

Polarized photoluminescence of highly oriented poly(*p*-phenylene-vinylene)

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ABSTRACT

We report on the anisotropic photoluminescence (PL) properties of stretch-oriented free standing films of poly(*p*-phenylene-vinylene) (PPV) at different temperatures. The PL quantum efficiency is strongly dependent on the pump polarization; it is higher when the pump is polarized perpendicularly to the polymer chain orientation. Independently of the pump polarization, we find that the PL emission spectra are mainly polarized along the polymer chain axis. The PL spectra show high-energy features, close to the onset of the HOMO-LUMO transition, that are significantly affected by self-absorption of the emitted light in the optically thick samples as well as by refractive effects at the polymer-air interface. In order to clarify the origin of these features, we have made a detailed characterization of the anisotropic optical constants of the PPV film. The optical constants have been derived from polarized reflectance and transmittance measurements and were used for the renormalisation of the PL spectra using the Fresnel equations. Frank-Condon analysis for the absorption oscillator strength and for the corrected emission spectra suggests that two different emitting states contribute to the optical properties. The connection of these states with film morphology and intermolecular interactions is described.

Keywords: poly(phenylene vinylene), photoluminescence, optical constants, intermolecular interactions.

1. INTRODUCTION

PPV and its substituted derivatives are widely used in optoelectronic devices. The investigation of their chemical and physical properties has been extensively studied over the past two decades. In spite of the impressive amount of work done on these materials, some aspects of their fundamental properties, such as the polarization dependent optical absorption spectra and the precise assignment of their various features have become clearer only recently [1,2] due to the availability of highly oriented samples [3]. Theoretical models proposed for the assignment of the absorption spectral properties of PPV and its derivatives were developed either within quantum-chemical or solid-state physics approaches only for isolated molecules. Even though this approximation may be suitable for describing most of the absorption properties [4], recent studies of the emission properties of PPV derivatives seem to indicate that intermolecular interactions, both in solution [5] and in silica nanoparticles composites [6], affect the emission spectra. In order to understand the role of interchain interactions on the electronic properties of PPV, we investigated the polarized photoluminescence of highly oriented PPV, a system previously used for a detailed characterization of the optical constants and their anisotropy [1]. The four possible polarization combinations in these measurements (i.e. polarization of the excitation and emission with respect to the chain axis) provide additional information, useful for an accurate assignment of the above spectroscopic features.

To evaluate the intrinsic emissive properties, a detailed knowledge of the refractive index as well as the absorption coefficient dispersion for the parallel and perpendicular polarizations is needed in order to determine the number of absorbed photons and correct for the optical losses of the emission, e.g. the self-absorption of the PL. This procedure has been already successfully adopted for the determination of the Raman cross sections of oriented polymers [7]. Additionally, we have measured the PL spectra at few temperatures in attempt to differentiate between the intrinsic intramolecular excitations from those affected by inter-molecular interaction.

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2. EXPERIMENTAL

Thick (14 μm and 18 μm), free-standing PPV samples used in this study were oriented by tensile drawing, with an elongation ratio between 3 and 5. Polarized transmission, reflectance, and diffuse reflectance spectra were recorded by a double-beam, double monochromator spectrometer (Varian Cary 5E), equipped with a closed-cycle liquid helium cryostat. During measurements, the samples were kept in an inert atmosphere of helium gas. Raman spectra with resolution of 2 cm^{-1} were recorded with a Bruker FT spectrometer (FRS 100) equipped with an Oxford Microstat cryostat; the detector was a Ge photodiode cooled by liquid nitrogen and the excitation was provided by an Adlas 300 Nd:YAG laser (1064 nm). IR polarized transmission spectra were recorded using a Bruker 113 FT spectrometer. The PL measurements were performed by exciting the samples with the 458 nm line of an Ar^+ laser (incidence angle 45°), while the samples were placed on a cold finger in the vacuum chamber of the cryostat, pumped to a pressure of $\sim 10^{-4}$ Torr. Part of the PL emission was collected (collection angle 45°), dispersed by a monochromator, and recorded by a CCD camera. The PL emission spectra were corrected for the anisotropic response of the measuring system. In the PL measurements, the four polarization combinations are denoted with the symbol (a,b) where the first symbol refers to the excitation polarization ($a=\perp$ or \parallel) while the latter to the emission polarization ($b=\perp$ or \parallel).

3. RESULTS AND DISCUSSION

Fig. 1 shows the room temperature polarized reflectance (R), transmittance (T) and photoluminescence spectra of oriented PPV films. Reflectance and transmittance spectra show similar characteristics to the ones previously described [1]. The parallel (\parallel) reflectance spectrum exhibits the electronic transition due to the $\pi-\pi^*$ transition followed by a well resolved vibronic progression. The purely electronic transition (0-0, where the first number refers to the ground state phonons and the second to phonons in the excited state involved in the transition), is located at a significantly long wavelength (500 nm), exhibiting a long conjugation length present in these samples. At lower wavelength, a shoulder assigned to conjugation chain ends [1] is observed at about 340 nm (usually referred as peak II), in addition to a broad transition around 260 nm (peak III). The perpendicular (\perp) reflectance spectrum is almost flat down to 280 nm, where the typical perpendicular component of peak III is present [1,8]. The intrinsic \perp component of the reflectance spectra in the visible and near ultraviolet regions is masked by a slight misalignment of the chain orientation around the stretching direction. This misalignment induces a \perp component of the dipole transition moment due to the projection of the \parallel component that scales as $\sin^2\phi$, ϕ being the misalignment angle [4]. Even a small misalignment angle of $\phi\sim 3^\circ$, obtained in our high quality samples, results in an apparent \perp absorption coefficient component of magnitude of 0.005 times the parallel one.

Optically thick samples used in this work do not allow a direct determination of the transmission spectra below 500 nm. However, we point out the remarkable difference in the onset of the transmission for the two polarizations, in the spectral region overlapped with the high energy PL emission peaks [9]. These observations suggest that the dispersion of the refractive index (n) and absorption coefficient (k) and their dependence on polarization strongly affect the measured PL emission spectra.

Among the four polarization combinations, the (\perp, \parallel) measurement exhibits the strongest PL intensity. Peaks at 560 and 602 nm, as well as a shoulder around 650 nm are detected. These PL peaks are red-shifted with respect to those previously observed in other PPV samples [6,10,11], further indicating the uniquely long conjugation length in our samples. In the (\perp, \parallel) spectrum, an additional shoulder can be identified at 530 nm. For all the other polarization combinations, the results of the PL data show much lower PL intensities and similar spectral features except in the 500-540 nm region. In this latter region, the (\parallel, \parallel) PL spectrum shows a well defined peak at 520 nm, while for the remaining polarizations (\parallel, \perp and \perp, \perp) there is no clear evidence for a transition underneath the tail of the main emission peak.

Fig. 2 compares the room temperature polarized PL spectra with those recorded at 80 K. Upon lowering the temperature, the PL signal intensity increases by a factor greater than three and spectra main peaks shift to longer wavelength (560 nm \Rightarrow 570 nm; 602 nm \Rightarrow 620 nm), indicating a more extended π -electrons delocalization at low temperatures, due to stiffening of the polymer chains. At the low temperature, the relative intensity of the four polarization combinations is almost unchanged, but the transition linewidths are slightly affected. At 80 K, the features at 520-530 nm are better defined, while the main peaks are unusually broadened with respect to the room temperature ones.

At first glance one could assign the 0-0 transition to the main PL peak at 560 nm (room temperature). The presence of the weak emission features around 520-530 nm, however, does not support this interpretation. For a better assignment, it is essential to correct the emission spectra for equal number of absorbed photons as well as for the self-absorption and

reflectivity losses. Considering the strong anisotropy of the optical properties as well as their spectral dispersion, considerable effects due to these corrections are expected. The correction formula [12] for the PL spectra can be deduced using the Fresnel equations for an anisotropic medium which depend on the real (ϵ_1) and imaginary (ϵ_2) part of the dielectric constant.

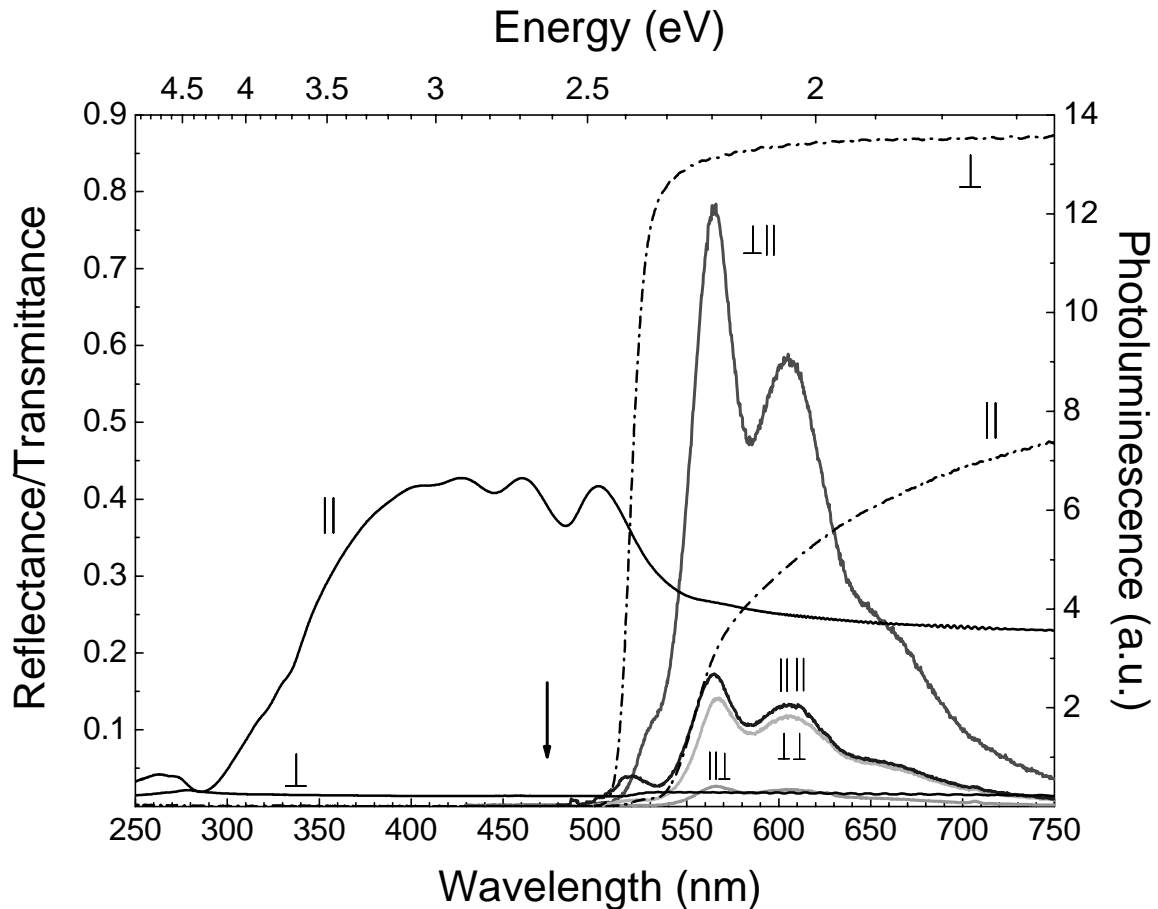


Fig. 1. Polarized reflectance (continuous line) and transmittance (dash line) and PL spectra of highly stretch oriented PPV. The arrow indicates the excitation wavelength ($\lambda_{exc}=458$ nm).

In order to deduce the anisotropic complex dielectric constants at different temperatures, Kramers-Kronig analysis of reflectivity, inversion of R and T spectra using Fresnel equation, and interferometry [12] have been used, taking into account the effects of diffused light. We find that light diffusion reduces the intensity of reflectance and transmittance spectra by about 10%. This effect is due to the formation of surface groves on the sample as a results of the tensile drawing (visible by optical microscopy) at high elongation ratios that considerably enhance light scattering. Note that self-absorption of PL spectra strongly depends on the absolute value of the polarized absorption coefficient at the absorption onset energy, where the determination of the optical constants is most critical. For this reason, a specific care has been taken in deducing the dielectric constant in this spectral region [9].

After correction, the PL spectra show a different shape (Fig. 3) with a different relative magnitude of the peak intensities. Remarkably, at the low wavelength region, in the range 520-530 nm, the two features seen in the (\perp, \parallel) and (\parallel, \parallel) configurations prior to the correction merge into a single peak centered at 517 nm at room temperature (530 nm at 80 K).

The correction also modifies the relative intensity of the PL spectra, where the (\perp, \parallel) component remains more intense than the (\parallel, \parallel) component, while (\parallel, \perp) and (\perp, \perp) reduced in magnitude and become identical (within the error in our measurements and the correction procedure).

The observation that the PL intensity for (\perp, \parallel) configuration after the above correction remains greater than the (\parallel, \parallel) one may seem unexpected. However, a similar intensity ratio (termed pump polarization anisotropy) has been observed also in photoinduced absorption due to charged states in polydiacetylene [13] and in photoconductivity measurements of oriented polyacetylene [4] and PPV [14]. These observations can be understood in terms of charged carrier-induced exciton quenching, as indeed is supported by the high charge photogeneration efficiency and the relatively low PL quantum efficiency measured in these films (<10%). For the \parallel polarization, the small absorption depth results in relatively high concentration of excitations near the sample surface which increases the probability of carrier induced exciton quenching. On the other hand, for \perp polarization the light penetration depth is significantly enhanced (by a factor of ~ 100) and thus the probability for charged carrier-induced exciton quenching is strongly reduced. Enhanced oxidation at the sample surface can in principle also explain the above observation, but our IR measurements (not shown here) have not revealed any mode related to the carbonyl group.

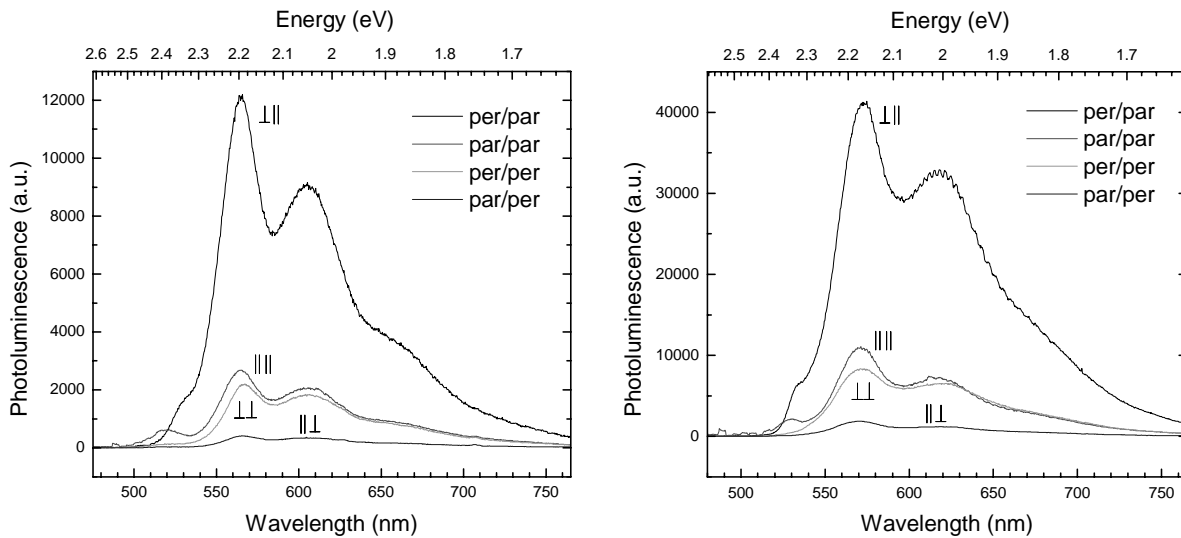


Fig. 2. Polarized PL spectra of highly oriented PPV excited at 458 nm at room temperature (left panel) and 80 K (right panel).

We now address the spectral characteristics of the PL data. The main consequence of the correction of the PL spectra is the increased relative intensity of the band at 517 nm, which raises some difficulty in the assignment of the 0-0 transition. In order to understand the vibronic structure of the spectra, we fitted the oscillator strength for the absorption process ($\int \omega \epsilon_2(\omega) d\omega$), for parallel polarization, with a Frank-Condon progression. Then the fitting was extended to the PL spectra and the corresponding Huang-Rhys parameters were compared. This procedure has been used for the spectra recorded at room temperature as well as 80 K.

The Frank-Condon progression depends on the energies of the phonons (E_{phj}) coupled to the electronic transition, the linewidth (w , assumed identical for all the transitions) and the Huang-Rhys parameters (S_j) which are related to the displacement of the ground and excited states along the normal coordinate system. In the emission process, phonons involved in the transition are those detected by resonant Raman spectroscopy. Raman spectra (not shown here) with excitation at 1064 nm (632.8 nm) show that five modes are excited at 1170 cm^{-1} (1172 cm^{-1}), 1328 cm^{-1} (1330 cm^{-1}), 1546 cm^{-1} (1548 cm^{-1}), 1582 cm^{-1} (1584 cm^{-1}), and 1624 cm^{-1} (1626 cm^{-1}), whose assignment is reported in Table 1 [15]. For the fitting of the vibronic progression, we used the two strongest Raman modes at 1170 cm^{-1} (0.145 eV) and 1582 cm^{-1} (0.196 eV). Even though our excitation lines are not resonant, the sharpening of the electronic transition suggests a negligible variation of their frequencies upon resonant excitation.

TABLE I

Mode assignment	Raman shift
C-C stretching + C-H bending of the phenyl ring	1174 cm^{-1}
C=C stretching + C-H bending of the vinyl group	1330 cm^{-1}
C=C stretching of the phenyl ring	1550 cm^{-1}
C-C stretching of the phenyl ring	1586 cm^{-1}
C=C stretching of the vinyl group	1625 cm^{-1}

Tab. 1. Raman modes for PPV, according to Ref. 15.

It is much more difficult to determine the phonon frequencies for the absorption process. Vibrational modes coupled to excited electronic states can be observed by coherent vibrational dynamics upon ultrafast impulsive excitation [16]. Since these data are not currently available for oriented PPV [17], we assume that the phonon frequencies for the absorption process are the same as those for the ground state.

From the fitting procedure we find that the oscillator strength for the absorption process (Fig. 4) cannot be fully reproduced within the Frank-Condon progression neither at room temperature nor at 80 K, as a broad transition at about 400 nm (hereafter referred as “ghost” band) must be added to obtain a satisfactory fit. This additional band has a different origin than peak II or peak III. The fitting parameters obtained (S_j and the linewidth w) are reported in the inset of the Fig. 4.

The fitting of the emission spectra requires to take into account the strongly dispersive $n^3(\omega)(\hbar\omega)^3$ term, which accounts for the influence of the environment on the emission rate [18]. We could not fit the PL spectra with a unique vibronic progression originating from the 517 nm band, indicating that two distinct radiative states must be involved in the emission process. Even when we tried to fit the PL spectra by arbitrarily fixing the 0-0 transition at 563 nm and by using the same parameters obtained from the absorption fit, the resulting fit of the PL was not satisfactory. Only when the constraint on S_j and w were relaxed, a satisfactory result could be obtained (Fig. 4). In Fig. 4 we also report a simulated Franck-Condon progression with the parameters deduced by the absorption fit and by assuming the 0-0 transition at 517 nm.

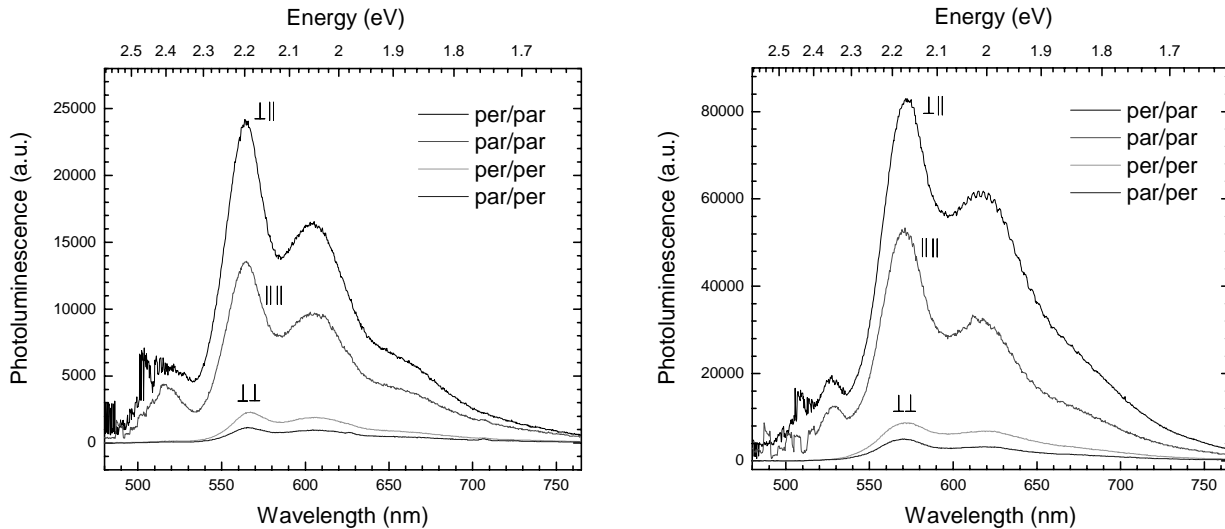


Fig. 3. Polarized PL spectra of highly oriented PPV at room temperature (left panel) and 80 K (right panel) normalized for the same number of absorbed photons and corrected for self-absorption and refractive effects.

Independently of the assignment of the 0-0 transition, the total Huang-Rhys factor ($S=S_1+S_2$) is quite low (absorption: 1.25 and 1.12; emission: 1.48 and 1.31 at room temperature and at 80 K, respectively), confirming the extended electronic delocalization. By comparing both the 0-0 transition energy for the ε_2 (2.47 eV) and the separation between the Raman modes relative to C=C vinyl group and phenyl ring stretching (1545 cm^{-1} and 1624 cm^{-1} , respectively) with the corresponding data for PPV oligomers [11,19], we conclude that the average conjugation length in our sample is greater than 15 repeat units.

Assigning the PL 0-0 transition to the peak at 563 nm implies different S_j values for the emission and absorption processes; this indicates that the two processes are not correlated. This conclusion is also supported by the large Stokes shift that would be inferred from the above assignment. Such a large Stokes shifts are typical of conjugated molecules in polar solvents, [20] where a strong relaxation (often due to flattening of the backbone) of the excited state geometry is induced by interactions with the solvent. However, a strong relaxation is not expected in the solid state. The large apparent Stokes shift could also arise from spectral diffusion of the photoexcited states toward lower energy sites originated at the longest conjugated segments [21]. Although the spectra shown in Fig. 1 as well as those previously reported for similar samples [1] clearly indicate that the distribution of conjugation length in the PPV samples used in this study (the 0-0 absorption peak has HWHM=0.06 eV), is very narrow. The existence of very long conjugated segments (compared with the average conjugation in the PPV sample) is supported by the observation of a PL background in the Raman spectra excited at 632.8 nm [1].

The assignment of the PL band at 517 nm is more problematic. One could conjecture the existence of a bimodal distribution of conjugation length, narrowly peaked at very long conjugation segments (absorbing at 500 nm) and at ~ 6 repeat unit segments (absorbing at 400 nm), a model that has been used for the interpretation of optical spectra of PPV/carbon nanotubes composites [10,15]. In this case, the short conjugation length segments could be responsible for both, the “ghost” absorption at about 400 nm and the emission at 517 nm. However, a bimodal distribution of conjugation lengths does not seem compatible with the high degree of crystallinity [22] and the very sharp spectral features observed in our highly ordered samples.

The data reported here may be understood considering the morphology of our PPV films. These films are composed of crystalline regions (70 % of the volume) and amorphous regions [22]. Within each crystallite (about 20 nm size), chains are packed in an orthorhombic structure with intermolecular separations of either 5 Å (translational periodicity along the b-axis) or 3.9 Å (between benzene ring layers inside the unit cell). Even though the highest interchain coupling is predicted to take place in the cofacial arrangement, such intermolecular separations can allow significant intermolecular interactions [23]. Thus, the two emitting/absorbing states we observed may be correlated to the amorphous and crystalline phases co-existing in the oriented PPV samples. In the amorphous phase, the electronic transitions stem mainly from isolated macromolecules, while in the crystalline phase intermolecular interactions must be considered including the details of the crystalline structure [24]. Recently, a similar interpretation has been proposed for PPV-silica nanoparticles composites, where PL spectra could be understood only when assuming emission from two distinct states [6, 11], where the high-energy emission stems from a molecular state while the low-energy emission stems from aggregates [11]. We then can tentatively assign the main absorption at 500 nm (room temperature) and its vibronic replica to a molecular transition from single chains in the amorphous regions of the sample.

According to recent findings on PPV oligomers [25], the inter-chain interaction can split the single molecular states into allowed-high-energy (H) states and forbidden-low-energy (L) states that may become weakly allowed due to disorder. The H transition can be identified with the “ghost” absorption band observed at about 400 nm. Preliminary results suggest that L may be underneath the 0-0 absorption transition [9]. According to this interpretation, the emission at 563 nm would arise from a molecular state occupied through spectral migration while the weak emission at 517 nm from the weakly allowed L state.

Finally, we remark that the description of highly oriented and ordered PPV samples where the electron delocalization is enhanced and the distribution of conjugated lengths is narrow, as inferred from the optical data reported here, requires advanced theoretical tools. Even though a quantum chemical approach, which deals with relatively short oligomers, provided successful hints for the assignment of optical transition in PPV [1], it may not be sufficiently powerful for a complete description of this system. Theoretical methods applied to inorganic semiconductors may address the three dimensional character of the polymeric system [26,27]. Even though these models do not include self-trapping due to the electron-phonon coupling, they point out the importance of the dielectric screening of the medium, the role of the crystallographic structure, as well as the spatial extensions of excitons. According to [27] the absorption spectrum of isolated PPV chains is modified by the presence of the intermolecular interactions. A dark state appears at energies slightly below the allowed transition, in agreement with the relatively low PL quantum yield of PPV as compared to the

one in its substituted derivatives. Moreover, charge transfer states, due to the presence of two non-equivalent chains in the crystallographic cell, appear at high energies and may be responsible for the “ghost” band detected in our spectra. The exciton binding energy in PPV is also strongly affected by both, the dielectric screening and the intermolecular interactions. The dielectric constant, in particular its perpendicular components[28], strongly reduces the exciton binding energy. For crystalline PPV, the calculated binding energy is reduced due to the 3D effects from 0.7 eV to 0.2 eV [27], a value close to the one proposed for these samples (<0.1 eV) [2].

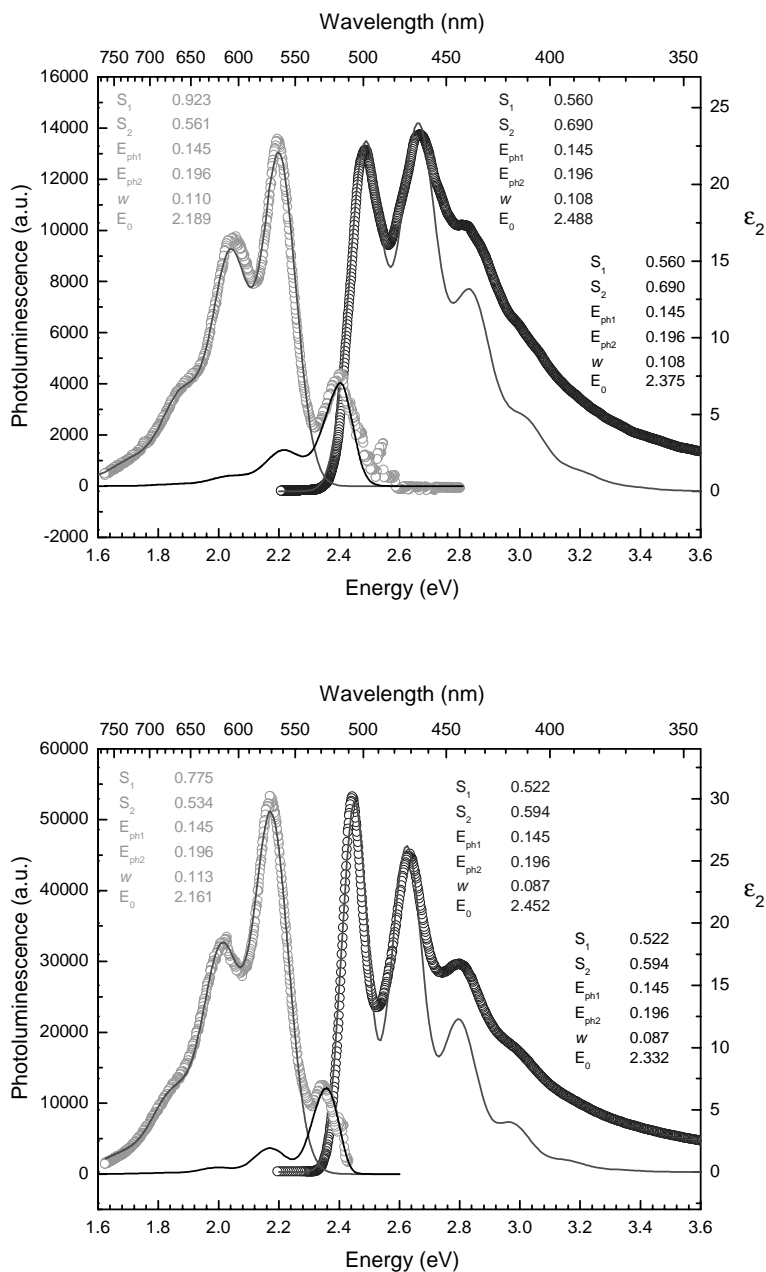


Fig. 4. Frank-Condon fitting of || absorption and (||,||) PL spectra at room temperature (top) and 80 K (bottom). Fitting parameters are reported in the insets.

4. Conclusions

We present a detailed characterization of the polarized optical and emission properties of highly oriented PPV samples at various temperatures derived from the analysis of polarized transmission, reflectance, and PL spectra. The analysis of the data requires corrections due to PL self-absorption and refractive losses in the various measuring polarization configurations. A Frank-Condon analysis indicates the existence of two distinct contributions to the PL emission that may originate from the presence of two structural phases in our PPV samples, i.e. an amorphous phase and a crystalline phase where intermolecular interactions cannot be neglected.

Acknowledgments

We thank Dr. A. Mikhailovsky for his help in the photoluminescence measurements. We are also grateful to Prof. A. J. Heeger for ongoing interactions. This work was supported by the National Science Foundation under DMR 0096820.

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