

Photoreactivity of *N*-*iso*-propylcinnamamide, a model for cinnamoylated polyvinylamine

Xavier Coqueret *

Laboratoire de Chimie Macromoléculaire-URA CNRS No 351 Université des Sciences et Technologies de Lille, F-59655 Villeneuve D'Ascq Cedex, France

Received 7 January 1998; accepted 23 February 1998

Abstract

The influence of solvent composition (water–THF 30:70 or 80:20 v/v) and irradiation wavelength (254/312 nm) on the photoisomerisation of pure (*E*)-*N*-*iso*-propylcinnamamide (NIPC) in solution was examined. The differences in photoreactivity were interpreted, not only on the basis of differences in the absorption characteristics of the *E* and *Z* isomers, but also in terms of isomerisation quantum yield. The data obtained from NIPC as a model compound were used to determine the progress of competing isomerisation and dimerisation processes in cinnamoylated polyvinylamine irradiated in water–THF solution, or as a thin solid film. © 1998 Elsevier Science S.A. All rights reserved.

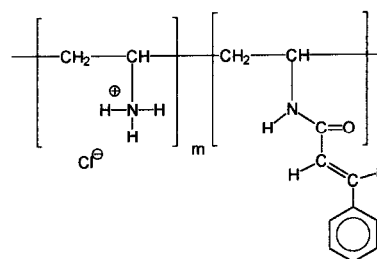
Keywords: Photoreactivity; *N*-*iso*-propylcinnamamide; Cinnamoylated polyvinylamine

1. Introduction

We have recently reported on the synthesis and on some photochemical properties of cinnamoylated polyvinylamines (Scheme 1) [1]. This novel class of photopolymers undergo efficient crosslinking via [2+2] photocycloaddition of the cinnamide side-groups. By analogy to the well-documented photoreactivity of poly(vinylcinnamate) [2,3], it is reasonably admitted that polymer chains are bridged by cyclobutane formation in the form, among other isomers, of α -truxillic diamide (Scheme 2) [4].

The photosensitivity of cinnamoylated polyvinylamines has been examined by means of photoresist tests that are based on the determination of the minimum UV light energy for obtaining incipient insolubilisation of the irradiated film [5]. The observed variations of the practical photosensitivity as a function of the cinnamide content and on the ionisation state of the amino units in the copolymers revealed a strong dependence of photoreactivity in the solid state on these two constitutional parameters [1].

For gaining a deeper insight into the photochemical process, the kinetic analysis of the modifications taking place and their analysis in conjunction with the physical characteristics of the material is a rational approach that usually provides pertinent information for systems involving

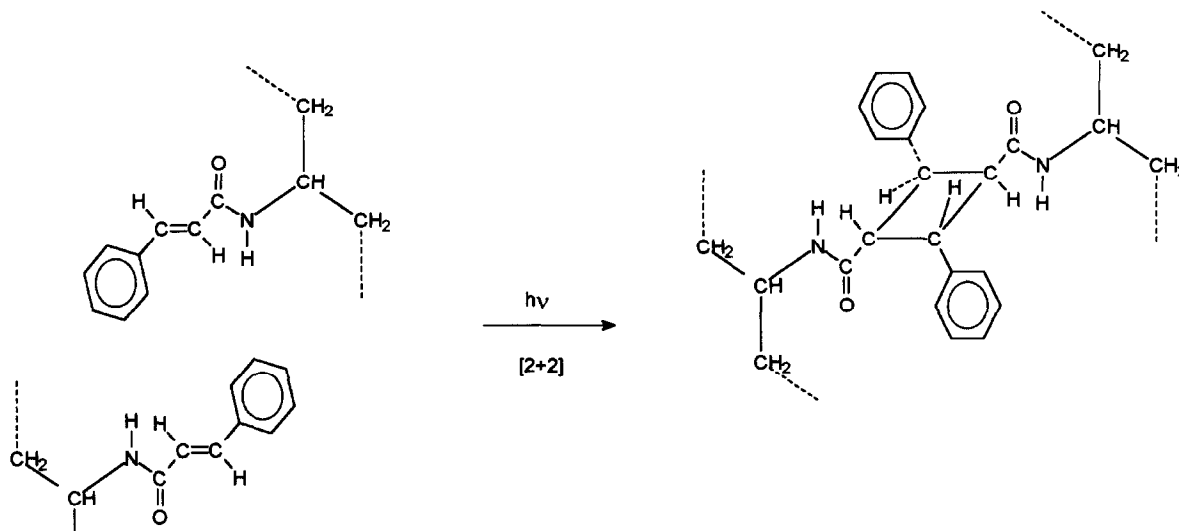


Scheme 1.

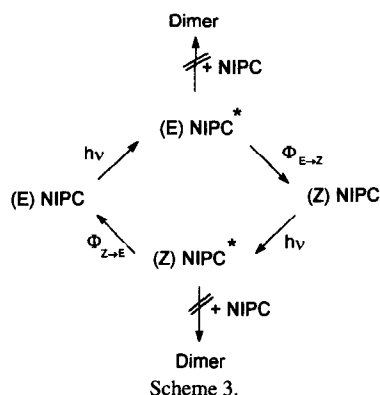
chromophores of the cinnamic type [6,7]. The events depicted in Scheme 3 take place in the solid state phototransformation of polyvinylcinnamate and are likely to occur similarly with polymer-bound cinnamide groups initially in the *E* form exclusively. The profiles of the concentration in *E*, *Z* and dimerised chromophores as a function of the time of exposure can be determined by monitoring at two wavelengths the changes in the UV spectra of the photoirradiated films.

We have therefore undertaken a basic study of the photoisomerisation of *N*-*iso*-propyl cinnamamide (NIPC) in water–THF solutions, initially in the pure *E* configuration, as a low molecular weight model for polyvinylcinnamamide. Since the photoreactions induced in photosensitive polymer films are generally carried out in air, the present study was performed without any effort to exclude air oxygen from the solutions, or from the solid films submitted to photoirradiation.

* Corresponding author.



Scheme 2.



Scheme 3.

tion. Indeed, there are some indications that the unsensitised photoreactivity of some simple cinnamic derivatives is not affected by the presence of oxygen [8].

2. Experimental

2.1. Starting materials

(*E*) *N*-iso-propylcinnamamide (NIPC) was prepared by reacting (*E*) cinnamoyl chloride with a 2-fold excess of freshly distilled isopropylamine in anhydrous ether solution. After stirring for 1 h at room temperature, the solution was concentrated by evaporation in vacuo. The white solid was washed three times with water and recrystallised from ethanol. The pure (*E*) amide was isolated as white needles (m.p. 101.5°C) in 95% yield.

IR (2 wt.% in KBr): ν/cm^{-1} : 3270, 3080, 2960, 1650, 1610, 1540, 1450, 1360, 1230, 980, 720; ^1H NMR (80 MHz, CDCl_3): δ/ppm = 1.60 (d, 6H, $J=7$ Hz), 4.45 (hept., 1H, $J=7$ Hz), 6.35 (d, 1H, $J=15$ Hz), 7.2–7.5 (mult., 5H), 7.65 (d, 1H, $J=15$ Hz); ^{13}C NMR (20.15 MHz, CDCl_3): $\delta/$

ppm = 22.5 (q), 41.4 (d), 121.6 (d), 127.5 (d), 128.5 (d), 129.2 (d), 134.9 (s), 140.1 (d), 165.2 (s); Mass spectrum [m/e (%)]: 189 $\text{M}^{+\bullet}$ (61), 146 (19), 131 (100), 103 (50), 77 (39), 58 (34), 51 (15).

Elemental analysis $\text{C}_{12}\text{H}_{15}\text{NO}$ (189.26)

Calculated	C	76.16	H	7.99	N	7.40
Found	C	76.00	H	8.02	N	7.26

Cinnamoylated polyvinylamine with cinnamamide content of 3.72 mmol g^{-1} was prepared from a polyvinylamine sample of $\bar{M}_n = 50,000$, [9] as described elsewhere [1]. The photosensitive polymer was isolated in the hydrochloride form.

2.2. UV spectroscopy measurements

Spectro grade THF and bidistilled water were used to prepare the solutions. A Varian Cary 219 spectrophotometer was used to record the spectra of starting (*E*) NIPC. Photoisomerisation kinetics was monitored on a Uvikon apparatus.

2.3. Photoisomerisation experiments

Fluorescent lamps with light emission centered at 254 nm or at 312 nm were used as monochromatic sources monitored by a RMX processor coupled to photometric detectors. The diluted solutions (ca. 60 $\mu\text{mol l}^{-1}$) of *N*-iso-propylcinnamamide were treated in 1-cm thick *Suprasil* cells for spectrophotometric analysis. For the chromatographic determination of the *E/Z* content in the photoisomerised mixtures, large volumes (200–250 ml) of the diluted solutions placed in a large diameter reaction vessel so as to obtain a thickness not exceeding 1 cm were treated under the frontal beam of the same UV source for 8–12 min. The solvents were evaporated in vacuo and the solid NIPC residue diluted for subsequent spectroscopic and chromatographic analyses.

2.4. Chromatographic analysis

The mixture of NIPC isomers obtained after photoirradiation was submitted to analytical HPLC on a Waters apparatus (C18 modified stationary phase, water–THF 80/20 as an eluent) with a UV detector set at 250 nm.

3. Results and discussion

3.1. Absorption spectrum of (*E*) *N*-iso-propylcinnamamide

The absorption spectrum of NIPC in water–THF mixtures was recorded for various compositions of the solvent. The mixtures used in the adequate proportions proved to have good solvating properties for modified polyvinylamines with cinnamamide content ranging from 4 to 72 mol%. The data collected in Table 1 reveal a bathochromic shift of approximately 15 nm for the absorption maximum wavelength upon increasing the water content over the whole range of compositions. This is a common feature of polar chromophores with higher dipole moment in the excited state [10]. However, the molar absorption coefficient of the cinnamamide chromophore is not greatly affected by the changes of solvent compositions, the variations being in the range of experimental errors. A slight deformation by shoulder on the long wavelength side of the main absorption band is observed, whatever the solvent composition.

3.2. Photoisomerisation of *N*-iso-propylcinnamamide

In order to prevent competing dimerisation that can take place at moderate dilution, the solutions prepared for studying photoisomerisation had a low concentration in NIPC ($59.3 \mu\text{mol l}^{-1}$). Two particular solvent compositions of water and THF in volume ratios 30:70 and 80:20 were selected to examine the effects of solvent polarity on the photoreactions. The changes in the UV spectrum of the (*E*) NIPC solution submitted to 312 nm irradiation are plotted in Figs. 1 and 2, respectively. By analogy to the well-documented photochemistry of cinnamates, the observation of an isobestic point between 240 and 260 nm confirms that photoisomerisation is the single chemical process in both solutions. The isobestic wavelength is 247.5 nm for the THF-rich solution and 250 nm for the water-rich solution as consequence of the solvent dependence of the absorption of both isomers, as will be discussed in a following section. The initially strong decrease of absorbance at the wavelength of the (*E*) isomer absorption maximum λ_{max}^E takes place with a shift of the spectrum absorption towards shorter wavelengths. Upon increasing the absorbed UV dose, the cinnamamide solutions approach their steady state composition with a more important spectral deformation for the water-rich mixture.

Table 1
Ultraviolet absorption characteristics^a of *N*-iso-propylcinnamamide in water–THF solutions

Solvent composition water–THF (vol/vol)	λ_{max}^b (nm)	ϵ^c ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)
0–100	269	24,500
30–70	271.5	24,700
50–50	273	24,550
80–20	274.5	24,600
95–5	275	24,450

^aAverage values determined for cinnamamide concentrations in the range of $10\text{--}50 \mu\text{mol l}^{-1}$.

^bWavelength of absorption maximum.

^cMolar decadic absorption coefficient.

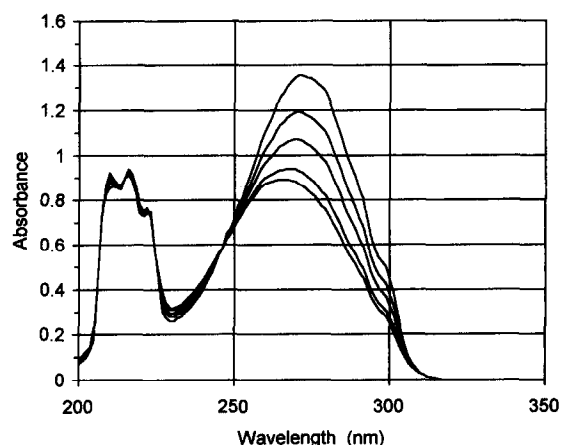


Fig. 1. Changes in the UV spectrum of a solution of NIPC (10 mg l^{-1}) in water–THF (30:70 v/v) upon exposure to 312 nm light (0, 30, 60, 120, 300 s).

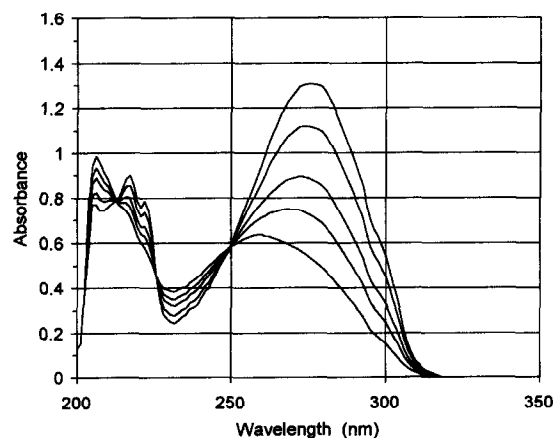


Fig. 2. Changes in the UV spectrum of a solution of NIPC (10 mg l^{-1}) in water–THF (80:20 v/v) upon exposure to 312 nm light (0, 5, 20, 40, 300 s).

3.3. Determination of *N*-iso-propylcinnamamide UV absorption spectrum

Various procedures permit to determine the absorption spectra of mixed isomers without requiring their separation

[11,12]. In the present case, the molar absorption coefficient of the (Z) isomer at λ_{\max}^E can be calculated from the changes of absorbance at λ_{\max}^E of the NIPC solution upon UV irradiation by coupling these data to the (E)/(Z) content in the photoisomerised mixtures. Preliminary analytical separation by reverse phase HPLC have shown that good separation of the two isomers was achieved by elution with water–THF mixtures in 80:20 volume proportions. Setting the wavelength of the UV detector at 250 nm, the wavelength of equal light absorption by both isomers, the corresponding areas are directly proportional to their mole content in the analyzed mixture. Three diluted solutions of (E) NIPC for each type of solvent mixture were submitted to photoisomerisation under 312 nm radiation. The absorbance at λ_{\max}^E of the diluted isomerised mixture $A_{\lambda_{\max}^E}^{E+Z}$ is dependent on the mole fraction of (Z) isomer f_Z determined from HPLC analysis for each experiments:

$$A_{\lambda_{\max}^E}^{E+Z} = [f_Z \cdot \varepsilon_{\lambda_{\max}^E}^Z + (1-f_Z) \varepsilon_{\lambda_{\max}^E}^E] l \cdot c_{\text{NIPC}} \quad (1)$$

where $\varepsilon_{\lambda_{\max}^E}^Z$ and $\varepsilon_{\lambda_{\max}^E}^E$ are the molar absorption coefficients at λ_{\max}^E of the Z and E isomer of NIPC, respectively, l is the cell thickness and c_{NIPC} , the overall NIPC concentration in the solution. Combining the absorbance values measured for the isomerised mixture $A_{\lambda_{\max}^E}^{E+Z}$ to that measured for the pure (E) isomer $A_{\lambda_{\max}^E}^E$, $\varepsilon_{\lambda_{\max}^E}^Z$ is given by Eq. (2).

$$\varepsilon_{\lambda_{\max}^E}^Z = \frac{\varepsilon_{\lambda_{\max}^E}^E}{f_Z} \left[\frac{A_{\lambda_{\max}^E}^{E+Z}}{A_{\lambda_{\max}^E}^E} - 1 + f_Z \right] \quad (2)$$

The average values for $\varepsilon_{\lambda_{\max}^E}^Z$ deduced from repeated experiments were 9400 and 5950 $\text{l mol}^{-1} \text{cm}^{-1}$ for the 30–70 and 80–20 water–THF mixtures, respectively. It is possible to go further in the knowledge of the spectral characteristics of the Z isomer by simply achieving the deconvolution of the isomerised mixture spectrum with weighing the contribution of the (E) isomer by its mole fraction in the solution. The resulting spectra of (Z) NIPC are shown in Fig. 3, and the corresponding spectral data are collected in Table 2. While for (E) NIPC, increasing the water content in the solvent mixtures was shown to induce the bathochromic shift of λ_{\max}^E without significant modification of the absorption coefficient, the two spectral parameters are affected by changing the solvent composition for the (Z) isomer. The peculiar conformation of the (Z) derivative with a *s-trans* enone conformation in the ground state may give rise to complex absorption patterns involving both the styrene like $\pi-\pi^*$ and the amide $n-\pi^*$ transitions [13].

3.4. Progress of the isomerisation

The spectral changes observed upon 254 nm irradiation for the two selected water–THF solutions of NIPC are initially observed with apparent conservation of the isobestic point located at the wavelength reported in Table 2. For prolonged irradiations of several minutes, the isobestic point is lost as a consequence of the occurrence of another competing process,

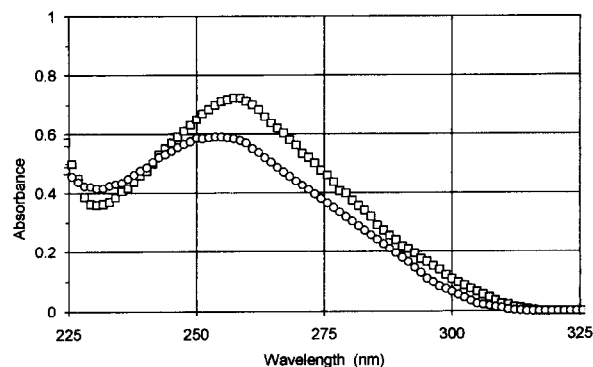


Fig. 3. Computed spectra of (Z) NIPC (10 mg l^{-1}) in water–THF mixtures, 80:20 v/v (○) and 30:70 v/v (□).

Table 2
Spectral characteristics^a of (Z) *N*-iso-propylcinnamamide

Solvent composition water–THF (vol/vol)	λ_{\max}^b	λ_{iso}^c (nm)	ε^d ($\text{l mol}^{-1} \text{cm}^{-1}$)	
			At λ_{\max}^Z	At λ_{\max}^E
30–70	258	247.5	14,000	9400
80–20	253	250	11,200	5950

^aAverage values determined for cinnamamide concentrations of ca. $50 \mu\text{mol l}^{-1}$.

^bWavelength of absorption maximum.

^cWavelength of the isobestic point of Z–E interconversion.

^dMolar decadic absorption coefficient.

likely a dimerisation or oligomerisation of the cinnamate styryl group [14]. When the solutions are submitted to 312 nm irradiation, the spectral changes take place with strict conservation of the isobestic point until a photostationary state is reached after 500–600 s. The progress of the isomerisation reaction is easily deduced from the recorded spectra, the decrease of absorbance at λ_{\max}^E being related to the content in (E) and (Z) isomers by Eq. (1).

The appearance of (Z) NIPC in the solutions submitted to 254 nm and 312 nm irradiation is presented on the plots of Figs. 4 and 5, respectively. The initial rates of formation of

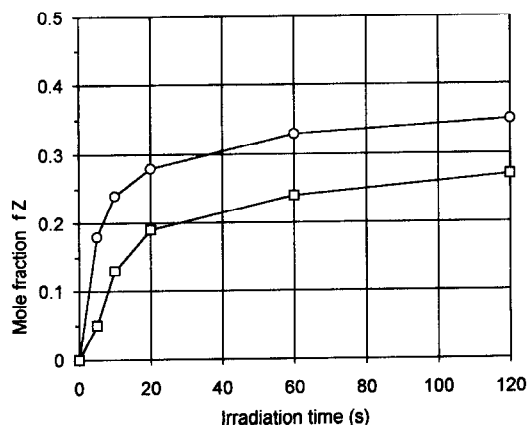


Fig. 4. Progress of the Z–E interconversion of (E) NIPC in water–THF solution (80:20 (○) or 30:70 (□) v/v) upon exposure to 254 nm light.

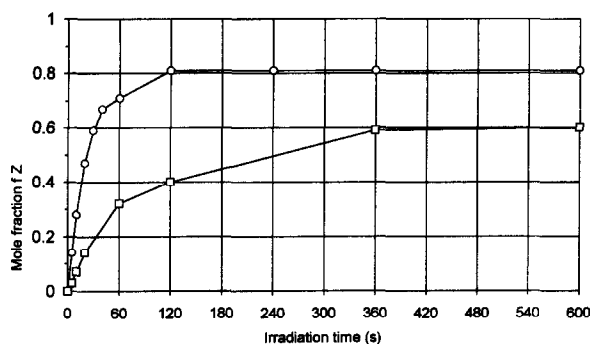


Fig. 5. Progress of the *Z*-*E* interconversion of (*E*) NIPC in water-THF solution (80:20 (○) or 30:70 (□) v/v) upon exposure to 312 nm light.

Table 3
Competing absorption characteristics of the *E* and *Z* isomers of NIPC

Ratio of molar absorption coefficients	Solvent composition water-THF (v/v)	
	80:20	30:70
$(\epsilon_E/\epsilon_Z)_{254\text{ nm}}$	1.1	1.2
$(\epsilon_E/\epsilon_Z)_{312\text{ nm}}$	7 ± 1.5	0.9 ± 0.1

the (*Z*) isomer are obviously dependent on both the nature of the solvent and the irradiation wavelength.

3.5. Photostationary composition and quantum yield for photoisomerisation

The photostationary compositions observed upon 312 nm irradiation of the two types of solvent mixtures reveal the existence of a single and presumably reversible process. The interconversion pattern of Scheme 3 takes place to produce a steady state with a $[E]/[Z]$ ratio expressed by Eq. (3), where ϵ_Z and ϵ_E are the molar decadic absorption coefficient of the two isomers at the wavelength of irradiation, and $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$ are the quantum yield for isomerisation [15].

$$\left(\frac{[Z]}{[E]}\right)_{ps} = \frac{\epsilon_E \Phi_{E \rightarrow Z}}{\epsilon_Z \Phi_{Z \rightarrow E}} \quad (3)$$

The competition for light absorption by the isomers is deduced from the spectral data determined in the above sec-

tions. The values of the ratio ϵ_Z/ϵ_E reported in Table 3 clearly indicate that changes in solvent composition will affect strongly the photostationary concentrations of the two isomers submitted to 312 nm irradiation.

Owing to the low absorbance of the pure (*E*) NIPC solution at 312 nm, the absorbed intensity in quanta per second and per surface unit, I_{abs} , is uniform in the depth l of the irradiated cell, and can be approximated to $2.303 \cdot A_0 I_0$ in the initial conditions. $\Phi_{E \rightarrow Z}$ was thus deduced from the initial slope of plots representing the appearance of the (*Z*) isomer with irradiation time by using Eq. (4). The resulting quantum yields are given in Table 4.

$$\Phi_{E \rightarrow Z} = \left(\frac{l}{I_{abs}} \frac{d[Z]}{dt} \right)_0 \quad (4)$$

The values for $\Phi_{Z \rightarrow E}$ were in turn approximated from Eq. (3) by using the absorption factors of Table 3. The dependence of NIPC photoreactivity upon the solvent composition is obviously complex. The absorption characteristics of the two isomers have a prominent role on steady-state compositions. However, the quantum yields for isomerisation are also sensitive to the composition of the medium. Such effects are well documented for a number of substituted ethenes, stilbene and others derivatives undergoing *E*-*Z* interconversion [16]. Obviously, the general interpretation of the $\Phi_{E \rightarrow Z}$ dependence upon the medium polarity based on the opposing effect of stronger polar interactions taking place between the excited state and the surrounding solvent molecules does not apply to NIPC *E* \rightarrow *Z* photoisomerisation. However, the quantum yields for methyl cinnamate two-way isomerisation were also shown to increase with solvent polarity [17]. The dissymmetry of the cinnamic chromophore compared to diaryl ethenes is certainly at the origin of this peculiar feature that would require additional investigation.

3.6. Photoreactivity of cinnamoylated polyvinylamine

Cinnamoylated polyvinylamines of various amide contents are not soluble in pure THF nor in pure water, but their hydrochloride form readily dissolves in water-THF mixtures of appropriate composition [1]. The polymer sample examined for this study had an average degree of polymerisation

Table 4
Influence of reaction conditions^a on the photoisomerisation of (*E*) *N*-iso-propylcinnamide

Solvent composition water-THF (vol/vol)	λ_{irr}^b (nm)	$([Z]/[E])_{ps}^c$	$(\Phi_{E \rightarrow Z})_{Solvent}^d$	$(\Phi_{Z \rightarrow E})_{Solvent}^d$
30-70	254	0.26	—	—
30-70	312	1.45	0.19	0.15-0.30
80-20	254	0.43	—	—
80-20	312	4.6	0.38	0.35-0.45

^aAverage values determined for cinnamide solutions ($60 \mu\text{mol l}^{-1}$).

^bWavelength of irradiation.

^cRatio of the photostationary concentrations of *Z* to *E* isomers.

^dQuantum yield for isomerisation.

$\overline{DP}_n = 1170$ and an amide content of 45 mol%. The UV spectrum of its 27 mg l⁻¹ solution in 30:70 v/v water-THF mixture is similar to that of NIPC in the same solvent. Upon 312 nm irradiation at the same molar concentration, the UV spectrum changes without conservation of the isomerisation isobestic point observed with the low molecular weight model. Because of the low macroscopic average concentration of cinnamamide units (< 100 μmol l⁻¹), intermolecular coupling by dimerisation is extremely unlikely but the close proximity of styryl moieties in adjacent cinnamoylated repeat units permits chemical deactivation of some excited chromophores, as observed with the *O*-analogue polymer, namely poly(vinylcinnamate) [14,18].

By monitoring at two wavelengths, the progress of concurrent isomerisation and dimerisation of polymer bound chromophores, it is possible to determine the variations with the exposure duration *t* of the mole ratio of *E*, *Z* and dimerised (*D*) cinnamamide by using Eqs. (5)–(7) [17,18] with the appropriate light absorption coefficients:

$$\frac{[E]_t}{[E]_0} = \frac{\varepsilon_{\lambda_{\max}^E}^E}{\varepsilon_{\lambda_{\max}^E}^E - \varepsilon_{\lambda_{\max}^Z}^Z} \left[\frac{A_{\lambda_{\max}^E}^E}{A_{\lambda_{\max}^E}^0} - \frac{\varepsilon_{\lambda_{\max}^Z}^Z \cdot A_{\lambda_{\max}^Z}^Z}{\varepsilon_{\lambda_{\max}^E}^E \cdot A_{\lambda_{\max}^E}^0} \right] \quad (5)$$

$$\frac{[Z]_t}{[E]_0} = \frac{\varepsilon_{\lambda_{\max}^Z}^Z}{\varepsilon_{\lambda_{\max}^E}^E - \varepsilon_{\lambda_{\max}^Z}^Z} \left[\frac{A_{\lambda_{\max}^E}^E}{A_{\lambda_{\max}^E}^0} - \frac{A_{\lambda_{\max}^Z}^Z}{A_{\lambda_{\max}^Z}^0} \right] \quad (6)$$

$$\frac{[D]_t}{[E]_0} = 1 - \frac{A_{\lambda_{\max}^Z}^Z}{A_{\lambda_{\max}^E}^0} \quad (7)$$

As expected, the corresponding plots of Fig. 6 show that polymer-bound cinnamamide isomerisation proceeds at a rate similar to that observed for (*E*) NIPC placed in the same conditions. However, the slow dimerisation process, possibly accompanied by oligomerisation, consumes more than 25 mol% of cinnamamide groups after 5 min of 312 nm irradiation (3.5 mW cm⁻²). A thin film of the same sample of cinnamoylated polyvinylamine was casted in the hydrochloride form on a quartz plate and irradiated under identical conditions. The spectrum of the unirradiated film presents a

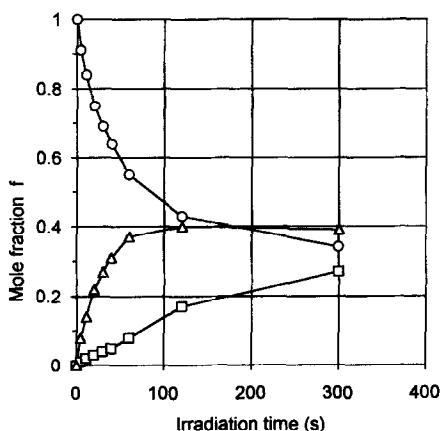


Fig. 6. Progress of the *Z*-*E* interconversion and concurrent dimerisation of cinnamoylated polyvinylamine in water-THF solution (30:70 v/v) upon exposure to 312 nm light (3.5 mW cm⁻²): *f*_E (○), *f*_Z (Δ), *f*_D (□).

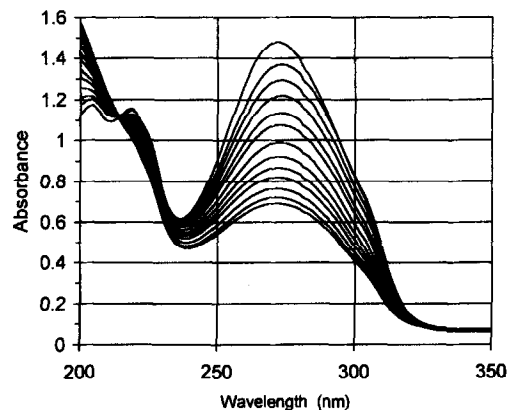


Fig. 7. Changes in the UV spectrum of a solution of cinnamoylated polyvinylamine as a solid film exposed to 312 nm light (0, 5, 10, 15, 25, 35, 55, 75, 105, 135, 195, 255, 315 s).

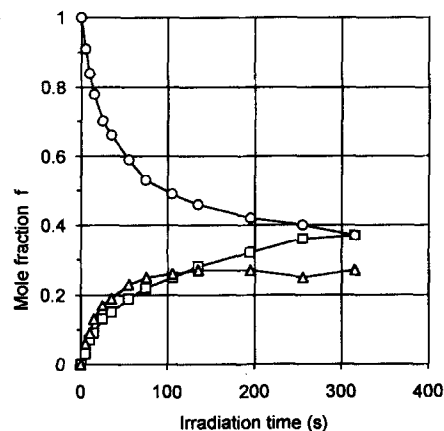


Fig. 8. Progress of the *Z*-*E* interconversion and concurrent dimerisation in cinnamoylated polyvinylamine as a solid film exposed to 312 nm light (3.5 mW cm⁻²): *f*_E (○), *f*_Z (Δ), *f*_D (□).

shape similar to that of NIPC in 30:70 v/v water-THF solution, with the absorbance maximum at 271.5 nm (Fig. 7). Analysis of the changes in the UV spectrum by using Eqs. (5)–(7) with the absorption characteristics determined for the free chromophore on this particular solvent mixture yield the conversion profiles of Fig. 8. The plots indicate a fast dimerisation process taking place at rate similar to that of isomerisation, dimerisation being obviously favoured in the bulk material. Interestingly, the rate of disappearance of the (*E*) cinnamamide side groups appear unaffected by the bulk or dissolved state of the photosensitive polymer, the changes appearing only in the partition of reaction products influenced by the reduction of free volume and the close proximity of the reactive chromophores.

4. Conclusion

The efficiency of NIPC photoisomerisation in water-THF mixtures was shown to be dependent on solvent composition, as a consequence of changes in the absorption characteristic of the two interconverting isomers and because of the higher

values of isomerisation quantum yields $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$ in water-rich mixtures. The spectroscopic data deduced from this study, particularly those concerning (Z) NIPC are of high interest for further examining the solution and solid state photochemical behaviour of cinnamoylated polyvinylamines.

Acknowledgements

The author is indebted to Mrs. A.-M. Cazé for her assistance in performing analytical experiments.

References

- [1] A. El Achari, X. Coqueret, *J. Polym. Sci., Polym. Chem.* 35 (1997) 2513.
- [2] L.M. Minsk, I.G. Smith, J.F. Wright, *J. Appl. Polym. Sci.* 2 (1959) 303.
- [3] G.A. Delzenne, *Encyclopedia of Polymer Science and Technology*, Suppl. Vol. 1, Wiley, New York, 1976.
- [4] P.L. Egerton, E.M. Hyde, J. Trigg, A. Payne, P. Beynon, M.V. Mijovic, A. Reiser, *J. Am. Chem. Soc.* 103 (1981) 3859.
- [5] J.L. Decout, A. Lablache-Combier, C. Loucheux, *Photogr. Sci. Eng.* 23 (1979) 309.
- [6] X. Coqueret, A. El Achari, A. Hajaiej, A. Lablache-Combier, C. Loucheux, L. Randrianarisoa, *Makromol. Chem.* 192 (1991) 1517.
- [7] J.M. Buisine, X. Coqueret, C. Lahamamssi, *Mol. Cryst. Liq. Cryst.* 281 (1996) 295.
- [8] Y. Shindo, K. Horie, I. Mita, *Chem. Lett.*, 1983, p. 639.
- [9] A. El Achari, X. Coqueret, A. Lablache-Combier, C. Loucheux, *Makromol. Chem.* 194 (1993) 1879.
- [10] Ch. Reichardt, *Solvent Effects in Organic Chemistry*, Springer, Berlin, 1986.
- [11] E. Fisher, *J. Chem. Phys.* 71 (1967) 3704.
- [12] J. Blanc, D.L. Ross, *J. Chem. Phys.* 72 (1968) 2817.
- [13] F.D. Lewis, J.E. Elbert, A.L. Uthagrove, P.D. Hale, *J. Am. Chem. Soc.* 110 (1988) 5191.
- [14] P.L. Egerton, E. Pitts, A. Reiser, *Macromolecules* 12 (1979) 670.
- [15] D. Schulte-Frohlinde, *Liebigs Ann. Chem.* 615 (1958) 114.
- [16] H. Görner, H.J. Kuhn, in: D.C. Neckers, D.H. Volman, G. von Büna (Eds.), *Advances in Photochemistry*, Vol. 19, Wiley, New York, 1995.
- [17] Y. Shindo, K. Horie, I. Mita, *J. Photochem.* 26 (1984) 185.
- [18] P.L. Egerton, E. Pitts, A. Reiser, *Macromolecules* 14 (1981) 95.