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Liquid Crystals

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Photoinduced orientation in poly(vinylcinnamate) and poly(7-methacryloyloxycoumarin) thin films and the consequences on liquid crystal alignment

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Thin films of poly(vinylcinnamate) and poly(7-methacryloyloxycoumarin) have been exposed to linearly polarized UV light. The resulting anisotropic films have been characterized by using UV, conventional and polarization modulation FTIR spectroscopies. In particular, several internal vibrational modes have been used as structural probes to examine the orientation of groups in the irradiated polymers. These experiments provide new information about the photoinduced anisotropy in these photocrosslinkable polymers upon irradiation with linearly polarized UV light, and an orientation mechanism is proposed. This mechanism is confirmed by studying the liquid crystal alignment induced by PVCi and poly(7-methacryloyloxycoumarin). Finally, the stability of the photoalignment process is discussed.

1. Introduction

Poly(vinylcinnamate) (PVCi) has been playing a prominent role in the field of photoresists since its synthesis in 1959 [1]. More recently, much attention has been paid to its ability to orient liquid crystals homogeneously after being irradiated by linearly polarized UV light [2]. Uniaxial orientation of liquid crystals is one of the most important prerequisites for liquid crystals display (LCD) technology. Nowadays, liquid crystal alignment is almost exclusively achieved by mechanical rubbing of any substrate coated with polyimides. The success of this technique lies mainly in its ease of integration into the manufacturing process. But its inherent drawbacks (creation of dust particles and static electricity during rubbing...) make rubbing-free techniques very attractive. In addition, optical processes allow one to induce as many alignment directions as desired over the display area [3] and open the way to more complex LCD structures with wider viewing angle [4]. Recent advances in photoalignment technology have been obtained by using new coumarin-based photopolymers [5]. The generated alignment has been reported to be thermally and optically stable. Moreover, oblique irradiation of these polymers with linearly polarized UV light has been shown to induce a homogeneously tilted alignment of liquid crystals.

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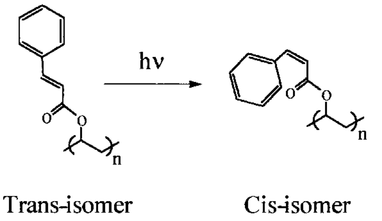
In this paper, the photochemical reactivity of PVCi and a new coumarin-based polymer are compared. PVCi has been extensively studied, but in contrast little information is available on the behaviour of coumarin-based polymer thin films upon irradiation. In spite of this lack of data, this family of photopolymers seems to be of special interest because of its simple photoreactivity. Moreover, we know that PVCi induces liquid crystal alignment perpendicular to the direction of polarization, whereas coumarin-based polymers orient liquid crystals parallel to the direction of polarization [5]. Consequently, in the field of molecular orientation, coumarin-based polymers and PVCi should behave in a different manner. Hence, we expect that a comparative study of PVCi and poly(7-methacryloyloxycoumarin) (PMC) would facilitate understanding of the mechanisms of photoinduced anisotropy in these polymer systems. The requirements for liquid crystal alignment could then become better understood. One of the main difficulties is to identify clearly the orientation of both unreacted and reacted chemical species in the films. Since UV absorption bands are often wide and overlapped, UV spectroscopy is unlikely to provide this information. On the contrary, IR spectroscopy should afford information at a vibrational level about the different species. In this paper, after reviewing the photochemical reactivity of PVCi and coumarin-based photopolymers, we present new results on the side group distribution in irradiated polymer thin films by using UV and IR spectroscopies. Consequently, a model explaining liquid crystal alignment on PVCi and PMC will be proposed. Finally, liquid crystal alignment stability on these polymer films is discussed.



Scheme 1. *trans-cis*-photoisomerization of PVCi upon UV irradiation.

2. General comments

2.1. *Behaviour of PVCi and PMC exposed to unpolarized UV light*

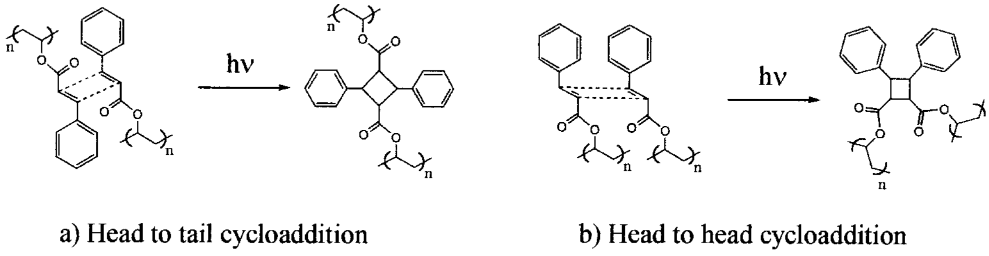
2.1.1. *PVCi*

When exposed to UV light, the *trans*-isomers of unsaturated chromophores such as cinnamates can photoisomerize to the *cis*-isomers (scheme 1).

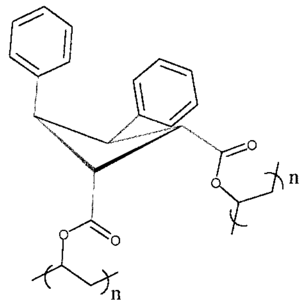
This intramolecular process is generally favoured in dilute solution. Indeed, Coqueret *et al.* [6] have shown that isomerization is the only photochemical process during ethyl cinnamate irradiation in dilute solution, at least in the early stages of irradiation. A similar result has been obtained by Rennert [7] with a dilute solution of PVCi. In this case, an isobestic point is observed at a wavelength λ_i equal to 249 nm. On the contrary, in confined systems such as films of PVCi, Egerton *et al.* [8] have shown by using UV measurements that isomerization produces less than 10% of the photoproducts. This result can be explained by constraint considerations, because the free volume for phenyl rotation is no longer available in thin films. The photochemical process in such polymer films has been attributed to crosslinking between polymer chains as inferred by the insolubility of the compound after irradiation [1]. The photoreactivity of PVCi thin films arises essentially from head to head and head to tail [2+2] cycloaddition between the double bonds whose relative geometry is favourable (scheme 2). It is noteworthy that cycloaddition induces an angular reorientation of the phenyl axis. For instance, in the head to tail photodimers, the phenyl axis has rotated from the direction in the starting chromophores.

Because of the very brief lifetime of the excited states of benzene derivatives [9], two chromophores have to be very close to each other for reaction to occur. As shown by Egerton *et al.* [8], the polymer film can be described as a set of sites with a quasi-continuous range of configurations that leads to a quasi-continuous distribution of reactivities. The most reactive sites are likely to correspond to chromophore pairs whose relative geometry is favourable for cycloaddition.

For PVCi thin films, it has been shown [8] that the β-truxinate (head to head dimer, scheme 3) is the major product among the eleven possible photodimers.



Scheme 2. Structures of the photodimers of PVCi.



Scheme 3. Structure of the β-truxinate.

As irradiation proceeds, the reactive sites are gradually depleted and light may finally be absorbed by unreactive sites. In that case, photochemical changes are essentially due to the isomerization process. Finally, it is important to note that no preferential orientation of the photoproducts (photodimers, *cis*-isomers...) is observed when thin films are irradiated by unpolarized UV light, because of the isotropic orientation of the electric field.

2.1.2. *Coumarin-based polymers*

The reactivity of coumarin has been less extensively studied. However, it has been mentioned [10] that coumarins have a good ability to crosslink in solution, but to our knowledge no study has been performed on thin films. It is noteworthy that the endocyclic position of the photosensitive double bond prevents an isomerization process in coumarin derivatives. Moreover, one can observe (scheme 4) that cycloaddition induces no angular reorientation of the coumarin chromophores: the photodimer axes remain along the axis of the initial coumarin side groups.

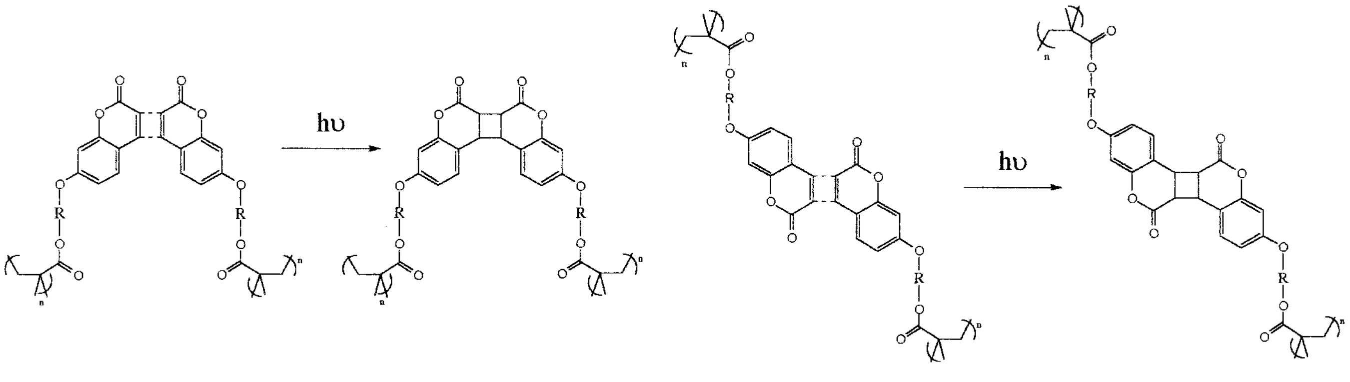
2.2. *Behaviour of PVCi and PMC exposed to linearly polarized UV light*

Compared with polymers irradiated with an unpolarized UV light, the photochemical reactivity of PVCi and PMC upon irradiation with linearly polarized light will present some differences. Indeed, in the last case, the probability for a chromophore to absorb a quantum of light is proportional to $I\cos^2\theta$ where I is the intensity of the laser pump and θ the angle between the electric vector of the incident electromagnetic wave and the electric dipole transition moment of the photosensitive chromophore [11, 12]. Consequently, as irradiation proceeds, this selective optical pumping (the so called angular hole burning process) is responsible for the preferred depletion of the chromophores in the direction of polarization. On the contrary, chromophores whose dipole transition moment is perpendicular to the polarization direction do not undergo photoreactions. Two consequences result from this process:

(1) crosslinked species will be formed in a preferential orientation in contrast to that observed using unpolarized light irradiation;
(2) a large amount of chromophore will remain unchanged as compared with the photochemical process with unpolarized light.

Consequently, the irradiated film will become more anisotropic.

In the field of LCDs, the film anisotropy is of great importance since the orientation of liquid crystals is governed by anisotropic interactions with the alignment layer. Most authors characterize the angular distribution of the chromophores in PVCi thin films either by measuring the birefringence ($\Delta n = n_{\parallel} - n_{\perp}$) or the UV linear dichroism ($\Delta A = A_{\parallel} - A_{\perp}$), where $A_{\parallel}$ and $A_{\perp}$ represent the absorbances of the irradiated film measured with the UV radiation polarized parallel or perpendicular to the direction of the laser pump polarization, respectively. In this respect, we summarize below the main results reported in the literature for PVCi and PMC.



a) Head to head cycloaddition

b) Head to tail cycloaddition

Scheme 4. Structures of the photodimers of coumarin-based polymers, R = spacer.

2.2.1. *PVCi*

Previous results concerning PVCi thin films have shown that both the birefringence and the UV linear dichroism are negative [13, 14], and their absolute values slowly increase upon irradiation and reach a maximum. The negative sign of the UV linear dichroism indicates that the chromophores are preferably oriented perpendicular to the polarization direction. Although the UV absorption spectrum of PVCi does not allow the identification of the different species, the negative dichroism observed for poly(vinyl-4-methoxycinnamate) [3] for both the unreacted chromophores and the photodimers leads to the proposition of the model of orientation, illustrated in scheme 5.

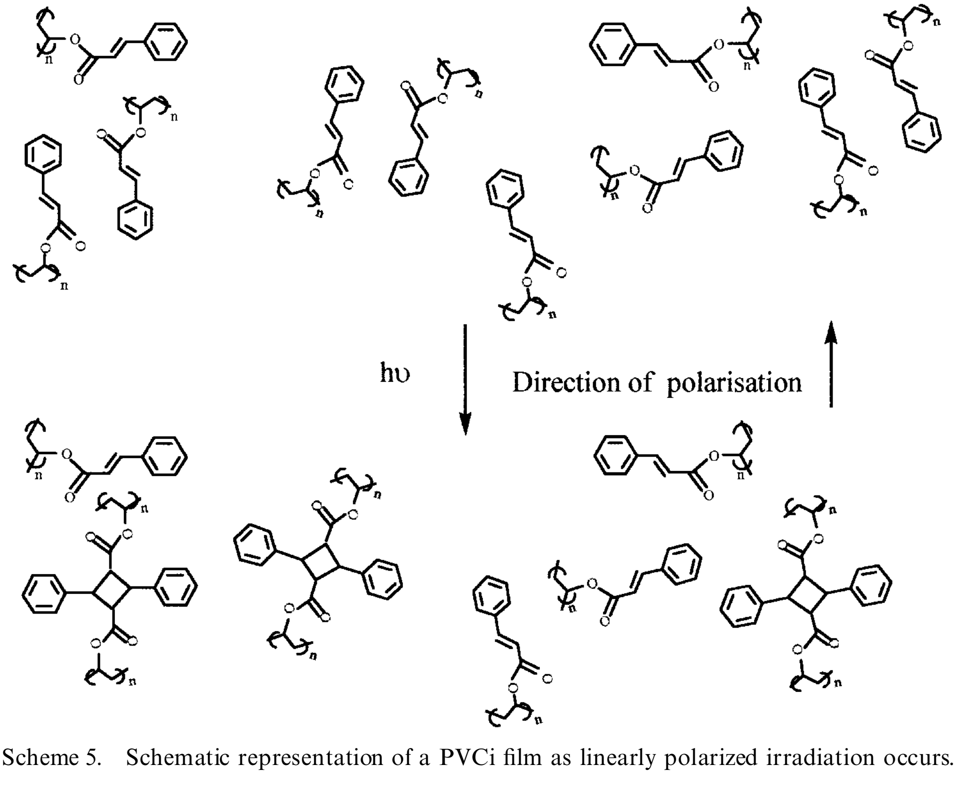
As irradiation proceeds, the negative dichroism of the unreacted cinnamates indicates a preferred depletion of the *trans*-chromophores along the direction of polarization; this effect is due to both the cycloaddition process which gives rise to photodimers from mainly *trans*-cinnamates oriented along the direction of polarization, and the selective optical pumping on unreacted chromophores (molecular reorientation of *trans*-cinnamates or the *trans*-/*cis*-isomerization process). In addition, the negative dichroism of the photodimers indicates that the molecular axis of the species formed is preferentially perpendicular to the direction of polarization. This arrangement is due to an angular reorientation of the phenyl moieties (scheme 2) with a majority of photodimers in a head to tail association. This model has been very recently confirmed by STM measurements [15] and has been assumed by most authors to be effective for PVCi.

The photoproduct distribution has been evaluated by Ichimura *et al.* [13] according to the method proposed by Egerton *et al.* [8]. The proportions of photoproducts after linearly polarized irradiation of PVCi thin films were: 40% of unreacted *trans*-cinnamates, 20% of *cis*-isomers and 40% of photodimers.

Irradiated PVCi thin films are known to orient liquid crystals in the direction perpendicular to the direction of polarization. Thus, the preferential orientation of liquid crystals on PVCi films has been attributed to anisotropic interactions with photodimers and/or unreacted *trans*-cinnamate side chains. Nevertheless, further experiments have shown that hindered PVCi derivatives, which did not undergo dimerization, were able to induce homogeneous liquid crystal alignment.

By comparison with photoreactive azobenzenes, Ichimura *et al.* [13] have assumed that liquid crystal alignment was due to the selective optical pumping which produces a preferential orientation of unreacted *trans*-isomers perpendicular to the direction of polarization. Under this last assumption, any cycloaddition mainly contributes to an increase in the thermal stability.

Iimura *et al.* [16] have shown that rubbing induced a preferred orientation of PVCi side groups along the direction perpendicular to the direction of rubbing.



Scheme 5. Schematic representation of a PVCi film as linearly polarized irradiation occurs.

Consequently, perpendicular orientation of liquid crystals has been attributed to anisotropic interactions with the *trans*-cinnamate side groups having a preferred orientation perpendicular to the direction of rubbing. This assumption has been confirmed by irradiating a rubbed PVCi film with randomly polarized UV light whereby non uniform alignment was obtained.

Thus, whatever the technique used for producing the film anisotropy, the preferred orientation of the *trans*-cinnamate side groups obtained seems to be responsible for the subsequent liquid crystal alignment.

2.2.2. *PMC*

As far as we know, no report has been published on the angular distribution of the chemical species in a coumarin-based polymer thin film irradiated with linearly polarized light. In contrast with the above results, it is only mentioned that irradiated coumarin-based polymer films induce a homogeneous alignment of liquid crystals in the direction of the polarization [5].

3. Experimental

3.1. *Synthesis*

PVCi was purchased from Polysciences Inc., while PMC was prepared in a two step procedure as described in Patent [17].

7-Methacryloyloxycoumarin (**1**) was first prepared by a conventional procedure from 7-hydroxycoumarin (Aldrich) and methacryloyl chloride in pyridine in the presence of di-*tert*-butylphenol to give a white solid (yield 73%). ^{1}H NMR δ: 7.7 ppm (d, $J = 9.5$ Hz, 1H, Ar–C$\underline{H}$=CH–), 7.5 ppm (d, $J = 8.4$ Hz, 1H, C_6H_3–), 7.15 ppm (sd, $J = 1.9$ Hz, 1H, –C_6H_3–), 7.09 ppm (dd, $J = 8.4$ Hz, 1H, –C_6H_3–), 6.4 ppm (d, $J = 9.5$ Hz, 1H, Ar–CH=C$\underline{H}$–), 6.39 ppm (s, 1H, $C\underline{H}_2$=C(CH_3)–), 5.83 ppm (s, 1H, $C\underline{H}_2$=C(CH_3)–), 2.08 ppm (s, 3H, CH_2=C($C\underline{H}_3$)–). IR: 1732 cm^{-1} (νC=O), 1616 cm^{-1} (νC=C).

Poly(7-methacryloyloxycoumarin) was then prepared by radical polymerization of (**1**) in the presence of 2,2′-azobisisobutyronitrile (AIBN). A solution of the monomer (1.0 g) and AIBN (1 wt %) in dry degassed DMF (10 ml) was stirred for 24 h at 60°C under vacuum. The solution was then diluted in 10 ml of DMF, precipitated into acetone (500 ml) and filtered off. This operation was repeated twice. The polymer was then filtered and dried under vacuum (yield 75%), T_g 180°C. IR: 1741 cm^{-1} (νC=O), 1617 cm^{-1} (νC=C). λmax$_1$: 309 nm (ε_1: 7200 l mol^{-1} cm^{-1}); λmax$_2$: 275 nm (ε_2: 9200 l mol^{-1} cm^{-1}).

3.2. *Thin film preparation*

The polymers were deposited onto convenient substrates (quartz for UV spectroscopy, NaCl for IR spectroscopy, and glass for liquid crystal cells) by spin coating of a 2 wt % solution in 1,1,2-trichlorethane. The films were then dried at 120°C for 2 h under vacuum. Irradiation of the polymers was performed by exposing the films to linearly polarized UV light at 300 nm. A metal halide lamp in conjunction with an Oriel UV-Visible sheet polarizer and a 300 nm interference filter provided an irradiance on the sample of 0.25 mW cm^{-2}. The films thickness was about 100 nm.

3.3. *Spectroscopic measurements*

The UV spectra of thin films and of dilute solutions were recorded as a function of irradiation time using a Perkin Elmer Lambda 9 spectrophotometer. Because of the low solubility of PMC in THF, UV spectra of Coumarin in diluted media were obtained with the corresponding monomer (7-methacryloyloxycoumarin). IR spectra of the thin films were recorded as a function of the irradiation time with a Perkin Elmer FTIR 2000 spectrophotometer. Infrared linear dichroism (IRLD) spectra obtained by polarization modulation (PM) were recorded between 1900 and 900 cm^{-1} using a Nicolet 740i spectrophotometer with the optical set-up and the two-channel electronic processing previously described [18]. By using a proper calibration procedure, any PM-IRLD spectrum can be related quantitatively to the dichroic difference spectrum, $\Delta A = A_{\parallel} - A_{\perp}$. All thin films were irradiated for 2 h before any PM-IRLD measurement.

3.4. *Liquid crystal cells*

Liquid crystal cells were prepared by sandwiching a liquid crystal mixture between two photopolymer coated glass substrates. The thickness was set by 10 µm thick mylar spacers. The cells were then sealed in a plastic bag under vacuum to prevent the glue from entering the cell by capillarity during polymerization. The final thickness of the cells was around 12 µm. The cells were filled with different nematic liquid crystal materials 5CB, ZLI 4792, ZLI 3086 or ZLI 1132 (Merck, table 1) at a temperature where the material was in the nematic state. The direction of the preferential alignment of the liquid crystals was determined with an optical compensator. Tilt angles were measured by the crystal rotation method [19].

4. Results and discussion

4.1. *UV spectroscopy*

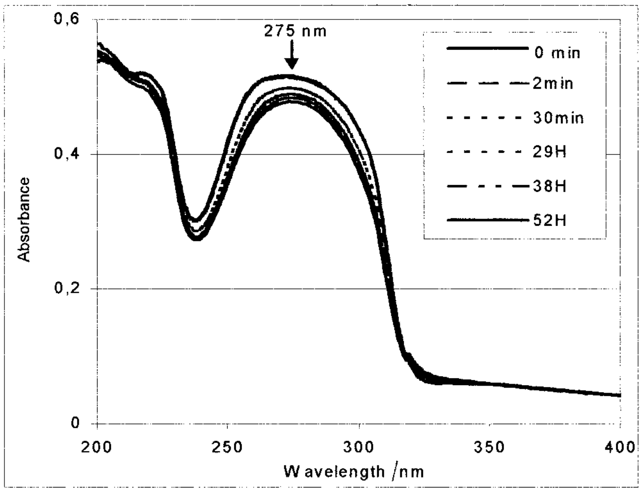
4.1.1. *PVCi*

The UV absorption spectra of thin films and dilute solutions of PVCi have been extensively studied by many groups as described previously. Here, we shall mainly discuss the time variation of these spectra upon irradiation.

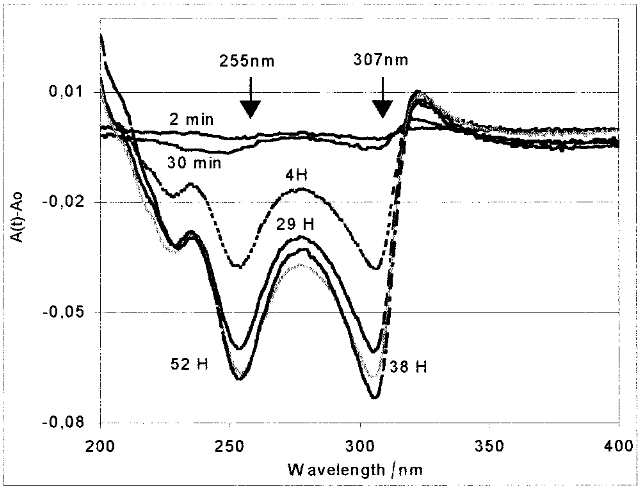
Table 1. Nematic liquid crystals.

Name	T_{NI}/°C	$\Delta\varepsilon$	Δn	Remarks
5CB	35.3	11	0.184	(4-Pentyl-4′-cyanobiphenyl)
ZLI 3086	72	0.1	0.113	Low polarity
ZLI 4792	92	5.2	0.097	Fluorinated terminal groups, medium polarity
ZLI 1132	71	12.9	0.141	Nitrile terminal groups, high polarity

First, as shown figure 1 (*a*), the absorption spectrum of a PVCi thin film displays a very broad band centred at about 275 nm which slowly decreases upon irradiation. Moreover, differences in reactivity among various species are evident from figure 1 (*b*) in which variations in the differential spectra $A(t) - A_0$ are shown at different times. In agreement with previous studies [20–22], this indicates the existence of different arrangements in addition to isolated chromophores (absorbing at about 275 nm): head to head arrangements (blue shifted to about 255 nm) and head to tail arrangements (red shifted to about 307 nm). Finally, the absorption spectra display no isobestic point indicating that the PVCi thin film undergoes a multiplicity of reactive paths, including the [2 + 2] cycloaddition and *trans*/*cis*-isomerization processes.



(*a*)



(*b*)

Figure 1. (*a*) Conventional spectra of a PVCi thin film irradiated with linearly polarized UV light from 0 to 52 hours. (*b*) Differential spectra of a PVCi thin film irradiated with linearly polarized UV light from 0 to 52 hours.

In agreement with the description reported by Egerton *et al.* [8], the PVCi film may thus be described as a set of sites with a quasi-continuous distribution of reactivities, the most reactive sites corresponding to chromophore arrangements (255 and 307 nm) whose relative geometry is favourable for [2 + 2] cycloaddition, while the less reactive sites correspond to isolated chromophores which slowly undergo isomerization (275 nm). In addition, it is noteworthy that head to head arrangements (255 nm) are as reactive as head to tail arrangements (307 nm). Consequently, both head to head and head to tail photodimers should co-exist equally in the irradiated film (scheme 2).

4.1.2. *PMC*

The UV absorption spectrum of PMC exhibits two bands, at 282 and 312 nm. Upon irradiation, the intensity of each band gradually decreases, and the spectra display an isobestic point at 250 nm (figure 2). These results are in agreement with the well-known photoreactivity of coumarins which can only undergo [2 + 2] cycloaddition.

4.2. *FTIR spectroscopy*

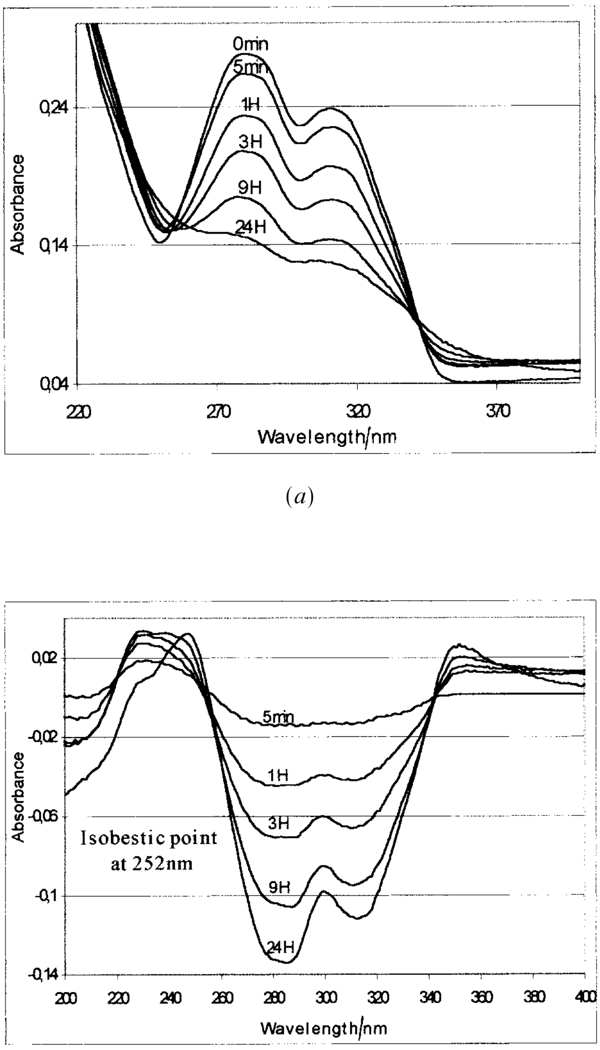
4.2.1. *Variation of IR spectra during irradiation*

PVCi and PMC thin films were irradiated for various periods of time with linearly polarized UV light in order to record the IR spectral changes during the photochemical process. The most characteristic IR vibrations of PVCi and PMC are reported in table 2.

Qualitatively, both spectra show a rather similar behaviour upon irradiation. The intensity of the bands attributed to the C=C double bonds and to the conjugated carbonyls decreases, while a new peak corresponding to unconjugated carbonyls increases at a higher

Table 2. Characteristic IR bands of thin films of PVCi and PMC.

Polymer	ν (C=O)/cm^{-1}	ν (C=O)/cm^{-1} vinylene		ν (C=C)/cm^{-1} aromatic		γ C–H/cm^{-1} ethylenic	γ C–H/cm^{-1} aromatic
PVCi	1713	1683 (*trans*)	1603	1580	1498	979	862
PMC	1745	1617 (endocyclic)	1617	1571	1498	989	889



(*a*)

(*b*)

Figure 2. (*a*) Conventional spectra of a PMC thin film irradiated with linearly polarized UV light from 0 to 24 hours. (*b*) Differential spectra of a PMC thin film irradiated with linearly polarized UV light from 0 to 24 hours.

wavenumber. The phenyl band at around 1500 cm^{-1} remains roughly unchanged in both cases. Finally, most bands in the spectral region between 1400 and 900 cm^{-1} decrease; they are due to ester groups, aliphatic groups and substituted benzene vibrations.

4.2.2.1. *PVCi*. As shown in figure 3, the most striking features are the following: (i) the vinylene C=C intensity gradually vanishes as the irradiation proceeds, in agreement with the observations made by other groups [23–25]; (ii) a few very weak bands appear at 1422, 1375, 750 and 697 cm^{-1} and can be attributed to the photoproducts.

The complete disappearance of the vinylene C=C band at 1638 cm^{-1} cannot be attributed only to the cycloaddition. Indeed, we assume that *trans*-/*cis*-isomerization is partly responsible for the decrease of intensity either because *cis*-isomers absorb at a different wavenumber or because the IR molar absorption coefficient of the *cis*-isomers is far lower than that of the *trans*-isomers at this wavenumber.

Since both isomerization and cycloaddition may induce similar changes in the IR spectra of PVCi and since no isolated band can be confidently attributed to the photodimers or the *cis*-isomers, it is hardly possible to follow the photoreaction kinetics by IR spectroscopy. Nevertheless, to a first approximation, one can estimate the amount of remaining *trans*-isomers of PVCi as irradiation proceeds, by calculating the integrated intensity ratio of the vinylene C=C band at various times to the initial band before irradiation. Such results are summarized in table 3.

4.2.1.2. *PMC*. Qualitatively, the changes in the IR spectra (figure 4) of PMC thin films are similar to those for PVCi, but appear weaker. As mentioned previously, PMC only undergoes cycloaddition and steric hindrance

Table 3. Proportion of remaining unchanged chromophores in PVCi and PMC thin films as linearly polarized irradiation at 300 nm proceeds.

	Remaining unchanged *trans* chromophores/%	
Irradiation time	PMC	PVCi
0	100	100
5 min	99.8	59
15 min	94.2	53
30 min	90.5	38
2 h	68.4	19
16 h	46.3	8

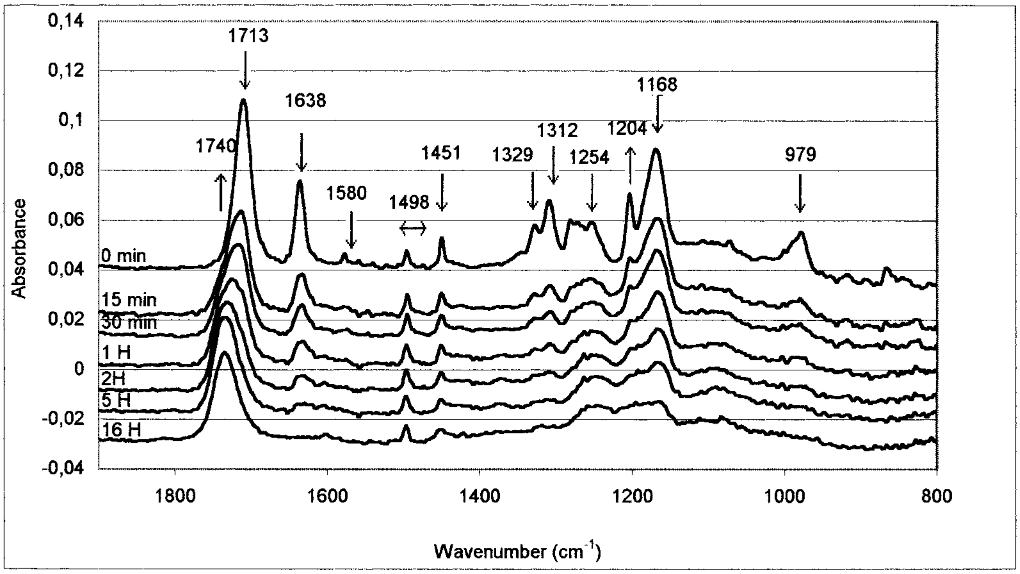


Figure 3. Variation of IR absorbance spectra of a PVCi thin film during irradiation with linearly polarized UV light from 0 to 16 hours.

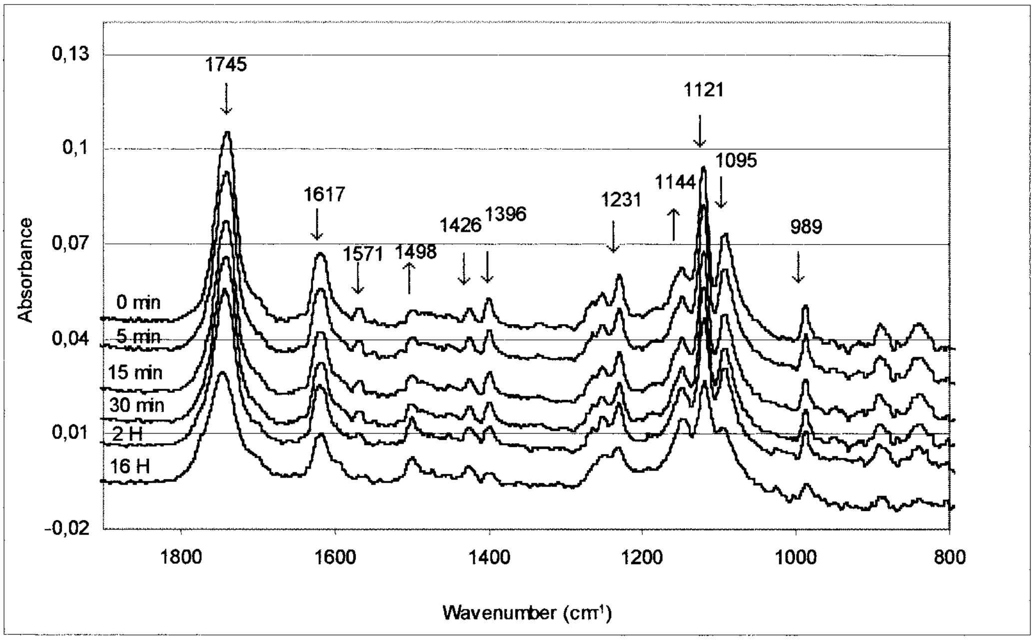


Figure 4. Variation of IR absorbance spectra of a PMC thin film during irradiation with linearly polarized UV light from 0 to 16 hours.

may slow down chromophore conversion. In this case, the spectral changes are due only to photodimer formation and to the disappearance of the initial chromophores. A few very weak new bands are observed at 1498, 1196, 1144 and 1020 cm^{-1}. In contrast with the previous results on PVCi, one cannot use the intensity variation of the band at 1617 cm^{-1} as a probe of the photoconversion kinetics. Indeed this band is not a pure vinylene ν(C=C) mode and its variation is not consistent with the UV results (figure 2). Under these conditions, we have used the γCH mode at 989 cm^{-1} to follow the cycloaddition kinetics; results reported in table 3 show that the conversion yield is equal to about 0.46 after 16 h of irradiation, i.e. significantly lower than that in PVCi.

It is noteworthy that the time variation of the percentage of unchanged chromophores can be satisfactorily fitted by a bi- or multi-exponential function. This confirms the existence of sites with different reactivity in the inhomogeneous polymer films. On the other hand, we notice that the overall change in absorbance under irradiation is very small for PVCi and quite large for PMC, whereas the conversion yield deduced from the IR spectroscopy is in favour of a chemical modification more significant in PVCi than in PMC. As dimerization can only take place in PMC, this result could mean that isomerization leading to a moiety having a molar extinction coefficient very close to that of the *trans*-isomer, is the main photoreaction which occurs in PVCi.

4.2.2. *PM-IRLD spectra of PVCi and PMC thin films after irradiation*

4.2.2.1. *PVCi.* The absorbance spectra of PVCi before and after a 2 h irradiation are reported in figure 5 along with the dichroic difference spectrum, $\Delta A = A_{\parallel} - A_{\perp}$: (i) Even though the dichroic difference data are noisy and scattered, significant very weak and negative linear dichroism effects are evidenced ($\Delta A \leqslant 6 \times 10^{-4}$); (ii) The most pronounced effects are observed for bands corresponding to conjugated carbonyl (1709 cm^{-1}), vinylene C=C (1634 cm^{-1}), phenyl ring (1495 cm^{-1}) and esters bands (1166 cm^{-1}); (iii) No dichroism is detected at wavenumbers corresponding to photoproducts.

To obtain more quantitative information about the orientation of the different bands associated with the chromophores, the normalized orientation function $F = \Delta A/3A_0$ is calculated. The limiting values of F, often called the order parameter, are 1.0 or -0.5 if the transition moments are perfectly oriented parallel or perpendicular to the polarization direction of the laser, respectively, or equal to zero for random orientation. The corresponding results are summarized in table 4.

The negative dichroism at 1634 cm^{-1} of the band due to unreacted *trans*-cinnamate demonstrates a preferred orientation of the chromophores in the direction perpendicular to the direction of polarization. This is in agreement with the fact that linearly polarized light depletes *trans*-isomers along the direction of polarization. Moreover, we know that after a 2 h irradiation, less than

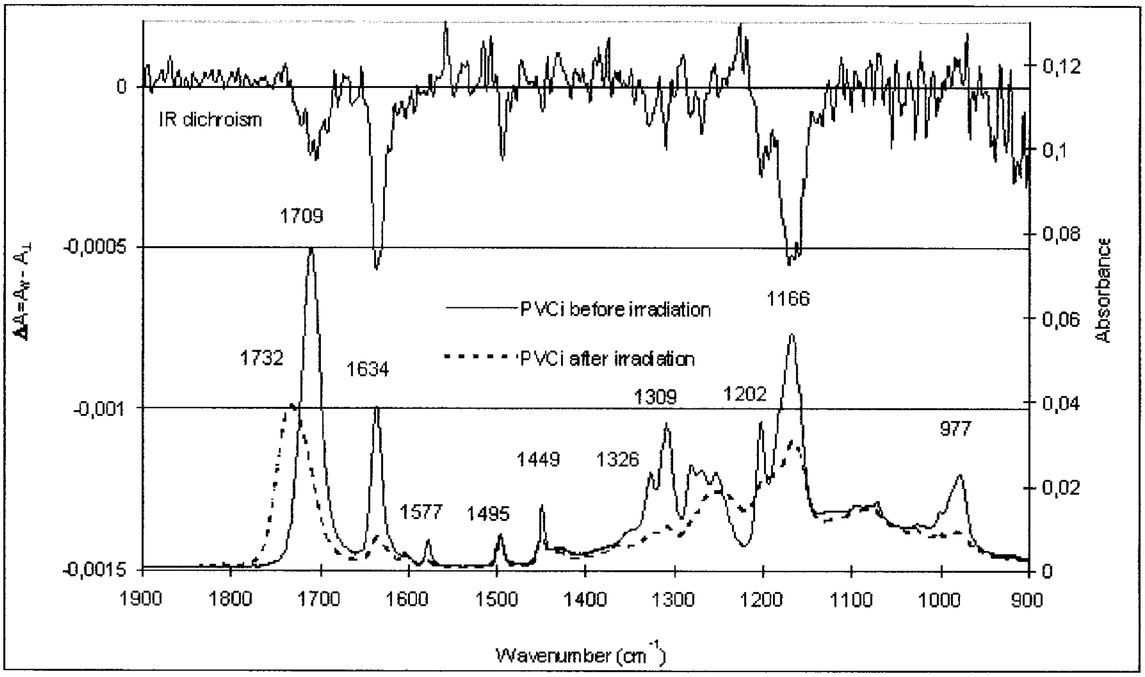


Figure 5. Above: IR dichroic difference spectrum of a two hour irradiated PVCi thin film. Below: Conventional IR absorbance spectra of a PVCi thin film before and after irradiation.

Table 4. IR dichroism of the PVCi thin film.

Wave number/cm^{-1}	Attribution	IR dichroism $\Delta A = A_{\parallel} - A_{\perp}$	Orientation function $F = \Delta A/3A_0$
1709	conjugated C=O	-2×10^{-4}	-0.0036
1634	vinylene C=C	-5.5×10^{-4}	-0.0236
1495	aromatic C=C	-2×10^{-4}	-0.009
1166	ester	-5.6×10^{-4}	-0.006

20% of *trans*-isomer remains in the film, while 80% has reacted. Since no dichroism signal has been detected for this 80%, the photoproducts are likely to be isotropically distributed. This conclusion is reinforced by the fact that the other bands due to phenyl rings which come from cinnamates, as well as photodimers, display an even weaker orientation function.

To conclude, the above results are in agreement with a preferential orientation of the *trans*-cinnamates along the direction perpendicular to the direction of polarization and with no preferential orientation of the photoproducts. Nevertheless, as no clearly isolated bands of photodimers can be observed by IR spectroscopy, no quantitative results can be obtained for the orientation function of the photoproducts.

4.2.2.2. *PMC*. Similarly, we have compared the IR absorbance spectra of a PMC thin film before and after 2 h of irradiation and extracted the dichroic difference spectrum of the irradiated film, as shown in figure 6. In contrast with the previous results, we observe positive and negative weak linear dichroism effects: (i) positive bands at 1773 cm^{-1} (unconjugated carbonyls), 1500 cm^{-1} (phenyl rings) and 1190 cm^{-1} (photoproducts); (ii) negative bands at 1733 cm^{-1} (conjugated carbonyls), 1613 cm^{-1} (vinylene and aromatic C=C), 1563 cm^{-1} (phenyl rings) and 1229 cm^{-1} (esters); (iii) a dispersion shape is observed in the 1150–1050 cm^{-1} spectral range due to the overlapping of different modes with orthogonal directions of their transition moments.

In addition, the corresponding orientation functions ($F = \Delta A/3A_0$) have been calculated and the results are reported in table 5.

It appears that bands relative to the unsaturated chromophores (endocyclic vinylene C=C and conjugated carbonyls) show a weak negative dichroism. Accordingly,

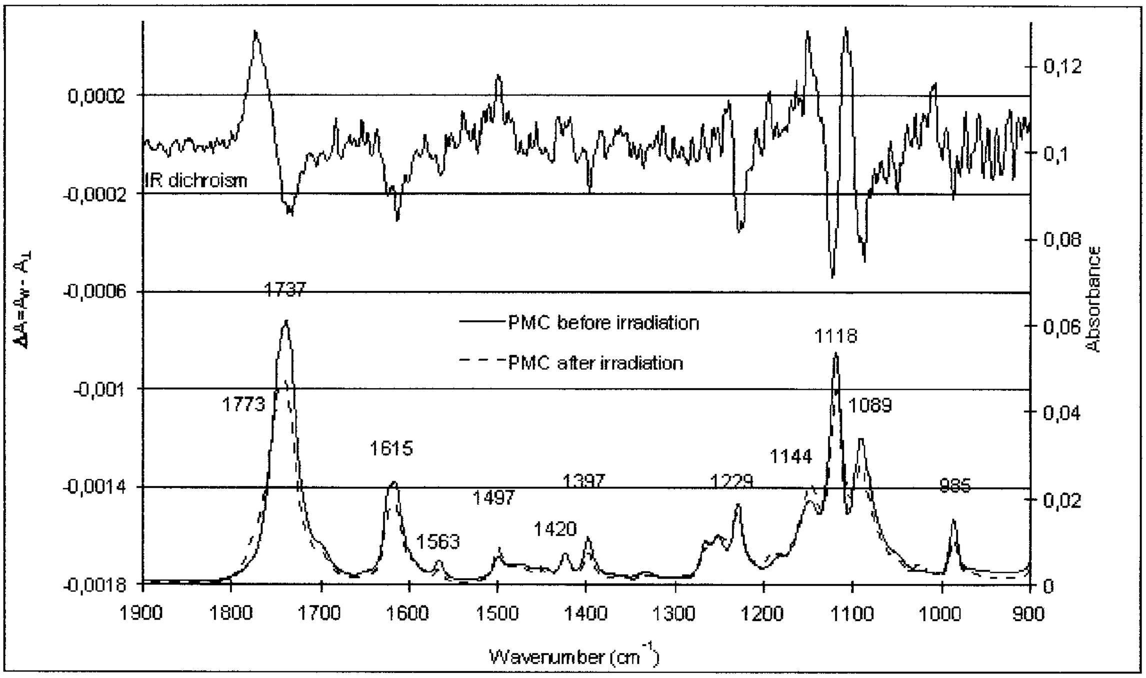


Figure 6. Above: IR dichroic difference spectrum of a two hour irradiated PMC thin film. Below: Conventional IR absorbance spectra of a PMC thin film before and after irradiation.

Table 5. IR dichroism of the PMC thin film.

Wave number/cm^{-1}	Attribution	IR Dichroism $\Delta A = A_{\parallel} - A_{\perp}$	Orientation function $F = \Delta A/3A_0$
1773	unconjugated C=O	4.5×10^{-4}	0.0043
1733	conjugated C=O	-3×10^{-4}	− 0.0026
1613	vinylene and aromatic C=C	-3×10^{-4}	− 0.0053
1563	aromatic C=C	-1×10^{-4}	− 0.0099
1500	aromatic C=C	3×10^{-4}	0.0107
1229	ester	-3×10^{-4}	− 0.0059
1196	photodimers	2×10^{-4}	0.0099

initial chromophores are preferentially oriented along the direction perpendicular to the direction of polarization. The weak value is consistent with the large amount (68%) of remaining unreacted side groups after a 2 h exposure. On the contrary, dichroism related to the dimers (unconjugated carbonyls at 1773 and 1196 cm^{-1}) is positive. Similarly, bands at 1500 (positive) and 1563 cm^{-1} (negative) can be assigned to the photodimers and the unsaturated chromophores, respectively. Nevertheless, the absolute value of their orientation function is similar and very close to the value of the photodimer orientation function at 1196 cm^{-1}. We conclude that dimers are preferentially oriented along the direction of polarization.

4.3. *Liquid crystal alignment on PVCi and PMC irradiated thin films*

In this study, we have paid special attention to the influence of irradiation time on the homogeneity of the cells and to the cell ageing. We obtained the following three main results: (i) PVCi orients liquid crystals perpendicular to the direction of polarization whereas PMC orients liquid crystals parallel to the direction of polarization; (ii) the longer the irradiation, the more homogeneous the alignment is; (iii) the liquid crystal alignment is not stable.

4.3.1. *Liquid crystal alignment*

The direction of liquid crystal alignment can be related to the anisotropy of the polymer thin films as shown in table 6.

First, it appears that the preferential orientation of liquid crystals on PVCi thin films is due to anisotropic interactions with the unchanged chromophores. Consequently, the ability of PVCi to induce a preferred alignment of liquid crystals upon irradiation with linearly polarized UV light is mainly governed by selective depletion of *trans*-cinnamates along the direction of polarization. This means that both isomerization and cycloaddition are responsible for the mechanism of photoinduced anisotropy, since they both deplete side groups along the direction of polarization. Moreover, this is consistent with the fact that only a poor alignment is obtained with short irradiation times since, in these conditions, many unreacted *trans*-cinnamates are still randomly oriented in the film (after half an hour, more than 50% of *trans*-cinnamates remain unchanged); these randomly oriented side groups then represent as many possible ‘anchoring sites’ for liquid crystals. On the contrary, after long irradiation times, *trans*-isomers are more selectively oriented perpendicular to the direction of polarization (after two hours, less than 20% of *trans*-cinnamates remain unreacted) and a more homogeneous alignment is obtained.

This orientational effect could explain results obtained by Schadt *et al.* [3] and Ichimura *et al.* [13]. Moreover, it is in agreement with the ability of rubbed PVCi to induce homogeneous alignment of liquid crystals along the direction perpendicular to the direction of rubbing [16].

Secondly, in the case of the coumarin-based polymer, the preferential orientation of liquid crystals seems to be due to anisotropic interactions with the photodimers (table 6). Consequently, liquid crystal alignment essentially results from the selective cycloaddition of chromophores along the direction of polarization. It is noteworthy that this would not occur if an angular reorientation of the photodimer axes were involved in the cycloaddition process as happens in PVCi. Finally, since a poor alignment is obtained for short irradiation times, we believe that a minimum number of photodimers is necessary to induce homogeneous alignment.

In this respect, it is important to underline the influence of the chemical structure of the photopolymer on its liquid crystal alignment ability. First, the exact chemical structure of the side groups influences its photoreactivity and in particular the relative proportions of isomerization and cycloaddition. Then, the interactions with the liquid crystals depend on the chemical nature of the photoproducts; in contrast to the case of rubbed surfaces in which the alignment direction can be predicted, the photoalignment process is more system dependent.

4.3.2. *Liquid crystal alignment stability*

Among the optical methods for liquid crystal alignment, simple irradiation of photocrosslinkable polymers

Table 6. Characteristics of polymer thin films and of the induced liquid crystal alignment after a 2 h irradiation with linearly polarized UV light.

	Angular distribution in thin films relative to the direction of polarisation			
Polymer	Unchanged chromophores	*cis*-isomers	Photodimers	Liquid crystals alignment relative to the direction of polarisation
PVCi	perpendicular	isotropic	isotropic	perpendicular
PMC	perpendicular	perpendicular	parallel	parallel

seems very attractive, since crosslinking could confer stability to the final alignment. Actually, none of our cells has shown alignment stability for a longer period than three months. After this time randomly aligned microdomains appear and they slowly increase upon ageing, meaning that the surface anisotropy is unstable.

Under these conditions, crosslinking of thin films is heterogeneous. The surface instability can then be attributed to diffusion of liquid crystal into the films resulting in the loss of the preferred orientation of the side groups. The swelling of the alignment film by liquid crystal has been confirmed for another polymer [26] and a similar behaviour seems effective in PVCi and PMC thin films.

5. Conclusion

We have characterized poly(vinylcinnamate) (PVCi) and poly(7-methacryloyloxycoumarin) (PMC) thin films irradiated with linearly polarized UV light by using UV, conventional and modulation polarization FTIR spectroscopies. In the case of PVCi, we have shown that chromophores are involved in the photoisomerization and cycloaddition reactions. Photoreactions induce no preferred orientation of the photoproducts, but deplete chromophores along the direction of polarization. Consequently, the photoinduced anisotropy is essentially due to the unreacted *trans*-cinnamates which are preferentially oriented perpendicular to the direction of polarization. In the case of PMC, unreacted chromophores were also roughly oriented along the direction perpendicular to the direction of polarization. But contrarily to PVCi thin films, photodimers show a preferred orientation along the direction of polarization. All these conclusions have been reached thanks to the selectivity of IR spectroscopy for the different chemical groups and to the very high sensitivity of the PM-IRLD technique. Even though the anisotropy effects were rather low, we have been able to detect different behaviours in PVCi and PMC. Furthermore, we have shown that irradiated PVCi thin films induce homogeneous liquid crystal alignment perpendicularly to the direction of polarization. This alignment is essentially governed by the preferred orientation of *trans*-cinnamates. Conversely, irradiated PMC thin films align liquid crystals parallel to the direction of polarization. In this case, photoalignment is attributed to liquid crystal interactions with photodimers. Such experiments highlight the importance of the photoreactivity, and hence the chemical structure of the photopolymer, for the liquid crystal alignment properties. Finally, we have shown that liquid crystal alignment on these photopolymers is not stable. Stability of photoalignment is one of the main prerequisites for further industrial applications, and for this reason, we still need to find either highly photocrosslinkable and stable materials or a way to prevent liquid crystals from swelling the anisotropic films.

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