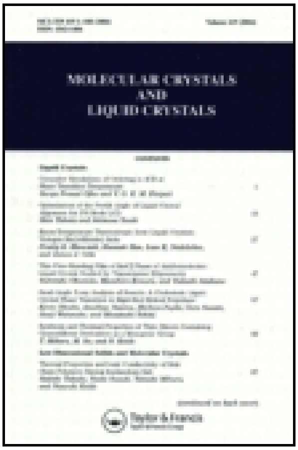

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Raman Spectroscopy Evidence of Phototransformation in Poly (Vinyl-para-fluorocinnamate)

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Raman Spectroscopy Evidence of Phototransformation in poly (vinyl-para-fluorocinnamate)

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Poly (vinyl cinnamates) are known to be phototransformable. We present in this work the Raman spectroscopy evidence of phototransformation in the case of poly (vinyl-para-fluoro-cinnamate). The relative intensity evolution of the C=C double bond stretching mode reflects strongly the polymer transformation under irradiation. Some other modes are also affected but the effects are less marked. We show also that phototransformation occurs both under UV and visible linearly polarized radiations.

Keywords : Raman spectroscopy, polymer, film, phototransformation, poly (vinyl cinnamate)

INTRODUCTION

Poly (vinyl-para-fluoro-cinnamate) (p-PVCN-F) is composed by fluorinated cinnamoyl photosensitive side chains linked to a vinyl chain skeleton. Poly (vinyl cinnamates) are well known for undergoing phototransformation under UV irradiation. The resulting modification of their physical properties were widely exploited for example in microelectronic's industries, where poly (vinyl cinnamates) are usually used as resin for photolithography [1-3], or since few years as tunable orientant for liquid crystals [4-15]. Vibrational spectroscopy is a suitable tool to understand the mechanisms involved in the phototransformation. In this paper, we present polarized Raman spectroscopy studies for various organization states of p-PVCN-F and the first Raman evidence of the phototransformation of p-PVCN-F.

EXPERIMENTAL SETUP

Our experiments were performed on p-PVCN-F powder and on p-PVCN-F films coated on glass plates. For the powder micro-Raman studies, the samples consisted in small elongated polyhedric grains, the size of which was a few microns and that look like small crystals, so we call them "crystallites" although such samples were probably not small mono-crystals. In case of such "crystallites" we can define a long axis and a short axis with respect to their shapes.

The films coating were performed as follow : p-PVCN-F was dissolved in dichloroethane at a ratio of 100 g/l, a droplet of solution was spread onto a glass plate and spinned during 10-30 s at 2000 rd/minute. Five layers of coating were deposed onto the same plate in order to obtain sufficient thick films to have get a suitable Raman signal. Finally, the obtained coated films were dried at 80 °C during 30 minutes. The phototransformation of the film was achieved by illuminating only half of the film area during 1 hour with linearly polarized UV light from a Hg-lamp providing 5-10 mW/cm^2. This procedure allowed us to study the effects of phototransformation by comparison between the Raman spectrum of the irradiated part of the films and the non-irradiated one. In order to verify the phototransformation we proceed to a cross-polarized observation of the samples through an optical microscope. Indeed the phototransformed polymer is optically anisotropic[4,8,13,6-19]. This feature is the most important mechanism in the tunable alignment of liquid crystals [5-15].

Our Raman experiments were performed with a XY 800 DILOR spectrophotometer, used in the micro-probe configuration. An Argon laser pump beam supplying a power of 4 mW was focused onto a 1 μm^2 area of the sample through a 100× microscope objective. In our experiments, we explored the spectral range between 200 cm^{-1} and 1800 cm^{-1} with a 2 cm^{-1} spectral resolution. The laser excited point on the sample was changed after 500 s exposure time in order to avoid any transformation (destruction or possible phototransformation) of the material by the laser beam; this point will be discussed in the following.

RESULTS AND DISCUSSION

We present on figures 1 and 2 the spectra obtained with a "crystallite" of p-PVCN-F. The spectra labeled (||) were obtained as the polarization of the excitation beam was nearby parallel to the direction of the "crystallite" long axis, and for the spectra (⊥) the polarization was perpendicular.

Previously, we presented Raman studies on various fluoro-substitued poly (vinyl cinnamates), and we assigned some modes of PVCN-F with specific known vibration modes [20]. The spectra shown in figure 1 exhibit some very weak peaks not easily observable, two spectral ranges look very bushy : the first between 750 cm^{-1} and 950 cm^{-1} and the second between 1100 cm^{-1} and 1400 cm^{-1}. It appears unambiguously that some modes are polarized. In table 1 we report the observed modes with tentative assignments together with the polarization status.

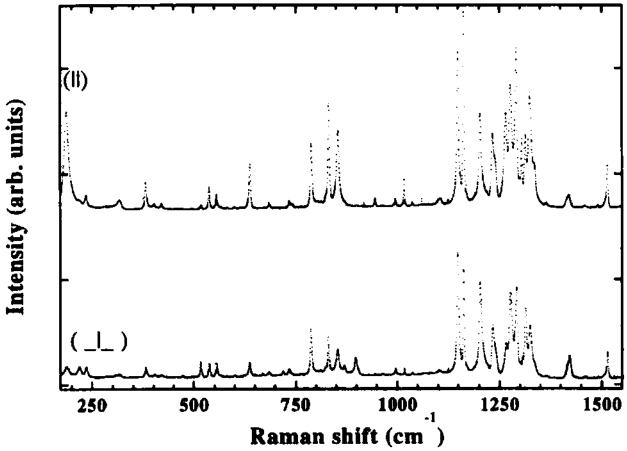

FIGURE 1 Raman spectra of p-PVCN-F. The excitation polarization was parallel to the crystallite axis (see text) for the spectrum (||) and perpendicular for the spectrum (⊥). The excitation wavelength was 514.5 nm.

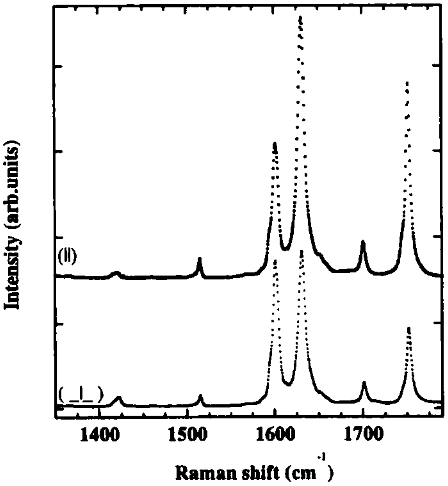

FIGURE 2 Raman spectra of PVCN-F in the C=C double bond stretching region. The excitation polarization was parallel to the crystallite axis (see text) for the spectrum (||) and perpendicular for the spectrum (⊥). The excitation wavelength was 514.5 nm.

TABLE 1 Tentative assignments (vs : very strong, s : strong, m : medium, w: weak, vw : very weak), and polarization status (p) of the Raman modes observed in p-PVCN-F. Para and mono are the type of substitution (mono is residual) and the brackets determine grouped assignments.

Frequencies (cm^{-1})	Status		Tentative assignment	Frequencies (cm^{-1})	Status		Tentative assignment
188	m	p		1137	m sh		C-C skeletal strech
220	w	p		1149	s	p	para ring stretch mixed with CH in plane bend
237	w	p		1156	m sh		
318	w			1164	s	p	
382	w			1171	w sh		
402	w		ring deformation by quadrant	1193	w sh		
421	w			1204	m	p	C-O strech unsatureted ester
471	w	p		1221	w sh		
518	w	p		1234	m		φ-F strech
538	w	p		1239	m sh		
566	vw			1266	m	p	
584	vw	p		1277	m	p	C-O conjugated ester
600	vw			1292	s	p	=C-H in plane rock
615	vw		ring bend by quadrant	1306	m	p	-$(CH_2)_n$- twist
639	m		para ring bending	1314	m	p	-O-CH or C-H. rock
671	vw	p		1325	m		
686	w			1336	m sh		
720	vw	p		1366	w		CH_2 &CH_3 bending mode
736	w			1416	w		para ring semi-circle stretch
743	vw sh			1420	w		n-alkane -CH_3 asym. bend
764	vw			1459	w		mono ring semi-circle stretch
789	m			1490	w		
794	vw sh			1506	w sh		mono ring semi-circle stretch
803	vw	p		1515	m		para ring semi-circle stretch
813	vw	p	C-H wag	1567	w		
823	w sh			1586	w sh		mono ring quadrant bend
833	m	p	C-C-C stretch	1595	m sh		
856	m	p		1602	s		para ring quadrant bend
866	vw sh		CH wag	1604	s		
873	w	p		1612	m sh	p	C=C strech conjugated with C=O and φ
884	vw			1631	vs	p	
900	m	p	C-H wag or stretching C-C ?	1648	w sh	p	
947	w	p	para C-H out of plane wag	1660	vw sh		
966	vw		C-H wag CHR_1=CHR_2	1702	m	p	C=O strech conjugated with C=C and φ
997	w		ring strech	1715	vw		
1004	vw	p	ring strech mono	1745	w sh	p	
1016	w	p	ring strech	1753	s	p	
1038	w		C-O ?				

Figure 2 shows the C=C double bond stretching region. This spectral range is of particular interest when considering phototransformation processes. An important point is that, whatever the polarization is, the quadrant stretch aryl ring mode at 1604 cm^{-1} is less intense than the C=C double bond stretching modes structure centered at 1640 cm^{-1} [20].

We show on figure 3 the p-PVCN-F films spectra. The spectrum labeled (a) corresponds to the UV irradiated zone of the sample and (b) to the non-UV irradiated zone of the same sample. In opposite to the "crystallite" spectra, no polarization effects were observed on the film spectra, UV irradiated or not.

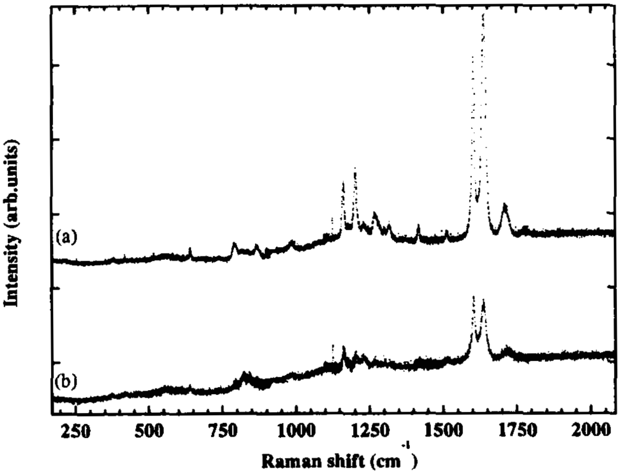

FIGURE 3 Raman spectra of a p-PVCN-F film; (a) without UV exposure, (b) after UV light exposure (see the experimental section for the details of the UV exposure procedure).

Comparing the spectra of the "crystallite" (figures 1 and 2) to those of the film (figure 3) two features come out : first, it is obvious that all the spectra are similarly shaped, secondly the film spectra are less resolved and the modes intensities are weaker. These two observations lead us to assume that our p-PVCN-F films are weakly ordered, this is compatible with the used coating procedure. In the case of the irradiated part of the film, the mode intensities are lowered with respect to the non-irradiated one.

Among various processes, dimerization occurs during the phototransformation of poly (vinyl cinnamates) [4, 8, 13, 16-19], the structural organization of the polymer is modified [22-a]. The structural modifications are partially induced by the crosslinking between adjacent cinnamoyl groups [21] and are able to affect the mode intensities. In case of photodimerization, C=C double bonds disappear, so we expect that the C=C stretching mode reveals strongly this evolution. Moreover the modes of the other side chains bonds should also express the photodimerization but in a less marked manner. After an UV exposure of the film we observe a strong relative intensity variation between the quadrant stretch aryl cycle mode at 1604 cm^{-1} and the C=C double bond stretching modes structure centered at 1640 cm^{-1}. Indeed, the intensity of the C=C mode at 1640 cm^{-1} decreases significantly relatively to the aryl mode at 1604 cm^{-1} intensity; we observed an intensity ratio inversion between the spectra (a) and (b) of the figure 3. As mentioned previously the polymer film presents no polarization effects, so the intensity decrease of the C=C stretching mode can only be attributed to the lowering of the C=C bonds number implied by the photodimerization process. In the spectral ranges around 800 cm^{-1} and 1200 cm^{-1}, the UV lightening induces relative intensity variations more or less pronounced (figure 3).

On an other hand we tested the samples stability under laser illumination. These studies were realized as follow : our samples were continuously illuminated by the laser pump beam with the same beam parameters as in the previous experiments. The linearly polarized beam was focused on the same sample point during the 200 minutes of exposure. We have limited our studies to arange around 1600 cm^{-1} as the C=C double bonds are involved in all the phototransformation processes. We present in figure 4 the more stricken result. These spectra were obtained after exposure; (a) with a "crystallite" for a parallel polarization (as defined in the experimental setup) and (b) with a non-UV exposed film.

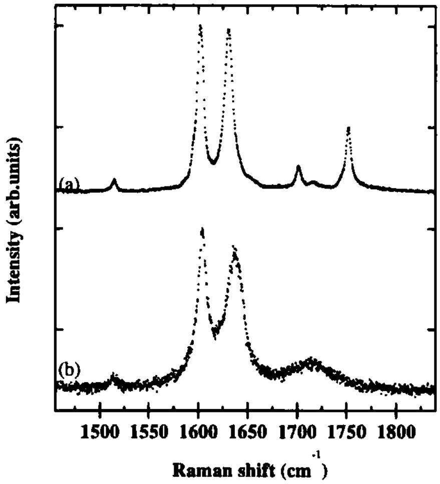

FIGURE 4 Raman spectra of p-PVCN-F in the C=C double bond stretching region after 200 minutes exposure under a 514.5 nm laser beam of : (a) for a crystallite (beam polarization parallel to the crystallite axis), (b) for a non-UV irradiated film.

Comparing figure 4 (a) with figure 1 (||) and figure 4 (b) with figure 3 (a), in the same way than for the UV-irradiated sample of p-PVCN-F film we observe a ratio inversion between the intensities of the modes at 1604 cm^{-1} and at 1640 cm^{-1}. As already argued, this effect can not be attributed to a polarization effect. It is well known that dimerization is not the only process of the phototransformation, and that the photoisomerization plays a notable role in the process [4, 8, 13]. Ichimura et al. have reported that during UV exposure, in a first step a selective isomerization occurs in case of polymers with cinnamate side chains [13] and if the irradiation time is long enough, in a second step a photodimerization begins when the appropriate isomer is present. The photoisomerization occurs at UV wavelengths for poly (vinyl cinnamates)[22, 23]. Preliminary calculations of poly (vinyl cinnamate) configurations [24], allow us to suppose that such isomerization could also occur in the case of PVCN-F for wavelengths in order of 500 nm. The para-position of the Fluor atom on the aryl cycle is indeed fairly propitious to provoke a large conjugation due to its strong electronegativity, weakening the C=C double bond energy, in a same manner as for halogenated compounds [25-29]. Thus the para-fluoro-substitution could cause a lowering of the energy gap between isomeric states. Assuming this hypothesis we can imagine that in the case of our polymer, the energy at 514.5 nm is sufficient to isomerize and/or dimerize the cinnamoyl side chains explaining the Raman spectra observed after 200 minutes exposure. This point is open and further experiments and calculations should clarify the status of the different species present in these polymers.

CONCLUSION

In this study, we have shown the first evidence of phototransformation of poly (vinyl-para-fluoro-cinnamate) by Raman spectroscopy. Considering the intensities variations especially in the C=C stretching mode spectral range, we have determined unambiguously the Raman spectroscopy signature of the phototransformation : the C=C modes intensity decreases significantly after UV irradiation. Moreover our work evidences that Visible as UV wavelengths are able to phototransform p-PVCN-F. These results show that Raman spectroscopy investigations can help to the comprehension of the complex processes occurring during the phototransformation of poly (vinylcinnamates).

Acknowledgments

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