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Characterization of photochemically converted poly(*para*-phenylene vinylene)

Jany Wéry[a],*, Bertrand Dulieu[a], Jacques Bullot[a], Mimouna Baïtoul[a], Philippe Deniard[b], Jean-Pierre Buisson[a]

[a]*Laboratoire de Physique Cristalline, Institut des Matériaux de Nantes, Université de Nantes, UMR 6502, 2, rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*

[b]*Laboratoire de Chimie des Solides, Institut des Matériaux de Nantes, Université de Nantes, UMR 6502, 2, rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*

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Abstract

The assisted photochemical conversion of precursor polymer synthesized via the procedure using tetrahydrothiophenium group is studied, particularly the influence of the substrate temperature and duration of the illumination period followed by optical absorption measurements. The optimal experimental conditions are obtained for a substrate temperature $T = 110°C$ and an illumination period of at least 30 min. The characterization of the optimized photochemically converted poly(*p*-phenylene vinylene) [PPV] has been investigated by means of optical absorption, infrared absorption, X-ray diffraction and resonant Raman scattering spectroscopy. We find that optical and structural properties of the optimized photoconverted are rather close to those of standard PPV. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: UV-Vis-NIR absorption; Infrared and Raman spectroscopy; X-ray diffraction

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1. Introduction

For several years, conjugated polymers have attracted interest due to their potential applications in electronic, optoelectronic and non-linear optics [1,2]. Poly(*p*-phenylene vinylene) [PPV] is one of the most studied conjugated polymers [3,4] since the discovery of synthetic routes via a soluble precursor polymer, containing either dimethyl sulfonium [5,6] or tetrahydrothiophenium groups [7] and the discovery of high efficiency electroluminescent emission at low bias voltages from sandwich structures [8–10].

Some recent studies show that light-assisted conversion under vacuum of the tetrahydrothiophenium precursor polymer of PPV is easily achieved [11,12]. The polymer obtained has optical absorption and photoluminescence properties very close to those of thermally converted PPV [11]. In contrast, UV illumination in air at room temperature of the precursor polymer yields oxygenated defects and degradation [13–15].

In this paper, we report on an experimental study of photochemical conversion. The influence of the substrate temperature and duration of the illumination period are followed by optical absorption measurements. The optimized photoconverted PPV, i.e. the material having the lowest absorption onset energy, is characterized by means of optical absorption, infrared (IR) absorption, X-ray diffraction and Resonant Raman Scattering (RRS) spectroscopy and compared with standard PPV, converted at 300°C under dynamic secondary vacuum.

2. Experimental

The precursor polymer was synthesized in our laboratory via the standard procedure using the tetrahydrothiophenium group described elsewhere [7]. Films of precursor polymer were cast from a methanolic solution under a nitrogen flow onto silica substrate for UV/VIS optical absorption and Raman scattering studies and onto silicon [1,0,0] single crystals for IR absorption and X-ray diffraction measurements. Beforehand, all substrates were cleaned in an ultrasonic bath with deionized water and ethanol.

Photochemical conversion was carried out under the experimental conditions previously described [11]. The precursor film was first submitted to a 3-h heating period, under vacuum of $\sim 2 \times 10^{-6}$ mbar, in order to eliminate solvent

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* Corresponding author.

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traces and subsequently illuminated with the light flux emerging from a 150-W XBO xenon arc lamp. A water filter was used to cut IR from the light beam in order to avoid any overheating of the illuminated film. The resulting spectral range of the light source thus extends from UV (190 nm) up to near IR. In this experimental configuration, the light power falling on the film (1.2 × 1.2 cm) is of the order of 0.6 mW/cm^2. We emphasize that due to the high absorption coefficient of the tetrahydrothiophenium group in the near UV region ($\alpha \sim 2-3 \times 10^{-5}$ cm^{-1}), this process is restricted to thin films, typically ~100 nm thick.

Thermal conversion at various temperatures was carried out under the same conditions of film thickness, in dark and under dynamic secondary vacuum (2×10^{-6} mbar).

The optical absorption spectra were recorded by means of a Varian CARY 2300 double beam spectrophotometer between 200 and 600 nm. IR absorption measurements were made by means of a NICOLET interferometer with an energy resolution of 4 cm^{-1}. The diffraction patterns were obtained with a SIEMENS 5000 diffractometer (Cu K$_\alpha$, 40 kV, 30 mA) in a Bragg Brentano geometry. Resonant Raman spectra were recorded on a multichannel JOBIN-YVON T 64000 spectrometer connected to a CCD Camera and detector. The excitation light was supplied by the 676.4-nm laser line in the visible (backscattering configuration) and by the 363-nm laser line in near UV (scattering configuration at 90°). The energy resolution of resonant Raman spectra was estimated to be 2 cm^{-1}.

3. Results and discussion

Fig. 1 shows the evolution of the optical absorption onset E_0 as a function of the substrate temperature T and the illumination period t. E_0 is measured by extrapolating the linear regime of the absorption to the baseline.

The following results were obtained: at $T = 23°C$ and $t = 180$ min, $E_0 = 2.50$ eV; at $T = 90°C$ and $t = 90$ min, $E_0 = 2.44$ eV. Optimal photoconversion, $E_0 = 2.41$ eV, was obtained at $T = 110°C$ and $t = 30$ min. Some experiments were performed at higher temperatures, up to 160°C, without improving E_0. In Fig. 1 the double axis allows us to compare these results with standard thermal conversion and to follow the gradual decrease of E_0 with the conversion temperature.

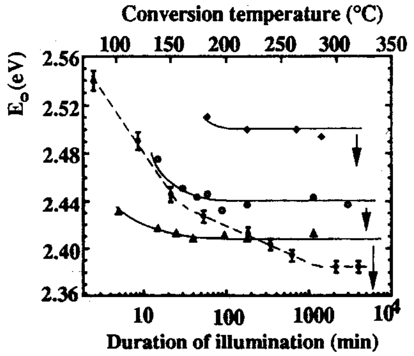

Fig. 1. Evolution of the optical absorption onset E_0 as a function of the illumination period at a constant temperature T (lower axis): $T = 23°C$ (lozenge); $T = 90°C$ (circle) and $T = 110°C$ (triangle) in the case of optimized photoconverted PPV and as a function of temperature in the case of thermal conversion (solid circle; upper axis; the broken curve is a guide to the eyes). The arrows indicate the x-axis to use.

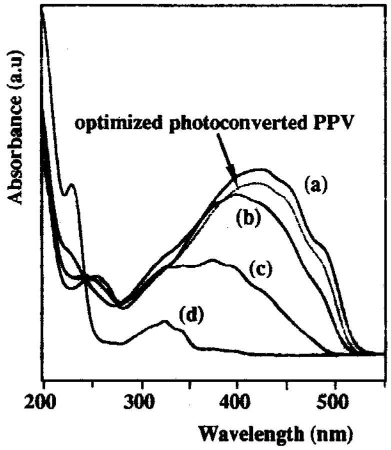

Fig. 2. Room temperature optical absorption spectra recorded in thermally converted samples at (a) 300°C; (b) 180°C; (c) 120°C; (d) 23°C and in optimized photoconverted PPV.

Fig. 2 shows the optical absorption spectra of films converted at various temperatures and of the optimized photoconverted film. The optical absorption of the latter is close to that of the material thermally converted at 220°C–240°C. If we consider the $\pi \rightarrow \pi^*$ electron transition onset reported in the literature for the six first oligomers of PPV [16,17], we may conclude that the effective conjugation length of optimized photoconverted PPV is of the order of 7–8 units, as compared to about 8–9 units for standard PPV. It has to be noted that in the 240–290 nm region, the spectrum of optimized photoconverted PPV is structureless and less well developed than standard PPV. We do not have any clear interpretation regarding this point.

Infrared absorption measurements were performed in order to detect the eventual presence of chemical defects. We found that the IR spectrum of photoconverted PPV (Fig. 3) is quite similar to that of standard PPV [4,16]. The presence of the 3024 cm^{-1} strong peak attributed to trans-vinylene C–H stretching vibrational mode and the absence of the 632 cm^{-1} peak attributed to C–S stretching vibrational mode [4,13,14] indicates that the elimination reaction is achieved. Also the absence of the peaks at 1690 and 1278 cm^{-1}, attributed to the carbonyl and carboxyl stretching vibrational modes respectively [13–15], shows that the photoconversion process under vacuum does not result in the creation of oxygenated defects, in contrast with what happens during illumination in the presence of air [13].

Information on the structural modifications (interchain distance related to lattice parameters) induced by illumination were obtained from X-ray diffraction studies. The corrected (background substracted) diffraction patterns

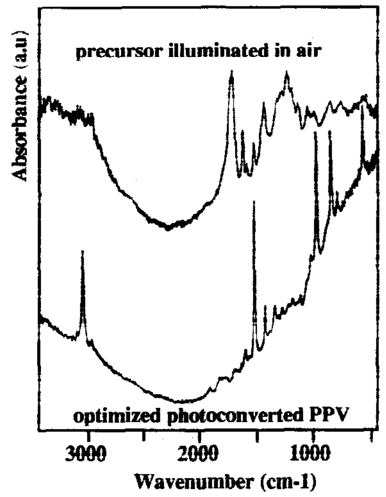

Fig. 3. Infrared spectra of optimized photoconverted PPV and of a precursor sample illuminated in the presence of air.

(Fig. 4) clearly show well defined peaks corresponding to (110/200) indexations [18,19]. The peak location depends upon the conversion procedure; we found $2\theta = 20.9^\circ$, 22.5° and 20.7° for thermal conversion at 180°C, thermal conversion at 300°C (standard PPV) and for optimized photochemical conversion, respectively. Thus, during thermal conversion, a peak shift to higher 2θ values is observed, in good agreement with the X-ray results obtained elsewhere [18]. In the case of photoconversion, the (110/200) peak shift towards lower 2θ values indicates a high inter-reticular distance in the $\vec{a}$ and $\vec{b}$ directions. Assuming that the chains are aligned along the $\vec{c}$ direction, in a monoclinic unit cell [19], we are led to conclude that the interchain distance is higher in the case of photoconversion. Thus, standard PPV appears to be more packed than optimized photoconverted PPV, which is close to thermoconverted at 180°C. Due to the low signal/noise ratio, information on the coherence length is not significant.

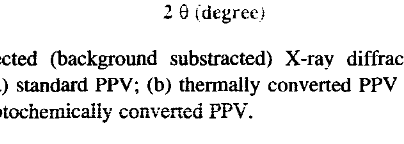

Fig. 4. Corrected (background substracted) X-ray diffraction patterns recorded in (a) standard PPV; (b) thermally converted PPV at 180°C; (c) optimized photochemically converted PPV.

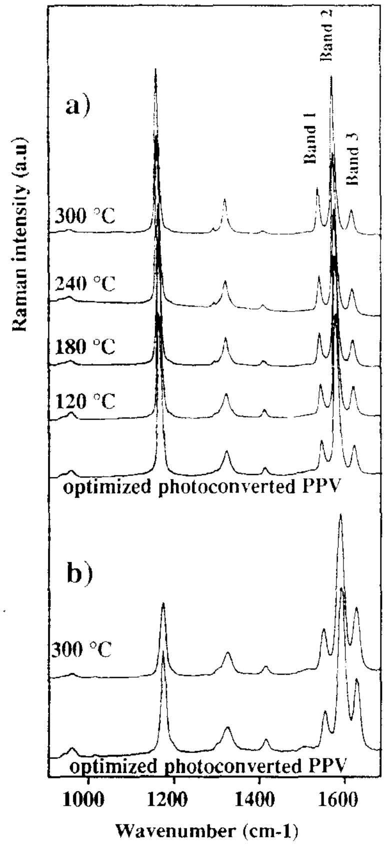

Fig. 5. (a) Resonant Raman spectra recorded in thermally converted films at various temperatures (300, 240, 180 and 120°C) and in optimized photoconverted PPV with the 676.4-nm laser line. (b) Resonant Raman spectra recorded in standard PPV and optimized photoconverted PPV with the 363-nm laser line.

In order to obtain further information on the conjugation lengths distribution, Resonant Raman Scattering studies were undertaken. The RRS technique allows one to selectively enhance different species by matching the laser line with the energy of the species absorption. By exciting in the UV-visible absorption range, a rather strong photoluminescence signal is observed, therefore, it is possible to use the 676.4- and 363-nm laser lines. These lines allow one to selectively excite the $\pi \rightarrow \pi^*$ electron transitions in long conjugated segments and mainly in short conjugated segments, respectively.

Fig. 5(a) shows the Raman spectra recorded at $\lambda = 676.4$ nm, with optimized photoconverted PPV and with thermally converted films at 120, 180, 240 and 300°C (standard PPV). Fig. 5(b) shows significant Raman spectra recorded at $\lambda = 363$ nm, with optimized photoconverted and standard PPV. As can be seen, the RRS spectra of optimized photoconverted film and of thermoconverted films at various temperatures are similar. Only the strong triplet around 1600 cm^{-1} shows significant differences. In standard PPV, at $\lambda = 676.4$ nm, the three bands, labelled 1, 2 and 3 are respectively located at 1547.1, 1583.6 and 1625.4 cm^{-1}. Bands 1 and 2 are attributed mainly to the phenyl group A_g mode (stretching of C–C bond) and band 3 mainly to vinyl group A_g mode (stretching of C=C bond) [20–22].

In Tables 1 and 2, at $\lambda = 676.4$ and 363 nm, the frequency, FWHM (Full Width of Half Maximum) of each band and the ratio $R = A_1/A_3$ of the integrated intensities

Table 1
Centre, width of bands 1, 2 and 3 and ratio $R = A_1/A_3$ of the integrated Raman intensities of bands 1 and 3 for thermally converted PPV at 120, 180, 240 and 300°C and for optimized photoconverted PPV with 676.4 nm laser excitation

		Band 1 centre (width) cm^{-1}	Band 2 centre (width) cm^{-1}	Band 3 centre (width) cm^{-1}	$R = A_1/A_3$
Themal conversion at various temperatures	120°C	1550.0 (11.5)	1586.3 (12.5)	1627.1 (12.8)	0.82
	180°C	1548.5 (11.4)	1585.2 (12.3)	1626.4 (12.5)	1.10
	240°C	1548.0 (10.8)	1584.5 (12.2)	1626.0 (12.4)	1.16
	300°C	1547.1 (10.4)	1583.6 (12.3)	1625.4 (12.4)	1.20
Optimized photoconverted PPV film		1550.2 (12.0)	1586.5 (12.6)	1627.4 (12.8)	1.09

$\lambda_{exc} = 676.4$ nm

of bands 1 and 3 are reported. The triplet is fitted by using a mixture of Gaussian and Lorentzian. At $\lambda = 676.4$ and 363 nm, when the conversion temperature is increased, the triplet undergoes a slight Raman frequency dispersion towards low frequencies and R increases; these results are in good agreement with those previously reported in PPV and its oligomers [22]. Such an evolution as a function of the conversion temperature may be interpreted as being due to changes in the intercycle electronic distribution inducing conjugation extension. Moreover, it is observed that, when using the 363-nm line instead of the 676.4-nm one, the triplet is slightly broadened and shifted towards higher frequencies. In addition, the frequency dispersion and the R increasing are less important, probably because short conjugated segments are partly excited. We note that in photoconverted PPV, excited at $\lambda = 676.4$ nm, $R = 1.09$, a value which corresponds to PPV converted at a temperature close to 180°C; this is accompanied by a slight broadening and a slight shift towards higher frequencies of the triplet. In near UV, we measured $R = 0.37$, a value close to that of PPV converted at 120°C and observed a small narrowing of the triplet as compared to standard PPV. These results indicate that the distribution of conjugation lengths is different in photoconverted PPV from these of thermoconverted and particularly in standard PPV. In optimized photoconverted PPV, the short conjugated segments distribution is similar to that of PPV converted at 120°C and the long conjugated segments distribution similar to that of PPV converted at 180°C. This distribution might result from the two-step photoconversion process we used, i.e heating in the dark at 110–120°C followed by illumination, the short segments being formed essentially during the first step and the long segments during the second one.

So photochemically converted PPV is more disordered than standard PPV. As reported elsewhere [23], this feature induces significant changes in the charge transport process which follows photon absorption as compared to standard PPV, in particular in the low temperature range.

4. Conclusion

In view of optical absorption measurements, the study of the influence of substrate temperature and illumination duration allowed us to obtain the optimal experimental conditions of assisted photochemical conversion: a substrate temperature 110°C and an illumination period of at least 30 min under dynamic secondary vacuum.

The optical absorption, infrared absorption, X-ray diffraction and Resonant Raman Scattering spectra of optimized photoconverted film are similar to those of standard PPV. We found that photochemically converted PPV has an effective conjugation length of about 7–8 units, with a distribution of conjugated segments which differentiate from these of thermoconverted PPV films, and contained no obvious chemical defects and is less packed than standard PPV. In order to complete this physical properties study of photochemically converted PPV, detailed charge transport measurements are in progress.

Table 2
Centre, width of bands 1, 2 and 3 and ratio $R = A_1/A_3$ of the integrated Raman intensities of bands 1 and 3 for thermally converted PPV at 120, 180, 240 and 300°C and for optimized photoconverted PPV with 363 nm laser excitation

		Band 1 centre (width) cm^{-1}	Band 2 centre (width) cm^{-1}	Band 3 centre (width) cm^{-1}	$R = A_1/A_3$
Themal conversion at various temperatures	120°C	1553.0 (15.1)	1592.5 (18.3)	1629.3 (16.2)	0.38
	180°C	1552.4 (15.6)	1592.32 (19.2)	1629.4 (16.5)	0.44
	240°C	1551.7 (16.0)	1591.5 (19.3)	1629.0 (17.0)	0.45
	300°C	1551.2 (16.4)	1591.0 (20.2)	1628.5 (18.0)	0.47
Optimized photoconverted PPV film		1553.1 (15.9)	1593.0 (19.3)	1628.9 (16.8)	0.37

$\lambda_{exc} = 363$ nm

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