Line Shape of Emission Spectra of the Luminescent Polymer Poly(*p*-Phenylene Vinylene)

A. Marletta, F. E. G. Guimarães, and R. M. Faria
Instituto de Física de São Carlos, Universidade de São Paulo,
Caixa Postal 369, CEP 13560-970, São Carlos - SP, Brazil

Received on 5 December, 2001

The influence of electron-phonon coupling in the emission spectra of self-assembly (SA) films of poly(*p*-phenylene vinylene) (PPV) is discussed. PPV is an important polymeric system because it exhibits strong luminescence effect. A semi-empirical model was used to analyze the photoluminescence spectra of PPV. This model assumes that defects along the molecule give rise to a distribution of conjugated segments of different lengths. In addition, it was considered that electronic transition was essentially coupled with three effective phonon modes with correspondent energies at 62, -139 and 192 meV, which were observed experimentally.

I Introduction

Optical and electrical properties of conjugated polymers have been extensively investigated due to their technological interest in optoeletronic devices such as light-emitting devices [1-2]. The progress in the chemical synthesis of poly(*p*-phenylene vinylene) (PPV), and its derivative, was followed by a similar development in experimental and theoretical electronic structure studies of such materials [3-5]. Optical and electronic properties of conjugated polymer have been investigated by absorption and photoluminescence (PL) spectroscopies [6-7]. In particular, spectroscopic investigations of PPV (and its derivatives) thin films have shown a strong dependence on their structural order, on intrinsic defects, and on molecular aggregations. The conventional procedure to obtain PPV films via the soluble PPV-precursor route should follow a thermal treatment at relatively high temperatures (>250 °C), which can be a source of a great amount of intrinsic defects by thermal-oxidation, i. e., the formation of carbonyl groups [8-11]. These defects, which are efficient non-radiative centers and that reduce the effective chain length [12-14], impose a physical limit in the spectra resolution. Typically, the PL spectrum of casting-PPV film presents high electron-phonon coupling with a line-width of zero-phonon transition of approximately 250 meV [15]. This value is much higher than the phonon energy measured by infrared and Raman spectroscopies, 100 meV [16-17], indicating that the disordered structure of the solid-film contributes to the line enlargement. As a result, the necessary resolution to measure the phonon energy directly from the emission spectra depends on having films highly ordered and with less intrinsic defects.

In a previous paper we developed an alternative process that allows obtaining PPV converted at relatively low temperature (110 °C), which, in addition, strongly reduced the number of carbonyl groups. Concomitantly, we show that thin films prepared by SA and Langmuir-Blodgett (LB) techniques are much more ordered [15,18-19]. Photoluminescence studies of such films showed an enhancement of the PL spectral resolution. Both, SA and LB films presented well-resolved vibronic PL spectra with a line-width of approximately 65 meV, measured at low temperature (30 K). In the present paper we analyze emission line shapes, measured at 30 K and at room temperature, of SA-PPV converted at 110 °C, using an empirical model assuming a Gaussian distribution of conjugated segment lengths.

II Experimental procedures

The PPV-precursor, poly(xylyliden tetrahydrothiophenium chloride) (PTHT), was synthesized using the precursor route described in the literature [8]. The concentration of polycation PTHT-solution was 0.16 mg/ml and the anion of dodecylbenzenesulfonate (DBS) solution was prepared with 10^{-1} M concentration. The solutions were diluted in pure water at pH = 5.0. Twenty layers SA-PTHT/DBS were deposited on hydrophilic quartz substrates through alternate immersion in the polycation solution for 1 min and anion solution for 30 s, and finally dried by N_2 flux. The substrate was rinsed in Milli-Q water after each immersion in the solution. The PTHT/DBS films were converted to PPV

films at low temperature (110 °C) during 30 min under atmospheric conditions.

The optical properties of these films were investigated by UV-Vis and photoluminescence spectroscopies. For absorption experiments we used a Hitachi U-2001 spectrometer. PL measurements in the visible region, were obtained exciting the samples by a 458 nm line of an Ar^+ laser with an average excitation of 5 mW/cm^2. The selective excitation spectroscopy (SES) experiments were carried out using a very narrow excitation-line (FWHM~1 nm) by dispersing the light of a 450 W Xe-lamp, which allows the variation of the excitation wavelength (Exc.) from 495 nm to 527 nm. PL and SES spectra were obtained using a photomultiplier mounted on a 0.5 m monochromator controlled by the lock-in technique. The temperature could be varied from 30 to 300 K using a closed-cycle helium cryostat.

III Theory analysis

The line shape of the emission was calculated via Fermi's golden rule containing the coupling between localized molecular states and vibrational modes. The analytic expression was obtained using Condon approximation. The emission coefficient can be calculated considering the electronic transition from excited state b to ground state a ($b \longrightarrow a$) as in the following expression [20-24]:

$$I_n(\omega) = \frac{2a_m \pi \omega^3}{3c\hbar} |\overrightarrow{\mu_n}|^2 \int_{-\infty}^{+\infty} dt \exp\left(it(\omega_n - \omega) - \frac{d^2t^2}{2}\right) \prod_j G_j^*(t) \quad (1)$$

where $\overrightarrow{\mu_n}$ is the electronic transition moment, a_m describes the medium effect, c the speed of light, $\hbar\omega_n = E_b^n - E_a^n$ is the difference between LUMO (E_b^n) and HOMO (E_a^n) of a conjugate PPV segment with n units, and d represents the inhomogeneous spectral line broadening described by a Gaussian distribution. The function $G_j^*(t)$ is the Frank-Condon factor in harmonic approximation and in the case of pure displacement can expressed as [21,25]:

$$\prod_j G_j^*(t) = \exp\left[\sum_{j=1}^{N} S_j \{(\overline{n}_j + 1)\exp(it\omega_j) + \overline{n}_j(\exp(-it\omega_j) - 1)\}\right] \quad (2)$$

where S_j is the Huang-Rhys factor, ω_j is the j^{th}-phonon energy, and $\overline{n}_j = 1/(\exp(\hbar\omega_j/2kT) - 1)$.

IV Results and discussions

Figure 1a shows the absorbance spectra of a SA-PPV film as function as the temperature (10 K to 300 K). At low temperatures the spectra exhibit well-resolved vibronic structures near the band edge (between 450 and 510 nm at 10 K). As the temperature increases these structures become less resolved, broadening the peaks, owing to the thermal induced structural disorder. Similar behavior is observed in the PL spectra (Fig. 1b). Compared with the absorption of LB-films, the SA-spectra present lower absorption in the region of low wavelength. This is an indicative that SA-PPV films converted at low temperature technique [26] exhibits a narrow distribution of the conjugated lengths increasing, therefore, the amount of effective degree of conjugate PPV segments along the polymer chain. Since HOMO-LUMO gaps are lower for large segments the absorption peaks move towards lower energies. On the other hand, the emission peak of SA-PPV at 300 K is very similar to that of LB-films. However, at low temperature (30 K) it presents a well-resolved line at 521 nm with line-width of about 65 meV. As the temperature increases the PL spectrum decreases slightly in intensity, owing to thermal activation of non-radiative processes, and is blue-shifted due thermal molecular motions which simulates a reduction of the PPV effective conjugation length. The PL spectrum of LB-PPV film at room temperature is shifted to high energies causing a low Stockes-shift in comparison to SA film (Fig. 1).

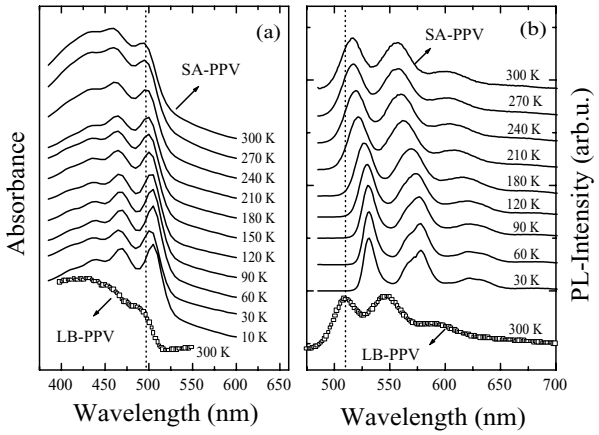

Figure 1. Absorbance (a) and emission (b) spectra of a SA-PPV film as function of the temperature. The spectra of a LB-PPV film at room temperature are present for comparison.

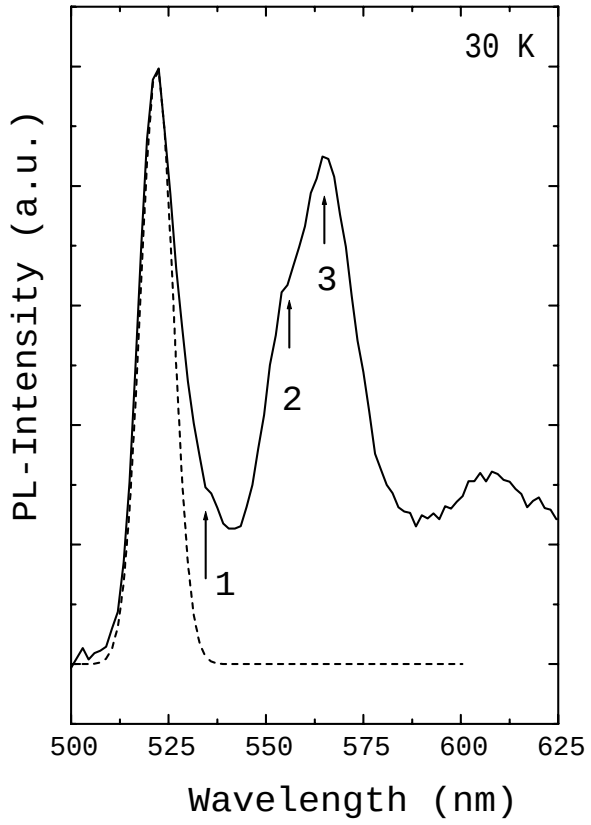

Figure 2. Line shape of PL spectrum at low temperature (30 K) of SA-PPV film. Three unresolved structures (1, 2 e 3) are indicated with energy about 535, 555 and 570 nm with are related with vibrational modes. The zero-phonon line (- - - -) is plotted using the equation 1 and $S_j = 0$.

The PL spectrum at 30 K of a SA-PPV film is now displayed in Fig. 2 in the 500-625 nm spectral range, showing in detail the well resolved peak around 521 nm that is fitted by the zero-phonon transition (dashed line). This fit was obtained assuming a negligible electron-phonon coupling, i.e., the Huang-Rhys parameter S_j equal 0 in Eq. 2. The result is a Gaussian function centralized in zero-phonon peak widened by the parameter d (non-homogeneous widening parameter).

Superimposed to the emission spectra it is also observed other small peaks, at 535, 555 and 570 nm that shall correspond, respectively, to ω_1=500 cm^{-1} (62 meV), ω_2=1170 cm^{-1} (139 meV) and ω_3=1550 cm^{-1} (192 meV). Infrared and Raman measurements [16-17] have identified spectral features of PPV vibronic modes of C-H plus C-C ring out-of-plane bend (522 and 555 cm^{-1}), C-H ring in-plane-bend (1005, 1135 and 1174 cm^{-1}) and C-C ring stretch (1518, 1543, 1550 and 1584 cm^{-1}). Then, we used in our calculations these three effective phonons coupled with the electronic transitions as parameters, for which S_1, S_2 and S_3 are the Huang-Rhys factors respectively.

Figure 3 shows PL spectra obtained from SES measurements, carried out at 30 K, of a SA-PPV sample. The sharp peaks in the left are the excitation lines, which was varied from 495 nm to 527 nm. The excitation energy was scanned over the zero-phonon spectral region selecting only long conjugated PPV segments. As the excitation energy goes through the zero-phonon transition (521 nm), two spectral lines, at 555 nm and 570 nm, become well defined showing the existence of two effective modes that were not resolved in the normal PL spectra of Fig. 2.

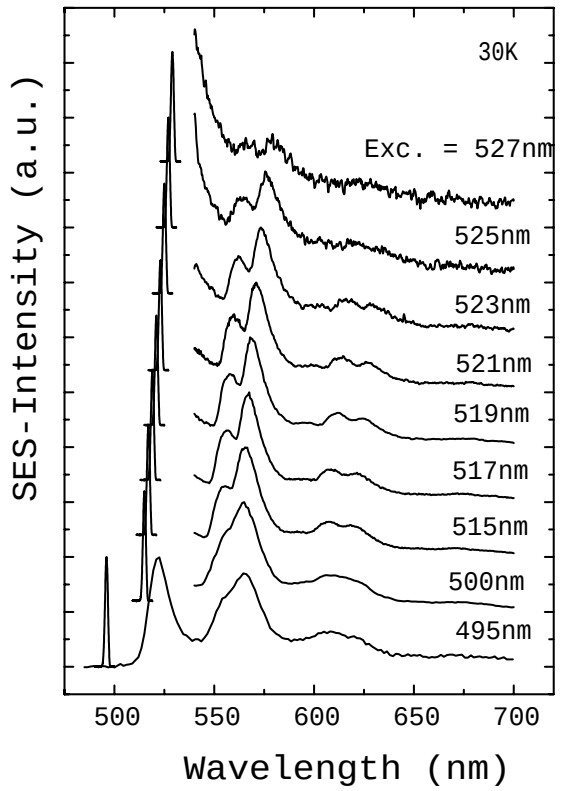

Figure 3. SES experiment with excitation (Exc.) varing from 495 nm to 527 nm at low temperature (30 K) of a SA-PPV. A definition in the first phonon replica is observed.

The theoretical model, expressed by Eq. 1, was applied to fit the PL spectra presented in Fig. 1. In the fitting, we fixed, based on the experimental result of Fig. 2, the phonon frequencies (500 cm^{-1}, 1170 cm^{-1} and 1550 cm^{-1}), but we varied the Huang-Rhys parameters (S_j), the homogeneous widening (d) and the zero-phonon position (ω_n). Figure 4 shows that the theoretical model presents a reasonable agreement with the experimental data (at 30 K). The contribution of each vibrational mode is also shown in the Fig. 4. The used parameters were: the width d is equal (580 cm^{-1}), ω_n equal 2.34 eV, and the Huang-Rhys parameters S_1=0.14, S_2=0.48, and S_3=0.80. The two first parameters, d and ω_n were extracted from the experimental results. The relatively low Ruang-Hys parameter values ($S_j < 1$) confirm that SA-PPV has rather long conjugated segments and low molecular disorder [24]. Considering the efficient carrier migration mechanism to lower energy states (HOMO and LUMO molecular states), the radiative recombination occurs at high PPV conjugate segments (~10 units) [27].

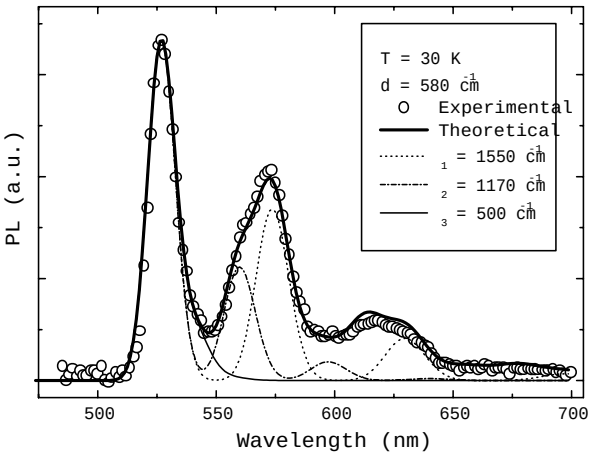

Figure 4. PL spectrum at low temperature (30 K) of SA-PPV film (—O—) and theoretical spectrum (——) considering the contribution of three effective phonons at 500 cm^{-1} (——), 1170 cm^{-1} (- - - -) and 1550 cm^{-1} (· · · · ·).

Similar fitting were carried out with the spectrum obtained at 300 K, shown in Fig. 5. In this fitting the adjusted parameters were: S_1=0.22, S_2=0.60 and S_3=0.85, whereas d equal to 840 cm^{-1} and ω_n is equal 2.39 eV. The broadening of the zero-phonon linewidth d and the ω_n-blue-shift of 50 meV reflects the thermal disorder induced by the temperature. The enhancement of S_1 and S_2 values shows that the electron-phonon coupling also depends on the temperature, which indicates that the electronic molecular states are more sensitive to the ring vibration (phenylene ring) in the PPV unit. Since ω_1 and ω_2 are associated, respectively, with the bend vibration of the ring out-of-plane and the ring in-plane-bend [16], we may expect that these phenomenon undergoes intermolecular interactions, being higher for high temperatures.

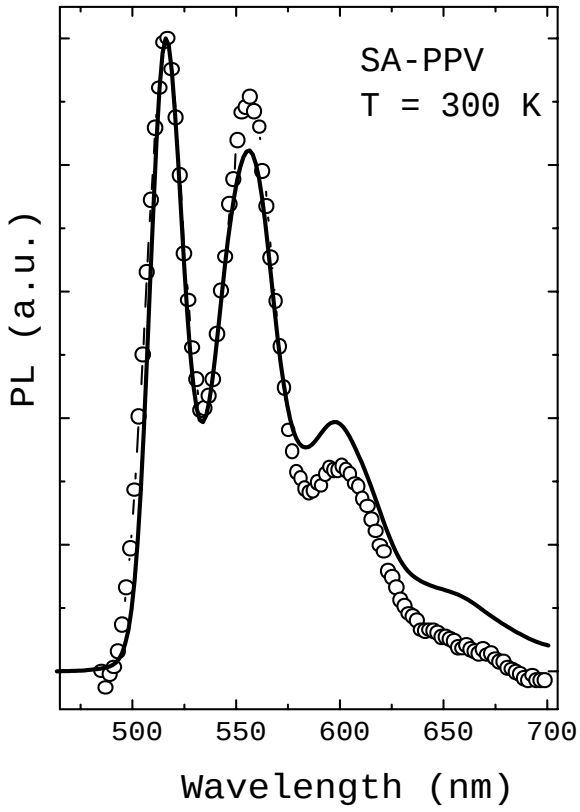

Figure 5. PL spectrum at room temperature (300 K) of SA-PPV film (—O—) and theoretical spectrum (——).

V Conclusions

In this paper we show that SA-PPV films display absorption and emission curves with high resolution, mainly at low temperatures, allowing a quantitative study of the emission spectrum considering its vibronic structures. In addition, by the use of the SES technique we were able to resolve the vibrational mode associated with the first replica of zero phonon transition. Calculations of electronic transition rates were obtained by a model based on the Condon approximation taking into account electron-phonon coupling and a distribution in lengths of conjugated lengths along the polymeric chain. By the analysis of the Huang-Rhys parameters and the zero-phonon line-width and its position in the spectrum we fitted, with great accuracy, the experimental emission curve at low temperature. The small Huang-Rhys coupling-parameters (smaller than the unity) confirms the quality of the produced SA-PPV films when compared to that made by conventional casting procedure. The slight difference observed between the theoretical and the experimental curves in Fig. 5 indicates that other interactions need to be considered, as, for example, interchain interactions and the effect of clusters of molecules [14,28-30].

Acknowledgement

The financial support from Brazilian agency Fundação de Apoio à Pesquisa do Estado de São Paulo (FAPESP) is acknowledged.

References

[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, Nature **397**, 121 (1999).

[2] M. T. Bernius, M. Inbasekaran, J. O'Brien, and W. Wu, Adv. Mat **12**, 1737 (2000).

[3] S. C. Graham, D. D. Bradley, R. H. Friend, and C. W. Spangler, Synth. Met. **41-43**, 1277 (1991).

[4] T. W. Hagler, K. Pakbaz, and A. J. Heeger, Phys. Rev. B **44**, 8652 (1991).

[5] K. Pichler, D. A. Halliday, D. D. Bradley, P. L. Burn, R. H. Friend, and A. B. Holmes, J. Phys.: Condens. Matter **5**, 7155 (1993).

[6] K. Pakbaz, C. H. Lee, A. J. Heeger, T. W. Hagler, and D . Mcbranch, Synth. Met. **64**, 295 (1994).

[7] J. Obrzut and F. E. Karasz, J. Chem. Phys. **87**, 2349 (1987).

[8] D. A. Halliday, P. L. Burn, R. H. Friend, and A. B. Holmes, J. Chem. Soc. Chem. Commun. **22**, 1685 (1992).

[9] B. H. Cumpston and K. F. Jensen, TRIP **4**, 151 (1996).

[10] F. Papadimitrakopoulos, M. Yan, L. J. Rothberg, H. E. Katz, E. A. Chandross, and M. E. Galvin, Mol. Crys. Liq. Crys. **256**, 663 (1994).

[11] W. Holzer, A. Penzkofer, M. Pichlmaier, D. D. C. Bradley, and W. J. Blau, Chem. Phys. **248**, 273 (1999).

[12] L. J. Rothberg, M. Yan, F. Papadimitrakopoulos, M. E. Galvin, E. W. Kwock, and T. M. Miller, Synth. Met. **80**, 41 (1996).

[13] R. Kersting, U. Lemmer, R. F. Mahart, K. Leo, H. Kurz, H. Bässler, and E. O. Göbel, Phys. Rev. Lett. **70**, 3820 (1993).

[14] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **73**, 744 (1994).

[15] A. Marletta, D. Gonçalves, O.N. Oliveira Jr., R.M. Faria, and F.E.G. Guimarães, Macromolecules **28**, 7107 (1995).

[16] D. Rakvié, R. Kostié, L. A. Gribov, and I. E. Davidova, Phys. Rev. B **41**, 10744 (1990).

[17] S. Lefrant, E. Perrin, and J. P. Buisson, Synth. Met. **29**, E91 (1989).

[18] A. Marletta, D. Gonçalves, O. N. Oliveira Jr., R. M. Faria, and F. E. G. Guimarães, Synth. Met. **119**, 1447 (2001).

[19] A. Marletta, D. Gonçalves, O. N. Oliveira Jr., R. M. Faria, and F. E. G. Guimarães, Synth. Met. **119**, 629 (2001).

[20] S. H. Lin, J. Chem. Phys. **44**, 3759 (1966).

[21] A. D. Brailford and T. Y. Chang, J. Chem. Phys. **53**, 3109 (1970).

[22] J. Yu, W. S. Fann, F. J. Kao, D. Y. Yang, and S. H. Lin, Synth. Met. **66**, 143 (1994).

[23] J. Yu, M. Hayashi, S. H. Lin, K. K. Liang, J. H. Hsu, W. S. Fann, C. I. Chao, K. R. Chuang, and S. A. Chen, Synth. Met. **82,** 159 (1996).

[24] R. Chang, J. H. Hsu, W. S. Fann, K. K. Liang, C. H. Chang, M. Hayashi, J. Yu, S. H. Lin E. C. Chang, K. R. Chuang, and S. A. Chen, Chem. Phys. Lett. **317**, 142 (2000).

[25] R. Chang, J. C. Chang, R. Chang, J. H. Hsu, W. S. Fann, M. Hayashi, J. Yu, J. C. Jiang, S. H. Lin, Y. Z. Lee, K. R. Chuang, and S. A. Chen, Synth. Met. **106**, 139 (1999).

[26] A. Marletta, D. Gonçalves, O.N. Oliveira Jr., R.M. Faria, and F.E.G. Guimarães, Adv. Mat. **12**, 69 (2000).

[27] D. G. Cahill, M. Katiyar, and J. R. Abeldeson, Phys. Rev. B **50**, 6077 (1994).

[28] Y. Shi, J. Liu, and Y. Yang, J. Appl. Phys. **87**, 4254 (2000).

[29] J. W. Blatchford, S. W. Jessen, L. B. Lin, T. L. Gustafson, D. K. Fu, H. L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **54**, 9180 (1996).

[30] T. Q. Nguyen, V. Doan, and B. J. Schwartz, J. Chem. Phys. **110**, 4068 (1999).