

UV–visible and infrared characterization of poly(*p*-xylylene) films for waveguide applications and OLED encapsulation

Y.S. Jeong^a, B. Ratier^{a,*}, A. Moliton^a, L. Guyard^b

^aFaculté des Sciences, UMOP, University of Limoges, 123 Av Albert Thomas, 87060 Limoges, France

^bLaboratoire de Chimie et d'Electrochimie Moléculaire, University of Franche Comté, Route de Gray, La Bouloie, 25030 Besançon, France

Abstract

UV–visible and infrared transmission of three sorts of poly(*p*-xylylene) films obtained by vapor-deposition polymerization have been studied in order to appraise their opportunity in two optical applications: waveguide achievement by reactive ion beam etching (RIBE) and organic light emitting diode (OLED) encapsulation. Optical changes induced by etching or thermal annealing (needed for the former application) are reported. While the high visible or near infrared transmission (~95%) of the films is suitable for OLED encapsulation, the crystalline nature of these materials revealed by annealing could be a handicap for waveguide application. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Poly(*p*-xylylene); Infrared spectroscopy; UV–visible spectroscopy

1. Introduction

Vapor-deposition polymerization (VDP) is an attractive way to achieve polymer coating for integrated optics or device encapsulation, since it presents two major advantages compared with the classical processes: first, unlike wet processes (dipping, spin coating), it is a solvent-less method suitable for multilayer organic devices; second, unlike PVD or CVD, the formed films often show high molecular weight (and thereby good mechanical properties) and good transparency [1]. Two main roads are used depending on the number of evaporated monomers: when two reacting monomers are involved (polyimide coevaporation [2]), polymerization occurs immediately during condensation; when only a single kind of monomer is evaporated, pyrolysis is needed to induce reactivity before condensation. This latter process is used for the VDP of the poly(*p*-xylylene) (PPX) [3,4]. In a previous study [5], we have emphasized the film growth control by the substrate temperature (explained elsewhere by the condensation properties of the process [6]) of unsubstituted PPX and phenyl ring chlorinated PPX (parylene-*n* and -*c* respectively) and we have shown that these films can be etched by reactive ion beam etching (RIBE) with oxygen in order to achieve ribbon waveguides, provided oxygen ion beam parameters (mainly deposited energy) remain low to

prevent film delamination. The use of adhesion promoters allowed us to limit this sample delamination and to enhance etching rates of the films. These new results will be summarized in this paper.

Otherwise PPX films present good barrier properties to moisture and oxygen [7] and could be convenient for OLED encapsulation, since these latter devices are well known to have an enhanced lifetime when encapsulated [8]. Moreover, parylene encapsulation is suitable for flexible display technology and prevents, as a low temperature process, any impurity diffusion in the OLED device from the metallic contact electrodes to the emitting layer. Since a good film transparency is required for both waveguide application and OLED encapsulation, optical properties (UV–visible and infrared absorption) of deposited or RIBE-etched parylene films will be discussed here.

2. Experimental

Monomers used to produce parylene-*n* and chloride phenyl ring substituted PPX (parylene-*c*) are [2,2]-paracyclophane from Acros and dichloro-di-*p*-xylylene from Comelec, respectively. The two monomers were stirred with cold petroleum ether for 1 h. The insoluble solids was filtered and several recrystallizations of these solids in hot petroleum ether led to the pure monomers. PPX with bromine-substituted phenyl rings (PPX-Br) was obtained from dibromo-di-*p*-xylylene. This monomer was synthe-

* Corresponding author. Tel.: +33-555-45-74-32;

fax: +33-555-45-72-88.

E-mail address: ratier@unilim.fr (B. Ratier).

sized following this method: [2,2]-paracyclophane (19 mmol) was stirred with 20 ml of methylene chloride under N_2 atmosphere. Bromine (38 mmol) was added in several portions. The colored solution was stirred for 72 h at room temperature and then hydrolyzed. The aqueous layer was extracted with methylene chloride. The combined organic layers were washed with water, dried and the solvent was evaporated. The solid was recrystallized with petroleum ether several times (yield = 52%) to give the pure pseudo-para dibromo[2,2]-paracyclophane.

Film deposition is made under a primary vacuum (10^{-3} Torr) in our home-made reactor described earlier [5]: monomers are evaporated at a temperature ca. 200 °C, converted at 650 °C into reactive *p*-xylylene in the pyrolysis chamber, with a transit time assumed to be 0.25 s, so that the conversion ratio must be 100% using our 650 °C pyrolysis temperature [4], then polymerized during condensation on silicon or KBr substrates. The substrate holder is maintained at a temperature around 0 °C whereas the vacuum chamber is maintained at a temperature above the highest condensation temperature (i.e. 30, 90 and 130 °C [4] for parylene-n, -c and PPX-Br, respectively).

UV–visible and IR transmittance spectra have been taken (with an SAFAS 200 DES and a BOMEM MB series FT-IR spectrophotometers, respectively) on self-supported films (initially grown on polished Al substrates and then removed) or on silicon and KBr substrates when the films were etched by RIBE.

RIBE of the samples has been performed in a secondary vacuum chamber (under a 10^{-6} mbar pressure) with an oxygen ion beam produced by a microwave plasma source previously used for polyimide etching [9]. Since sputtering yield of parylene is low and almost independent of the ion energy [5], we used successively 6, 5 and 2.5 keV ion energies and a beam current density of 0.15 mA/cm². In order to compare the influence of the beam parameters, we exposed the sample to the same energy flux of 540 J/cm² (i.e. adjusting the irradiation time to 10, 12 and 24 min for the

decreasing energies). Two adhesion promoters, triethoxysilypropanamine (promoter 1) and phenyltriethoxysilane (promoter 2) were spin-coated prior to the film growth on the silicon substrates in order to limit film delamination during the sample etching. Etched depth were determined by a Dektak profilometer.

3. PPX RIBE etching

Etching rates of the samples are reported in Table 1. Excepted the case of parylene-n films which remained blistered by etching, using adhesion promoter prevents delamination encountered earlier [5] for the highest energy flux. These values remain lower than those obtained in the case of polyimide etching [9], but are sufficient to allow a few micrometer etching needed for waveguide application. The best values obtained in the case of PPX-Br could be attributed to the higher sputtering yield of bromine with the ion energies that we used.

4. UV–visible absorption of self-supported films

UV–visible transmission spectra of parylene-n and -c self-supported films are reported in Fig. 1. The films were obtained from nonpurified monomers and show a rather good transmittance in the visible domain, because of the

Table 1
Etching rates of PPX films on silicon substrates

O ⁺ ion energy (keV)	Parylene-c	Parylene-c + promoter 1 (Å/min)	Parylene-c + promoter 2 (Å/min)	PPX-Br + promoter 2 (Å/min)
2.5	15 Å/min	30	30	340
5	55 Å/min	40	40	160
6	Delamination	56	100	200

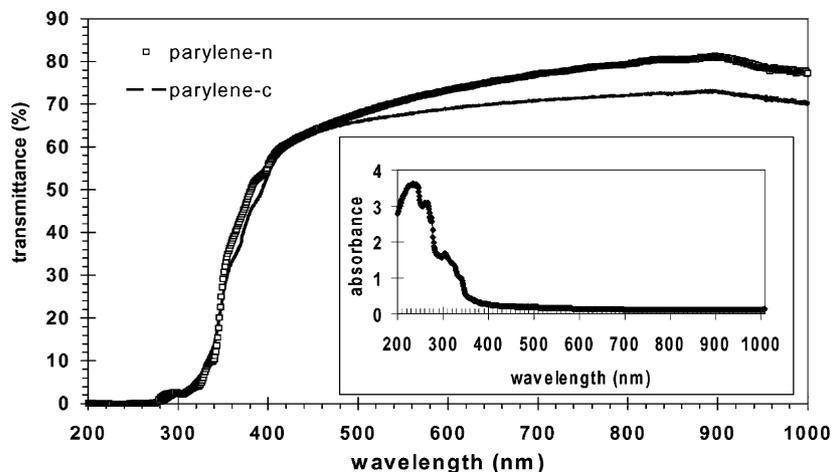


Fig. 1. UV–visible transmission spectra of parylene-n and -c self-supported films.

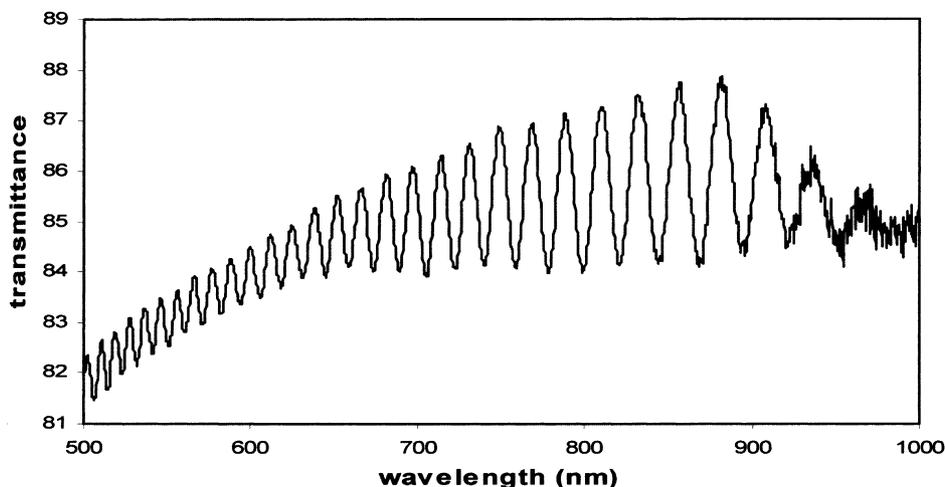


Fig. 2. Interference pattern of a 10 μm self-supported parylene-c UV-visible spectrum.

high optical gap value (around 300 nm (~ 4 eV); inset of Fig. 1), so that the films present a colorless behavior. This last property is important for OLED encapsulation, where the protective layer must neither affect the color of the emitted light nor the device efficiency. Nevertheless, these transmission ratios are lower than those obtained with purified monomers after recrystallization in hot petroleum ether: around 95% for 10 μm thick films, while only less than 1 μm thick film is needed for moisture or oxygen-barrier applications [10].

Refractive index (n) of the films were calculated from the comparison between the measured film depth (e) and the interference pattern period observed in the spectra, due to the good depth homogeneity of the films (Fig. 2 in the case of parylene-c), following the expression [7]:

$$e = \frac{m\lambda_1\lambda_2}{2n(\lambda_1 - \lambda_2)}$$

where m is the order between the constructive interference at wavelengths λ_1 and λ_2 . The index values were 1.63 and 1.66 for parylene-n and -c, respectively, at 700 nm and are consistent with results obtained by ellipsometry [11].

5. Infrared absorption of self-supported films

First, the comparison between polymerized films and monomer infrared spectra allowed us to verify that the grown films did not include unpolymerized species. Just few works on infrared absorption have been carried out that give the peak attributions of parylene films (Senkevich and Desu [12]). Infrared spectra of parylene-n and -c and PPX-Br self-supported films were taken from 6000 to 500 cm^{-1} and are presented in Fig. 3 (only parylene-n and -c are displayed for clarity). The absorption peaks in the 700–900 cm^{-1} domain are useful to determine the ring substitu-

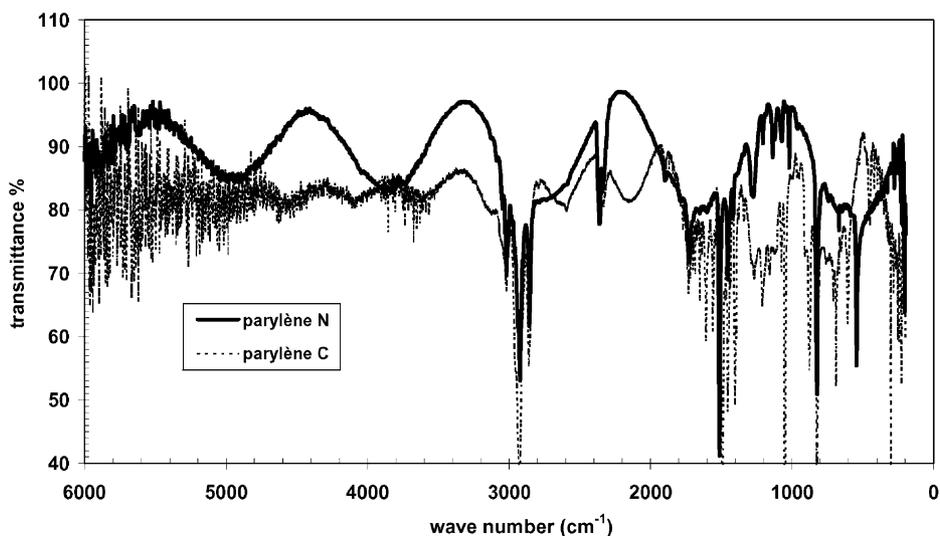


Fig. 3. Infrared transmission spectra of parylene-n and -c self-supported films.

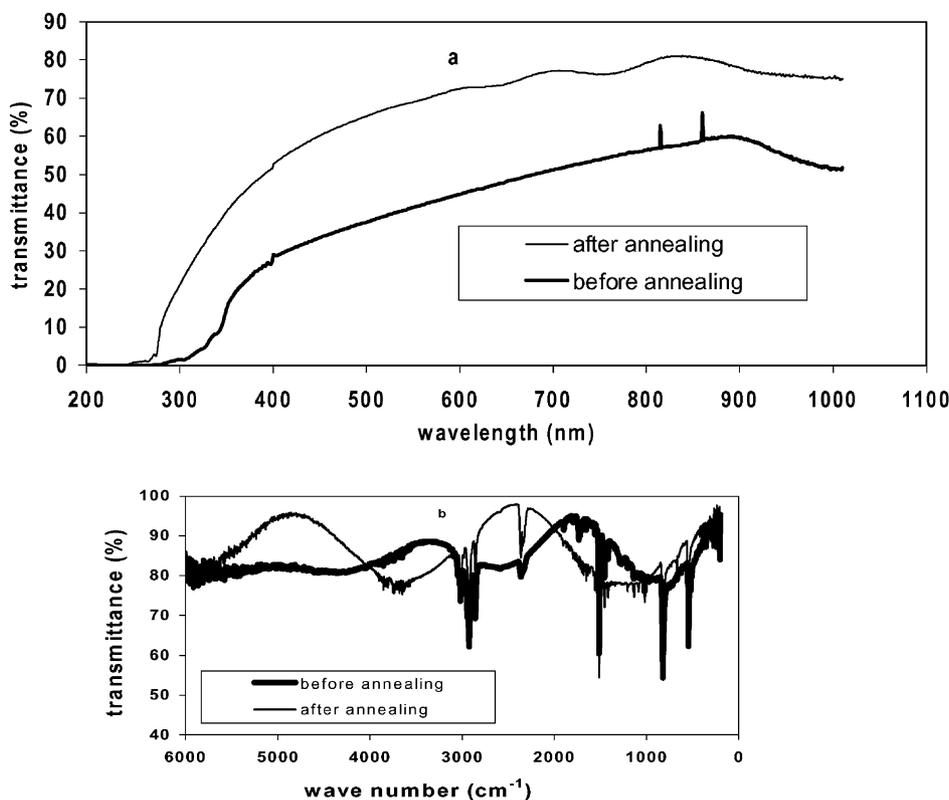


Fig. 4. UV-visible (a) and infrared (b) transmission of a self-supported parylene-n film before and after annealing.

tion by chlorine or bromine [13] (875 cm^{-1} peaks) and to characterize the molecular weight of the films, comparing the strength of monosubstituted ($\sim 750\text{ cm}^{-1}$) and disubstituted (825 and 875 cm^{-1}) C–H phenyl ring out of plane vibration: in our case, the 750 cm^{-1} peak was considerably weaker than the 825 cm^{-1} peak, indicating a higher degree of polymerization of the films.

Using parylene in telecommunication waveguides imposes that these materials are transparent in the near infrared domain. All the infrared spectra show a featureless behavior of these materials in the $6000\text{--}3200\text{ cm}^{-1}$ range, with a good transmission ratio around 95% for parylene-n and PPX-Br, and a little lower for parylene-c (85%). Although the wave number domain around 6000 cm^{-1} ($\lambda = 1.66\text{ }\mu\text{m}$) is close to the telecommunication range, we have measured with an infrared camera (Find-R-Scope 1800) a 90% transmission ratio of the light emitted by 1.32 and $1.55\text{ }\mu\text{m}$ wavelength laser diodes.

6. Thermal annealing effect

New functionalized paracyclophanes with nonlinear optical (NLO) properties have been synthesized [14], allowing the growth of electroluminescent or NLO parylene films. These latter materials will need thermal process to induce their polling. In order to predict the behavior of such

materials, we have observed the UV-visible and infrared transmission modifications induced by a $230\text{ }^\circ\text{C}$ annealing during 1 h of self-supported parylene-n films. A great enhancement of the transmission in the UV-visible domain is noticed in Fig. 4a, that we attribute to a film thickness diminution rather than a change of the refractive index (~ 0.003 according to Niegisch [15] in similar experiment), because of the great periodicity increase of the interference pattern observed in the infrared spectra as it could be seen in Fig. 4b.

This major change could be explained by an irreversible crystalline transition from the α -form (rectangular crystals typically encountered when film growth occurs toward $0\text{ }^\circ\text{C}$ as in our experiment) to the β -form (hexagonal crystals). Although, this behavior is rather good for OLED encapsulation (because of the transparency increase in the visible domain), high crystalline polymers ($\sim 60\text{--}80\%$) are not attempted for materials dedicated to waveguide application, because of the light scattering via the crystals. Crystallization during polymerization of parylene has been studied intensively [16], and it was shown that poor crystalline parylene films are opaque. A compromise between growth rate (which is increased at low substrate temperature around $-30\text{ }^\circ\text{C}$ [5,6]) and optical properties (a better transparency is obtained when the substrate temperature is just below the condensation temperature limit [16]) will be necessary for reasonable applications.

7. Changes in absorption due to the film etching

Ribbon-like waveguides are achieved by RIBE through a lithographed mask, so that the guide itself is constituted by the grown polymer. Nevertheless, the lateral guide walls are exposed to the ion beam side during the process and could induce light scattering (due to roughness or index variation), or absorption. Infrared and UV–visible transmission spectra of parylene-c and PPX-Br were taken before and after etching of the whole surface of the films grown on KBr substrates. An increase of the absorption, very low for PPX-Br and more important in the case of parylene-c, was noticed in the visible range and on the background of the infrared spectra after beam irradiation. Neither absorption peak areas in the infrared domain nor the UV $\pi\pi^*$ -absorption band were affected, indicating that only a sputtering of the film occurred during the process without any chain length shortening or polymer modification. Further experiment of diffusion loss measurement (carried out in our laboratory in the case of polyimide waveguides) are needed to know if this rather low absorption increase forbids the use of these materials for waveguide applications.

8. Conclusion

UV–visible and infrared absorption measurements were studied in order to estimate the opportunity of using parylene and its derivatives obtained by pyrolysis evaporation for optical applications: OLED encapsulation and waveguide achievement. A transmission around 95% in the visible range was obtained with the three materials that we have tested (parylene-n and -c and PPX-Br) when purified monomers were used. Moreover interference phenomenon observed because of the film thickness uniformity will not induce a loss of the device efficiency because of the

broad emission spectra of the OLED, so that the three materials could be good candidate for OLED encapsulation.

RIBE etching of parylene-c and PPX-Br films neither change their chemical constitution nor their near infrared absorption. Nevertheless, their thickness change when annealed reveals the crystalline nature of these materials that could be unsuitable for waveguide application, so that further optical characterization (diffusion loss measurements on waveguide structures) are needed.

References

- [1] A. Kubono, N. Okui, *Prog. Polym. Sci.* 19 (1994) 389–438.
- [2] J.R. Salem, F.O. Sequeda, J. Duran, W.Y. Lee, R.M. Yang, *J. Vac. Sci. Technol. A* 4 (1986) 369.
- [3] D.J. Cram, N.L. Allinger, *J. Am. Chem. Soc.* 77 (1955) 6289.
- [4] W.F. Gorham, *J. Polym. Sci., Part A-1* 4 (1966) 3027–3039.
- [5] B. Ratier, Y.S. Jeong, A. Moliton, P. Audebert, *Opt. Mater.* 12 (1999) 229–233.
- [6] G.R. Yang, S. Ganguli, J. Karcz, W.N. Gill, T.M. Lu, *J. Cryst. Growth* 183 (1998) 385–390.
- [7] W.F. Beach, C. Lee, D.R. Bassett, T.M. Austin, R. Olson, *Encyclopedia of Polymer Science and Engineering*, Vol. 17, Wiley/Interscience, New York, 1991, pp. 990–1025.
- [8] P.E. Burrows, V. Bulovic, S.R. Forrest, L.S. Sapochak, D.M. McCarty, M.E. Thompson, *Appl. Phys. Lett.* 65 (23) (1994) 2922–2924.
- [9] B. Lucas, C. Moussant, A. Moliton, J. Zyss, *Polym. Int.* 47 (1998) 210–214.
- [10] W.F. Gorham, *Encyclopedia of Polymer Science and Engineering*, Wiley/Interscience, New York, 1971, pp. 98–113.
- [11] J.F. Gaynor, S.B. Desu, *J. Mater. Res.* 11 (1) (1996) 236–242.
- [12] J.J. Senkevich, S.B. Desu, *Thin Solid Films* 322 (1998) 148–157.
- [13] M. Margoshes, V.A. Fassel, *Spectrochim. Acta* 7 (1955) 14–24.
- [14] L. Guyard, M. Nguyen Dinh An, P. Audebert, *Adv. Mater.* 13 (2) (2001) 133–136.
- [15] W.D. Niegisch, *J. Appl. Phys.* 37 (11) (1966) 4041–4046.
- [16] R. Iwamoto, R.C. Bopp, B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.* 13 (1975) 1925–1938.