

# Optical properties of nanosize aggregation of phenylene vinylene oligomers

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## Abstract

In this paper, we report the experimental results on the optical properties of oligo-phenylene vinylenes (OPVs) formed in nanosize pores of porous silicon substrates. Strong modifications of the photoluminescence properties of nanosize aggregation of OPVs were observed at room temperature, such as a blue shift of the PL spectra, whereas the structure of the oligomers is preserved as proved by Raman scattering experiments. However, the penetration of the oligomers into the nanopores was found to depend on the conformation of the chains, which is, in turn, conditioned by the solvents, used to dissolve the oligomer powder.

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## 1. Introduction

Recently, nanosize aggregation of polymer chains has attracted attention of researchers because of their peculiar and interesting properties, compared to those of bulk materials. These properties enable particular and potential applications in electronic nanodevice field. To obtain such materials, several techniques can be used [1]. One of these techniques consists in filling a template with a polymer solution, the template being made with inorganic oxides, such as aluminium or silicon oxide [2–5]. However, the difficulty to introduce the polymer solution into template pores lead to discrepancies in data and in interpretation of the physical processes. The penetration of the polymer solutions into the nanopores depends on several factors. Among them, the nature of the solvent used to dissolve the polymer powder [6,7] and the nature of the polymer itself [8] have been found to play an important role in the impregnation

process. In most of the previous studies, a particular material was used with several types of solvents, polar or non-polar and the penetration of the solution into the template pores was checked by optical characterization of the composite material.

In thick polymer films, the chains are stuck together resulting in a mutual energy transfer and the photoluminescence (PL) spectra exhibit a red shift as compared to those obtained in solution, where the polymer chains are separated and free to move. Inside a nanopore, when chains are entirely introduced into it, they behave as if they were independent and consequently, the corresponding PL spectra exhibit a blue shift as compared to those recorded in films. However, if the chains do not entirely penetrate the pores, the shift is expected to be small or negligible. Usually, the nature of the solvents is an important factor for the penetration of the polymer chains into the pores, i.e. their conformation depends greatly on the solvent used [9]. When a “poor” solvent is used, chains tend to coil and are not able to enter entirely the pores. Furthermore, the chain length of the polymer plays an important role in the penetration of the

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chains into the pores, and to our knowledge, this aspect has never been considered in previous investigations.

In this work, we have investigated optical properties of soluble oligo-phenylene vinylenes (OPV) formed in nanosize pores of porous silicon substrates. The oligomers possess high third-order non-linear optical (NLO) coefficients and are interesting for waveguide structure applications [10]. The influence of the solvents used to dissolve the oligomers and that of the oligomer chain length on the optical characteristics of the materials have been studied and discussed.

## 2. Experimental

The structure of the OPV is given in Fig. 1. Two different chain lengths were used ( $n=3$  and 5, the corresponding oligomers being labelled as OPV3 and OPV5, respectively). The synthesis and control of the chain length of the oligomers were reported in a previous paper [10]. Solutions of oligomers were obtained by dissolving the powder in two different solvents: chloroform and xylene, using an identical concentration for both solvents (5 mg/ml). Porous silicon substrates were fabricated by a standard anodization technique, using p-type(1 0 0) orientated silicon substrates and a HF:H<sub>2</sub>O:ethanol mixture electrolyte. The average pore size was 50 nm as determined by scanning electron microscopy (SEM) and the porous layer thickness was about 5  $\mu\text{m}$ . Substrates were immersed in the oligomer solution for 24 h, then taken out and dried in nitrogen. Approximately, one-third of the surface of the sample was then washed with the used solvent to obtain two distinct areas of the porous layer, denoted as A (washed part) and B (unwashed part) (Fig. 2). The unwashed part of the silicon wafer on which is formed the polymer film is denoted as part C. On area A, only oligomers located in the pores are present, while on area B, oligomers are found inside the pores and on the surface of the porous silicon layer. In order to analyze the oligomers inside the pores, the substrates were further cut to present a cross-section (CS) on which measurements were carried out.

Optical characterizations of the samples were performed on a BRUKER RFS 100 spectrophotometer in the range of 100–3500  $\text{cm}^{-1}$  for Raman experiments and on a Fluorolog HORIBA spectrophotometer for PL measurements. Micro-Raman inspection of the cross-section of the porous layer was carried on a T64000 Jobin Yvon spectrometer, coupled to

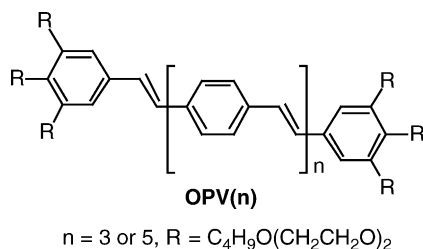


Fig. 1. Structure of OPV oligomers.

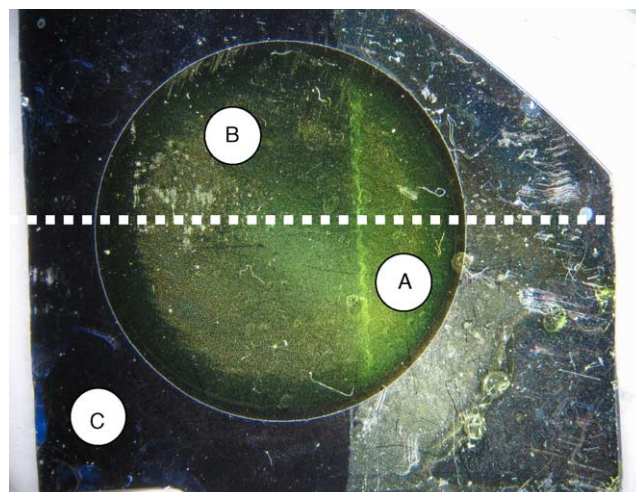


Fig. 2. A composite sample: (A) OPV on porous silicon, washed part; (B) OPV on porous silicon, unwashed part; (C) OPV on silicon, unwashed part.

an Olympus BH2 microscope and using a 514 nm excitation wavelength issued from an Ar<sup>+</sup> laser. With an appropriate magnification, the Raman spectra of regions separated by 1  $\mu\text{m}$  could be recorded. All experiments were performed in air and at room temperature.

## 3. Results and discussion

### 3.1. Optical properties of OPV films

Fig. 3 shows Raman spectra recorded on OPV3 and OPV5 thin films, which were prepared by using chloroform as solvent and deposited on glass substrates. In the 800–2000  $\text{cm}^{-1}$  range, three characteristic vibrational bands are observed at 1175, 1330 and 1590  $\text{cm}^{-1}$ . These bands are similar to those obtained in PPV thin films. The two first bands can be assigned to internal aromatic cycles [11,12], while the third one consists of a triplet with peaks centered at 1550  $\text{cm}^{-1}$  (band 1), 1590  $\text{cm}^{-1}$  (band 2) and 1630  $\text{cm}^{-1}$  (band 3). According to previous results obtained for PPV

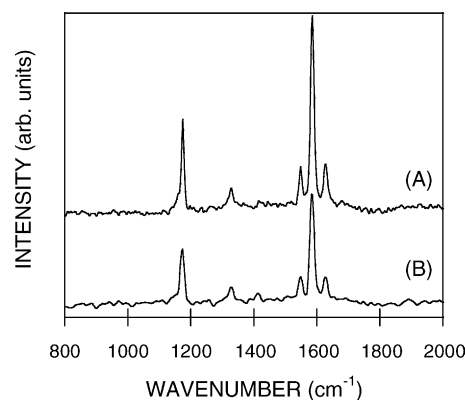


Fig. 3. Raman spectra of: (A) OPV3 film and (B) OPV5 film.

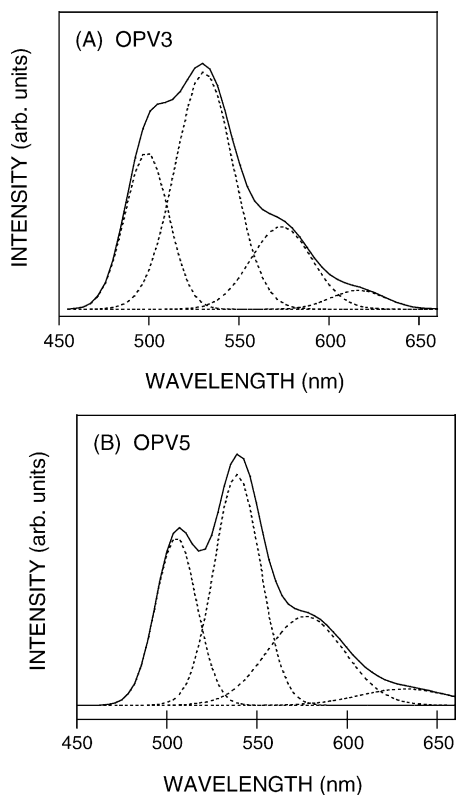


Fig. 4. Resolved PL spectrum of: (A) OPV3 film deposited on a glass substrate and (B) OPV5 film deposited on a glass substrate.

and its oligomers, the two first bands are attributed to the phenyl group (stretching of C–C) and the last to the vinyl one (stretching of C=C). On the other hand, the intensity ratio  $R$  (band 1/band 3) increases when the chain length increases. From the spectra, we have evaluated these ratios for both oligomer films, which appear in good agreement with their structure ( $\sim 0.9$  for OPV3 and  $\sim 1.0$  for OPV5).

Figs. 4 and 5 show PL spectra of the two films and their components. The spectral resolution was performed using a Gaussian–Lorentian combination. In both types of oligomer films, four components are determined. Their peak maxima are located at 490, 520, 555 and 605 nm for OPV3 film and 505, 540, 578 and 635 nm for OPV5 film. The red shift of the OPV5 spectrum with regard to the OPV3 one is in agreement with previous results obtained in similar PPV oligomers [11] as well as in intensity ratio [13] and can be assigned to the conjugation length effect.

Optical spectra of the oligomer films, prepared using xylene as a solvent, are similar to those prepared with chloroform. This result suggests that the nature of the solvent does not affect the structure of the oligomer films and their optical properties. The memory effect described in Ref. [6] in poly(2-methoxy-5-(2'-ethyl-hexyloxy)-phenylene vinylene) (MEH-PPV) thin films is not observed in the oligomer films studied here.

We note that Raman and PL spectra of the oligomer film formed on part C of the silicon wafer are almost identical to

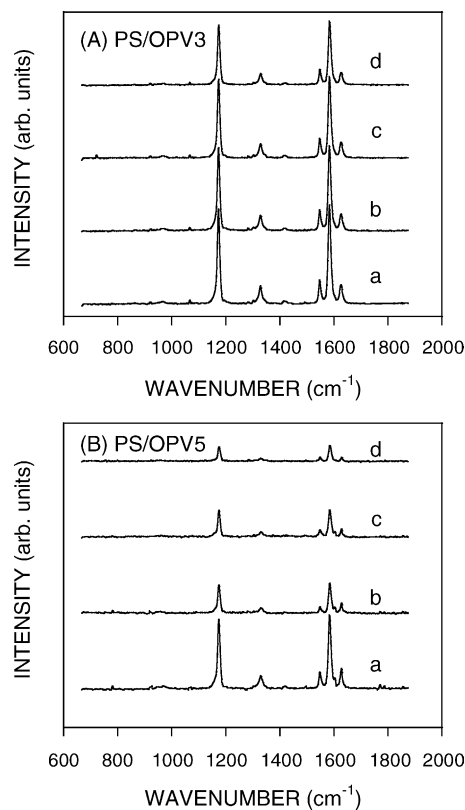


Fig. 5. Raman spectra recorded in the cross-section of: (A) a porous silicon/OPV3 composite and (B) a porous silicon/OPV5 composite.

those described above, indicating that the optical characteristics of the oligomer are independent of the nature of the substrates it was deposited on.

### 3.2. Optical properties of OPV films in porous silicon nanopores

#### 3.2.1. Influence of the conjugation length

The two oligomer solutions, OPV3 and OPV5, prepared with chloroform as solvent were used in this experiment. Spectroscopic analyses were performed on different parts of the silicon wafer (A–C and CS) as described in Section 2.

Raman spectra on the cross-section of the porous silicon layer were recorded by focusing the laser beam on different locations of the layer. In this manner, the spectra evolution along the thickness of the porous layer gives information on the structure of the oligomers inside the pores as well as their penetration level.

For both oligomers, Raman spectra recorded on the washed and unwashed surface or on the cross-section do not show significant change in the shape and position of the vibrational bands, indicating that the structure of the nano-size aggregation film is similar to that of the bulk one and the formation inside the silicon pores does not affect the structural backbone of the material. On the contrary, the intensity variation of the recorded spectra is different depending on the oligomer chain length. Fig. 5 shows the evolution of the

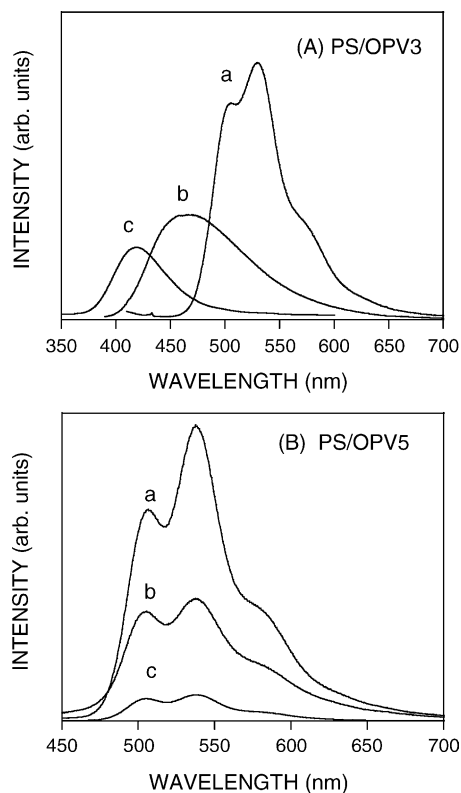


Fig. 6. Photoluminescence spectra recorded in: (A) a porous silicon/OPV3 composite and (B) a porous silicon/OPV5 composite. Curves (a–c) correspond to: (a) OPV on silicon, unwashed part; (b) OPV on porous silicon, washed part; (c) OPV on porous silicon, in the cross-section. The oligomer was dissolved in chloroform.

Raman spectra in the porous layer for the two oligomers. We note that the intensity of OPV3 is fairly constant in the porous layer, indicating a rather uniform distribution of the oligomer. For OPV5, the Raman intensity decreases from the top of the layer and vanishes significantly inside the silicon wafer. This observation suggests that the OPV5 oligomer does not completely penetrate the porous layer.

Fig. 6 shows the PL spectra of OPV3 and OPV5 recorded on the surface and on the cross-section of the porous silicon layer. The corresponding PL spectra of the oligomer films are also shown for comparison. The porous silicon layer exhibits negligible PL activity at room temperature compared to those of the oligomers. Compared to the OPV3 film, the spectrum of the oligomer recorded on the surface of the substrate is blue shifted of 67 nm. The shift was evaluated by measuring the difference peak maxima between the components of the resolved spectra. The corresponding shift is much higher in the spectrum recorded on the cross-section of the sample and reaches 111 nm. Shift in wavelength of PL spectra was observed in several nanosize aggregations of polymers and was assigned to the confinement of the materials [14]. In the case of OPV3, the behavior of the film was different when examined on the surface or in the cross-section of the sample. In the cross-section measurement, the PL spectrum originates from the emission of the oligomer inside the porous layer. In

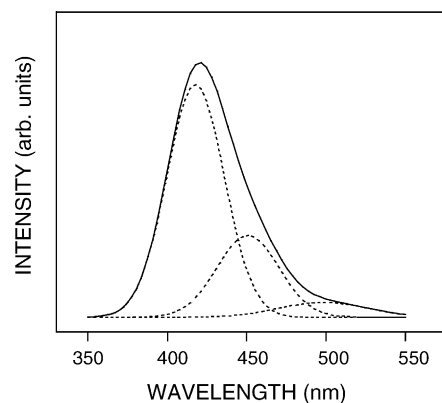


Fig. 7. Photoluminescence spectra recorded in the cross-section of a porous silicon/OPV3 composite. The oligomer was dissolved in chloroform.

the case of the surface measurement, the PL contribution can come both from the oligomers inside the pores and those formed on the surface of the porous substrate. This supposes that a number of the oligomer chains are coiled and have not penetrated into the pores. The chain conformation can be described as a “drawing pin” [15] which has most of its units adsorbed at the outer surface of the pores and some on the inner surface.

The deconvoluted PL spectrum of OPV3 in the sample cross-section (Fig. 7) shows three components with peak maxima located at 418, 450 and 511 nm, the high energy peak being not retrieved in the spectrum. Compared to the film, the component at 418 nm is dominant, presumably suggesting that the cross-section emission for this transition is enhanced in such a confined environment of the oligomer. This result is in agreement with those previously obtained in different polymer-based nanocomposites [3].

In the case of OPV5, we note that PL spectra are practically unchanged in position when recorded on the surface of the sample or on its cross-section, as compared to the spectrum of the film. On the other hand, there is no noticeable difference between the relative intensity of the components in the resolved spectra. This observation suggests that the polymer does not penetrate the porous silicon layer, in agreement with results obtained by Raman spectroscopy.

Comparing the results obtained for the two oligomers that were both prepared by using chloroform as a solvent, we note that the shorter conjugation length material has a more adapted conformation for penetrating the nanosize pores. Their formation inside the porous silicon results in a blue shift of the PL spectrum.

### 3.2.2. Influence of the nature of the solvent

In order to examine the influence of the solvent on the conformation of the oligomer chains, we performed similar measurements as previously described by replacing chloroform by xylene. Raman and PL spectra were recorded on the surface and the cross-section of porous silicon substrates filled with OPV3 and OPV5.

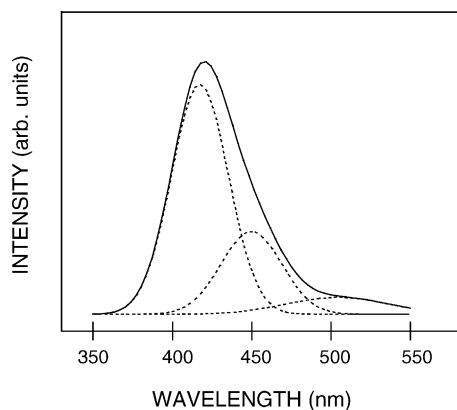


Fig. 8. Photoluminescence spectra recorded in the cross-section of a porous silicon/OPV5 composite. The oligomer was dissolved in xylene.

As in the case of chloroform, Raman spectra for both oligomers deposited on the porous layer have features similar to those observed in films, indicating that their structure does not change after deposition on the silicon substrates. Here, Raman spectra recorded along the porous layer shows fairly constant intensity and suggest that oligomers are uniformly distributed in the silicon thickness. The PL results show in Fig. 8 that OPV5 is formed inside the pores and a blue shift of the spectrum is obtained when dissolving the oligomer in xylene. This penetration was not obtained for the same oligomer when using chloroform as a solvent. Therefore, xylene seems to better dissolve the long-chain oligomer (OPV5) than chloroform, i.e. in this case, the viscosity of the oligomer solution is higher with xylene, possibly because of the presence of benzene rings in both the solvent and the oligomer. For short-chain oligomer (OPV3), the difference is not significant because the penetration results are similar for both solvents.

PL spectra of OPV3 and OPV5 recorded on the cross-section of the sample are almost identical. The resolved spectra of both oligomers are similar to that previously obtained for OPV3 dissolved in chloroform. This result may suggest that the conformation of the oligomer chains inside the pores is independent of the initial conjugation length and the effective conjugation length of both oligomers inside the pores is identical. In other words, the silicon pores can be thought as acting as a filter and prevent the aggregation of OPV5 oligomers, allowing only short segments to penetrate into the porous layer [16]. If it is the case, then modifications of Raman spectra ( $R$  ratio) should be observed in the cross-section measurements. However, the values of  $R$  for the oligomers are very close and do not clearly confirm the filtering of the aggregates in OPV5. Alternative explanation for the similarity of OPV3 and OPV5 PL spectra in the porous silicon can be the conformational disorder of the oligomers resulting from the use of the solvents, as suggested by theoretical calculations on PPV oligomers [17]. In fact, planar and non-planar structures can be both present in oligomers and the used solvents can create a disorder between these

structures, which leads to a shortening of the conjugation length. Such a formation can be favored when oligomers are deposited in the silicon pores by the interactions between the oligomer chains and the silicon, as suggested in the case of porous alumina/MEH-PPV systems [3]. In fact, the surface of porous silicon was found to be oxidized in air and probably contains Lewis acid groups, which can undergo interactions with the oligomers [18]. Although the structure of the contact is not known, we may suppose that the interfaces between the silicon wall and the oligomers are similar, leading to identical conformation disorder of the chains and, consequently identical PL spectra. However, we believe that further studies using different conjugation lengths are needed to fully understand the changes observed in PL spectra of the porous silicon-oligomer systems.

#### 4. Conclusion

The formation of nanosize aggregation of oligo-phenylene vinylenes inside porous silicon layers has been investigated through several properties, such as solvent nature and chain length. The penetration of the oligomers into the silicon pores is found to depend on these properties. For the process used, short-chain-length oligomers are formed inside the porous layer independently of the nature of the solvent. Introduction of long-chain-length polymer into the nanopores was made possible by using appropriate solvent, which is believed to increase the viscosity of the oligomer solution. However, no clear conclusion can be drawn from this study on the exact role of the solvent on the penetration of the solution into the porous layer. The optical properties of the oligomers were strongly modified in nanosize aggregation form with a large blue shift of the photoluminescence spectra as compared to those recorded in thick films. The structures of the oligomers are, however, preserved as already observed in several polymer-based composite systems.

#### References

- [1] L.L. Beecroft, C.K. Ober, *Chem. Mater.* 9 (1997) 1302.
- [2] T.Q. Nguyen, J. Wu, V. Doan, B.J. Schwartz, S.H. Tolbert, *Science* 288 (2000) 652.
- [3] D. Qi, K. Kwong, K. Rademacher, M.O. Wolf, J.F. Young, *Nanoleters* 3 (2003) 1265.
- [4] Y. Zhao, D. Yang, C. Zhou, Q. Yang, D. Que, *J. Lumin.* 105 (2003) 57.
- [5] R.P. Jia, Y. Shen, H.Q. Luo, X.G. Chen, Z.D. Hu, D.S. Xue, *Solid State Commun.* 130 (2004) 367.
- [6] T.Q. Nguyen, V. Doan, B.J. Schwartz, *J. Chem. Phys.* 110 (1999) 4068.
- [7] T. Huser, M. Yan, L.J. Rothberg, *Proc. Natl. Acad. Sci. U.S.A.* 97 (2000) 11187.
- [8] H. Xi, B. Wang, Y. Zhang, X. Qian, J. Yin, Z. Zhu, *J. Phys. Chem. Solids* 64 (2003) 2451.
- [9] H. Zhang, X. Lu, Y. Li, X. Ai, X. Zhang, G. Yang, *J. Photochem. Photobiol. A Chem.* 147 (2002) 15.

- [10] M.S. Wong, Z.H. Li, M.F. Shek, M. Samoc, A. Samoc, B. Luther-Davies, *Chem. Mater.* 14 (2002) 2999.
- [11] T.P. Nguyen, V.H. Tran, P. Destruel, D. Oelkrüg, *Synth. Met.* 101 (1999) 633.
- [12] I. Orion, J.P. Buisson, S. Lefrant, *Phys. Rev. B* 57 (1998) 7050.
- [13] E. Mulazzi, A. Ripamonti, J. Wery, B. Dulieu, S. Lefrant, *Phys. Rev. B* 60 (1999) 16519.
- [14] J. Wu, A.F. Gross, S.H. Tolbert, *J. Phys. Chem. B* 109 (1999) 2374.
- [15] G.F. Hermesen, N.F.A. van der Vegt, M. Wessling, *Soft Mater.* 1 (2003) 295.
- [16] C.E. Halkyard, M.E. Rampey, L. Kloppenburg, S.L. Studer-Martinez, U.H.F. Bunz, *Macromolecules* 31 (1998) 8655.
- [17] J.B. Lagowski, *J. Mol. Struct. (Theochem.)* 589–590 (2002) 369.
- [18] S.H. Yang, T.P. Nguyen, P. Le Rendu, C.H. Hsu, *Thin Solid Films*, 471 (2005) 230.