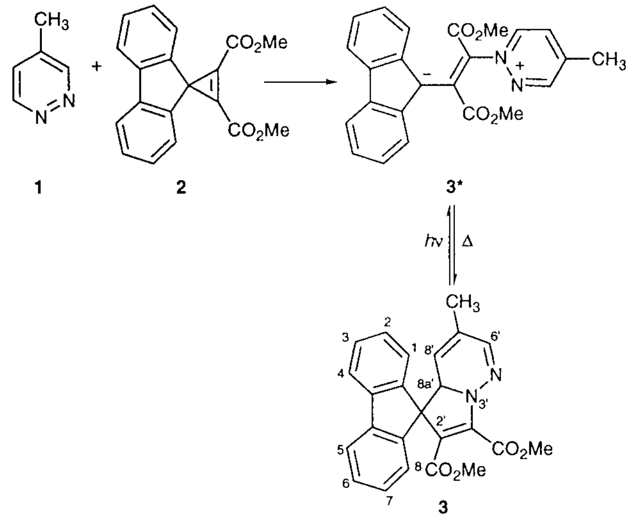
New cooligomers **5** of styrene and 4-vinylpyridazine have been prepared by the controlled free radical polymerization technique. The addition of spirocyclopropene has led to cooligomers **6** in which the pendant pyridazine subunits are transformed into photochromic spirodihydroindolizines. Characterisation by NMR and SEC was carried out with **5** and **6**. Molecular masses (M) of **5** and **6** have been found to be in the range of oligomers. Studies by UV–VIS-spectroscopy have shown the photochemical properties of **6** and of the reference compound **3**. The absorbance of **6** is similar to that of **3**. The fatigue resistance ($Z_{80} = 4$–10) of the cooligomers **6** shows **6** to be more stable than **3**. The half life of the cooligomers **6** was found to be (100 ± 20 s).

For optical applications, *photochromic substances* are normally embedded in polymers in which they are dispersed by intermolecular forces.[1] However for better control of their incorporation, it might be useful for some applications such as dental surgery[2,3] to graft the photochromic molecules by covalent links, and it was shown that a short spacer between the photochromic antenna and the polymer backbone was desirable. Such direct linkage has been demonstrated particularly with spiropyrans, spirooxazines and fulgides, having normally rather long, and flexible spacers.[4–6] During our study in the field of spirodihydroindolizines (denoted DHI)[2,7–11] and related compounds, which by molecular tailoring could be used to produce a wide range of different photochromic properties, attempts to polymerise derivatives of DHI using the classical free radical initiation techniques in solutions have led to photochromic polymers, whose structures are not clearly defined. Owing to the reactivity of DHIs with free radicals, part of these photochromic molecules may be degraded during the process.

Different synthetic routes have been reported for the DHIs, reaction of an azaheterocycle, such as pyridine, with an appropriate spirocyclopropene derivative, as depicted in Scheme 1, being the most employed.[2,7–9] Thus, a two-step procedure, *i.e.* copolymerization of vinylpyridine and styrene followed by reaction with a spirocyclopropene was considered to build well characterized photochromic oligomers, and preliminary successful results were reported earlier.[12] A preceding extensive study of DHIs has shown that the lifetime of the coloured form in solution is much longer for those which contain a *pyridazine* skeleton than those having a *pyridine* subunit.[2,7–9] Therefore, in order to improve the colouring properties and the photostability of these materials, we used 4-vinylpyridazine to prepare new photochromic oligomers. Here we report the synthesis, the structure, and the spectroscopic and photochromic properties of the new substances.



Scheme 1 Preparation of the reference compound (DHI) **3**; **3*** is the zwitterionic open form (betaine).

Experimental

Instrumentation

Mps were taken with a hot stage microscope (Gallenkamp MFB-595) and are uncorrected. For Size Exclusion Chromatography (SEC) (Spectraphysics P100) the samples were dissolved in THF. Calibration of SEC was carried out with Etalon (Toyo Soda MFG. CO. LTD, Standard polystyrene). Irradiation for photophysical measurements were achieved with a UV-lamp (2×8 W, $\lambda = 254$ or 366 nm). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC 250 instrument. The UV/VIS spectra were recorded with a Hitachi U-3300 spectrophotometer. The samples were degassed by the freeze–pump–thaw technique using a secondary vacuum pump (10^{-6} Torr) and the tubes were sealed. No elemental analysis was taken for the cooligomers.

Materials

All solvents were distilled before use, except the spectroscopic grade solvents.

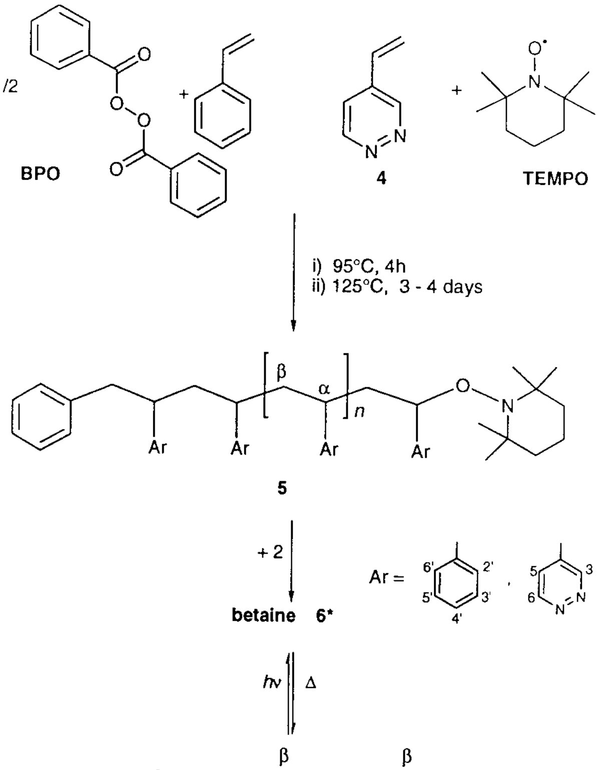
Spirodihydroindolizine (DHI) 3. 4-Methylpyridazine **1** (94.1 mg, 1 mmol) was reacted with the known 2′,3′-bis(methoxycarbonyl)spiro[fluorene-9,1′-cycloprop-2′-ene] **2** (306.3 mg, 1 mmol) in ether at ambient temperature[13,14] (see Scheme 1), and was purified by column chromatography on a silica gel column with CH_2Cl_2 as eluent, providing DHI **3** as a yellow-green powder, mp 106 °C;[13] yield: 43 mg (11%); $\lambda_{max}(CH_2Cl_2)$ 383.0 nm (log ε 3.97); δ_H(250 MHz) 7.73 (d, 2H, H-4,5), 7.57–7.20 (m, 6H, H-fluorene), 6.81 (d, 1H, H-6′), 5.24 (t, 1H, H-8a′), 4.70 (d, 1H, H-8′), 4.03 (s, 3H, 3′-

CO_2CH_3), 3.31 (s, 3H, 2′-CO_2CH_3) and 1.59 (s, 3H, CH_3) ppm; δ_C(62.9 MHz) 141.9, 128.5, 128.2, 127.8, 127.2, 126.6, 124.8, 123.6, 120.7, 120.1, 119.8, 65.7, 53.4 (C spiro), 51.2 and 18.1 ppm; IR(KBr) 3040, 2960, 1750 (C=O), 1700 (C=O) cm^{-1}; *m/z* 401 (25%, $M^+ + 1$), 400 (100, M^+), 341 (33, $M^+ - CO_2CH_3$), 247 (50), 59 (25); Found: C, 71.84; H, 5.08; N, 6.88. $C_{24}H_{20}N_2O_4$ requires C, 72.00; H, 5.03; N, 7.00%.

Preparation of cooligomers 5

A 50 ml three necked tube containing a mixture of the monomer 4-vinylpyridazine **4** which was prepared according to a described procedure,[15] styrene (**St**) and the starter molecules BPO (benzoyl peroxide) and TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) was evacuated with a pump and flushed with nitrogen. The mixture was then heated under nitrogen at 95 °C for 4 h, the temperature being subsequently increased to 125 °C and maintained for 4 days (Scheme 2). After cooling to ambient temperature, the crude product was dissolved in methylene chloride and ether was added in excess. The precipitate formed was filtered. After repeating this procedure three times the solvent was evaporated and cooligomers **5** were dried under vacuum.

Copolymer 5a. Ochre coloured powder, mp 175 °C; yield: 440 mg (13%); M_n 750 g mol^{-1}, PD 1.19; $\lambda_{max}(CH_2Cl_2)$ 388.0 nm; δ_H(250 MHz) 9.2–8.6 (1H, H-6), 8.6–8.1 (1H, H-3), 7.3–6.8 (3H, H-3′-5′), 6.8–6.1 (3H, H-2′,6′,5) and 2.3–1.2 (3H, H-α,β) ppm; δ_C(62.9 MHz) 151.1 (C-3,6), 128.6 (C-3′,5′), 127.4 (C-1,2′,6′), 40.7 (C-α) and 38.1 (C-β) ppm; ratio (**4**/**St**) = 49/51.



Scheme 2 Synthesis of the cooligomers **5** and then photochromic cooligomers **6** using the 'controlled free radical' polymerization technique. **6*** is the zwitterionic open form.

Copolymer 5b. Ochre coloured powder, mp 160 °C, yield: 680 mg (23%); M_n 1925 g mol^{-1}, PD = 1.66; $\lambda_{max}(CH_2Cl_2)$ 390.0 nm; δ_H(250 MHz) 9.1–8.5 (1H, H-6), 8.5–8.1 (1H, H-3), 7.2–6.8 (3H, H-3′-5′), 6.7–6.1 (3H, H-2′,6′,5) and 2.4–1.3 (3H, H-α,β) ppm; ratio (**4**/**St**) = 27/73.

Copolymer 5c. Ochre coloured powder, mp 156 °C, yield: 450 mg (23%); M_n 1075 g mol^{-1}, PD = 1.64; $\lambda_{max}(CH_2Cl_2)$ 390.0 nm; δ_H(250 MHz) 9.2–8.6 (1H, H-6), 8.6–8.0 (1H, H-3), 7.5–6.6 (3H, H-3′-5′), 6.9–6.1 (3H, H-2′,6′,5) and 2.4–1.2 (3H, H-α,β) ppm; ratio (**4**/**St**) = 36/ 64.

Preparation of the photochromic cooligomers 6

The DHI cooligomers **6** were prepared according to the procedure described for the DHI monomer **3**. The appropriate copolymer **5** was dissolved in distilled methylene chloride and 2′,3′-bis(methoxycarbonyl)spiro[fluorene-9,1′-cycloprop-2′-ene] **2** was added. The solutions were stirred in a dark tube under nitrogen at ambient temperature for a few days to produce polymers **6**, as shown in Scheme 2, which were purified by precipitating the solutions in ether to result in an ochre powder.

Photochromic copolymer 6a. Beige powder, mp 263 °C, yield: 120 mg; M_n 2908 g mol^{-1}, PD 1.30; $\lambda_{max}(CH_2Cl_2)$ 390.5 nm; δ_H(250 MHz) 8.1–5.7 (15 H, H-1–8,6′, H-2″-6″ and H-5‴) [7.74 (2H, H-4,5), 7.39 (H-3,6), 7.07 (H-3″,5″)], 5.6–4.5 (2H, H-8′,8a′), 4.3–3.7 (3H, 3′-CO_2CH_3), 3.6–3.0 (3H, 2′-CO_2CH_3) and 2.1–0.7 (3H, H-α,β) ppm; DHI-units: >95% (calculated: 100%).

Photochromic copolymer 6b. Beige powder, mp 238 °C, yield: 90 mg; M_n 4032 g mol^{-1}, PD 1.55; $\lambda_{max}(CH_2Cl_2)$ 390.5 nm; δ_H(250 MHz) 7.9–5.7 (15 H, H-1–8,6′, H-2″-6″ and H-5‴) [7.73 (2H, H-4,5), 7.34 (H-3,6), 7.06 (H-3″,5″)], 5.3–4.5 (2H, H-8′,8a′), 4.3–3.7 (3H, 3′-CO_2CH_3), 3.5–3.0 (3H, 2′-CO_2CH_3) and 2.2–0.5 (3H, H-α,β) ppm; DHI-units: >95% (calculated: 100%).

Photochromic copolymer 6c. Beige powder, mp 242 °C, yield: 130 mg; M_n 2393 g mol^{-1}, PD 1.35; $\lambda_{max}(CH_2Cl_2)$ 389.5 nm; δ_H(250 MHz) 8.0–5.7 (15 H, H-1–8,6′, H-2″-6″ and H-5‴) [7.73 (2H, H-4,5), 7.35 (H-3,6), 7.07 (H-3″,5″)], 5.4–4.5 (2H, H-8′,8a′), 4.3–3.7 (3H, 3′-CO_2CH_3), 3.6–3.1 (3H, 2′-CO_2CH_3) and 2.3–1.0 (3H, H-α,β) ppm; DHI-units: >95% (calculated: 100%).

Photochromic copolymer 6d. Beige powder, mp 205 °C, yield: 110 mg; M_n 2026 g mol^{-1}, PD 1.35; $\lambda_{max}(CH_2Cl_2)$ 389.5 nm; δ_H(250 MHz) 9.3–8.1 (2H, H-3‴,6‴), 8.0–5.7 (15 H, H-1–8,6′, H-2″-6″ and H-5‴), [7.71 (2H, H-4,5), 7.35 (H-3,6), 7.08 (H-3″,5″), 6.58 (H-2″-6″ and H-5‴)], 5.6–4.6 (2H, H-8′,8a′), 4.2–3.6 (3H, 3′-CO_2CH_3), 3.5–3.1 (3H, 2′-CO_2CH_3) and 2.1–0.8 (3H, H-α,β) ppm; DHI-units: 40% (calculated: 50%).

Results and discussion

For the reasons indicated in the introduction, the strategy adopted was first to polymerise the vinylpyridazine and to form the DHI subunits in the second stage. In order to avoid possible congestion owing to the bulk of DHI, it was deemed preferable to prepare a copolymer 'styrene/4-vinylpyridazine'. In order to get the minimum polydispersity (PD) of molecular weights, the recent controlled free radical polymerization technique using benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was implemented according

Table 1 Composition (estimated by ^{1}H-NMR), yields and SEC data of cooligomers **5**

	Ratio (TEMPO/ BPO)	Starting ratio (**4**/**St**)	Observed ratio (**4**/**St**)	M_n, theor./ g mol^{-1}	M_n, exp./ g mol^{-1}	Yield [%]	PD
5a	1.51	30/70	49/51	60 000	750	13.3	1.19
5b	1.67	20/80	27/73	60 000	1925	23.0	1.66
5c	1.24	20/80	36/64	30 000	1075	23.0	1.64

to Georges *et al.*[16] In the first step, **4**, styrene and the starters BPO and TEMPO are heated in a degassed tube under nitrogen at *ca.* 95 °C without solvent (see Experimental section for details). At this temperature, BPO is decomposed and the resulting phenyl radicals react with one of the monomers, the newly formed free radical is immediately trapped by TEMPO [17] and the mixture is then heated at 125 °C for several days (*ca.* 120 h) which allows other monomers to be incorporated. This process allows the initial formation of all growing chains and affords relatively low polydispersity. Compound **3** was prepared as a standard in order to compare its structural and photochromic properties with those of the cooligomers.

Variation of the monomer ratio **4**/**St** (see Scheme 2) allows the preparation of different cooligomers **5a**–**c**. The yields are shown in Table 1. The chemical yield was low and dependent on the TEMPO/BPO ratio. The pyridazine subunit content was found to be higher in the product than in the starting materials.

Characterization of cooligomers 5 and 6

The ^{1}H-NMR data of 4-vinylpyridazine **4** are given in Table 2 as a reference to establish the structure of the cooligomers. They clearly show the downfield shift of protons H-3 and H-6, centred at 9.08 and 9.01 ppm respectively, which are *ortho* to the –N=N– group. Proton H-5 appears at 7.32 ppm, *i.e.* in the range of the styrene aromatic proton signals (7.5–7.1 ppm).

^{1}H-NMR spectra of polymers show broad signals as a result of the influence of surrounding aromatic rings on each proton. ^{1}H-NMR spectra of **5** have been recorded in $CDCl_3$ and their assignment studied by the 2D analysis. This is illustrated for **5a** in Fig. 1 (see also Table 2). An important feature is the presence of broad signals in the 8.2–9.2 ppm range which are characteristic of H-3 and H-6 (the chemical shifts are inverted in comparison with the monomer). The aliphatic protons appear at 1.3–2.4 ppm. Unexpectedly, no signal for the protons of TEMPO could be detected probably because the termination process involves self-proportionation or coupling.

Table 2 ^{1}H-NMR data of **4**, styrene and cooligomers **5** in δ [ppm]

	H-6	H-3	H-3′-5′	H-2′,6′,5	H-α	H-β
4-Vpz **4**	9.01	9.08	—	7.32	6.54	6.01, 5.56
Styrene	—	—	7.5–7.1		6.65	5.67, 5.15
5a	9.2–8.6	8.6–8.1	7.3–6.8	6.8–6.1	2.3–1.2	
5b	9.1–8.5	8.5–8.1	7.2–6.8	6.7–6.1	2.4–1.3	
5c	9.2–8.6	8.6–8.0	7.5–6.9	6.9–6.1	2.4–1.2	

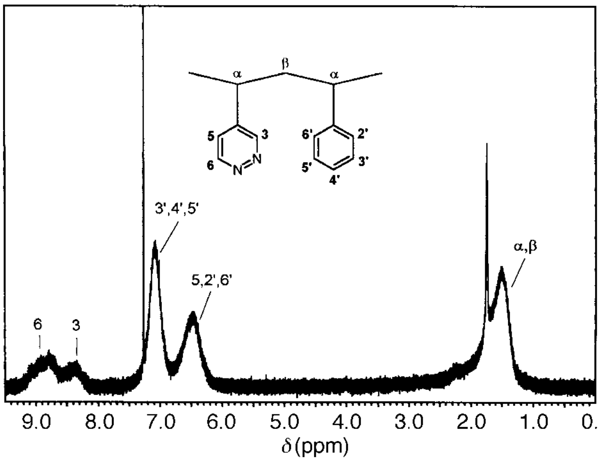


Fig. 1 ^{1}H-NMR spectrum of **5a** in $CDCl_3$; the assignments are based on a 2D ^{1}H-^{1}H TOCSY spectrum (Bruker, 250 MHz).

^{1}H-NMR spectra of **6** have been recorded in the same manner as **5**. The assignment rests on comparison of the chemical shift range with the data known for monomers (see Table 3). A spectrum is shown in Fig. 2 (see also Table 4) from which it is clear that there is partial formation of DHI in the copolymer (**6d**); the signals intensity for H-3‴ and H-6‴ allow a crude estimation of 40% of DHI and 60% of pyridazine subunits. For the other cooligomers **6a–c** there is no pyridazine subunit left unreacted within the limit of errors ($\approx$5%). The ^{13}C-NMR gave no further clarification for the assignment or the determination of monomers because the signal to noise ratio was found to be too low.

The molecular mass (M_n) and the polydispersity (PD) of the cooligomers **5** and **6** have been determinated by size exclusion chromatography (SEC). The values of M_n and PD for the cooligomers **5** are listed in Table 1. The conversion rate of these reactions was less than 5%. Molecular masses less than 2000 g mol^{-1} point to the presence of *oligomers*. The origin of this small conversion might be attributed to 4-vinylpyridazine **4** because former studies on copolymerization with 4-vinylpyridine or pure polymers on styrene basis by ‘controlled free radical polymerization’ led to conversions of about 30%[12] but the reasons for the small molar masses obtained are not clear at the moment. Polydispersity (PD) values are in the range 1.0–2.0, typical for this polymerization technique; however they should be improved. The SEC data of the photochromic cooligomers **6** are listed in Table 3. The M_n values are between 2000 and 4100 g mol^{-1}.

Table 3 shows the percentage of the (expected) theoretical photochromic (pc) subunits and the obtained photochromic subunits in the polymers **6**. For instance, 100% of theoretical photochromic subunits means that all the pyridazine groups in the polymer should react with the spiro alkene added in a stoichiometric amount. In all cases studied, more than 80% of the pyridazine groups were transformed into photochromic subunits.

Photophysical and photochromic properties

The UV–VIS spectra of the cooligomers **5**, the photochromic cooligomers **6** and the DHI **3** (reference) were studied in methylene chloride solutions. The concentrations were taken between 10^{-4} and 10^{-5} mol l^{-1} depending on the validity of the Lambert–Beer law. The spectrum of DHI **3** is shown in Fig. 3.

All cooligomers **5** exhibit a shoulder at $\lambda = 390$ nm and a maximum at $\lambda = 317$ nm. The monomeric reference DHI (**3**) has an absorption at $\lambda = 383$ nm in its closed form. After irradiation with the UV-lamp for 3 min another absorption appears at $\lambda = 534$ nm for the open form (Fig. 3). It should be noted that this spectrum is a superposition of the closed and open form in the photochemical equilibrium established between an ultra fast photochemical opening and a fast thermal cyclization (*vide infra*).

All photochromic cooligomers **6** have an absorption at $\lambda =$

Table 3 SEC data and repartition of photochromic subunits in the cooligomers **6**

	Starting material	M_n, exp/ g mol^{-1}	PD	Theoretical pc units (calc) [%]	^{1}H-NMR signal in 9.2–8.0 ppm	Obtained pc^a units (exp) [%]
6a	**5a**	2900	1.30	100	–	>95
6b	**5b**	4050	1.55	100	–	>95
6c	**5c**	2400	1.35	100	–	>95
6d	**5c**	2050	1.35	50	+	40

^{a}The experimental % yields are based on NMR determination which lacks accuracy (see Fig. 2).

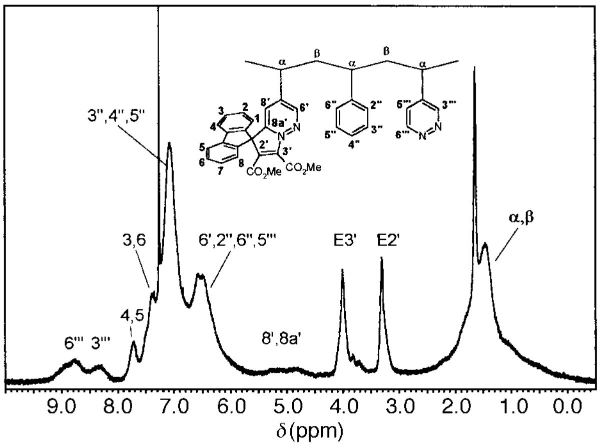


Fig. 2 ^{1}H-NMR spectrum of the photochromic cooligomer **6d** in $CDCl_3$.

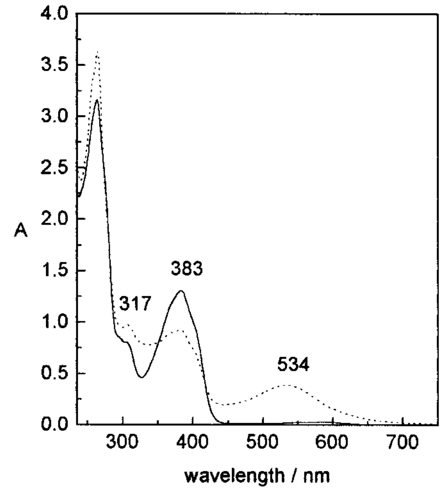


Fig. 3 Electronic absorption spectrum of the reference DHI (**3**) in CH_2Cl_2 in its closed (—) and open coloured (···) (Betaine) forms at ambient temperature, conc. $\cong 1.4 \times 10^{-4}$ M.

Table 5 UV–VIS data, fatigue resistance (Z_{50} and Z_{80}) and half life of the 1,5-electrocyclization of the reference **3** and the photochromic cooligomers **6**

	Closed form	Betaine				
	λ_{max}/ nm	λ_{max}/ nm	Z_{50} (Z_{80})	$t_{1/2}$/ s	τ^a/s (β)	Solvent
3	383	534	6 (2)	99	CH_2Cl_2	
6a	391	539	>10 (5)	91	102 (0.80)	CH_2Cl_2
6a	390	537	>10 (10)	124	149 (0.85)	THF
6b	391	540	>10 (5)	75	87 (0.80)	CH_2Cl_2
			>10 (10)			CH_2Cl_2 degassed
6b	389	541	>10 (10)	85	91 (0.90)	THF
6c	390	539	>10 (7)	114	167 (0.83)	CH_2Cl_2
6d	390	534	8 (4)	111	128 (0.77)	CH_2Cl_2

^{a}Fitted using eqn. (1).

390 nm in the closed form coming from the DHI units but slightly red shifted; the tail of the band is at the origin of the ochre colour of the cooligomers **6**. The former maximum of the reference monomer at $\lambda = 317$ nm appears only as a small shoulder at $\lambda = 310$ nm. The spectra were not found to be structured enough to determine the proportion of DHI subunits in the cooligomers **6**. After irradiation with the UV-handlamp for 3 min the spectra of the open form could be recorded. The spectra also show the superposition of the open and closed forms. All betaines have an absorption at about $\lambda = 539$ nm responsible for the red colour of the solutions. In THF, in the same concentration range, the UV spectra show no significant change, compared with the methylene chloride solutions. All data are listed in Table 5.

Photochromic cooligomers resistance to fatigue and kinetics of the 1,5-electrocyclization

The reversibility and fatigue behaviour of the photochromic cooligomers **6** have been tested by effecting several cycles of UV light induced opening and thermal back cyclization as illustrated in Fig. 4.

The absorbance of the solutions were measured at the maximum absorption wavelength (see Table 5) for each copolymer at ambient temperature. The solutions were then irradiated for one minute with a UV-lamp. Subsequently the solutions were held in darkness for three minutes. After each operation the absorbance was measured, and the same procedure was repeated several times. Ten cycles were determined for the betaines of **6* a–d** and the reference **3***. The Z_{50} value,[18] which denotes the number of cycles undergone until the absorbance of the solution has been reduced to 50% of the starting value, is a good indicator of the fatigue behaviour. Table 5 shows that the photochromic cooligomers **6** have not reached their Z_{50} values after ten cycles except for **6d** ($Z_{50} =$

Table 4 ^{1}H-NMR data of the reference **3** and the photochromic cooligomers **6** in δ [ppm]

	H-3''',6'''	H-1–8,H-6', H-2''-6'', H-5'''	H-4,5	H-3,6	Fluorene, Aromatics	Aromatics, Heteroaromatics	H-8a',8'	3'-ester	2'-ester	Hα,β
3	—	7.8–7.1 6.81 (H-6')	7.75	7.56	7.5–7.1	—	5.25, 4.70	4.05	3.31	1.60 (7'-Me)
6a	—	8.1–5.7	7.74	7.39	7.07	—	5.3–4.5	4.3–3.7	3.6–3.0	2.1–0.7
6b	—	7.9–5.7	7.73	7.34	7.06	—	5.3–4.5	4.3–3.7	3.5–3.0	2.2–0.5
6c	—	8.0–5.7	7.73	7.35	7.07	—	5.4–4.5	4.3–3.7	3.6–3.1	2.3–1.0
6d	9.3–8.1	8.0–5.7	7.71	7.35	7.08	6.58	5.6–4.6	4.2–3.6	3.5–3.1	2.2–0.8

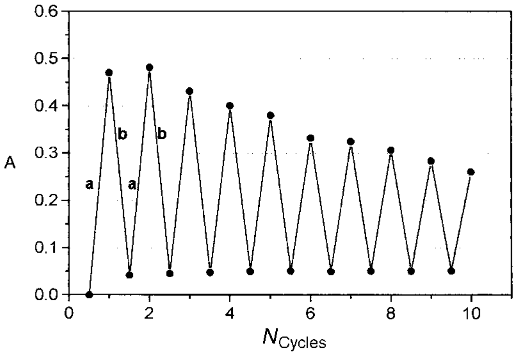


Fig. 4 Behaviour of the cooligomer **6*b** during the photochromic process at $\lambda = 540$ nm in CH_2Cl_2 at room temperature. **a**, 1 min irradiation under UV (lamp on): opening; **b**, 3 min darkness (lamp off): closing.

8). Therefore the Z_{80} values are also listed in Table 5. The cooligomers **6** show Z_{80} values of *ca.* 4 to 10. This is more than the monomer **3** ($Z_{80} = 2$). A reason for this better resistance could be an intramolecular stabilisation of the system by the neighbouring subunits. All Z_{50} values are reported in Table 5.

Further insight into the influence of the nature of the solvents frequently used to dissolve the oligomers (CH_2Cl_2 and THF) as well as the role of oxygen in the degradation was gained by plotting the difference in absorbance of the open and closed forms (obtained under the experimental conditions described in Fig. 4) *versus* the cycle number (see Fig. 5). Methylene chloride was degassed by freeze and thaw cycles (see Experimental). The slopes of the curve clearly show that oxygen accelerates the degradation and that (non degassed) THF behaves like degassed CH_2Cl_2. THF appears to stabilise the open form probably by specific solvation of the positive centre of the betaine. This is reflected in the kinetics $t_{1/2}(\mathrm{THF}) > t_{1/2}(CH_2Cl_2)$ (Table 5).

The kinetics of the 1.5 electrocyclization of the cooligomers **6*** (open form) and of **3*** was studied using UV–VIS spectroscopy. Thus, the absorbance (A) of each solution was measured at the maximum absorption wavelength of the betaine (**6*** or **3***, see Table 5) at 20 °C after irradiation for three minutes with a UV-lamp. The thermal decay could be followed by taking the absorbance every 10 s. Fig. 6 shows the decay of absorbance. The half life ($t_{1/2}$) at which the absorbance has decreased to half of the initial value were determined for the reference DHI (**3**) and for **6a–d** (Table 5).

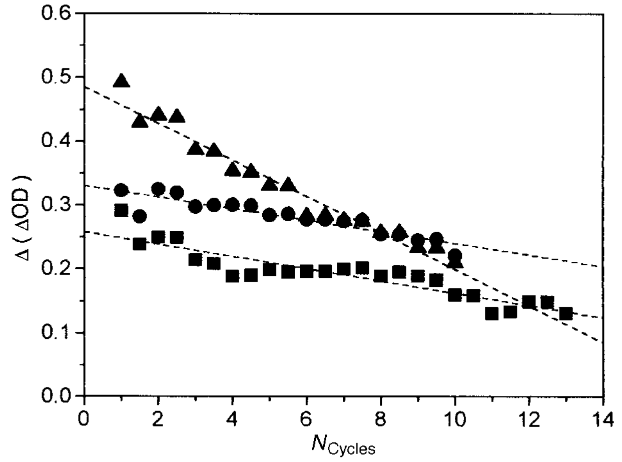


Fig. 5 Comparison of the fatigue resistance in CH_2Cl_2 (▲), degassed CH_2Cl_2 (■) and THF (●) of **6*b** under the experimental conditions detailed in Fig. 4. The dotted lines result from a linear regression from the experimental data.

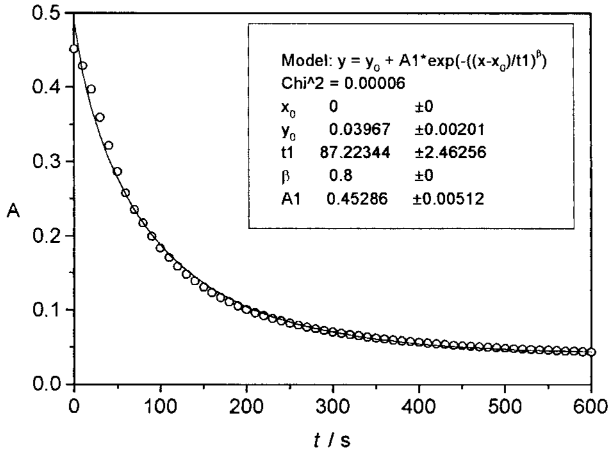


Fig. 6 Kinetics of the thermal 1,5-electrocyclization of **6*b** at $\lambda =$ 540 nm in CH_2Cl_2 (20 °C) after 3 min UV-irradiation. (○ ○ ○) experimental curve, (——) fitted curve using eqn. (1).

One observes half lives of the photochromic cooligomers **6** in the range of 100 ± 20 seconds, a value similar to that of the reference molecule **3**. All cooligomers show a complex kinetic behaviour for thermal cyclization of their photochromic units after irradiation in contrast to the photochromic monomer **3**, whose cyclization follows first order kinetics. The decay rate of each photochromic subunit is different, because it depends on its environment in the polymer; this has been observed in other cases.[4] The decay curves can be approximately fitted using eqn. (1) following the 'Kohlrausch–Williams–Watts' (KWW) function employing β-values of 0.7 to 0.9.[19] This is shown in Fig. 6 and Table 5.

$$y = y_0 + A1 \cdot \exp\left(\left(-\frac{(x - x_0)}{\tau}\right)^{\beta}\right) \qquad (1)$$

Comparison of photochromic cooligomers formed from 4-vinylpyridazine and 4-vinylpyridine

The main results of this study are grouped in Table 6 together with those of a preceding study on cooligomers based on the *4-vinylpyridine* subunits.[12] One notes the following features:

- The 'controlled' free radical polymerization has higher polymer rates with vinylpyridine (3800–19 000) than with vinylpyridazine (700–2000). No satisfactory explanation can be proposed for the moment.
- The yield of spirocyclopropene with the cooligomers to form the DHI subunits was found to be higher for the

Table 6 Comparison between the photochromic copolymer systems formed from 4-vinylpyridine and 4-vinylpyridazine

	4-vinylpyridine/ styrene	4-vinylpyridazine/ styrene
Non grafted copolymer		
Best monomer ratio	30/70	20/80
Max. yield [%]	60	23
M_n/g mol^{-1}	$3800 < x < 19000$	$700 < x < 2000$
Polydispersity (PD)	1.4–1.7	1.2–1.7
Degree of polymerization (max. conv. [%])	~32	3.5
Photochromic copolymers		
Photochromic yield [%]	5–6	80
M_n/g mol^{-1}	> 10000	$1600 < x < 4200$
Polydispersity (PD)	> 1.7	1.4 ± 0.2
$\lambda_{\mathrm{max,\ DHI}}$/nm	388	390
$\lambda_{\mathrm{max,\ Betaine}}$/nm	600	540
$t_{1/2}$/s	80	100
$Z_{50}(CH_2Cl_2)$	6	$30^a > Z_{50} > 10$

[a] Estimated value.

pyridazine systems (80%) than for the pyridine cooligomers (5–6%) presumably because the reactive centres are more accessible in low molecular weight species.

- The photochromic properties of the pyridazine systems proved to be better than the pyridine cooligomers as borne out by higher half life ($t_{1/2}$) and cycle numbers (Z_{80}).

Conclusion

We have prepared cooligomers of 'pyridazine DHI' and styrene for the first time. Despite their low degree of polymerization, these oligomers were found to show improved properties as compared with the DHI reference molecule and the pyridine–DHI/styrene cooligomers described previously: the half life of their open form ($t_{1/2}$) and the fatigue resistance (Z_{80}) proved to be higher. The results of this study justify further investigations to improve the degree of polymerization and study the photochromic properties in the solid state.

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