

Thin Films of Insoluble Copolymer Derived from Poly(phenylene-vinylene) Obtained by Thermal Evaporation Under Vacuum

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ABSTRACT: A new copolymer, referred to as poly(phenylene-vinylene) (PPV)-ether, built as PPV a polymer with some (—CH=CH—) links changed into (—CH₂—O—CH₂—) ethylic-ether links, is insoluble in common solvents. PPV-ether films are deposited by the thermal evaporation technique. X-ray photoelectron spectroscopy for chemical analysis measurements indicate that the surface contamination decrease in the case of vacuum-evaporated PPV-ether. The scanning electron micrographs indicate that the surface of these vacuum-deposited PPV-ether are uni-

form. By comparison to the reference powder, the modification of the properties of the evaporated PPV-ether are related to the decrease of the chain length and surface contamination. The results of the photoluminescence measurements reveal a shifting of the luminescence to blue in the vacuum-evaporated PPV-ether. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3091–3099, 2003

Key words: IR spectroscopy; luminescence; insoluble; poly(phenylene-vinylene); X-ray photoelectron spectroscopy

INTRODUCTION

In recent years, considerable efforts have been dedicated to the development of electroluminescent polymers and organic materials to be used in light emitting diodes (LEDs). Poly(phenylene-vinylene) (PPV) was the first conjugated polymer in which electroluminescence was observed.¹ The results obtained with LEDs, using PPV as the emissive layer,^{2–15} have stimulated the synthesis of new copolymers based on PPV derivatives.^{16–18} Luminescent polymer-based devices have a simple structure: a thin film of organic luminescent material is sandwiched between two electrodes. For soluble polymers or oligomer precursors, different methods have been used to incorporate polymer in the structure of LEDs, such as spin coating or sol-gel. But the use of solvent could make the realization of multilayer devices very difficult. Furthermore, when the polymer used is insoluble, the only way to make thin films is the thermal evaporation under vacuum. This process permits not only to prepare a homogeneous multilayer with a desirable thickness but also to reduce the oxidation of the interface of the polymer-

electrode. It also allows protecting the achieved devices by evaporation of a protective thin film without oxygen contamination.

The new copolymer, referred to as PPV-ether,¹⁶ used to achieve transparent thin films, is insoluble. Thus, as previously mentioned, only thermal evaporation under vacuum permits the realization of PPV-ether thin films. In order to justify obtaining evaporated copolymer thin films under vacuum, a proper characterization by different techniques is absolutely necessary. In this article we describe a simple vacuum evaporation technique to deposit the insoluble PPV-ether, which permits to obtain continuous and uniform thin films with the desired thickness. The PPV-ether vacuum-deposited films have been characterized by optical absorption (IR absorption, visible, and near-UV absorption), X-ray photoelectron spectroscopy (XPS analysis), electron microscopy and photoluminescence measurements (PL).

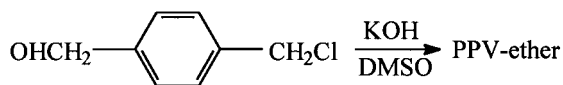
EXPERIMENTAL

The new copolymer derived from PPV, referred to as PPV-ether, is a macromolecular material obtained by homopolycondensation of 1-chloromethyl,4-methoxybenzene (Scheme 1).

The synthesis of this insoluble copolymer (PPV-ether) has been previously described¹⁶ and its structure, showed in Scheme 2, is supported by IR mea-

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Scheme 1 The homopolymerization of 1-chloromethyl,4-methoxybenzene to obtain PPV-ether.

surements, raman scattering, XPS and optical density (OD) analysis.

In our first article¹⁶ we showed from the gravimetric thermal analysis results (GTA) Figure 1, that no important deterioration occurs below 573 K but there is a 10% decrease in weight at 523 K that is due to the departure of HCl or the termination molecule ($\text{OCH}_2\phi\text{CH}_2\text{Cl}$). Then the PPV-ether chain lengths and sequences were very difficult to estimate because no reliable quantitative chemical analysis was available.

The thin films were obtained by evaporation of PPV-ether powder under vacuum $\sim 10^{-3}$ Pa from a molybdenum boat and using the same method for obtaining poly(*N*-vinylcarbazole) (PVK) thin films.¹⁹ This boat has a special configuration (two superposed multihole covers) in order to avoid the qualification of the copolymer and so that the evaporated PPV-ether remains focused on the substrates. During the evaporation, the substrate and the boat temperature was respectively 300 K and less than 500 K. It was controlled by a copper-constantan thermocouple attached to the surface of the sample (substrates or boat) by silver paste. The substrates were glass for the electron microscopy and PL measurements, and CaF_2 single crystals for optical absorption measurements. Before the evaporation, the substrates were chemically cleaned and then heated at 400 K for 1 h to desorb the water vapor. The evaporation rate and film thickness were measured in situ using the vibrating quartz method. The evaporation rate was optimized to 0.1 nm/s. The thickness varied from 1 to 5 μm and was also controlled by interferometry. The optical measurements were carried out at room temperature for visible and near-UV domains using a Bruker Vector 22 spectrophotometer for IR and a Cary 2300 spectrometer for the OD. For IR measurements, only characteristic bands of PPV-ether samples were selected. Those of CaF_2 for evaporated copolymer or KBr for powder were eliminated through a subtraction of CaF_2 or KBr from the final spectrum. Band positions are expressed in terms of wavenumbers for IR and wavelengths

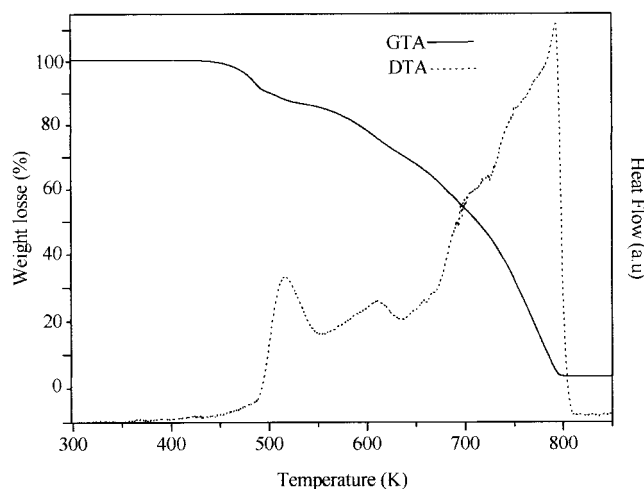
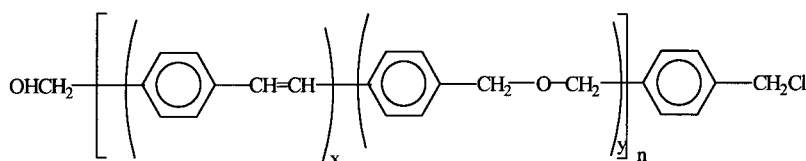


Figure 1 Thermograms by dynamic and gravimetric thermal analyses of PPV-ether powder.

from 2 to 0.2 μm for OD. Observations of the surface topography were performed using a Jeol 6400F field-effect scanning electron microscope. The XPS data were obtained with a Leybold LHS-12 spectrometer equipped with magnesium radiation source (1253.6 eV) operating at 10 kV and an electric current of 10 mA. The pass energy was set at 50 eV. High resolution scans with a good signal to noise ratio were obtained in the C1s, O1s, and Cl2p regions of the spectrum. In order to decrease the charge effect, the sample was deposited on a sheet of indium placed on the substrate holder. The quantitative analysis were based on the determination of the C1s, O1s, and Cl2p peak areas with sensitivity factors of 0.2, 0.6, and 0.58, respectively. The sensitivity factors of the spectrometer were provided by the manufacturer. The vacuum in the analysis chamber was around 10^{-6} Pa. All spectra were recorded under identical conditions. The deconvolution of the XPS peaks into different components and the quantitative interpretation were made after subtraction of the background using the Shirley method.²⁰ The developed curve fitting programs permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half-maximum, and the position and the intensity of the contribution. A curve-fitting program optimized these parameters in order to obtain the best fit. In the PL measurements the substrate covered with vacuum-evaporated copolymer films was placed in a conical hole under a SiO_2



Scheme 2 The structure of PPV-ether.

TABLE I
XPS Quantitative Analysis of PPV-Ether Powder and Vacuum-Evaporated PPV-Ether

	C1s	O1s	Cl2p
PPV-ether powder			
Binding energy (eV)	285.42	533.23	200.83
Relative atomic percentage	86	11	2
Vacuum-evaporated PPV-ether thin films			
Binding energy (eV)	284.7	532.2	199
Relative atomic percentage	95.6	4.1	0.3

window in the cryostat at 10 K. An argon laser with 1-mW excitation was used ($\lambda = 4579, 4765, 4880, 4965, 5017, \text{ and } 5145 \text{ \AA}$).

DISCUSSION

The characterization of the previously discussed PPV-ether powder¹⁶ was used as an argument to analyze the results obtained in case of vacuum-evaporated PPV-ether films.

Physical and chemical characterization analysis of vacuum-evaporated PPV-ether

Compared to the PPV-ether powder, the XPS quantitative analysis reported in Table I, revealed a decrease of the binding energies in the case of evaporated PPV-ether which means that the charge effect decrease during XPS measurements. The surface composition of the samples, reported in Table I, showed an increase in the relative atomic percentage of carbon and a decrease of those of oxygen and chlorine in the case of vacuum-evaporated PPV-ether. Moreover, it can already be shown that this excess of carbon was systematically present in this family of polymers. The results obtained by deconvolution of the peaks are reported in Table II after subtraction of the charge effect. It appears that, in the case of vacuum-deposited films, the deconvolution of the peak of carbon shows that, apart from the main component (at 285 eV), two other contributions are present and situated at 285.8 and 287.3 eV. The excess of carbon and the shape of its

peak, which is narrow permit its deconvolution into three contributions. The component at 285 eV is due to carbon in an environment with C—C links. The second component (at 285.8 eV) corresponds to a C—O—H environment but some C—Cl links can also be present. The last one, at 287.3 eV, can correspond to some COOR links with a relative intensity equal to 4%. The deconvolution of oxygen peaks shows two contributions whose binding energies are 530.5 and 532.8 eV. The components corresponding to the highest binding energies (532.8 eV) can be assigned to C—O—C. The peak appearing at lower energy (530.5 eV) originates from the indium (In_2O_3) used as a support. Based on the XPS results, we noted that the contribution attributed to C=O (originate from the surface contamination) disappeared for O1s in the case of evaporated PPV-ether but appeared for C1s with very small relative intensity we could also conclude that the surface contamination is reduced.

The approach followed in optical analysis was to study at first the PPV-ether powder, used in preparing evaporated copolymer, then CaF_2 single crystals covered by vacuum-deposited PPV-ether films. Figure 2(a,b) shows the IR spectra of the evaporated layer as well as the powder that used to realize it. The comparison of the IR is essentially based on the PPV^{21,22} and ether²² characteristic peaks (Table III). The latter two are present in both spectra. However, some modifications are obvious. In fact, peaks situated at 920 and 1638 cm^{-1} , present in the case of PPV-ether powder, disappear in the case of vacuum-evaporated PPV-ether. Those peaks are probably due to impurities. An absorption band situated at 2734 cm^{-1} also appears in the case of evaporated PPV-ether. This probably results from a change in the evaporated PPV-ether crystallinity.²³ The peak intensity situated at 630 cm^{-1} , identified as C—Cl have diminished compared to the same peak in powder (spectra are normalized according to C=C peak intensity). We could also find that the peak located at 3440 cm^{-1} and attributed to OH (the terminal of PPV-ether as mentioned in Scheme 1) was not present in the case of vacuum-deposited PPV-ether films. The disappearance of IR impurity peaks and contamination surface decrease, qualitative XPS

TABLE II
XPS Qualitative Analysis of PPV-Ether Powder and Vacuum-Evaporated PPV-Ether

	C1s			O1s			Cl2p	
	C—C	C—O—H	C—Cl	COOR	In_2O_3	C=O	C—O—C	Cl
PPV-ether powder ($\Delta E = 0.4 \text{ eV}$)								
Binding energy (eV)	285	286.5	—	—	530	531.2	533	200.2
Relative atomic percentage	86.5	13.5	—	—	13.5	21.5	65	100
Vacuum-evaporated PPV-ether thin films ($\Delta E = 0.05 \text{ eV}$)								
Binding energy (eV)	285	285.8	287.3	—	530.5	—	532.8	200.2
Relative atomic percentage	91	5	4	—	36	—	64	100

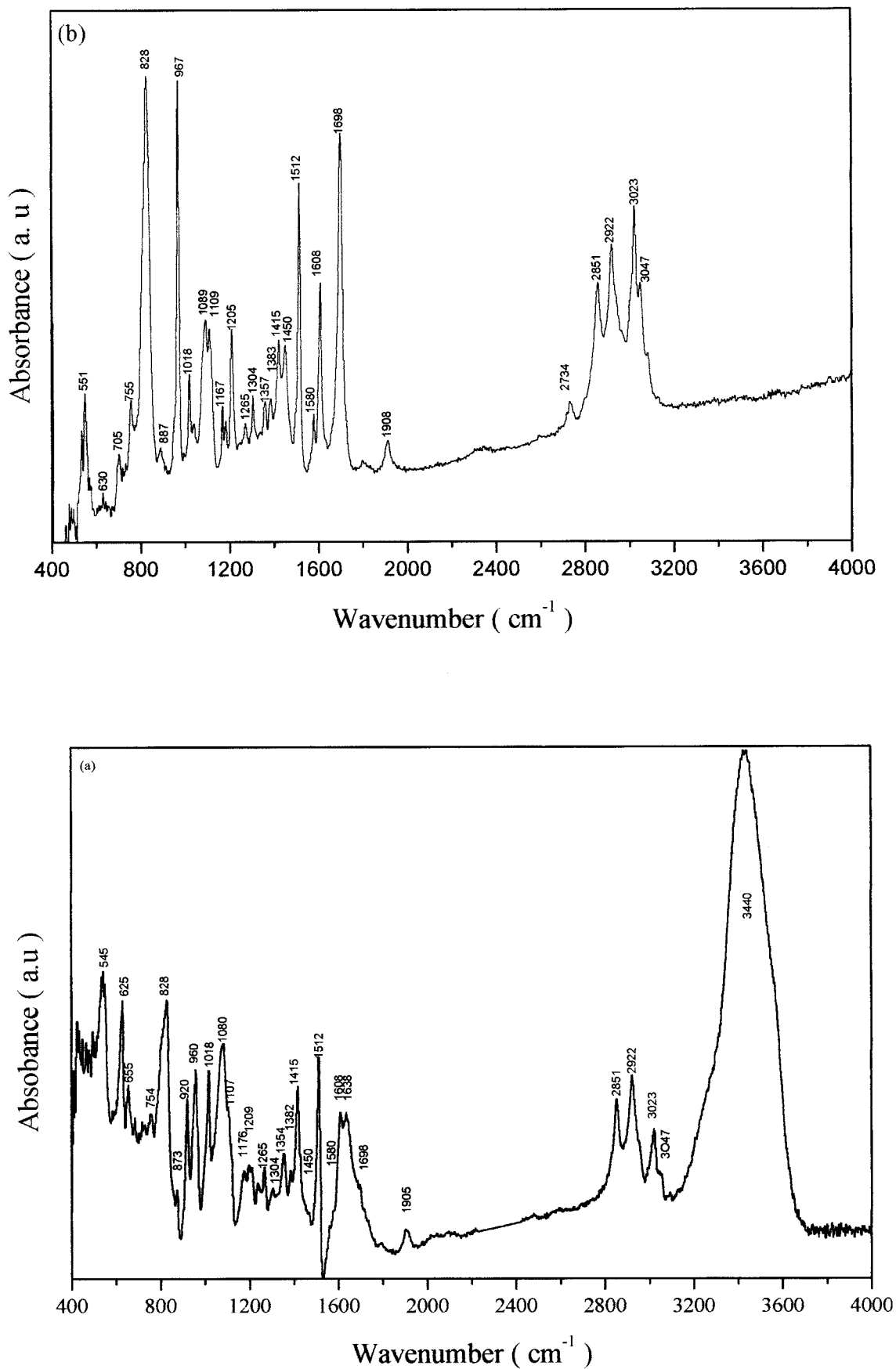


Figure 2 IR spectra of (a) PPV-ether powder and (b) vacuum-evaporated PPV-ether films.

TABLE III
FTIR Analyses: Characteristic Vibration Bands for PPV-Ether Powder and Vacuum-Evaporated PPV-Ether

Assignment	PPV-Ether Powder		Vacuum-Evaporated PPV-Ether	
	Frequency (cm ⁻¹)	Intensity	Frequency (cm ⁻¹)	Intensity
C—H phenylene out of plane	545, 828, 1018	s, s, m	551, 828, 1018	s, vs, w m, w,
<i>p</i> -Phenylene C—H in-plane bend	1107, 1176, 1265	m, w, w	1109, 1167, 1265	vw
C—C ring stretch	1354, 1415, 1450	m, s, vw	1357, 1415, 1450	w, vs, m
C=C ring stretch	1512, 1608, 1698	vs, s, m	1512, 1608, 1698	vs, s, vs
C—H aliphatic stretch	2851, 2922	m, m	2851, 2922	m, m
C=O stretch	920, 1638	s, s	—	—
Aromatic C—H stretch	960, 3023, 3047	s, m, vw	967, 3023, 3047	vs, s, m
CH ₂ —O—CH ₂ (ether)	1080, 1209	s, vw	1089, 1205	s, m
C—Cl and OH stretch (chain ends)	625, 3440	s, vs	630, —	vw, —
Origin unknown	—	—	2734	w

The assignments are according to the literature,^{21,22} s, strong; vs, very strong; w, weak; vw, very weak; m, medium.

analysis, could help us conclude that evaporated powder purity is better than the initial powder.

In parallel with these studies, the evolution of the solubility of the PPV-ether layers in different organic solvents has been studied. As said before, the PPV-ether powder is insoluble in common solvents while after vacuum evaporation, the evaporated PPV-ether is soluble in acetone. (One minute is needed to dissolve the evaporated PPV-ether having a thickness of

about 1.5 μm.) This confirms that the copolymer chains decrease during evaporation process.

According to the IR results it was evident that the peaks characterizing PPV as well as those of ether were present in the case of vacuum-deposited PPV-ether films. Furthermore, we could note from the XPS analysis the presence of the elements that make up PPV-ether (C, O, and Cl), so we could firstly conclude that PPV-ether did not decompose during vacuum evaporation. However, the chain length and the terminal groups (OCH₂φCH₂Cl) of the initial PPV-ether were affected by heat during the vacuum evaporation.

Morphology of vacuum-evaporated PPV-ether

The scanning electron micrographs were made for two types of vacuum-deposited PPV-ether, one having a thickness of less than 1500 Å (Fig. 3) and a second one with a thickness of more than 2000 Å (Fig. 4). It could

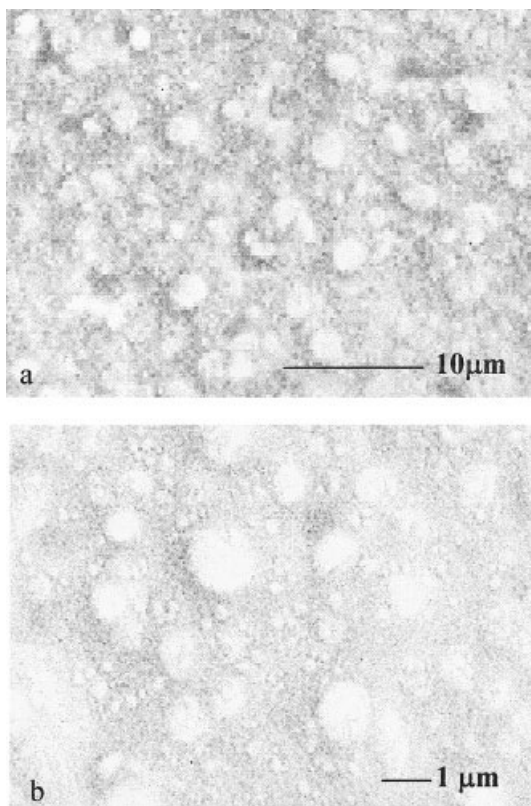


Figure 3 SEM micrographs of vacuum-evaporated PPV-ether films with a thickness of <1500 Å: (a) low magnification and (b) high magnification.



Figure 4 SEM micrographs of vacuum-evaporated PPV-ether films with a thickness of >2000 Å.

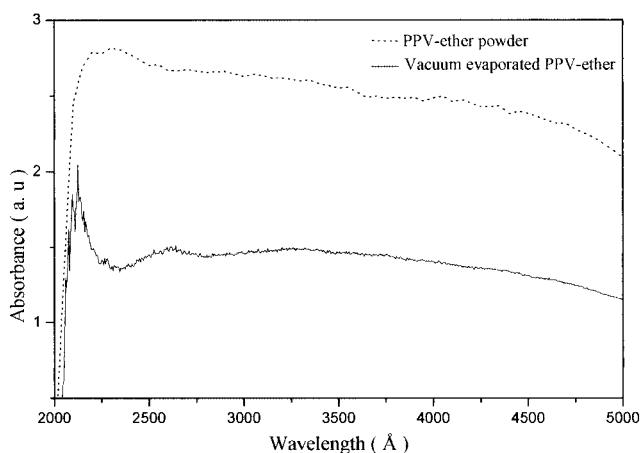


Figure 5 Optical density measurements of PPV-ether powder and vacuum-evaporated PPV-ether.

be seen that the substrate was covered with PPV-ether layer. Figures 3 and 4 show thin evaporated layers that grow regularly. We also noted two contrasting regions, which could be probably attributed to a discrimination between PPV and ether sequences or to the surface of the film not being flat but presenting hills and valleys as an orange skin. This contrast is more important in Figure 4 where the layer is thicker.

Optical properties of vacuum-evaporated PPV-ether

It can be seen from the results of OD, reported in Figure 5, that the absorption band for PPV-ether pow-

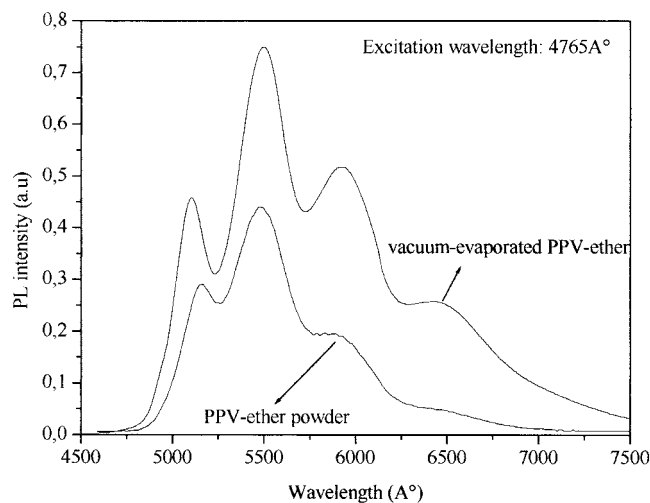


Figure 6 Photoluminescence measurements of PPV-ether powder and vacuum-evaporated PPV-ether.

der is larger than the vacuum-evaporated PPV-ether. Consequently the absorption edge in the case of evaporated PPV-ether (4493 Å, 2.76 eV) is slightly higher than PPV-ether powder (4900 Å, 2.51 eV), which is in agreement with the decrease of the band gap expected with the chain length increases.²⁴ It is clear from the PL analysis shown in Figure 6 that the shape of the samples' PL spectra (PPV-ether powder and vacuum-evaporated PPV-ether film) is similar. The PL results, shown in Figure 6, reveal the presence of at least three peaks in this domain varying from 4700 to 7500 Å and

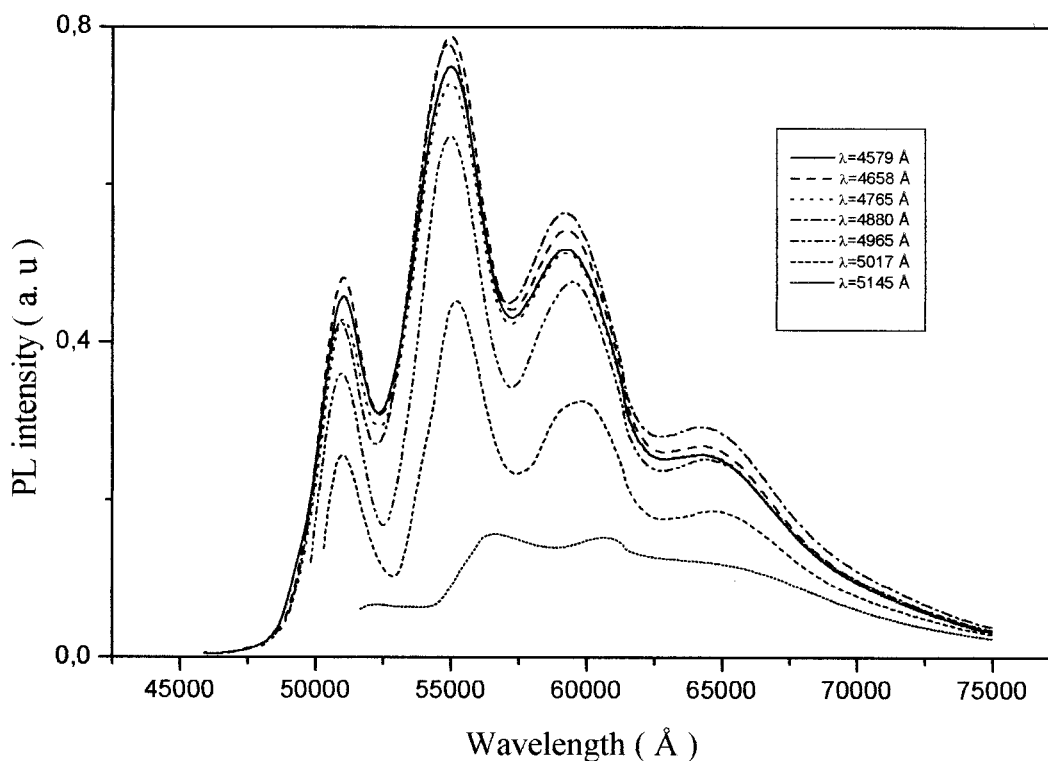


Figure 7 The variation of the photoluminescence under variable excitation energies in vacuum evaporated PPV-ether.

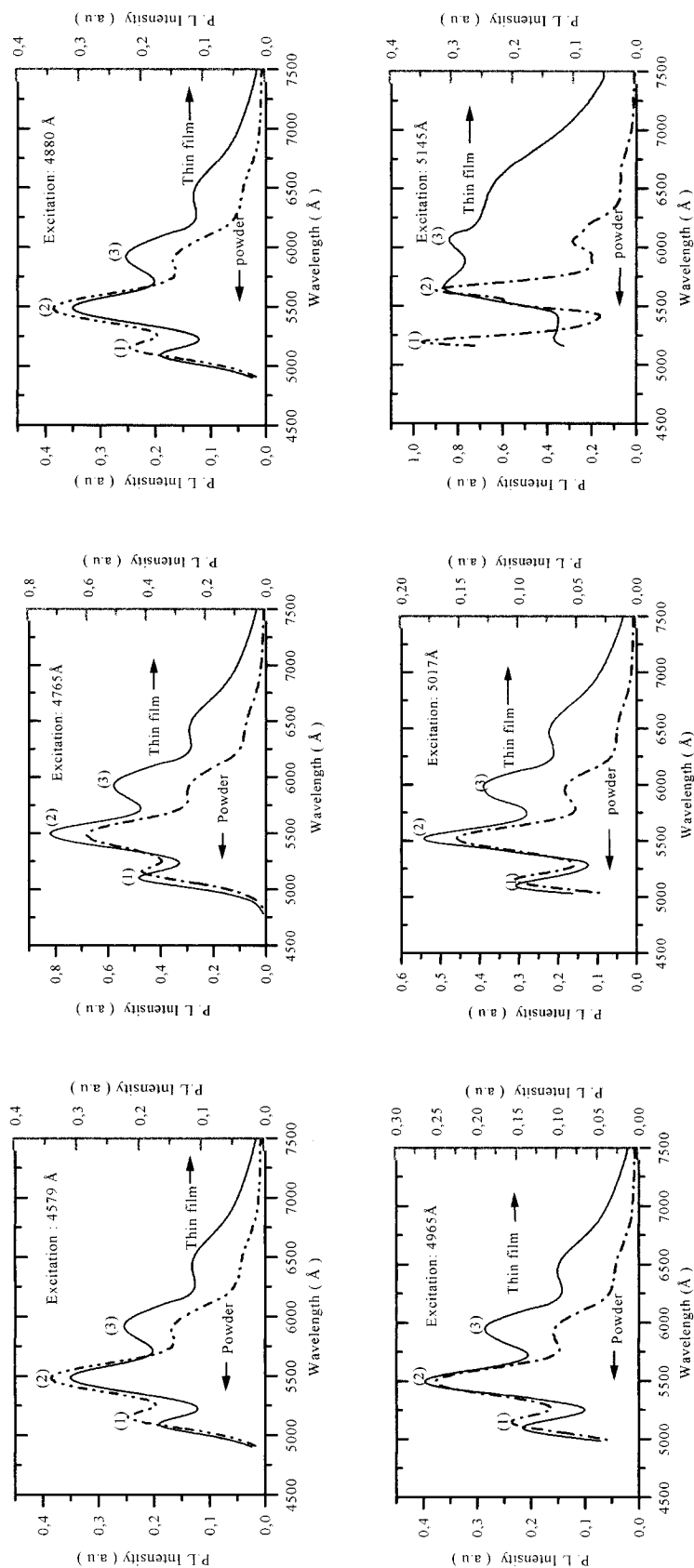


Figure 8 A comparison of the peaks positions versus the excitation between PPV-ether powder and vacuum-evaporated PPV-ether.

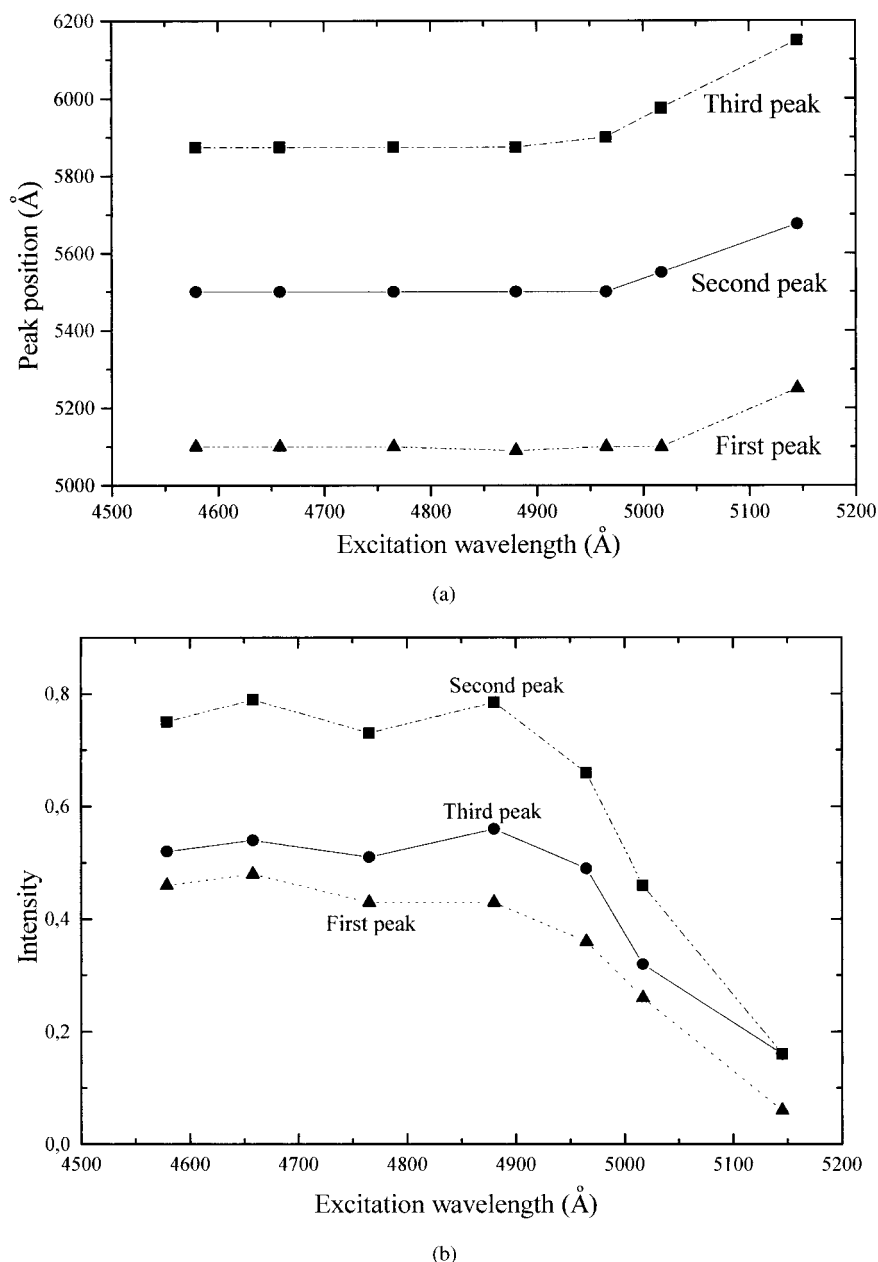


Figure 9 The variation of the (a) peak position and (b) intensity under variable excitation of vacuum-evaporated PPV-ether.

centered at 5200, 5550, and 5980 Å. The first two strong peaks are identified as zero S_0 and 1-phonon S_1 emission lines for 0–0 and 0–1 transitions. The third peak is the weak one, which is identified as a 2-phonon emission line. It is interesting to check directly the PL intensity and the peak positions under a variable excitation in order to have an idea about its spectrum of excitation. On the one hand, we noted the peak positions (Fig. 7) in the PL are still constant when the excitation energies vary from 4579 to 5145 Å. The same phenomenon was observed in the case of PPV-ether powder.¹⁶ On the other hand, by comparing the positions of the peaks in the PPV-ether powder and those of the vacuum-deposited PPV-ether (Fig. 8), we noted

a decrease in PL intensity then a shift of the luminescence toward the blue in the case of thin films which can be related to the decrease of the chain length during vacuum deposit. The same phenomenon was observed in the case of vacuum-deposited PVK thin films.¹⁹ According to the variation of intensity or peak position under a variable excitation, shown in Figure 9(a,b), these analysis suggest that the conjugated parts of thin films absorbed at 2644/3313 Å and emitted around 5072/5493 or 5930 Å. It is clear from the PL analysis that according to wavelength excitation we favor certain emission chains to emit more than others. Therefore, vacuum-deposited films are sometimes nearer to the blue emission and sometimes nearer to

the red one. This may be correlated to the number of PPV blocks in the vacuum-deposited PPV-ether.

Without a reliable microanalysis, it has been difficult to quantify the chain length of the powder or thin film copolymers. Through the XPS is a surface characterization technique, XPS quantitative analyses have been used to estimate the chain length. If terminal groups are taken into account and for an aleatory repetition, it is deduced that two PPV blocks correspond to one ether block in the case of thin films. If the same reasoning is considered to estimate the powder copolymer chain length, we do not obtain any PPV blocks, which is in contradiction with IR results. Indeed, the oxygen excess percentage observed in the powder, which is probably due to the water absorption, does not allow a correct estimation of the powder copolymer chain length. However, if the chlorine percentage obtained in thin layers is used instead of oxygen, then a PPV block will correspond to each ether block. Consequently the evaporated copolymer is more aromatic in character than the powder. This is in accordance with IR, the PL results and solubility tests.

CONCLUSION

Because the polymer we studied is mainly insoluble and unprocessable by a liquid precursor, it is impossible to use a spin coating method. The only useful method in the case of a pulverulent insoluble sample remains a thermal evaporation under ultravacuum assisted or not by an ablation laser or magnetic field. Generally, copolymers are insoluble because they usually result from a simultaneous copolymerization of two oligomeric precursor (small size polymers). As the PPV limited polymerization is also insoluble, it is known that we use an water-soluble PPVRSO₃ oligo-precursor to realize PPV or PPV derivatives. The purpose is not an exhaustive study of the physical properties of the evaporated layers, but the validation of the evaporation techniques in the case of the double polymers having aleatory repetition units of PPV and ether previously studied. The XPS result, the optical absorption and electronic scanning microscopy show that our technique of obtaining of PPV-ether thin films (thermal evaporation under vacuum) allows to realize a good quality films. However, the chain lengths decrease during deposit. On the other hand, the results of PL confirm the resemblance between the powder

and the evaporated layer and there is a shift toward the blue.

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