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Molecular orientation and liquid crystal alignment properties of new cinnamate-based photocrosslinkable polymers

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Isotropic thin films of three original phenyl substituted cinnamate-based polymers, hereafter referred to as ‘Para’, ‘Meta’ and ‘Metamet’ have been exposed to linearly polarized UV light and their photoinduced molecular orientations have been studied. The resulting photocrosslinked anisotropic polymer films were characterized using UV, conventional and polarization modulation (PM) FTIR spectroscopies. From UV and PM-IR linear dichroism measurements, at least two simultaneous orientation processes appear to play a key role in these phenyl substituted cinnamate-based systems. On the one hand, isomerization reactions deplete chromophores along the polarization direction (**P**) of the UV light and induce a preferential orientation of remaining ‘*trans*’-isomers perpendicular to **P**; on the other hand, cycloaddition reactions lead to the formation of either head to head or head to tail photodimers aligned preferentially along **P** in the ‘Para’ and to a lesser extent in the ‘Meta’ and ‘Metamet’ systems. These last results are related to the different liquid crystal alignment properties of the films, and the influences of the chemical structure of the chromophores are discussed.

1. Introduction

Photoinduced anisotropy in photocrosslinkable polymers exposed to linearly polarized light is of great interest for liquid crystal display (LCD) technology. Since the discovery by Dyadyusha *et al.* [1] and Schadt *et al.* [2] of the aligning properties of irradiated poly(vinyl-cinnanmate) derivatives (PVCi), few other materials producing a homogeneous alignment of liquid crystals have been proposed. Indeed, a linearly polarized UV light may induce not only selective photo-orientations of the absorbing chromophores, but also various photochemical reactions leading to oriented photoproducts; the resulting anisotropic thin films may further have a great influence on the homogeneous alignment of liquid crystals.

Qualitatively, the more important photochemical reactions involve ‘*trans*↔*cis*’ isomerizations and/or [2 + 2] cycloadditions, but the relative influences of the different chemical species on the final properties of the aligning layers are not yet definitively established. Depending on the chemical structures of the chromophores and the photoproducts formed, at least three different mechanisms have been proposed: (i) anisotropic interactions of the liquid crystals with unchanged chromophores and photodimers [2]; (ii) anisotropic interactions between the liquid crystal and only unchanged ‘*trans*’-chromophores [3]; (iii) anisotropic interactions between the liquid crystals and the ‘*cis*’-isomers [4].

Obviously, a better understanding of these phenomena needs a better knowledge of the molecular orientation properties of the various chemical species in the irradiated polymer films. In this context, we have confirmed in a recent study [5] that PVCi films orient liquid crystals

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perpendicularly to the direction of polarization (that of unchanged chromophores), while poly(7-methacryloyloxycoumarin) films induce a parallel alignment (the direction of photodimers). Similarly, in this paper the molecular orientations in three new phenyl substituted cinnamate-based polymer films are investigated. Upon UV irradiation, intensity changes in the UV and FTIR spectra are followed and, more importantly, IR linear dichroisms are measured for various characteristic vibrational bands. Therefore, the molecular orientations and liquid crystal alignment properties of the irradiated polymer films are compared and some requirements on the chemical structure of the aligning layers are then discussed.

2. Experimental

2.1. *Polymers*

The syntheses of the three polymers investigated are described elsewhere [6]. Their structures are shown in scheme 1. The polymers were deposited onto convenient substrates (quartz for UV spectroscopy and NaCl for FTIR spectroscopy) by spin coating of a 2 wt % solution in 1,1,2-trichloroethane. 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 interferential filter provided an irradiance on the sample of 0.25 mW cm^{-2}. The film thickness was about 100 nm.

2.2. *Spectroscopic measurements*

The UV spectra of thin films and of diluted solutions were recorded as a function of exposure time using a Perkin Elmer Lambda 9 spectrophotometer. FTIR spectra 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 with a Nicolet 740i spectrophotometer using the optical set-up and the two channel electronic processing previously described [7]. By using a proper calibration procedure, any PM-IRLD spectrum can be related quantitatively to the dichroic different spectrum, $\Delta A = A_{\parallel} - A_{\perp}$. All thin films were irradiated for 3 h before any PM-IRLD measurements.

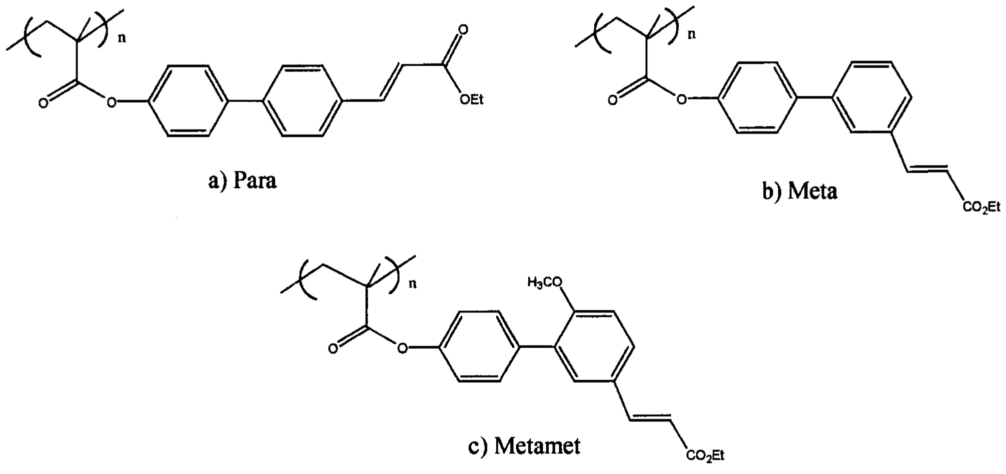
3. Results

3.1. *UV spectroscopy*

Inspection of the UV absorption spectra of photocrosslinkable polymers upon irradiation (thin films of diluted solutions) is a very common way to follow photoreactions and, sometimes, to distinguish different processes. Indeed, according to Egerton *et al.* [8], *para*-substituted PVCi thin films can be described as an ensemble of sites with a quasi-continuous range of configurations including isolated chromophores absorbing at about 300 nm, head to head arrangements absorbing at 290 nm and, also head to tail dimers absorbing at 320 nm. Such results can be used as reference starting indicators.

3.1.1. *'Para' photopolymer*

Before irradiation, the UV spectrum of a 'Para' solution exhibits a maximum at 305 nm, while that of a thin film maximizes at 295 nm and displays an absorption tail at higher wavelength (figure 1). These differences cannot be assigned to solvatochromy, but more probably indicate the existence of both head to head and head to tail dimer arrangements in the film. This is confirmed by the differential spectra $A(t) - A(t=0)$, where $A(t)$ represents the absorbance of the irradiated film at time t. As shown in figure 2, the whole absorption band does not decrease homogeneously with the irradiation time, indicating that the film contains differently reacting chromophores, the head to head arrangements decreasing



a) Para

b) Meta

c) Metamet

Scheme 1. Structures of the polymers investigated.

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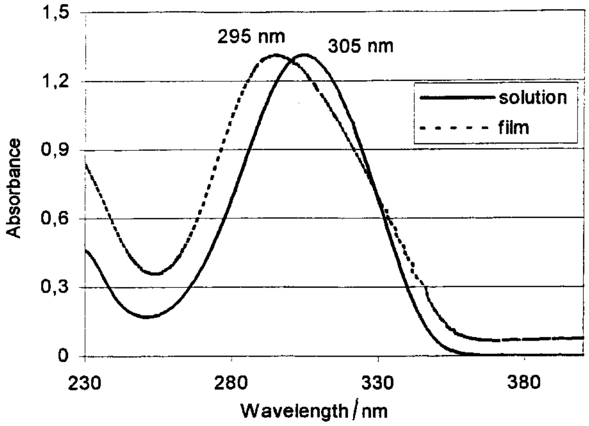

Figure 1. UV spectra of 'Para'.

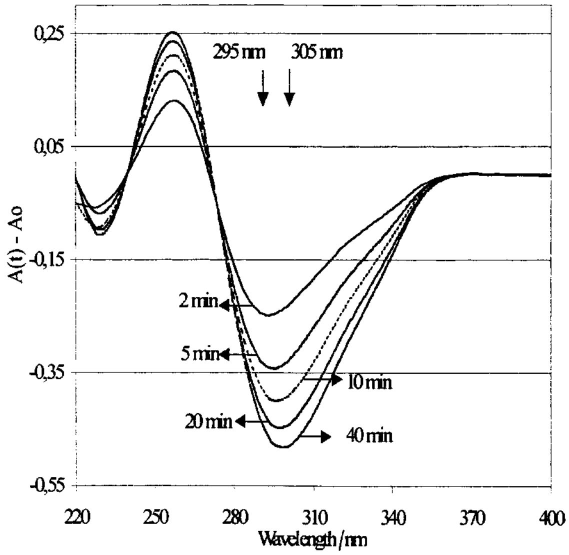

Figure 2. Differential spectra of a 'Para' thin film upon irradiation.

more rapidly at short times. These species must be in part responsible for the formation of the photoproducts and for the observed increases at higher energies, maximizing at 260 nm. As a result, all spectra intersect and display two isobestic points at 240 and 273 nm. Therefore, cycloaddition and isomerization reactions have occurred and one can suggest that head to head arrangements crosslink and isolated chromophores only isomerize. Moreover, it is noteworthy that the films become insoluble after irradiation, confirming that crosslinking has taken place.

Furthermore, we have investigated the UV linear dichroism ($\Delta A = A_{\parallel} - A_{\perp}$) in such irradiated 'Para' films. A negative value is observed at 300 nm ($\Delta A = -30 \times 10^{-3}$) indicating that the chromophores are preferentially oriented perpendicularly to the direction of the light polarization, **P**. In contrast, the positive value obtained at 260 nm ($\Delta A = 10 \times 10^{-3}$) reveals that the photoproducts are more likely oriented parallel to **P**. However, it is noteworthy that such orientation effects were maximizing after a 5 min irradiation and slowly decreasing with longer exposure.

3.1.2. *'Meta' photopolymer*

As shown in figure 3, the UV spectrum of a 'Meta' photopolymer thin film displays a broad absorption band with a maximum at near 255 nm and a shoulder at about 290 nm. As irradiation proceeds, the intensity at the maximum decreases very slowly and the shoulder exhibits larger decreases; also, a new weak band at 215 nm due to photoproducts is increasing (figure 4). An isobestic point is also located at 233 nm. Similarly, these results suggest that both isomerization and, to a lesser extent cycloaddition processes have occurred; the films again become insoluble after prolonged irradiation. However, we have been unable to reveal any significant UV linear dichroism, probably because the orientation effects are weak.

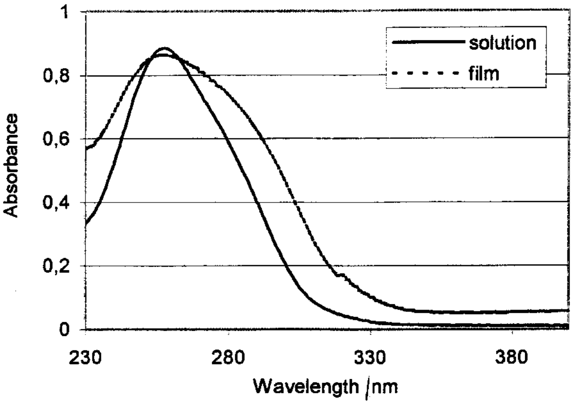

Figure 3. UV spectra of 'Meta'.

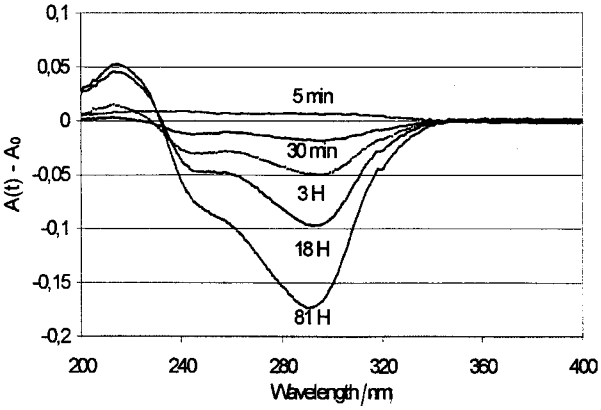

Figure 4. Differential spectra of a 'Meta' thin film upon irradiation.

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3.1.3. *'Metamet' photopolymer*

The UV absorption spectra of a 'Metamet' thin film and its solution exhibit two maxima at 260 and 303 nm and a shoulder at 320 nm (figure 5). The similarity of both spectra indicates that no preferential molecular arrangement exists in the thin film. All the bands gradually decrease upon irradiation with linearly polarized UV light, but those at lower energies decrease more rapidly; one can suggest that head to tail molecular arrangements are preferentially reacting. In addition, a new high energy band at 230 nm is developing and this leads to the observation of an isobestic point at 242 nm on the differential spectra (figure 6). The films becoming insoluble after irradiation, and we conclude that both cycloaddition and isomerization reactions have taken place; nevertheless, we have been unable to reveal any UV linear dichroism effect.

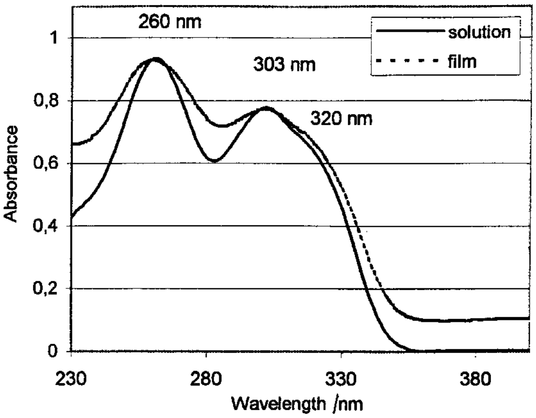

Figure 5. UV spectra of 'Metamet'.

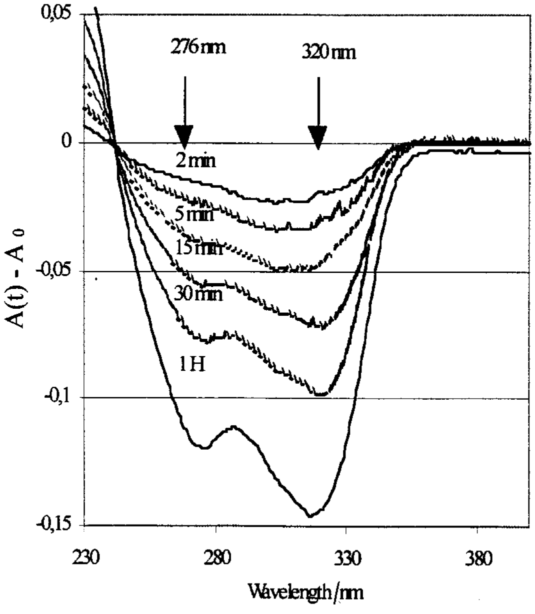

Figure 6. Differential spectra of a 'Metamet' thin film upon irradiation.

3.2. *FTIR spectroscopy*

3.2.1. *Evolution of FTIR spectra after irradiation*

Polymer thin films were irradiated for various periods of time with linearly polarized UV light in order to follow the IR spectral changes during the photochemical processes. The most characteristic IR vibrations of the chromophores in the 1800–800 cm^{-1} spectral range and their assignment [9] are reported in table 1. For each vibrational mode, the observed wavenumbers are very close for the three polymers, except for the band at 1511 cm^{-1} which is not active in the 'Para' polymer.

The behaviour of the IR spectra upon irradiation is similar for the three systems. As an illustrative example, we have reported in figure 7 several IR spectra, in the 1800–800 cm^{-1} region, of the 'Para' polymer for different irradiation times. The intensities of the phenyl bands (νC=C and δ_{ip}CH) remain roughly unchanged, indicating that no degradation processes occur during irradiation. The intensities of the bands due to the vinylene C=C groups (νC=C at 1635 cm^{-1} and δ_{op}CH at 981 cm^{-1}) continuously decrease with irradiation time. Moreover, we observe that the intensity of the band associated with conjugated carbonyls (at 1711 cm^{-1}) decreases, while the band corresponding to non-conjugated carbonyls (at 1751 cm^{-1}) increases and the resulting band is shifted down to 1742 cm^{-1}. These two effects can be attributed to cycloaddition which causes a decrease in the amount of vinylene C=C and, consequently, a decrease in the number of conjugated carbonyls. This result is confirmed by the presence of few very weak new bands at 1378, 1202 and 1068 cm^{-1} due to photodimers. The bands at 1378 and 1202 cm^{-1} can be attributed to in-plane bending

Table 1. Wavenumbers and assignments of the most characteristic IR bands of the polymer thin films.

Wavenumbers/cm^{-1}			
'Para'	'Meta'	'Metamet'	Assignments[a]
1751	1751	1751	ν(C=O) unconjugated
1711	1711	1707	ν(C=O) conjugated
1635	1639	1635	ν(C=C) vinylene
1604	1604	1601	ν(C=C) aromatic
	1511	1511	ν(C=C) aromatic
1495	1479	1495	ν(C=C) aromatic
1264	1269	1263	δ_{ip}(CH) aromatic
1166	1166	1166	δ_{ip}(CH) aromatic
1103	1102	1102	δ_{ip}(CH) aromatic
981	981	981	δ_{op}(CH) vinylene

[a] ν: stretching; δ: bending; ip: in-plane; op: out-of-plane.

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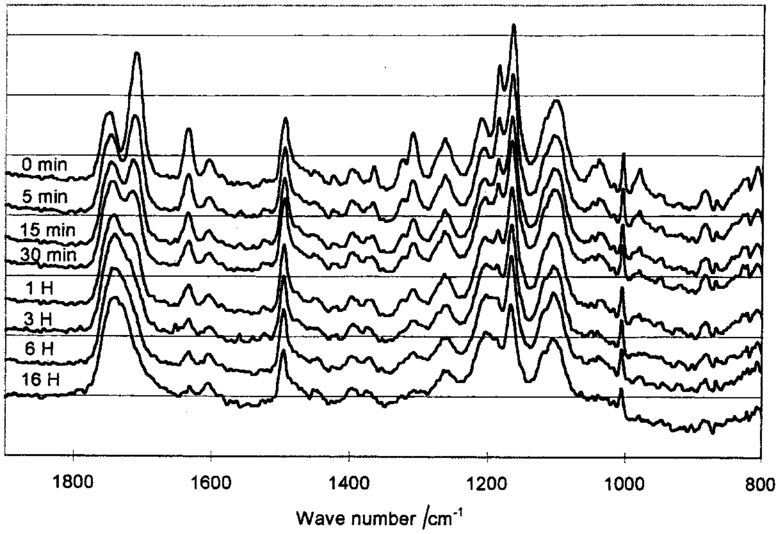

Figure 7. Variation of the IR absorbance spectra in the 1900–800 cm^{-1} region of a 'Para' thin film exposed to UV irradiation from 0 to 16 hours.

vibrations of CH (δ_{ip}CH) in cyclobutane rings, while the band at 1068 cm^{-1} has been attributed to a stretching mode of the cyclobutane ring [10]. Nevertheless, as discussed in a previous paper [8], crosslinking cannot explain the drastic decrease of vinylene C=C bands, since the cycloaddition yield is limited to 50%. In fact, the intensity decrease of the vinylene bands can also be due, in part, to isomerization of isolated chromophores. Indeed, the band associated with the vinylene C=C of '*cis*'-isomers is expected at a similar wavenumber, but with an extinction coefficient significantly lower than that of '*trans*'-isomers.

Since no isolated band can be confidently attributed to the '*cis*'-isomers and no intense bands are related to only photodimers, it is very difficult to monitor the photoreaction kinetics by IR spectroscopy. Nevertheless, the intensity variations of the vinylene C=C band, mainly due to the '*trans*'-isomers, can be used to obtain an estimate of remaining '*trans*'-species in the polymer films. The results reported in table 2 were calculated from the integrated intensity ratio of the band at 1635 cm^{-1}, at various times, with respect to its intensity before irradiation. The decreases in remaining unchanged chromophores are roughly the same in 'Meta' and 'Metamet' polymers. However, for the 'Para' polymer, this decrease is more rapid for short times of irradiation, but the conversion appears less efficient after prolonged irradiation.

Table 2. Proportion of remaining unchanged chromophores in the polymer thin films as linearly polarized irradiation at 300 nm proceeds.

	Remaining unchanged chromophores/%		
Irradiation time	'Para'	'Meta'	'Metamet'
0	100	100	100
5 min	68	77	77
15 min	57	66	64
30 min	46	46	47
1 h	42	38	40
3 h	27	22	18
6 h	22	18	14
16 h	14	10	8

3.2.2. *PM-IRLD measurements*

In order to obtain new information about molecular orientation effects upon irradiation, the PM-IRLD spectra ($\Delta A = A_{\parallel} - A_{\perp}$) of the three polymer thin films were recorded. The PM-IRLD spectrum after 3 h of irradiation and the conventional IR absorbance spectra before (A_0) and after irradiation are reported in figures 8, 9 and 10 for 'Para', 'Meta' and 'Metamet' photopolymers, respectively. To obtain more quantitative information about the orientation of the different bands,

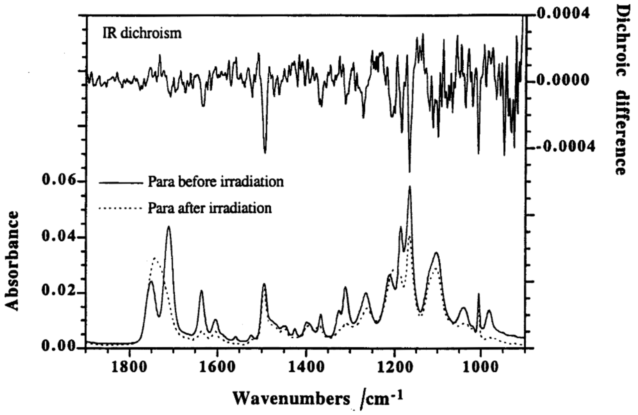

Figure 8. Above: IR dichroic difference spectrum of a two hour irradiated 'Para' thin film. Below: Conventional IR absorbance spectra of a 'Para' thin film before and after irradiation.

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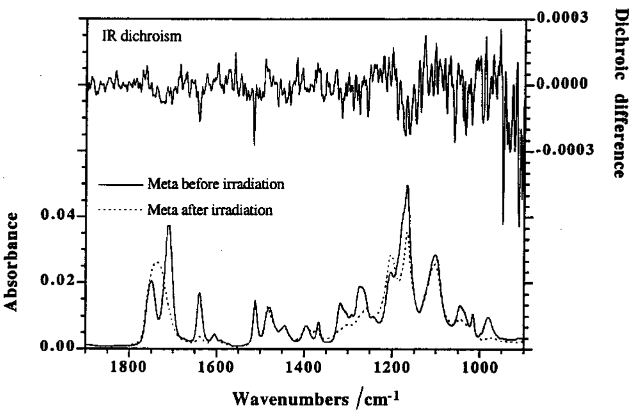

Figure 9. Above: IR dichroic difference spectrum of a two hour irradiated 'Meta' thin film. Below: Conventional IR absorbance spectra of a 'Meta' thin film before and after irradiation.

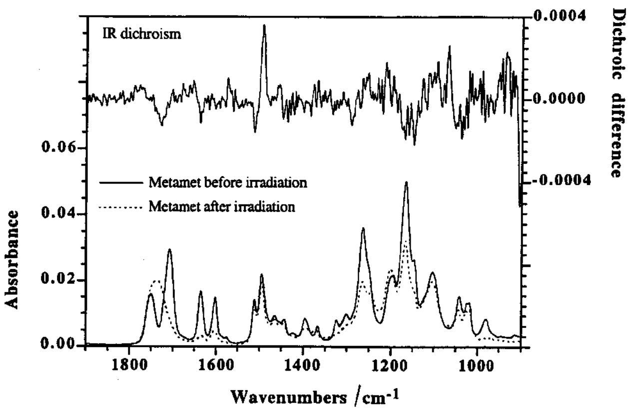

Figure 10. Above: IR dichroic difference spectrum of a two hour irradiated 'Metamet' thin film. Below: Conventional IR absorbance spectra of a 'Metamet' thin film before and after irradiation.

the normalized orientation function $F = \Delta A/3A_0$ is then calculated. The limiting values of F, often called the order parameter, are 1.0 or -0.5 if the transition moment is perfectly oriented parallel or perpendicular to the polarization direction of UV light, respectively, and equal to zero for random orientation. Values of the IR dichroism and the normalized orientation function are summarized in table 3 for several vibrational modes.

Whatever the polymer system, the linear dichroism observed on the most characteristic bands is very low ($|\Delta A| < 5\times10^{-4}$), indicating weak molecular orientation effects in these photocrosslinkable polymers. Nevertheless, thanks to the very high sensitivity of PM-IRLD spectroscopy, such results were found to be reproducible, so that some conclusions about the orientation of both remaining unchanged chromophores and photodimers

Table 3. IR dichroism and normalized orientation function for several vibrational modes of Para, Meta and Metamet polymer thin films.

Wavenumbers/cm^{-1}	Assignments	IR dichroism/ΔA	Orientation function F
'*Para*'			
1634	ν(C=C) vinylene	-1.5×10^{-4}	-0.0125[a]
1495	ν(C=C) aromatic	-4.0×10^{-4}	-0.0063
1378	photodimer	-1.5×10^{-4}	[b]
1202	photodimer	-2.0×10^{-4}	[b]
1166	δ_{ip}(CH) aromatic	-5.5×10^{-4}	-0.0047
'*Meta*'			
1631	ν(C=C) vinylene	-1.6×10^{-4}	-0.0181[a]
1515	ν(C=C) aromatic	-2.7×10^{-4}	-0.0075
1485	ν(C=C) aromatic	$+1.0\times10^{-4}$	$+0.0028$
1378	photodimer	$< +1.0\times10^{-4}$	[b]
1202	photodimer	$< +1.0\times10^{-4}$	[b]
1166	δ_{ip}(CH) aromatic	-2.2×10^{-4}	-0.0021
'*Metamet*'			
1635	ν(C=C) vinylene	-1.1×10^{-4}	-0.0156[a]
1513	ν(C=C) aromatic	-1.5×10^{-4}	-0.0040
1494	ν(C=C) aromatic	$+3.6\times10^{-4}$	$+0.0060$
1378	photodimer	$< +1.0\times10^{-4}$	[b]
1208	photodimer	$+1.5\times10^{-4}$	[b]
1166	δ_{ip}(CH) aromatic	-1.8×10^{-4}	-0.0020
1068	photodimer	$+2.6\times10^{-4}$	[b]

[a] In the particular case of vinylene C=C, the orientation function has been calculated considering for A_0 the amount of remaining '*trans*'-isomers after 3 hours of irradiation.

[b] Since A_0 is not known for the new bands of photodimers, we are unable to calculate their orientation function.

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can be drawn. For the three polymers studied, a negative linear dichroism is observed at the wavenumber corresponding to the vinylene C=C band. Since this band is essentially due to '*trans*'-isomers of unreacted chromophores, one concludes that a selective optical pumping has occurred upon irradiation. Indeed, this process is responsible for the depletion of the remaining chromophores in the polarization direction of the UV light.

The more negative value of the linear dichroism for the aromatic ring bands is obtained for the 'Para' polymer. As the transition moments associated with these bands are along the biphenyl axis, the 'Para' chromophores are preferentially oriented perpendicular to **P**. It must be pointed out in this result that the contributions of the aromatic rings of both remaining chromophores and photodimers are involved. It is also noteworthy that the dichroism of the new bands associated with the cyclobutane ring of photodimers displays similarly negative values.

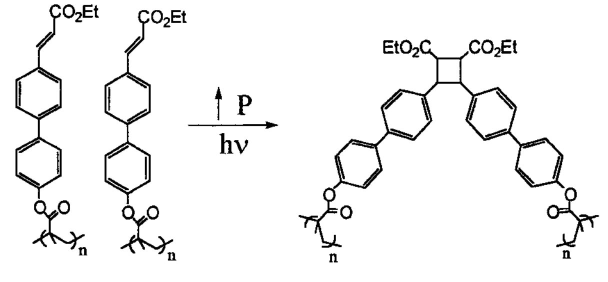
The interpretation of the observed linear dichroism in 'Meta' and 'Metamet' polymers is not straightforward. Indeed, it is now difficult to define a molecular long axis in these systems. Negative and positive dichroisms are observed for the aromatic ring bands at 1511 and 1490 cm^{-1}, respectively, indicating that their transition moments are orthogonal. Moreover, positive values of linear dichroism are observed for the new bands associated with photodimers at 1378, 1202 and 1068 cm^{-1}. The corresponding values are very weak in the 'Meta' polymer and relatively stronger in the 'Metamet' polymer, demonstrating the existence of weak orientation effects parallel to **P** for the photodimers in both systems.

4. Discussion

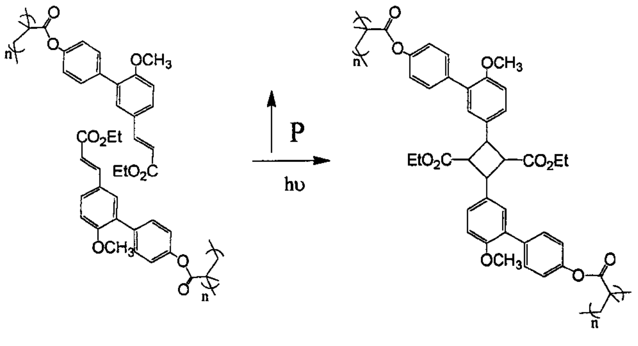
As demonstrated above, the behaviours of the three phenyl substituted cinnamate-based derivatives upon linearly polarized irradiation present similarities and differences. On the one hand, we have noted in all systems that, after a 3 h irradiation, nearly 30% of '*trans*'-isomers were remaining and their preferential orientation was always perpendicular to the polarization direction **P**. This reminds us of the photoinduced anisotropic processes in azobenzene-based polymer systems, extensively studied in the last decade [11–15]. As irradiation proceeds, successive '*trans*↔*cis*' isomerization cycles including spontaneous '*cis*→*trans*' relaxation lead to an increasing proportion of chromophores oriented perpendicularly to **P**; however, isomerization is thermally reversible in azobenzene compounds, a situation which does not apply to the present photocrosslinkable poly(cinnamate) derivatives.

On the other hand, in spite of the rather similar chemical structures of the starting polymers, we have noticed from UV results that the simultaneously formed photoproducts are aligned preferentially along **P** in the 'Para' derivative and exhibit very weak orientation effects in the 'Meta' and 'Metamet' compounds. These results seem in apparent contradiction to the negative infrared dichroism observed for the photodimers in the 'Para' system, but in our opinion this discrepancy comes from the related transition dipole moment direction. The distinct orientations observed for the three systems are probably due not only to differences in the direction of the transition dipole moment, along the biphenyl axis and the methoxycinnamate groups in the 'Para' and 'Metamet' chromophores, respectively, but also to the respective formation of corresponding head to head (scheme 2) and head to tail (scheme 3) photodimers. It is also noteworthy that in the latter head to tail configuration no angular reorientation of the biphenyl groups is imposed, and the main transition dipole moment remains along the direction of polarization **P**. In any case, the larger orientation effects observed in the 'Para' photopolymer are in accordance with the expected more effective electronic delocalization.

Now, it is possible to correlate these orientational effects with alignment properties observed for the same polymers in a previous study [6]. For this purpose, several liquid crystals were confined between two photopolymer coated glass substrates. Actually, 'Para' photopolymer was the only system which homogeneously oriented liquid crystals perpendicular to **P**; for the 'Meta' and 'Metamet' systems a parallel alignment was observed, but with a poor homogeneity in the former



Scheme 2. Head to head cycloaddition of Para.



Scheme 3. Example of head to tail cycloaddition of Metamet.

case. Furthermore, to test the alignment properties of the starting chromophores, several liquid crystals were confined between two rubbed photopolymer films. In such rubbed films, aromatic side group polymers generally lie perpendicular to the rubbing direction and lead to a perpendicular orientation of the liquid crystals via anisotropic van der Waals interactions [16, 17]. 'Para' polymer again induced a preferential alignment perpendicular to the rubbing direction, while no preferential alignment was observed with 'Meta' polymer. This result appears consistent with the mesogenic character of the '*trans*'-*para*-substituted isomers. We come thus to the conclusion that the interactions between '*trans*'-unreacted chromophores and liquid crystals are not sufficient to obtain a homogeneous alignment, since PM-IRLD measurements have shown that these chromophores exhibit similar orientations in the three systems. In contrast, the interactions with the photodimers must play also a key role, since in the 'Meta' and 'Metamet' photopolymers, the alignment direction is along the photodimer orientation.

From the above study it appears that at least two simultaneous and competing orientation processes are taking place upon irradiation in these photocrosslinkable poly(cinnamate) systems: (i) isomerization reactions deplete chromophores along the direction of **P** and induce a preferential perpendicular orientation of the remaining '*trans*'-isomers in all systems; (ii) cycloaddition reactions lead to the formation of photodimers along **P** in 'Para' and probably also in the 'Meta' and 'Metamet' derivatives. Both processes have an influence on the liquid crystal alignment properties but apparently the resulting molecular orientation effects are governed by the first process in the 'Para' system and by the second (weak) process in the 'Meta' and 'Metamet' systems. Such results complete our previous conclusions obtained on PVCi and PMC thin films, respectively [5].

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5. Conclusion

Molecular orientations in three original phenyl substituted cinnamate-based photopolymers irradiated by linearly polarized UV light were studied. UV measurements have shown the decrease of the '*trans*'-isolated chromophores and conversely the increase of photoproducts upon irradiation; head to head and head to tail molecular arrangements were observed in 'Para' and 'Metamet' systems, respectively. These photodimers are oriented along **P** for 'Para' polymer and show weak orientation effects in 'Meta' and 'Metamet' polymers. FTIR measurements have provided information on the preferential orientations of mainly the remaining '*trans*'-chromophores which always orient perpendicular to the polarization direction **P** in all systems. The photoinduced anisotropic effects are thus strongly dependent on the chemical nature of the chromophores and on the structure of the polymers. Furthermore, the great potential of the 'Para' photopolymer to align liquid crystals has been related to the molecular orientation of unreacted chromophores.

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