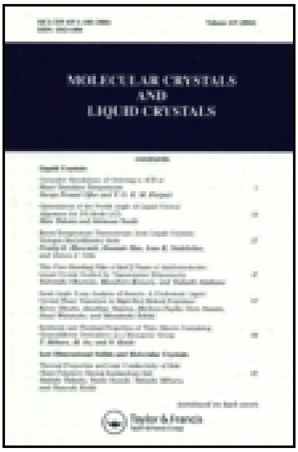

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Temperature Dependent Vibronic Structures in the Emission Spectra of Poly(p -Phenylene Vinylene)

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To cite this article: C. A. M. Borges, A. Marletta, R. M. Faria & F. E. G. Guimarães (2002): Temperature Dependent Vibronic Structures in the Emission Spectra of Poly(p -Phenylene Vinylene), Molecular Crystals and Liquid Crystals, 374:1, 427-432

To link to this article: http://dx.doi.org/10.1080/10587250210462

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 427-432
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1058-725X/02 $12.00 + .00

Temperature Dependent Vibronic Structures in the Emission Spectra of Poly(*p*-Phenylene Vinylene)

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We studied the effect of temperature on electron-phonon coupling in the emission spectra of poly(*p*-phenylene vinylene), PPV, prepared by self-assembly methodology. Site selective luminescence spectroscopy (SSE) was employed to resolve the fine structures of the vibracional modes. Using Franck-Condon analysis, the experimental vibronic progressions of PPV can be well described by three effective, inhomogeneous broadened vibrational modes with energies at 330, 1163 and 1550 cm^{-1}. As the temperature increases the electron-phonon coupling for the 1550 cm^{-1} mode remains constant while, for the other two modes, the S factor increases.

Keywords: Franck-Condon analysis; PPV; site selective luminescence; electron-phonon coupling;

INTRODUCTION

Optical properties of conjugated polymers are very sensitive to extrinsic structural and intrinsic thermal disorder. A variety of processing techniques have been developed which focus on large conjugation length and chain order [1-4] to an extent that intrinsic electronic properties of the macromolecular chains can be studied in such inhomogeneous broadened material. Useful insights into the fine details of the electronic structure of polymers have also been obtained in thin films of oligomers dispersed in an inert matrix or by using well-defined oligomers [5-7]. In this work we study experimentally and theoretically the dependence of the electron-phonon coupling on the sample temperature of poly(*p*-phenylene vinylene), PPV. The PPV films ware prepared joint a novel self-assembly methodology (SA) and low temperature conversion process [8]. The main advantage of this SA procedure is that thermal conversion may be performed at considerably lower temperatures (80-100 °C) in a few minutes, producing high conjugated PPV films with incredibly sharp and well-resolved vibronic structures in the photoluminescence (PL) and absorption spectra. Site-selective luminescence spectroscopy (SSE) was employed in order to better resolve the vibronic structures. The dependence of the electron-phonon coupling with temperature was quantified by using a Franck-Condon analysis of the emission spectrum.

EXPERIMENTAL DETAILS

The experiments were performed with high quality PPV films prepared by self-assembly (SA) methodology and converted 110 °C for 30 min [1]. The sample was mounted onto the cold finger of a close cycle cryostat and the temperature was varied form 40 to 120 K. Site-selective cw-luminescence were carried out using a very narrow excitation-line (spectral bandwidth of ~ 1 nm) which was obtained through the dispersion of the light of a 450 W Xe-lamp by a 1 m monochromator. A 0.5 m monochromator was employed for luminescence detection using photomultiplier tube and lock-in amplifier technique.

FRANCK-CONDON ANALYSIS

The emission coefficient for the electronic transition from a excited state b to the ground state a ($b \rightarrow a$) can be calculated by the golden rule, taking into account multiphonon processes [7-9]:

$$I_{ba}(\omega) = \frac{2\,\pi\pi\,a^{\;3}}{3\,c\,\hbar}\left|\vec{\mu}_{ab}\right|^2 \int_{-\infty}^{+\infty} dt \exp\left(it(\omega_{ba}-\omega) - \frac{d^2t^2}{2}\right)\prod_j G_j^*(t) \qquad (1)$$

where $\vec{\mu}_{ab}$ denotes the electronic dipole moment, a the factor which describes the medium effect, c the speed of light, $\hbar\omega_{ba} = E_b - E_a$, and d the inhomogeneous line width described by a Gaussian distribution of conjugated segments centered at ω_{ba}. In the harmonic approximation:

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

where $\mathrm{S_j = M\omega_j \Delta Q^2{}_j / 2}\hbar$ is the Huang-Rhys factor, ΔQ is the displacement in normal coordinates between the minimal of the ground and excited states, ω_j is the jth-phonon energy and $\bar{\mathrm{n}}_j = (\exp(\hbar\omega_j/2\mathrm{kT}) - 1)^{-1}$.

RESULTS

Figure 1(a) shows the low temperature (40 K) emission spectra of a PPV film (open circles). The highly resolved vibrational structures, with three overtones of different effective backbone stretching modes, correspond to emissions from PPV segments of at least ten uninterrupted phenylenevinylene units [10].

Using Franck-Condon analysis (eq. 1) we notice that the experimental vibronic progression can be well described by the overlapping of three effective, inhomogeneous broadened modes with energies 330, 1160 and 1550 $\mathrm{cm^{-1}}$ (continuous curve). The last two modes correspond to Raman bands due to stretching vibration of vinyl group and phenyl ring.[6] The around 330 $\mathrm{cm^{-1}}$ feature has been observed before[9,11] and needs further experimental identification.[12]

The contribution of each mode is given by dashed curves. The respective amplitudes and positions of the phonon progression are depicted in Fig. 1(b). The overall agreement further confirms the validity of the model and the quality of the PPV films used in this work. Note that no additional low-energy emission band in the red region of the spectrum, indicating the absence of aggregate luminescence in the SA PPV films.

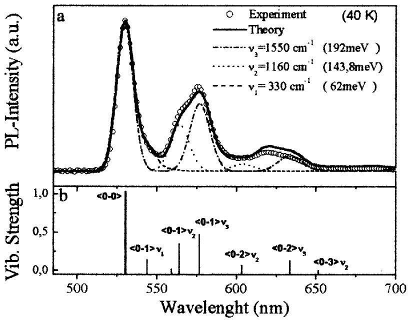

FIGURE 1. (a) Franck-Condon analysis of the emission line shape at 40 K (continue line) and (b) the respective vibrational strength and positions of the phonon progression used in the analysis.

SSE spectroscopy was used to better resolve the vibronic modes determined theoretically in Fig. 1. The insert of Figure 2 displays luminescence of a SA PPV film upon scanning the light excitation wavelength λ_{exc} across the low energy tail of the absorption that overlaps the luminescence spectrum. One observes that line narrowing occurs in the region of the vibronic bands once λ_{exc} moves into resonance (from 525 nm to 532 nm) with the zero-phonon line centered at 532 nm. The unresolved vibronic band splits into a doublet with energies that coincides with those for the two most energetic modes. Figure 2 shows the SSE emission spectra for different temperatures varying from 38 to 120 K. The decrease of spectral intensity is related to non-radiactive process activated by temperature. In this range there is no significant spectral shift and line broadening of the zero-phonon.

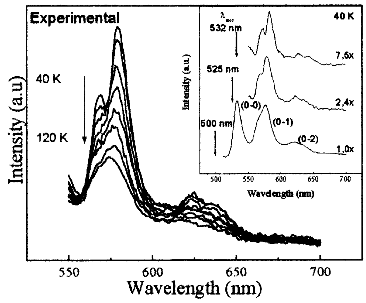

FIGURE 2. Temperature dependence of the SSE spectra in the region of vibronic progression. Insert show the dependence of the SSE spectra on $\lambda_{exc.}$.

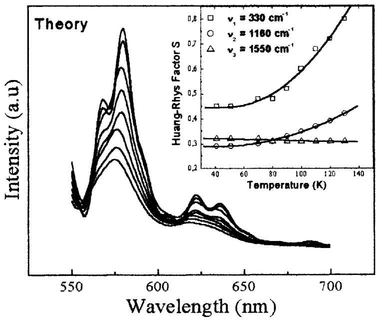

FIGURE 3. Theoretical fitting of experimental spectra of Fig.2 using Franck-Condon analysis, eq.2. (b). The insert shows the temperature dependence of the Huang-Rhys parameters S to three effective vibrational modes (330, 1160 and 1550 cm-1).

This will be of particular importance in the next theoretical analysis. The temperature dependence of each S_j is displayed in the insert of Figure 3. One observes that S_j increases for the two less energetic modes (330 and 1160 cm^{-1}). This result is consistent with the fact that S_j is correlated with the thermal disorder, that is, the higher the disorder of a system, the larger the S value. Conversely, the most striking result is the almost constant behavior of the higher energy mode with temperature. This trend is consistent with the result that high-energy vibrational modes are strongly localized with respect to the size of the effective conjugation length and, therefore, less sensitive to thermal disorder.

CONCLUSION

In conclusion, this work presented a joint of experimental and theoretical investigation of the electron-phonon coupling in function of the sample temperature for PPV. The experimental vibronic progressions of PPV can be well described by three effective, inhomogeneous broadened vibrational modes with energies at 330, 1160 and 1550 cm^{-1}. We find that the Huang-Rhys factor of each mode increases differently with the temperature, correlating thermal disorder and phonon localization.

The authors would like to thank the financial assistance from the Brazilian agencies FAPESP and CNPq.

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