

Photocrosslinkable polymers bearing pendant conjugated heterocyclic chromophores

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Dedicated to Professor Imanishi on the occasion of his retirement

Abstract

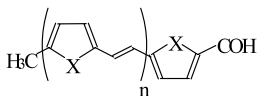
This article describes the synthesis of furan- and thiophene-based chromophores bearing a terminal aldehyde function which was used to append them to polyvinyl alcohol (PVA) and thus obtain photosensitive polymers. Because of their conjugated structure, the chromophores absorbed in the near-UV domain and only displayed two photochemical transformation, viz. a *trans*–*cis* isomerisation and a bimolecular cyclodimerisation. The latter reaction was exploited to induce the crosslinking of the modified PVAs. The application of these materials as photosensitive resins for lithographic plates is the practical issue of the present investigation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Furan and thiophene conjugated oligomers; Photodimerisation; Photocrosslinkable polymers

1. Introduction

Polymers bearing chromophore groups capable of coupling among themselves through photochemical activation have been known and used for several decades, particularly in the realms of photography, printing and microlithography [1]. The most rational approach consists of calling upon the bimolecular reaction of an excited species with its ground-state counterpart without the intervention of free radicals which usually give rise to undesired side reactions. Thus, for example, cinnamic moieties attached to a polymer backbone have been exploited successfully for some 50 yr, albeit in different structures according to the specific application sought [1].

Recent work in our laboratory [2] showed that 5-methylfurfural and its thiophene homologue can be readily oligomerised by nucleophilic self-condensations to give materials with the general structure **1**



and that the procedure can be adapted specifically to the synthesis of each individual species with $n = 1, 2$ and 3

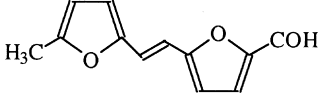
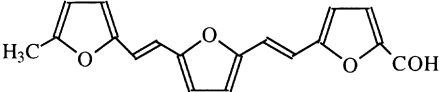
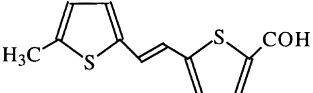
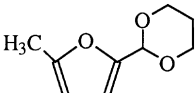
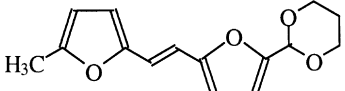
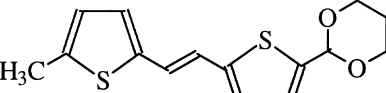
and $X = O$ and/or S (i.e. all furan, all thiophene and mixed structures). Mixtures of oligomers with $n > 3$ were also prepared and characterised. As expected, the absorption maximum in the electronic spectra of these series moved progressively to higher wavelengths as n increased, following the corresponding increase in the degree of conjugation, although this trend practically stopped for $n > 5$, suggesting a progressive loss of planarity beyond that chain length [2,3]. The protonation of these molecules produced an enhancement of intra- and inter-molecular electronic communication [3] as shown, respectively, by the bathochromic shift in the UV–visible spectra (extending now to higher oligomers thanks to a more extended planarity) and the conductivity of these doped materials. The photochemical behaviour of the crystalline O,O and S,S dimers was also briefly examined [4] and shown to yield the corresponding cyclobutane product arising from the coupling of the alkenyl moieties between the two heterocycles.

The presence of an aldehyde function at one end of each of these species is a peculiar feature of their synthesis which opens the way to chemical modifications based on reactions involving that function. Thus, the preparation of Schiff bases with different amines led to interesting products including plasticised conducting oligomers [5] and mesogenic structures [6,7].

The present investigation deals with the exploitation of the photochemical properties of some of these oligomers in

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Table 1
Structure of the compounds synthesised in this study

Compound	Structure
5-[2-(5-Methyl-furylvinylene)-furan-carbaldehyde] 2	
5-(2-{5-[2-(5-Methyl-furan-2-yl)-vinyl]-furan-2-yl}-vinyl)-furan-2-carbaldehyde 3	
5-[2-(5-Methyl-thiophen-2-yl)-vinyl]-thiophene-2-carbaldehyde 4	
2-(5-Methyl-furan-2-yl)-[1,3]-dioxane 5	
2-{5-[2-(5-Methyl-furan-2-yl)-vinyl]-furan-2-yl}-[1,3]-dioxane 6	
2-{5-[2-(5-Methyl-thiophen-2-yl)-vinyl]-thiophen-2-yl}-[1,3]-dioxane 7	

photosensitive polymers and more specifically thermo-plastic materials which can be rapidly crosslinked by near-UV irradiation. Among the applications sought in this context, lithographic printing plates were an obvious choice. The approach selected to prepare these polymers called upon the condensation of the aldehyde function of the oligomer with two OH groups borne by polyvinyl alcohol (PVA) in order to append the chromophores as side groups.

2. Experimental

Table 1 shows the different heterocyclic molecules prepared in this study. The synthesis and structural characterisation of dimers **2** and **4** and trimer **3** have already been reported [2]. It was confirmed by FTIR and ^1H NMR spectroscopy that these compounds were in their *trans* geometries. Acetals **5–7** were obtained in 80–90% yields from the condensation of the corresponding aldehydes 5-methylfurfural (commercially available), **2** and **4** with 1,3-propane-diol in methylene chloride using *p*-toluene

sulphonic acid as catalyst. After refluxing for several hours under nitrogen, the reaction mixture was neutralised with triethylamine, washed several times with distilled water and the organic phase dried over Na_2SO_4 before vacuum-evaporating the volatile components. The structure of each acetal was confirmed by FTIR, ^1H NMR and UV spectroscopy and elemental analysis. The relevant features in these spectra were (i) the disappearance of the carbonyl group (absence of peak around 1680 cm^{-1} and resonance around 9.5 ppm); (ii) the presence of the cyclic acetal moiety shown by the CH_2 and O-C-O bands around $2920/2860$ and 1110 cm^{-1} in the FTIR spectra and the three CH_2 protons at around 4 ($\text{O-CH}_2\text{-O}$, $i = 4$) and 2 ppm ($\text{CH}_2\text{-CH}_2\text{-CH}_2$, $i = 2$), respectively, in the NMR spectra; and (iii) the decrease in the maximum absorption wavelength by about 50 nm associated with the loss of conjugation caused by the elimination of the C=O function. The acetalisation of **2** and **4** did not alter the geometry around the central alkenyl function which retained its *trans* form, as shown by the spectra of **6** and **7**. The melting temperatures of the two solid acetals **6** and **7**, as determined by DSC, were both $87 \pm 1\text{ }^\circ\text{C}$.

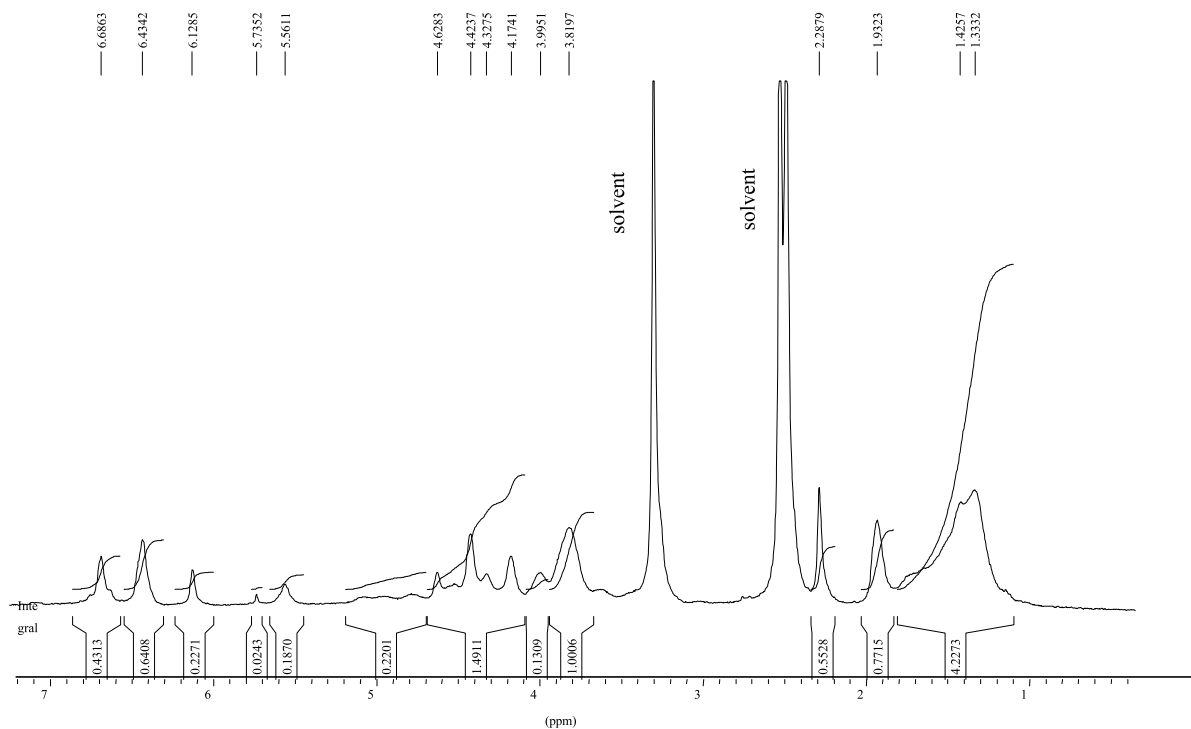
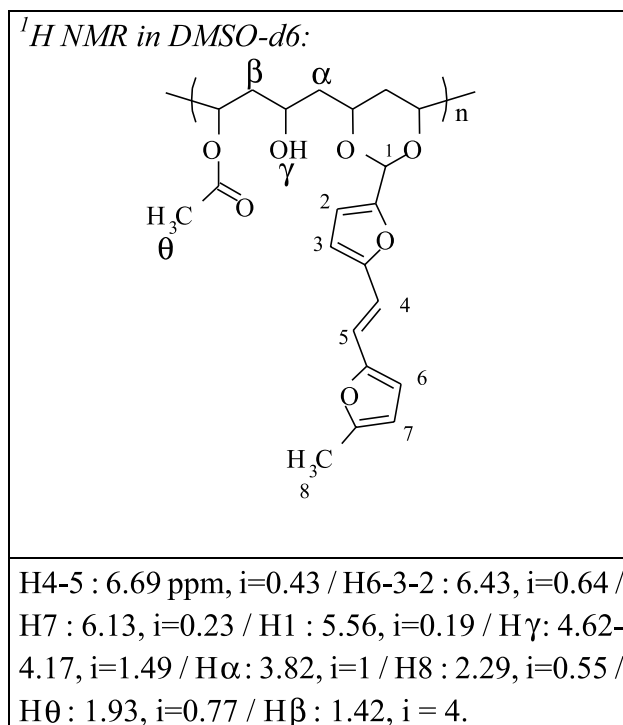


Fig. 1. ¹H NMR spectrum and assignments of a PVA grafted with 20% of **2**.

The PVA used in this work was a commercial product (Mowiol 8/88, Clariant) with $M_w = 67,000$ and a degree of hydrolysis of $87 \pm 1\%$ (confirmed by the determination of residual acetate moieties by ¹H NMR). It was acetalised

with **2** and **4** following the same procedure described earlier for the model diol, but using DMSO as the solvent at room temperature for 24 h in the dark. The modified polymers were precipitated into either acetone (low degree of

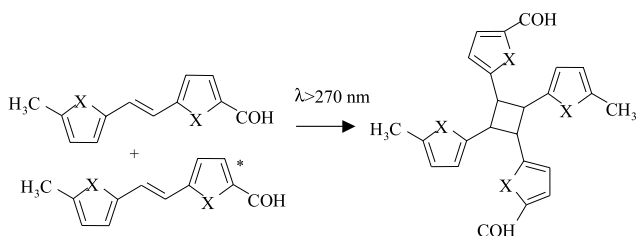
substitution) or water (higher substitution) depending on the extent of acetalisation. Different degrees of chromophore grafting were sought, namely 5, 10 and 20% and in each case the actual extents obtained, determined by ^1H NMR spectroscopy, were close to the expected ones, i.e. the acetalisations proceed to completion. Fig. 1 shows one such spectrum with the assignments of the characteristic resonances arising from the OH and acetate vinyl units of unmodified PVA and from the protons of the appended chromophores. Given the clearly distinct regions of the spectrum in which the PVA and the chromophore protons resonated, the quantitative assessment of the degree of substitution constituted an accurate procedure.

Most irradiations were conducted at room temperature using a 500 W medium-pressure mercury arc from Helios Italquarz. In order to avoid photochemical side reactions arising from high-energy excitations, the incident light was filtered through a Kodak 18A filter which eliminated all wavelengths below 300 nm. The substrate under photolysis was kept under vacuum or in a nitrogen atmosphere to avoid any photooxidation. For the experiments in which the photolysis kinetics were followed in NMR tubes (see later), the substrate was placed in the tube, degassed under high vacuum and then CD_2Cl_2 was added, frozen, degassed and the tube sealed off. Some of these latter runs were carried out for several months at room temperature using sunlight as the source of irradiation.

3. Results and discussion

Since the previous study on the photolysis of dimers **2** and **4** had been limited to irradiation in the solid state [4], a more detailed investigation was now envisaged using both diluted and concentrated solutions. Moreover, the study was extended to trimer **3** and model compounds **6** and **7** which simulated the situation of the heterocyclic chromophores appended to PVA. Compound **5** was only prepared in order to optimise the syntheses of the corresponding conjugated acetals: since it did not absorb above 260 nm, its irradiation in the present conditions was not meaningful.

In dilute CH_2Cl_2 open solutions ($\sim 2 \times 10^{-3}$ M) under nitrogen, **2**, **4** ($\lambda_{\text{max}} \sim 385$ nm) and their corresponding acetals **6** and **7**, were progressively isomerised under irradiation into their respective *cis* isomers, as shown by the corresponding changes in the coupling constants related



Scheme 1. Photocyclodimerisation mechanism of **2** (X = O) or **4** (X = S).

Table 2

Examples of the progress of cyclodimerisation as a function of irradiation time

Irradiation time (h)	Extent of cyclodimerisation of 2 (%)	Extent of cyclodimerisation of 4 (%)
1	5.1	0.8
2	8.5	9.6
3	16.8	17.9
4	19.5	–
5	23.5	–
6	24.0	22.2
7	24.8	–
8	33.3	–
9	–	31.2
15	38.8	37.4
25	39.3	45.6

to the alkenyl protons, until the thermodynamic equilibrium between the two forms was attained ($\sim 50\%$ of each). No evidence of other structural changes was detected, indicating that the filtering procedure had indeed prevented photolytic pathways involving the decomposition of the substrate.

In concentrated open solutions (~ 1 M) under nitrogen, **2** and **4** were converted progressively into their respective cyclodimers following the same $\pi 2 + \pi 2$ mechanism already observed when they were irradiated in the solid state, namely the coupling of an excited molecule with one in the ground state (Scheme 1). Table 2 shows the evolution of the yield of cyclodimer as a function of photolysis time for both compounds and the data suggest that their photoreactivities are similar. The quantum yield of these reactions was determined using an aqueous solution of potassium ferrioxalate as actinometer [8]. The values for both furan and thiophene derivatives were found to be 0.08 ± 0.01 . The kinetics of cyclodimerisation were also examined and Fig. 2 shows the second order plot relative to one of these experiments. Its reasonable linearity up to 40% conversion suggests that the mechanism invoked (Scheme 1) is correct. The contribution of *trans*–*cis* isomerisation was modest under these conditions (but see later). Again, no other product was detected suggesting the

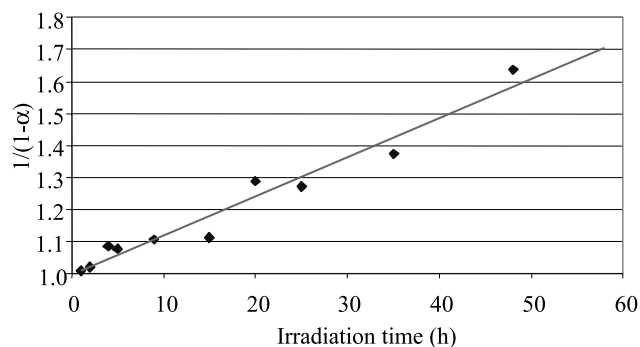


Fig. 2. Typical second-order plot for the cyclodimerisation of **2**; α is the fractional conversion.

absence of major photochemical side reactions. The lack of decomposition mechanisms involving free radical products was confirmed by the fact that the addition of free radical scavengers did not alter the course of the reactions.

In order to examine the behaviour of these systems at very high conversions, sealed NMR tubes containing 1 M solutions of **2** and **3** in CD_2Cl_2 were irradiated in sunlight for several months, namely until the starting compounds had practically vanished. With **2**, one experiment gave close to 100% cyclodimer, whereas with **3**, when 80% had been converted, the yield of cyclodimer and *cis* isomer were both close to 40%. These results suggest that isomerisation does indeed compete with cyclodimerisation in these concentrated solutions, but that the *cis* isomer of **2** can also dimerise, whereas it is not clear whether that of **3** can do the same (and even if it does, it certainly acts much more sluggishly).

Trimer **3** displayed an absorption maximum at 445 nm and minima close to the two major lines emitted by the medium pressure Hg lamp at 313 and 366 nm, whereas it absorbs strongly the 436 nm line. Its irradiation of a 1 M CH_2Cl_2 solution with the filtered emission from that lamp did not produce appreciable yields of coupling products, whereas isomerisation took place (up to 15% in 24 h). Irradiation of the same solution by sunlight did not alter this qualitative behaviour and gave 30% isomerisation within 1 week. It can be concluded that since the excitation of **3** required a much lower energy than that involved in the excitation of dimers **2** and **4**, the reaction of the ensuing excited molecule with a ground state counterpart could not take place, most probably because the system did not acquire the activation energy associated with the coupling reaction. The fact that the trimer was nevertheless excited was proved by the occurrence of its isomerisation. The failure to induce the dimerisation of **3** determined the lack of interest in its subsequent use as a potential chromophore on PVA and therefore its acetalisation with 1,3-propane-diol.

The photochemistry of model compounds **6** and **7** ($\lambda_{\text{max}} \sim 340$ nm) was only studied using them as pure solids

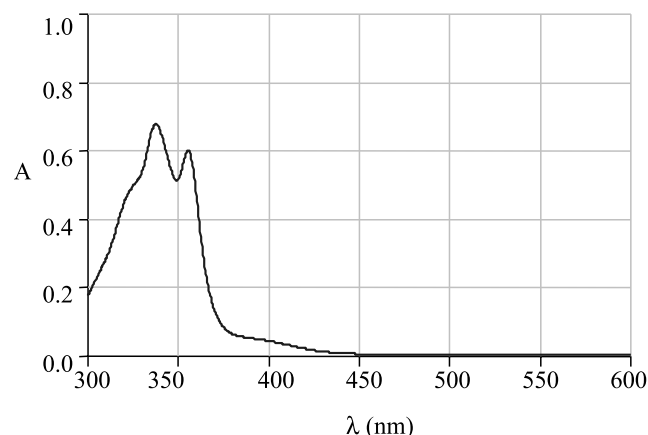
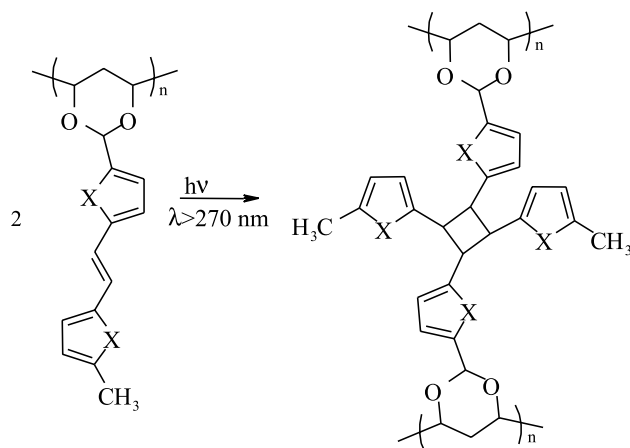


Fig. 3. UV-visible spectrum (DMSO) of a PVA grafted with 20% of **2**.



Scheme 2. Photocyclodimerisation mechanism of PVA grafted with **2** ($X = \text{O}$) or **4** ($X = \text{S}$).

(placed between NaCl plates) and in concentrated (~ 1 M) methylene chloride solutions. Dimerisation occurred in all instances, attaining typically 30–40% conversions after several hours under the effect of the Hg lamp. Thus, the decrease in conjugation did not play a significant negative role with respect to the reaction, which constituted the basis of the crosslink strategy.

The acetalisation of PVA with **2** and **4** proceeded smoothly within the range of substitutions chosen here, viz. between 5 and 20%. The T_g of the ensuing modified polymers was lower than that of the starting PVA (50°C), but the effect was modest because the decrease in intermolecular hydrogen bonding, associated with the corresponding decrease in OH groups, was in part counteracted by the stiffness of the chromophores introduced in their place. Thus T_g values ranging between 45 and 35°C were measured by DSC, as a function of the percentage of grafted moieties.

Although the extent of grafting was determined systematically and rather precisely by ^1H NMR spectroscopy, as pointed out earlier (Fig. 1), the UV spectrum of the modified polymers represented an alternative mode of evaluation, which confirmed the NMR results. Fig. 3 shows one such spectrum which bears the fingerprint of the chromophore, identical to that of the corresponding acetal model compound. The percentage of appended chromophore could thus be calculated using the extinction coefficient of the respective model compound.

These modified materials, dissolved in DMSO, were converted into thin films (~ 100 μm) by spin coating or spreading with a glass rod onto a polyethylene terephthalate surface, from which they could be readily peeled off. Irradiation of these films produced a progressive insolubilisation of the polymer reflecting its crosslinking by the intermolecular couplings between pendant chromophores (Scheme 2). Monitoring the UV spectrum of the film as a function of the irradiation time (or the equivalent energy) was a good way to show the gradual decrease in the concentration of chromophores, since the coupling reaction

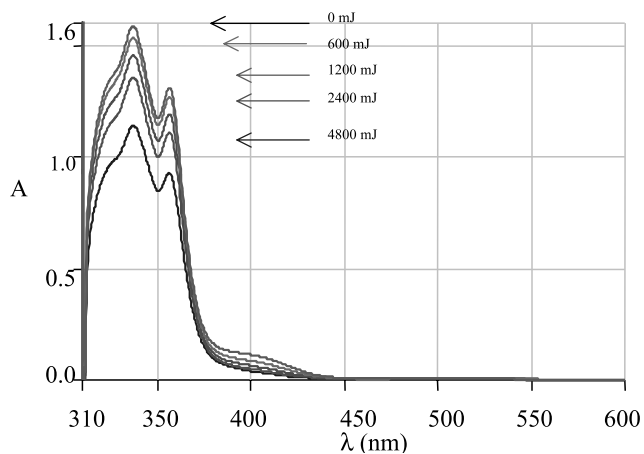


Fig. 4. UV-visible spectra of a PVA grafted with 20% of **2** irradiated with different energies.

destroys the conjugation leaving two independent furan or thiophene rings. Fig. 4 shows an example of this feature. The changes in the FTIR spectra were less pronounced because of the modest initial content of relevant moieties and the fact that the only group which was affected by the photochemical coupling was the alkenyl bridge between the heterocycles, i.e. a moiety associated with peaks displaying low extinction coefficients. The same applies to the formation of cyclobutane rings.

The logical extension of these results consisted in preparing polymers bearing the same basic structures in terms of the main chain and chromophores, but incorporating additional more specific moieties intended to optimise

their technical performance as photosensitive negative coatings for lithographic plates. These materials gave satisfactory performances in the context of workshop trials, when compared with commercial counterparts [9].

4. Conclusions

The straightforward preparation of 1,2-furan- and thiophene-substituted ethylenes bearing a reactive moiety and the subsequent grafting of these chromophores to PVA gave access to novel photosensitive polymers possessing potential applications as negative substrates for imaging technologies. Work is in progress to widen the scope of this investigation both to new chromophores and to other polymer backbones.

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