

# Pyrylium and thiopyrylium salts as electron transfer photosensitizers for the $[2\pi + 2\pi]$ cyclodimerization of poly(vinyl cinnamate) in solution<sup>1</sup>

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## Abstract

The photochemical cross-linking of poly(vinyl cinnamate) (PVCin, **1a–d**) mediated by pyrylium salts in solution has been investigated. 2,4,6-Triphenylpyrylium tetrafluoroborate (TPT, **2a**), a well-known electron-transfer photosensitizer, produces highly selective  $[2\pi + 2\pi]$  cyclodimerization between cinnamate units of PVCin: head-to-head dimers (truxinates) account for 98–99% of the cycloaddition products. Among all the identified dimers,  $\zeta$ -truxinate (**8**) seems to be specifically associated with the presence of TPT, since not even traces of this compound can be detected when no sensitizer is employed.  $\delta$ -Truxinate (**5**) and  $\beta$ -truxinate (**7**) are the major products, but their percentages are inverted in comparison with the unsensitized reaction. 2,4,6-Triphenylthiopyrylium perchlorate (**2b**) has been shown to be 3 to 4 times more efficient than TPT, as evidenced by UV–vis and <sup>1</sup>H NMR experiments. The use of several cross-linking additives such as 1,4-butanediol dicinnamate (**3a**), pentaerythritol tetracinnamate (**3b**), dimethyl *p*-phenylenediacrylate (**3c**), diethyl cinnamylidenemalonate (**3d**) and pentaerythritol tetraacrylate (**3e**), results in a significant enhancement of the intermolecular cycloaddition. © 1998 Elsevier Science S.A.

**Keywords:** Photochemical cross-linking; Poly(vinyl cinnamate); Pyrylium salt; Thiopyrylium salt

## 1. Introduction

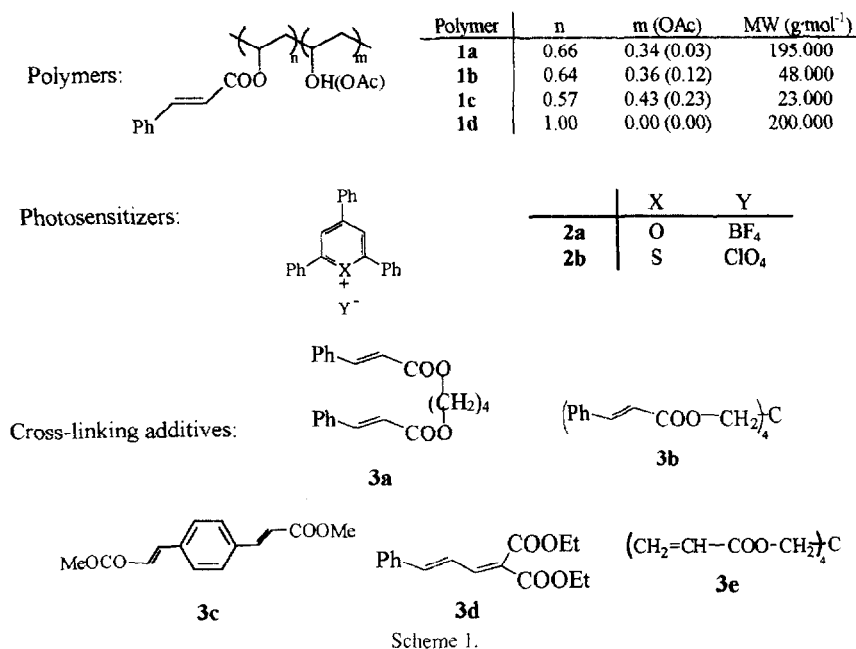
The use of light-sensitive polymers is widely extended in several practical applications (e.g., photographic processes, reprography) as revealed by the great number of patents appeared in the last decades [1–7]. Usually, photosensitizers are employed in order to achieve a higher performance in the photochemical reaction. In fact, the search for new sensitizers is a key step in the improvement and development of commercial photochemical processes.

Poly(vinyl cinnamate) (PVCin) is a simple photo-cross-linkable polymer which has been extensively studied [8–19]. It consists of a poly(vinyl alcohol) backbone esterified with photoreactive cinnamoyl groups. When a PVCin film is exposed to short wavelength light, hardening of the material occurs. In solution, irradiation of the polymer leads to insolubilization and concomitant gel formation. It has been shown that intermolecular  $[2\pi + 2\pi]$  cyclodimerization of the cinnamate moieties is responsible for the observed effects.

So far, photo-cross-linking of this polymer has been achieved both upon direct irradiation and under energy transfer conditions. However, the use of electron transfer sensitizers is much less known, probably because this is a more recent conception in photochemistry and specially in the field of the photosensitized reactions of polymers. Furthermore, most reports on PVCin deal with its photochemistry in the absence of any solvent. 2,4,6-Triphenylpyrylium tetrafluoroborate (TPT) is a powerful electron-transfer photosensitizer for fragmentations, rearrangements, oxygenations, cycloadditions and many other reactions [20]. Ramamurthy et al. [21], by means of laser flash photolysis have reported that excited TPT is able to accept an electron from *trans*-cinnamic acid in dilute solutions (acetonitrile), as indicated by the detection of pyryl radical. TPT-photosensitized photolysis under steady state conditions was found to result in the disappearance of *trans*-cinnamic acid, which was attributed to isomerization (from the TPT triplet) and cyclodimerization (from the TPT singlet), but no dimer was isolated. As a part of our work on photoinduced electron transfer mediated by pyrylium salts [20], we decided to undertake a systematic study on the reaction of PVCin in solution. In a previous work Mistr et al. [22] and Mistr and Zahradnik [23] measured the fraction of non-solubilizable polymer after light exposure (solid

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<sup>1</sup> Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday



film) in the presence of pyrylium and thiopyrylium salts, and interpreted the results in terms of energy transfer sensitization. In the present work it is clearly shown that PVCin can be photo-cross-linked by pyrylium and thiopyrylium salts in  $\text{CH}_2\text{Cl}_2$  solution and that this behaviour is due to cyclobutane dimer formation, involving an electron-transfer mechanism.

The sensitized reaction leads to dimer distributions markedly different from that obtained in the unsensitized one. Thus, the use of TPT enhances the formation of head-to-head (rather than head-to-tail) dimers and appears to be specifically associated with the appearance of  $\zeta$ -truxinate.

Finally, another aim of our work was to study the variations associated with the use of potential cross-linking additives. For this purpose, we have selected a series of compounds with two or more insaturations capable of undergoing  $\{2\pi + 2\pi\}$  cycloadditions, whose intercalation between polymer chains and subsequent irradiation could result in the formation of intermolecular bridges. It will be shown that addition of these compounds produced a significant enhancement of the photo-cross-linking efficiency, according to the expectations.

## 2. Experimental details

### 2.1. Materials

Poly(vinyl cinnamate) **1d** was purchased from Aldrich (catalog No. 18,264-8). The other polymers (**1a–c**) were synthesized by esterification of commercial poly(vinyl alcohol) (Aldrich, catalog Nos. 38,834-3; 36,317-0 and 36,062-7) with cinnamoyl chloride (Aldrich, catalog No. C8,110-1) in *N*-methyl-2-pyrrolidinone as solvent (Aldrich, catalog No. 32,863-4) [24]. As an example, 1.1 g of poly(vinyl alcohol)

97% hydrolyzed (ca. 25 mmol of OH) was dissolved in 15 ml of *N*-methyl-2-pyrrolidinone at 100°C and 5 ml of a cinnamoyl chloride (5 g, 30 mmol) solution in *N*-methyl-2-pyrrolidinone was added by means of a drop funnel. The addition was conducted at 55–60°C and the reaction mixture was maintained with stirring at that temperature for 4 h. The resulting poly(vinyl cinnamate) was purified by precipitation, pouring the dissolved mixture onto an alkaline aqueous solution ( $\text{Na}_2\text{CO}_3$ , 0.3 M) to obtain an orange coloured gum, which was dissolved in dichloromethane and precipitated with a large amount of ethanol. The same operation was repeated with dichloromethane and hexane. Finally the gum was dried overnight (10 h at 80°C). In this way 1.79 g of pure poly(vinyl cinnamate) was obtained (41% yield). <sup>1</sup>H NMR analysis showed the total absence of solvent or cinnamic acid in the product. The rest of polymers were synthesized in a similar way. The degree of substitution and the average molecular weight are shown in Scheme 1.

2,4,6-Triphenylpyrylium tetrafluoroborate (**2a**) was obtained from Aldrich (catalog No. 27,234-5). 2,4,6-Triphenylthiopyrylium perchlorate (**2b**) was synthesized in the following way [25]: 0.17 g (0.4 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (**2a**) were dissolved in 8 ml of acetone. Afterwards, a 2 ml solution of 10%  $\text{Na}_2\text{S}$  was added slowly and stirred for 30 min. The mixture was acidified with 2 ml of an aqueous solution of perchloric acid (20%) and diluted with water (8 ml). Immediately after the addition of acid and water a bulky precipitate of the thiopyrylium salt was formed which was filtered and washed with water. Precipitation with ether from a solution of **2b** in acetone afforded 96 mg (0.23 mmol, 58% yield) of yellow crystals (mp: 211–212°C, lit [25]: 210–211°C).

The cross-linking additives (**3a–d**) were synthesized by esterification of the corresponding alcohol with cinnamoyl

chloride (**3a** and **3b**) or synthesizing the appropriate acid chloride from the commercially available acid (Aldrich) prior to reaction with methanol or ethanol (cases **3c** and **3d**). The compound **3e** was purchased from Aldrich (catalog No. 40.826-3).

## 2.2. Irradiation procedures

For UV-vis spectral studies  $\text{CH}_2\text{Cl}_2$  solutions of polymer **1** (ca.  $6 \times 10^{-5}$  M of cinnamate) and sensitizer **2** (ca.  $3 \times 10^{-5}$  M) were placed in quartz cuvettes and irradiated for 30 min with a 400 W high-pressure mercury lamp, filtering with a  $2.1 \times 10^{-3}$  M solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 2%  $\text{H}_2\text{SO}_4$  ( $\lambda > 400$  nm). The UV-vis absorption spectra of the solutions were recorded every 5 min. In the experiments with the cross-linking additives **3a–e**, the latter were used in the necessary amount to provide  $6 \times 10^{-6}$  M of extra double bonds not belonging to the polymer.

On the other hand,  $\text{CDCl}_3$  solutions of **1a** (ca.  $7 \times 10^{-2}$  M of cinnamate) and **2a,b** (ca.  $10^{-3}$  M) were placed in NMR test tubes. The reaction progress was monitored by  $^1\text{H}$  NMR (300 MHz) every 5 min, up to 30 min. The irradiation was performed with a 125-W medium-pressure mercury lamp and using a cut-off glass filter (350 nm) for the sensitized reactions. For the experiment with cross-linking additive **3d**, its additional cinnamate concentrations was  $7 \times 10^{-3}$  M.

## 2.3. Dimer analysis

For product analysis dichloromethane solutions of **1d** and **2a** were irradiated for 8 h. The concentrations of these solutions are listed in Table 1. The light source was a 125-W medium-pressure mercury lamp, and a cut-off glass (320 nm) was used as filter for the sensitized reactions. The dry residue was hydrolyzed and reesterified (ethyl esters)

according to the method described in Ref. [15]. The dimer mixture was analyzed by means of gas-chromatography and the identification was made by comparison with the retention times of authentic samples.

## 3. Results and discussion

Four different poly(vinyl cinnamates) (**1a–d**) were studied in this work; their characteristics are presented in Scheme 1. The main differences are the average molecular weight and the degree of esterification.

Although 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) is the best known electron-transfer photosensitizer of the pyrylium salts family [20], there is a great variety of related salts which might also act as photosensitizers in photoinduced-electron-transfer (PET) processes. For this reason we have also included in this study 2,4,6-triphenylthiopyrylium perchlorate salt (**2b**), in order to test the ability of **2a** and **2b** to mediate photo-cross-linking of PVCin. The structures are presented in Scheme 1.

With regard to the above mentioned cross-linking additives, we have examined 1,4-butanediol dicinnamate (**3a**), pentaerythritol tetracinnamate (**3b**), dimethyl *p*-phenylene-diacrylate (**3c**), diethyl cinnamylidenemalonate (**3d**) and pentaerythritol tetraacrylate (**3e**) (Scheme 1).

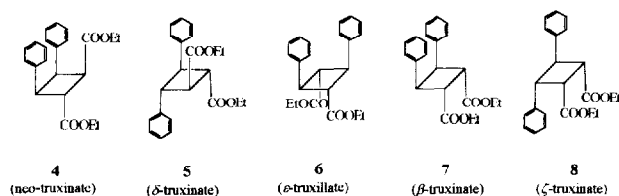
### 3.1. Photo-cross-linking of PVCin in solution sensitized by **2a** and **2b**

The activity of **2a** and **2b** as photosensitizers for PVCin was investigated, first under dilute conditions and later under concentrated ones. In the former case it was realized that both **2a** and **2b** were efficient but with striking differences. The measured parameter for following the reaction was the

Table 1  
Selectivity of the PVCin  $[2\pi + 2\pi]$  cycloaddition, as determined after hydrolysis and derivatization to give the ethyl cinnamate dimers

Entry	Sensitizer	Cinnamate conc. (M)	Sensitizer conc. (M)	$\lambda >$ (nm)	Distribution of dimers (%)				
					4	5	6	7	8
1	—	0.1	—	280	5	36	10	49	—
2	<b>2a</b>	0.1	$2.5 \cdot 10^{-3}$	320	8	53	—	23	16
3	—	0.01	—	280	8	30	8	54	—
4	<b>2a</b>	0.01	$2.5 \cdot 10^{-4}$	320	5	58	1	27	9
5	—	0.001	—	280	7	29	9	55	—
6	<b>2a</b>	0.001	$2.5 \cdot 10^{-5}$	320	8	51	2	37	2
7	<b>2a</b>	$0.1^a + 0.01^b$	$2.5 \cdot 10^{-3}$	320	8	46	—	28	18

<sup>a</sup>Cinnamate from the polymer **1d**. <sup>b</sup>Cinnamate from the cross-linking additive **3b**.



decrease of the 277 nm band corresponding to the cinnamate moiety by means of UV-vis spectroscopy. A 400 nm filter (potassium dichromate solution) was chosen in order to avoid direct irradiation of the polymer (see Section 2). A control experiment showed that the irradiation of an unsensitized solution of **1a** (ca.  $6 \times 10^{-5}$  M of cinnamate) for 30 min using the mentioned filter produced no variation in the 277 nm band. Conversely, on irradiating solutions ( $\text{CH}_2\text{Cl}_2$ ) of **1a** (same concentration) for 30 min in the presence of **2a** or **2b** (ca.  $3 \times 10^{-5}$  M) a substantial fall of the band was observed. This was much more remarkable when using the thiopyrylium salt (**2b**) than when TPT (**2a**) was the sensitizer. These results are depicted in Fig. 1.

As the polymer molecular weight might have some effect on the reactivity, different polymers (**1a**, **1b**, **1c**) were included in the study. The main difference between these polymers is the average molecular weight, calculated from the average molecular weight of the starting poly(vinyl alcohol) and their degree of esterification, determined by  $^1\text{H}$  NMR. The MW values (**1a**, 195,000; **1b**, 48,000 and **1c**, 23,000) were sufficiently different as to allow the observation of any effect of this parameter on the course of the reaction. Using **2b** as sensitizer and following the decrease of the 277 nm UV-band no such effect was observed (Fig. 1).

The absorption decrease at 277 nm can be attributable either to dimerization or to isomerization around the double bond, since the *cis* isomer has a molar absorptivity lower than the *trans* isomer at this wavelength. Since no clear isosbestic point was observed it is reasonable to think that dimerization is competing with isomerization. That is not unlikely as cinnamate moieties are anchored to a polymeric backbone which maintains the chromophores unavoidably in close proximity. Rennert et al. [26] have reported dimerization besides isomerization in the irradiation of 1,3-propanediol dicinnamate in

dilute conditions. In the polymer the situation of the cinnamate chromophores is not very different from that of the experiment of Rennert.

More conclusive evidences concerning the nature of the photosensitized reactions of PVCin were obtained by means of complementary experiments at higher concentrations of polymer. Thus,  $\text{CDCl}_3$  solutions of **1a** (ca.  $7 \times 10^{-2}$  M) and sensitizers **2a** or **2b** (ca.  $10^{-3}$  M) were irradiated. The reactions were monitored by  $^1\text{H}$  NMR. One of the olefinic protons of the *trans*-cinnamate (starting product) is characterized by a signal at  $\delta = 6.3$  ppm, while the corresponding proton in the *cis* isomer is more shielded ( $\delta = 5.8$  ppm). The integrated areas of those signals in the polymer were measured all along the reaction and compared with the integrated signal of the methine proton of the saturated backbone ( $\delta = 5.5$  ppm) which remains unchanged during irradiation. With the appropriate combination of these three signals it was possible to know the extent of the dimerization as well as the isomerization processes in the irradiated PVCin. Again, a filter for short wavelengths (350 nm) was employed in order to make sure that the observed reactions were mediated by the photosensitizers.

The results obtained are shown in Fig. 1. As it can be seen, both **2a** and **2b** were able to photosensitize the dimerization of PVCin, although, the efficiency of **2b** was again higher (more than four times) than that of **2a**. This agrees well with the results obtained by Mistr et al. [22] and Mistr and Zahradnik [23] for the reaction in solid film. One of the more striking observations made in the reactions followed by  $^1\text{H}$  NMR was the complete gelification of the solutions contained in the NMR test tubes. That observation can only be accounted for if a significant degree of cross-linking occurs. The resonance spectra seem to support this view. The considerable decrease (ca. 25%) of the 6.3 ppm signal (*trans* pro-

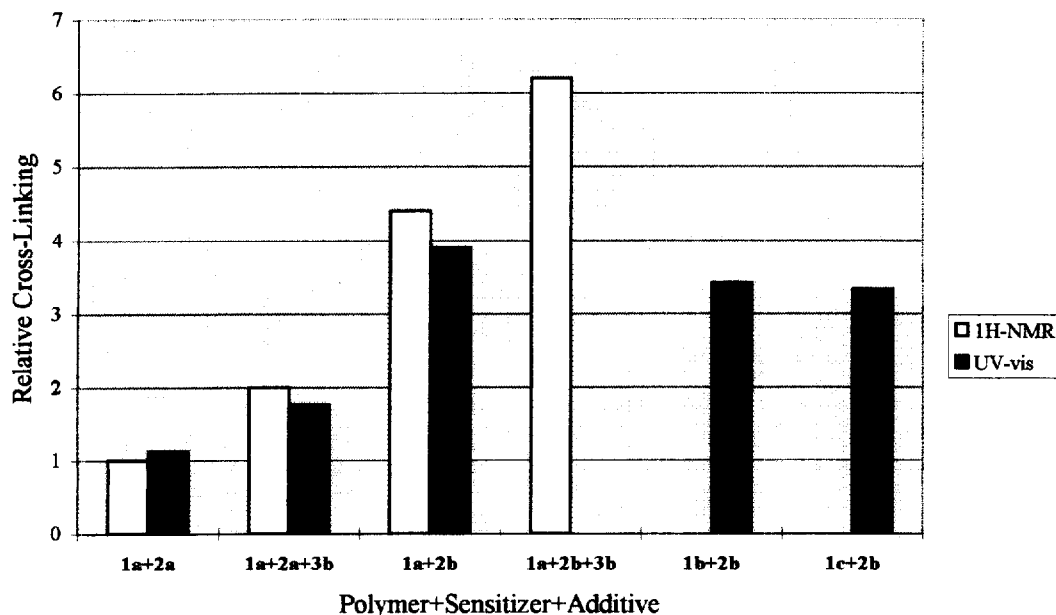


Fig. 1. Relative PVCin cross-linking under different irradiation conditions.

ton) was observed simultaneously to a quantitatively less important increase (ca. 5%) of the 5.8 ppm signal (*cis* proton). So, most of the disappearance of the *trans* signal must be attributed to dimer formation.

The ability of the studied sensitizers to convert in gel PVCin solutions in short periods of time with UV-A light ( $\lambda > 320$  nm) was remarkable. This effect, indicative of intermolecular photodimerization, was not achieved neither by direct irradiation of the solutions nor by the use of triplet sensitizers. As a matter of fact, dichloromethane solutions of PVCin (**1b–c**) (0.2 M of cinnamate) and sensitizers (**2a,b**) ( $5 \times 10^{-3}$  M) were completely gelified after only 20–25 min of irradiation with UV-A light (argon or air atmospheres). For comparison, also two triplet sensitizers were tested in the same conditions: Michler's ketone [9] and dichloran [27,28] (2,6-dichloro-4-nitroaniline). No gel formation was observed in these cases even after 15 h of light exposure.

The stability of the formed gels towards short wavelength radiations was also examined. It is known that gels formed at long  $\lambda$  by means of  $[2\pi + 2\pi]$  cycloadditions revert to the starting products when irradiated with short  $\lambda$  [29]. This was not our case, because exposure of a dry sample of the gel formed as above to the unfiltered light of a 125-W medium-pressure mercury lamp for 6 h resulted in no apparent cyclorversion, as indicated by the lack of solubilization in  $\text{CH}_2\text{Cl}_2$ .

### 3.2. Influence of cross-linking additives on the reaction efficiency

Addition of compounds **3a–e** in dilute solutions of **1a** had a significant effect on the overall photochemical reactivity, as evidenced by UV-monitoring of the process. In all cases the variation was higher than 20%, reaching in some cases a 40–60% improvement of the cross-linking efficiency. The most interesting effects were observed with 1,4-butanediol dicinnamate (**3a**) and pentaerithritol tetracinnamate (**3b**) which also posses the same cinnamic chromophore. Even though these compounds have the same absorption spectra as PVCin, the variations of the 277 nm band cannot be attributed to the sole reaction between additive units without participation of the polymer, since the concentration of reactive chromophore contributed by **3a** or **3b** was only 10% of that provided by **1a**. In other words, in a solution of **1a** containing  $6 \times 10^{-5}$  M cinnamate the amount of additives provided only  $6 \times 10^{-6}$  M of extra chromophores.

The influence of cross-linking additives was also determined by  $^1\text{H}$  NMR with **3b**, which produced the best results in the experiments monitored by UV-vis spectroscopy. Again, an improved efficiency was observed when **3b** was added to the solutions, in comparison with the same measurements in the absence of additive (Fig. 1).

### 3.3. Nature of the pyrylium salt-photosensitized $[2\pi + 2\pi]$ dimerization of cinnamate units

Besides determining the extent of photoreaction, it was of interest to establish the nature of the  $[2\pi + 2\pi]$  dimerization

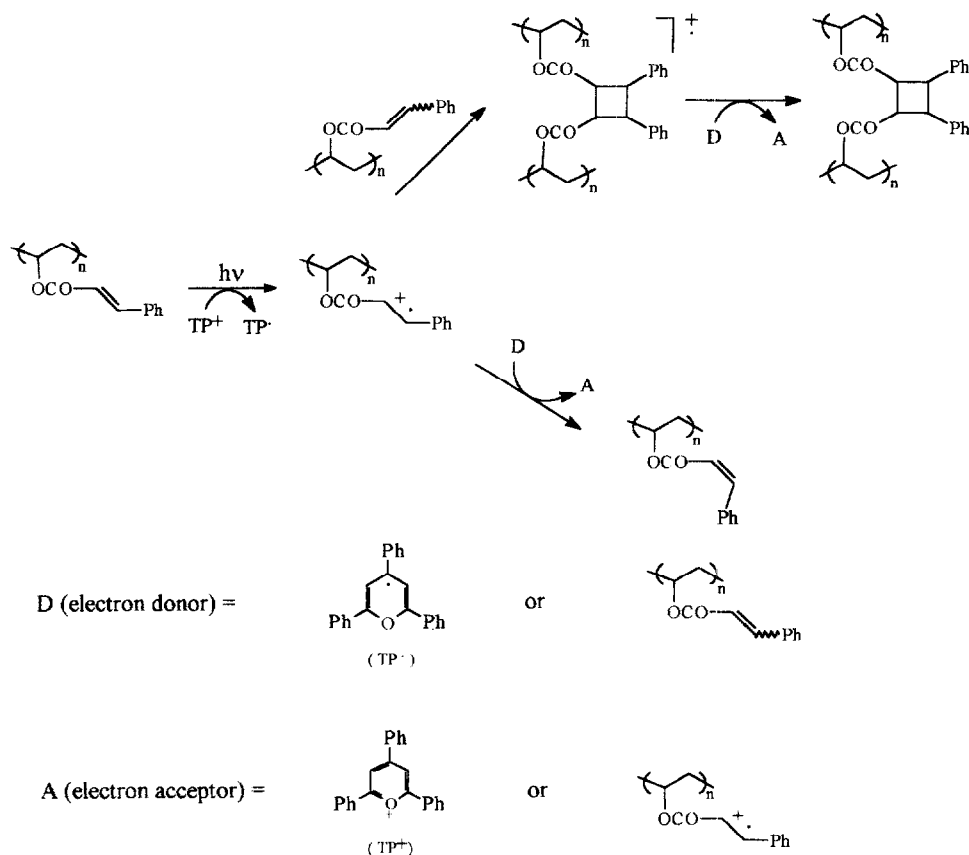
of cinnamates. In particular, a careful study of the dimer distribution might be highly informative from the mechanistic point of view, since different mechanisms are expected to be associated with characteristic product selectivities. A useful method (although time-consuming) to ascertain what kind of reactions take place during irradiation of poly(vinyl cinnamate) is to hydrolyze the photolysate and subsequently to analyze the reaction mixture by means of an appropriate technique. The hydrolysis step was achieved by the method described elsewhere [15] for the analysis of the unsensitized reaction of PVCin in solid films. This method employs relatively mild conditions and a phase transfer catalyst (tetraethylammonium hydroxide). Such a smooth method produces no change in the stereochemical configuration of the cyclobutane derivatives. After the hydrolysis, the mixture of cinnamic acid dimers was derivatized (ethyl esters) in order to make possible the gas-chromatographic analysis. A positive identification was done by comparison with authentic samples. Further details can be found in the Section 2.

The irradiation (and subsequent analysis) of dichloromethane solutions of the polymer **1d** containing the sensitizer **2a** was carried out at several concentrations in order to detect possible variations due to competition between intra- and intermolecular  $[2\pi + 2\pi]$  dimerization. For comparison, solutions of **1d** without sensitizer were also irradiated and analyzed in the same way. The dimers distributions presented in Table 1 were established by GC analysis of the hydrolysates. Control experiments showed that the 320 nm cut-off glass filter prevented the reaction in the absence of sensitizer. Thus, when a solution of **1a** (0.1 M of cinnamate) was exposed to the filtered light no dimer at all could be detected. Conversely, when this filter was substituted by Pyrex (cut-off at ca. 280 nm) the dimerization process did in fact occur. So, both filters were used alternatively depending on whether the reaction was sensitized (320 nm) or not (280 nm).

Three main outcomes are evident from the data in Table 1.

(a) Among all the possible ethyl truxinates (head-to-head dimers) and truxillates (head-to-tail dimers),  $\delta$ -truxinate (**5**) and  $\alpha$ -truxinate (**7**) were always the major products. Overall, they accounted roughly for 80% of the cyclobutane products, independently of the reaction conditions. However, a remarkable difference was observable between sensitized and unsensitized reactions. In the latter, **7** was the main product with 50% while **5** was obtained in a lower yield (30%). The reverse was true for the TPT-photosensitized dimerization: **5** was the major product (50%) and **7** was the minor product (30%).

(b) In the unsensitized irradiations there was always a noticeable amount (8–10%) of the  $\epsilon$ -truxillate (**6**). By contrast, this dimer disappeared almost completely when **2a** was used as photosensitizer. Scarcely a 1–2% of **6** could be detected in such conditions. So, the acquisition of 98–99% of truxinates in the photosensitized reaction represents a remarkable selectivity. Such a high selectivity towards head-to-head dimers is in agreement with an electron transfer mechanism [20].



Scheme 2.

(c) In comparison with the unsensitized reactions a new dimer appeared in the TPT-sensitized ones, which was identified as the  $\zeta$ -truxinate (**8**). Even so, five is a low number in comparison with the eleven possible isomers that can be formed. Of course the spatial restrictions imposed to the chromophores by the arrangement of the polymeric chains can be the reason for such a limited number of cycloaddition products. In the reactions where TPT is used, **8** accounted for up to 16% of the overall set of dimers, and was the only one whose yield varied dramatically with changes in cinnamate concentration: from 2.3% at  $10^{-3}$  M to 15.8% at 0.1 M. This is a strong indication that dimer **8** is taking part in the intermolecular photo-cross-linking process more than the other dimers, since the higher the concentration the higher the probability for two chromophores belonging to different chains to interact with each other. The data of entry 7 in Table 1 appear to support this view: the addition of **3b** increased slightly the percentage of **8**. A macroscopic observation also points to the same idea: at the end of the irradiations where **8** was formed in higher yield (16–18%, entries 2 and 7) the liquid became a complete gel whereas in the other cases (less concentrated cinnamate or no TPT) the solutions remained liquid.

### 3.4. Feasibility of the electron transfer mechanism

According to the knowledge on the mechanism of TPT-sensitized reactions [20], it is reasonable to assume that the

reaction with PVCin involves radical cations, generated after oxidation by photoexcited TPT (Scheme 2). These species can give rise both to *trans-cis* isomerization and to  $[2\pi+2\pi]$  cycloaddition. From the thermodynamic point of view the Rehm–Weller equation [30] for PET reactions is compatible with the proposed mechanism:

$$\Delta G = 23.06 (E_{D/D^{++}} - E_{A/A^{--}}) - E^* \quad (\text{kcal/mol})$$

Here  $E_{D/D^{++}}$  and  $E_{A/A^{--}}$  are the redox potentials (in V) of donor (D) and acceptor (A) species respectively, and  $E^*$  is the sensitizer excitation energy (in kcal/mol). If the pertinent data are introduced in this equation, negative  $\Delta G$  values are obtained from the singlet ( $-16.8$  kcal/mol) and from the triplet ( $-4.8$  kcal/mol) excited states of TPT.<sup>2</sup> So, this reaction is, in principle thermodynamically possible. In addition these values are far enough from the Marcus Inverted Region ( $\Delta G < -20$  kcal/mol), where kinetics is slow.

## 4. Conclusions

2,4,6-Triphenylpyrylium tetrafluoroborate (**2a**) and 2,4,6-triphenylthiopyrylium perchlorate (**2b**) are efficient sensitizers

<sup>2</sup> As redox potential of PVCin we have chosen the value of the model compound methyl cinnamate:  $E_{D/D^{++}} = 1.80$  V vs. SCE [21]. TPT data [20]:  $E_{A/A^{--}} = -0.29$  V vs. SCE,  $E_S = 65$  kcal/mol,  $E_T = 53$  kcal/mol.

ers for the photochemical cross-linking of poly(vinyl cinnamate). Analysis of the resulting cyclobutane dimers has revealed a selectivity different from that of the unsensitized reaction: a higher preference for head-to-head dimers (truxinates) and inversion of the percentages of  $\delta$ -truxinate (**5**) and  $\beta$ -truxinate (**7**) with the former as major product. In addition, significant amounts of  $\zeta$ -truxinate (**8**) are also formed in the presence of TPT. These results are in agreement with an electron-transfer mechanism involving cinnamate radical cations.

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