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Synthesis and characterization of copolymer derived from poly-phenylene-vinylene potentially luminescent copolymers

K. Alimi [a,f,*], P. Molinie [b], M. Majdoub [c], J.C. Bernede [d], J.L. Fave [e], H. Bouchriha [f], M. Ghedira [a]

[a] *Laboratoire des Matériaux, Faculté des sciences de Monastir, 5000 Monastir, Tunisia*
[b] *Institut des Matériaux Jean Rouxel, CNRS-UMR 6502, 2 rue de la houssinière, BP 32229, 44322 Nantes Cédex 3, France*
[c] *Laboratoire des Polymères et des Membranes, Faculté des Sciences de Monastir, 5000 Monastir, Tunisia*
[d] *Laboratoire de Physique des Solides pour l'Electronique, Faculté des Sciences de Nantes, 2 rue de la houssinière, 44072 Nantes Cédex 03, France*
[e] *Groupe de Physique des Solides, Université Paris 7 et 6, CNRS URA 17, tour 23, 2 Place Jussieu, 75251 Paris Cedex 05, France*
[f] *Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis, 1060 Tunis, Tunisia*

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Abstract

The objective of the present work, described in this paper, is to synthesize and characterize new conjugated materials with tunable properties, as well as to contribute to a better understanding of their structure and physical properties. This copolymer, derived from poly-phenylene-vinylene (PPV), denoted PPV–ether is amorphous and insoluble in common solvents. It was characterized by infrared absorption (IR), Raman scattering, optical density (OD), gravimetric thermal analysis (GTA), differential thermal analysis (DTA), X-ray photoelectron spectroscopy (XPS) and photoluminescence. After synthesis and purification the copolymer PPV–ether is obtained with oligomer (F3), a fraction of copolymer, which is soluble. The results of GTA and DTA show that this copolymer is very stable. The IR, Raman scattering, and XPS studies show the good purity of the materials and confirm the proposed structure. The OD and photoluminescence (PL) measurements show that this copolymer can be exploited in optoelectronic applications. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly-phenylene-vinylene; Copolymer; Thermally stable; Optoelectronic; Photoluminescent

1. Introduction

Today, the use of polymers as conductors and semiconductors is a well-developed area of research. The manufacture of electronic components such as diodes, light-emitting diodes (LEDs) or field effect transistors (FETs) based on polymer is a reasonable objective. The polymer used must show good conduction for FET and a good luminous output for LED applications and also a high stability.

Some new conjugated polymers can be used in the manufacturing of LEDs. Poly-phenylene-vinylene (PPV) was the first conjugated polymer where electroluminescence (EL) was observed [1–22]. Due to their good processability and high stability, PPV and its derivatives are still attractive candidates for future organic electroluminescent display applications. The results obtained with LEDs, using PPV as the emissive layer, have stimulated the synthesis of new copolymers based on derivatives of PPV [23–46]. The temperature of the glass transition, the solubility and the opto-electronics properties of the polymers or copolymers vary according to their method of synthesis and depend on the chain lengths. The oxygen contamination can be overcome by the choice of the synthesis method [47,48].

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[*] Corresponding author. Fax: +216-3-500-278.
E-mail address: kamel.alimi@fsm.rnu.tn (K. Alimi).

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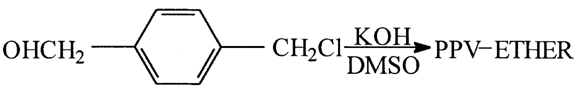


Scheme 1.

In the present paper, our study is focused on the properties of the soluble copolymer denoted "oligomer F3" and the insoluble copolymer "PPV–ether" (Schemes 1 and 2). The X-ray photoelectron spectroscopy (XPS) measurement combined with IR, Raman, GTA-DTA PL and OD studies give a description of the physical and optical properties for both organic compounds.

2. Experimental part

All chemicals and solvents used during the process were obtained from Aldrich, Merck and Fluka. Before being used, they must be purified by normal procedures. The resulting powders were characterized by XPS analysis. This was carried out at the University of Nantes-CNRS, with a Leybold LHS-12 spectrometer. The XPS data were obtained with a magnesium source radiation (1253.6 eV) operating at 10 kV and 10 mA with the energy window set at 50 eV. High resolution scans with a good signal to noise ratio were obtained in the C 1s, O 1s and Cl 2p regions of the spectrum. In order to decrease the charge effect, the powder was fixed to the substrate holder by pressing the copolymer powder onto a sheet of indium. The quantitative analyses were based on the determination of the C 1s, O 1s and Cl 2p peak areas with sensitivity factors of 0.2, 0.6 and 0.58, respectively. The sensitivity factors of the spectrometer were given by the manufacturer. The vacuum in the analysis chamber was around 10^{-6} Pa. All spectra were recorded under identical conditions. The decomposition of the XPS peaks into different components, and the quantitative interpretation, were made after subtraction of the background using the Shirley method [49]. The developed curve-fitting programs permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum (FWHM), and the position and the intensity of the contribution. These parameters were optimized by a curve fitting program in order to obtain the best fit.

Infrared spectra were obtained in a Brucker Vector 22 spectrophotometer. Band positions are expressed in wave number (cm^{-1}). The samples were pellets of KBr mixed with the organic compound under study. The optical measurements were carried out at room temperature using a Carry 2300 spectrophotometer. The optical density was measured at wavelengths from 0 to 3000 nm. The Raman spectra were recorded on a Fourier transform spectrometer Bruker RFS 100 with a 1064 nm-wavelength laser.

Dynamic thermogravimetric analyses were carried out in a Perkin–Elmer TGS-1 thermal balance with a Perkin–Elmer UV:1 temperature program control. Samples were placed in a platinum sample holder and the thermal degradation measurements were carried out at a temperature ranging from 20°C to 700°C at a rate of 5°C min^{-1} in air atmosphere.

Concerning the PL measurements, the powder is placed in a conical hole under a SiO_2 window in the cryostat at 10 K. The excitation of 1 mW is ensured by an argon laser.

3. Experimental results and discussion

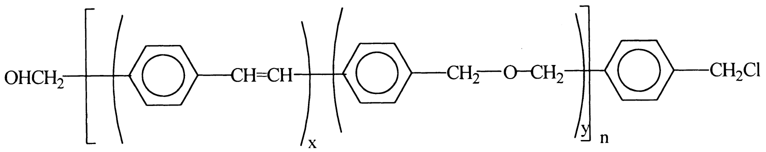
3.1. Synthesis and purification of the copolymer

This copolymer, PPV–ether, is a macromolecular material obtained by homopolycondensation of the 1-chloromethyl, 4-methoxylbenzene (Scheme 1).

The copolymer is obtained in the same way used elsewhere for poly-X synthesis [50] except that we have used here another base: KOH, as indicated in Scheme 1, then in the experimental protocol we have used microwaves for the activation of the reaction.

About 20 g of 1-chloromethyl,4-methoxylbenzene were dissolved in hot DMSO (100 ml) then an aqueous solution of KOH (12.5 M l^{-1}) was added by small quantities under quick agitation. A greenish yellow coloration appeared progressively. The mixture was then submitted to 600 W microwaves for a few minutes until a temperature of 470 K was reached. Then the mixture was left to regain the ambient temperature while the agitation was sustained for 6 h in order to obtain a homogeneous fine-granulated mixture.

Two litres of water were added under quick agitation to the resulting mixture. The precipitate obtained was



Scheme 2.

filtered and then washed with a diluted solution of hydrochloric acid. Next it was rinsed several times in boiling water. After filtration and high vacuum drying a raw polymer was obtained. Actually, this raw mixture was composed of three fractions which were dried under high vacuum until constant mass:

- A yellow fraction insoluble denoted "PPV–ether" in all common organic solvents, the yield of which was 43%.
- A white fraction soluble in $CHCl_3$ denoted "F2", the yield of which was 52%.
- A fraction yellow-green fraction denoted "oligomer F3" soluble in the CH_2Cl_2, the yield of which was 5%.

All the fractions were dried under high vacuum until constant mass, and built as PPV polymer with some links (–CH=CH–) changed in methylic-ether links ($–CH_2–O–CH_2$) (Scheme 2).

The structure of this copolymer is represented in Scheme 2.

The copolymer (PPV–ether) and the oligomer F3 have been characterized by GTA, DTA, XPS, IR-absorption, Raman scattering, OD and PL studies.

3.2. Thermal analysis

Thermal analysis was conducted on the PPV–ether and on oligomer F3. Results are presented in Fig. 1. A significant difference of thermal behavior between these two samples could be noticed. PPV–ether is more stable than oligomer F3 which degrades very quickly. The thermal degradation of oligomer F3 may be related to the presence of short chains. Hence it could be considered as an oligomer.

The result for PPV–ether, shown in Fig. 1, where the weight losses (in percent) and thermal analysis (microvolts) are reported versus the temperature of measurement. The GTA study shows for PPV–ether that there is a 10% decrease in weight at 530 K, followed by another 30% decrease at 620 K. We think that the weight losse observed at 530 K can correspond to the departure of HCl or the termination molecule ($OCH_2\varphi CH_2Cl$) of the copolymer. Between 580 and 620 K ruptures of the most fragile links, resulting in the departure of the methylic-ether and showing the beginning of the decomposition.

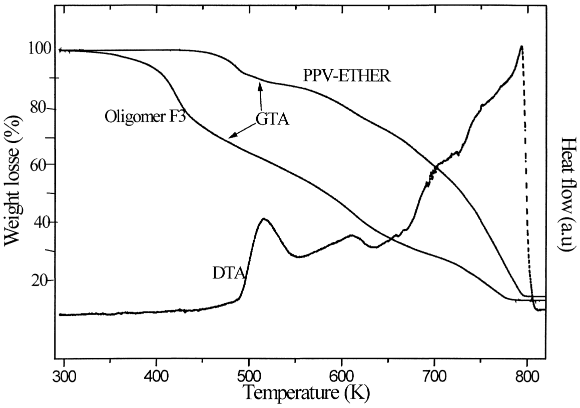


Fig. 1. Thermogram by GTA and DTA of PPV–ether and oligomer F3.

It can be seen from the DTA study that for both, PPV–ether and oligomer F3, no glass transition temperature is visible, therefore there is only an exothermic signal at about 490 K for PPV–ether which corresponds to a reaction of dehydrochlorination or terminal departure.

3.3. X-ray photoelectron spectroscopy analysis

We did some fine analysis in studying the windows of energies corresponding to the binding energy domains of the oxygen O 1s, carbon C 1s and chlorine Cl 2p. First of all, the quantitative analyses at the surface of the samples are reported in Table 1. The data on composition are presented as the ratio in percent of the element in question to the total amount of C, Cl and O. The quantitative analysis shows that the O 1s and Cl 2p peaks are similar for both compounds, while the carbon peaks are different. Indeed, one could notice a shoulder which appears at the highest energy side in the case of oligomer F3, probably a sign of links C–O–O–R present in the ends of chains, as shown below. It can be seen, in Table 1, that there is a strong excess of oxygen. It has already been seen that this surface excess is systematically present in this family of polymer [51].

Therefore for oligomer F3 sample, the O 1s peak is similar to the one obtained by PPV–ether. The same similarity is obtained with chlorine Cl 2p. In oligomer F3 sample, we observed that while the carbon peaks are particularly unchanged, the decomposition (Table 2) shows a new component located at 288.1 eV that will be discussed later. In order to compare the binding energy of the different components from one sample to another, the values reported in the XPS decomposition table (Table 2) have been estimated by using the energy of carbon–carbon bond as a reference, as it is often the case

Table 1

Quantitative analysis of different elements in PPV–ether and oligomer F3[a]

	C 1s	O 1s	Cl 2p
PPV–ether	86	11	2
Oligomer F3	89	10.3	0.7

[a] Relative concentration (at.%).

Table 2
XPS decomposition (the charge effect ΔE has been subtracted)[a]

	C 1s			O 1s			Cl 2p
	C–C	C–O–H	COOR	In_2O_3	C=O	C–O–H	Cl
PPV–ether	285	286.5	–	530	531.2	533	200.2
$\Delta E = 0.4$ eV	86.5	13.5		13.5	21.5	65	100
Oligomer F3	285	286.5	288.1	530.2	532.5	533.5	200.2
$\Delta E = 0.05$ eV	84.5	13	2.5	10	69	21	100

[a] First line: binding energy after correction of the charge effect (eV) and, second line: relative concentration (at.%).

in the literature [51], with 285 eV as carbon–carbon binding energy.

The results obtained by decomposition of the peaks are reported in Table 2, after subtraction of the charge effect. As said before the decomposition of the peak of carbon of PPV–ether is different from that of oligomer F3. However, those of the oxygen and chlorine are identical, but then, of course, we noted a little tracing off, less than 0.5 eV, of all peaks, which probabably means that the PPV–ether is more resistive than oligomer F3. It appears that the main carbon peak, present at 285 eV, corresponds to the carbon–carbon bonds, then there is another component at 286.5 eV which could correspond to some links C–O–H [51]. The decomposition of oxygen peaks shows three contributions, whose binding energies are 530, 531.2 and 533 eV. The components corresponding to the highest binding energies should be assigned to atoms of oxygen bound to carbon. The contribution situated at 533 eV is assigned to the atoms of oxygen forming a simple link C–O. It indicates the presence of alcohol function C–O–H. The component situated at 531.2 eV corresponds to the presence of oxygen bound to some double links with the carbon (C=O). The peak appearing at lower energy (530 eV) is assigned to the indium (In_2O_3) used as a support.

3.4. Infrared analysis

We systematically studied the granulated powder of PPV–ether mixed with KBr as well as that of oligomer F3. Fig. 2 shows the spectrum of PPV–ether and oligomer F3 for some wavenumbers between 400 and 3000 cm^{-1}. The main absorption peaks and their assignments are reported in Table 3. We find the end of PPV–ether as mentioned in Scheme 2 (OH and Cl). It could also be concluded that there is not a contamination by oxygen from the air since a peak situated at 1700 cm^{-1}, characteristic of carbonyl groups, is absent, whereas, the results of XPS, which is a surface analysis, show the opposite. So we think that the excess of oxygen at the surface justifies the presence of C=O. In the same way the assignment of the peak situated at 965 cm^{-1} is in agreement with the literature [52,53]. We note the presence of peaks characteristic of PPV as well as those of ether function, which confirms the synthesis of PPV–ether. The similarity of these two spectra confirms the validity of our preparation technique of PPV–ether.

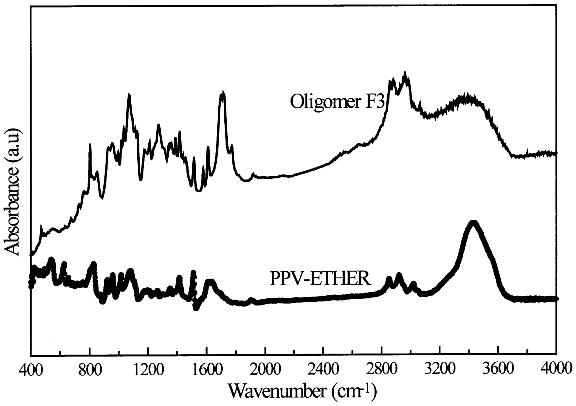


Fig. 2. IR spectra of PPV–ether and oligomer F3.

Table 3
Main lines, and their assignments, of IR spectrum of PPV–ether

Absorption band (cm^{-1})	Assignment
627 and 654	C–Cl chain ends
920	Trans-vinylene out of plane CH bending mode
1060	Torsion HCC terminal cycle in PPV
1364	Elongation of cycle
1512	Elongation of half of cycle
1609	Elongation of quadran cycle
2852	CH2
3021	CH3
3500	OH (chain ends)

3.5. Raman analysis

The Raman spectrum of PPV–ether as well as that of oligomer F3 is presented in Fig. 3. The comparison also shows the similarity of the two materials with supplementary peaks being less numerous than in infrared spectra. The main peaks are reassembled in Table 4. One

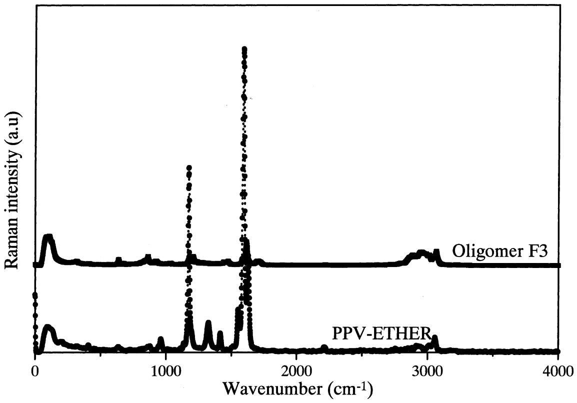


Fig. 3. Raman spectra of PPV–ether and oligomer F3.

Table 4
Main lines, and their assignments, of Raman spectrum of PPV–ether

Absorption band (cm^{-1})	Assignment
1624	Elongation of C=C trans vinyl
1583	Elongation of cycle symmetrical quadran
1514	Elongation of half symmetrical cycle
1414	Elongation of symmetrical hexant cycle
1326	Elongation of C=C trans vinyl
1170	Torsion of CH aromatic
960	Torsion of CH trans vinylen out of plane

could note in particular the presence of the intense peak at 1589 cm^{-1} which was very weak in infrared. This signals the presence of double links. Furthermore, one notices again the similarity between PPV–ether and oligomer F3. The main difference observed from the Raman result is the modification of the connections of intensity of the peaks at 1629 and 1550 cm^{-1} which could probably be related not only to the length of conjugation of the chain [54] but also to the change of molecule symmetry.

Once again we find most of the peaks expected from the PPV as well as those of ether, which confirms the synthesis of the copolymer. Firstly, working from the principle that our copolymer is ended at one side by some OH and at the other by some CCl, this is actually confirmed by the measurements of IR. Chain lengths and sequences of the copolymer were very difficult to estimate since no reliable quantitative chemical analysis was available.

3.6. Optical density measurements

The results of the measurements of optical density are reported in Fig. 4(a) concerning PPV–ether and Fig. 4(b) concerning oligomer F3. It can be seen that the absorption band for PPV–ether is larger than oligomer F3. It could be noted that the absorption edge in the case of oligomer F3 (2.76 eV), which is progressive, is slightly higher than PPV–ether (2.51 eV), which is in agreement with the decrease of the band gap expected with the chain length increases [55]. The spectra of optical density of oligomer F3 show an absorption at 320 nm probably due to the π–π^* transition.

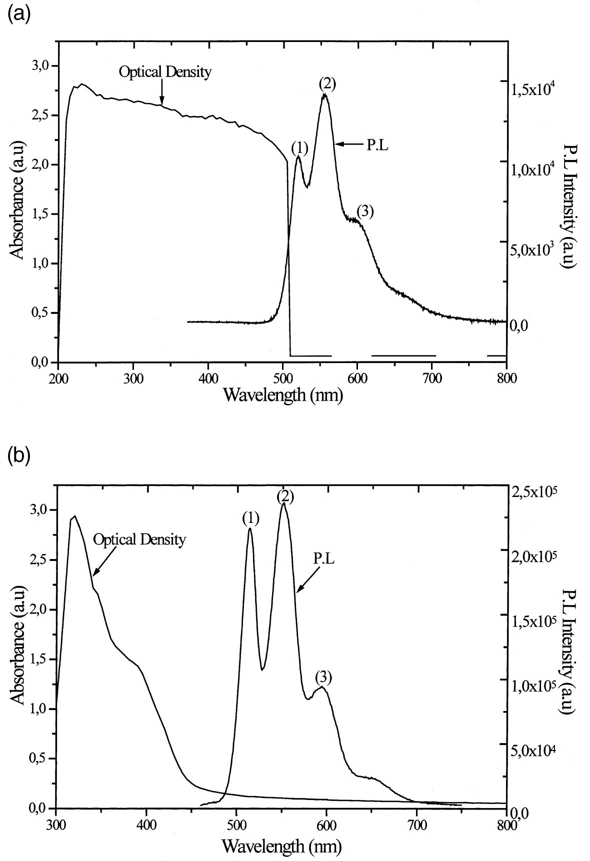


Fig. 4. Optical density and photoluminescence measurements of (a) PPV–ether and (b) oligomer F3.

3.7. Photoluminescence analysis

The PL spectra at 10 K of PPV–ether and oligomer F3 can be seen in Fig. 4(a) and (b), respectively. Both PL spectra are similar to those shown by Woo et al. [56]. The response of PPV–ether and oligomer F3 to a luminous excitation results in photoluminescence of wavelength ranging from 475 to 700 nm. The spectrum shows the presence of, at least, three peaks in this domain centered at 520, 555 and 598 nm. The differences between the PPV–ether and the oligomer F3 are essentially a variation of intensity, without significant modification of the wavelength and shape of the peaks. It can clearly

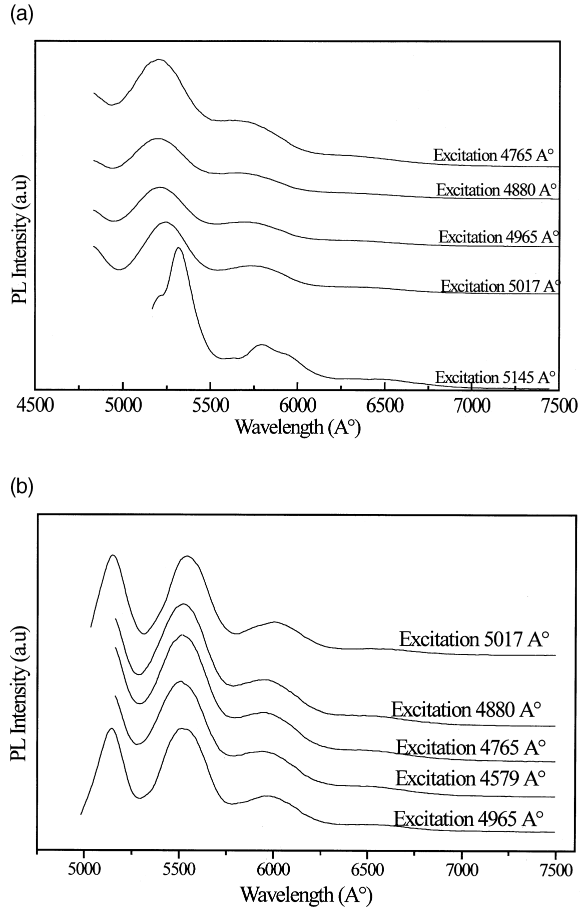


Fig. 5. Variation of photoluminescence under a variable excitation energies in (a) PPV–ether and (b) oligomer F3.

be seen that the shape of PL spectra (Fig. 4(a) and (b)) of both PPV–ether and oligomer F3 is identical. But the peaks in the case of oligomer F3 are considerably more intense, probably due to the length of chain. The first two strong peaks (1 or 2) are identified as zero S_0 and one phonon S_1 emission lines for 0–0 and 0–1 transitions and the weak feature (3) as a two phonons emission line. Another important factor for understanding the optical behavior of the copolymer is the dependence peak position under variable excitation energies (2.4, 2.6 eV). In our case of PPV–ether and oligomer F3 the position lines in the photoluminescence spectra (Fig. 5(a) and (b)) are regardless of the excitation energies performed.

4. Conclusion

The synthesis of sequenced or transplanted copolymers including some conjugated and no substituted sequences, with very definite lengths, remains a difficult problem. Our work was essentially focused on the synthesis and the survey of the properties of a copolymer derived from PPV. To compare, we also conducted in parallel a study on a fraction, oligomer F3, of this copolymer, which is soluble. The properties of the copolymer PPV–ether and the oligomer F3 are similar with the exception of the thermal behavior, which corresponds to the different chain lengths of both copolymers. The characterization by IR, Raman scattering, and XPS confirmed the purity of the materials and the advanced structures. In the same way, PPV–ether and oligomer F3 present some optic properties which could be exploited in the realization of electronic organic components. In this context, the study of electrical and optoelectronic performances of PPV–ether is in progress.

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