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

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Abstract

We report on the anisotropic reflectance (R), transmittance (T) and 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, being higher when the pump is polarized perpendicular to the polymer chain orientation. Independently of the pump polarization, we find that the PL emission spectra are mainly polarized along the polymer chain direction. The PL spectra have been corrected both for the number of absorbed photons and for self-absorption of the emitted light. Frank-Condon analysis of the oscillator strength for absorption and corrected emission spectra suggest that two different "chromophores" contribute to the optical properties.

Keywords: Poly(phenylene vinylene), Optical absorption and emission spectroscopy, Infrared and Raman spectroscopy

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1. Introduction

Poly(p-phenylene-vinylene) (PPV) and its substituted derivatives are widely used in optoelectronic devices. The chemical and physical properties of these materials have 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 its various features have become clearer only recently [1,2]. This has become possible due to the availability of highly oriented samples, which enabled the investigation of the intrinsic optical properties of these anisotropic systems [1,3]. Theoretical models proposed for the assignment of the absorption properties of PPV and its derivatives, either developed within quantum-chemical or solid-state physics approaches, are mainly based on the assumption of isolated molecules. Even though this approximation may be suitable for describing the absorption properties [4], recent findings on the emission of PPV derivatives suggest that intermolecular interactions may take place in these macromolecular systems both in solution [5] and in silica nanoparticles composites [6]. In order to understand in detail the photophysical properties of PPV, we started an extended investigation of the polarized photoluminescence spectra of highly stretch-oriented PPV, a system previously used for a fine 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 orientation direction) provide additional information for an accurate assignment of the above spectroscopic features.

Moreover, in order to evaluate the intrinsic emissive properties, a detailed knowledge of the refractive index and the absorption coefficient dispersion for parallel and perpendicular polarization is needed for determining the number of absorbed photons and the emission losses (e.g. correction due to self-absorption of the PL emission). We will therefore report on the temperature dependence of the polarized reflectance, transmittance and intrinsic PL properties of highly stretch-oriented PPV.

2. Results and Discussion

Fig. 1 shows the room temperature polarized reflectance, transmittance and photoluminescence spectra of thick (14 μm and 18 μm) free-standing PPV samples oriented by tensile drawing with an elongation ratio of 5. The parallel (||) reflectance spectrum shows the electronic transition (the π-π^* transition) followed by a well resolved vibronic progression. The purely electronic transition (0-0 where

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first number refers to the ground state phonons involved in the transition and the second to those in the excited state) is located at very low energy (500 nm), thus indicating a very long conjugation length in these samples. At lower wavelength, a shoulder at about 340 nm (usually called peak II) assigned to conjugation chain ends [1] is observed in addition to a broad transition at about 260 nm (peak III).

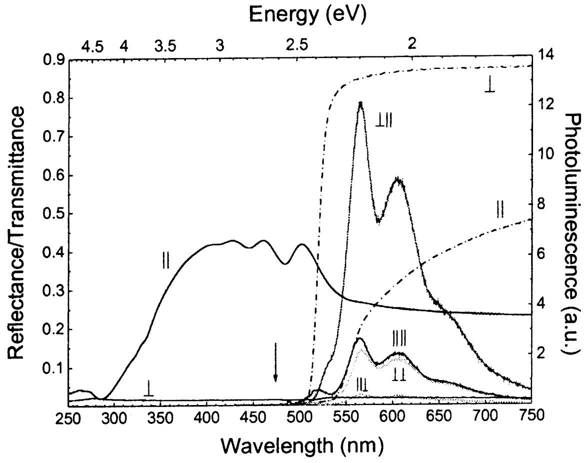

Fig. 1. Polarized reflectance (continuous lines) and transmittance (dash lines) and PL (in the low energy region) spectra of highly oriented PPV. The arrow indicates the excitation wavelength (λ_{exc}=458 nm).

The perpendicular ($\perp$) reflectance spectrum is almost flat down to 280 nm where the typical perpendicular component of peak III is detected [1,3]. The intrinsic $\perp$ component of the optical spectra in the visible and near ultraviolet is masked by the weak but unavoidable misalignment of the chain orientation around the stretching direction. The misalignment induces an apparent $\perp$ component of the dipole transition moment due to the projection of the $\parallel$ one through $\sin\phi$, ϕ being the misalignment angle [4]. Even though ϕ is estimated in high quality samples to be very low (about 3°), the $\perp$ absorption coefficient due to misalignment scales as $\sin^2\phi$, thus giving a contribution of 0.005 of the parallel one. As a matter of fact a comparable value (0.003) to the experimental anisotropy observed at the π-π^* transition region (see below for details). Optically thick samples used in this work do not allow a direct analysis of the transmission spectra below 500 nm. However, we point out the remarkable difference in the onsets of absorption for the two polarizations in the spectral region that overlaps with the high energy PL emission peaks [7]. These observations suggest that the dispersion of the refractive index and absorption coefficient as well as their dependence on polarization strongly affect the measured PL emission spectra.

In the PL polarized measurements, the four combinations of excitation and emission are denoted with the symbol (a,b) where the first symbol denotes the excitation polarization ($a=\perp$ or $\parallel$) while the latter for emission polarization ($b=\perp$ or $\parallel$). 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 structurally disordered PPV, indicating again an unusually long conjugation length in our samples with respect to those reported in the literature [8]. In addition, in this spectrum, a shoulder can be identified at 530 nm. For all other polarization combinations, the results of the PL data show much lower PL intensities and similar spectral features apart of the behavior in the 500-540 nm spectral region. Here, in the ($\parallel$,$\parallel$) PL spectrum a well defined peak at 520 nm is detected, while for the remaining polarizations ($\parallel$,$\perp$ and $\perp$,$\perp$) no clear evidence of such a transition is detectable underneath the tail of the main emission peak.

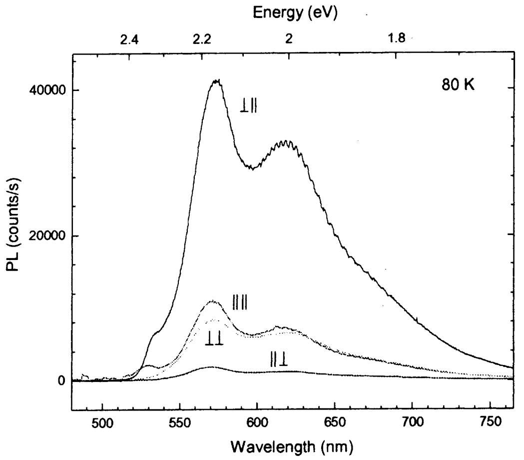

Fig. 2. Polarized PL spectra of highly stretch oriented PPV. Excitation at 458 nm, T=80 K.

Upon lowering the temperature down to 80 K the signal intensity increases and the PL spectra shift to longer wavelength (560 ⇒ 570 nm; 602 ⇒ 620 nm for the main peaks) indicating an extension of π-electrons delocalization (Fig. 2). The relative intensity of the four polarization combinations is almost unchanged. Varying the temperature slightly affects the transition linewidth. At 80 K, the feature at about 530 nm is better defined while the main peaks are broadened with respect to the room temperature data. At first glance, we could assign the 0-0 transition to the main PL peak at 560 nm (at room temperature). However, the presence of the weak features at 520/530 nm in the PL spectra does not support this interpretation. Then, in order to carefully determine the assignment of the PL spectral features, it is essential to normalize these spectra to the same number of absorbed photons as well as to correct for the self-absorption and reflectivity losses. The correction formula [9] was deduced from the Fresnel equations for an anisotropic medium whose main ingredients are the real (ε_1) and imaginary (ε_2) part of the dielectric constant. Anisotropic complex dielectric constant at different temperatures were determined by Kramers-Kronig analysis of reflectivity, inversion of R and T spectra through Fresnel equation, and a novel interferometric method, taking into account the effects of diffused light [9].

After correction, the PL spectra show a different shape (Fig. 3) with a different distribution of intensities among the features of the spectra. Remarkably, the high energy features observed for different polarizations in the range 520-530 nm for $(\perp,\parallel)$ and $(\parallel,\parallel)$ spectra, becomes a unique peak centered at 517 nm (530 nm) at room temperature (80 K) for both polarization configurations. It is also interesting to compare the intensities of the different PL spectra. The $(\perp,\parallel)$ component is still more intense than the $(\parallel,\parallel)$ one while $(\parallel,\perp,)$ and $(\perp,\perp)$ are identical (within the error in our measurements and correction procedure) and have also a much lower intensity than the others. The relative intensity for the different PL polarization configurations will be discussed in a forthcoming publication [9].

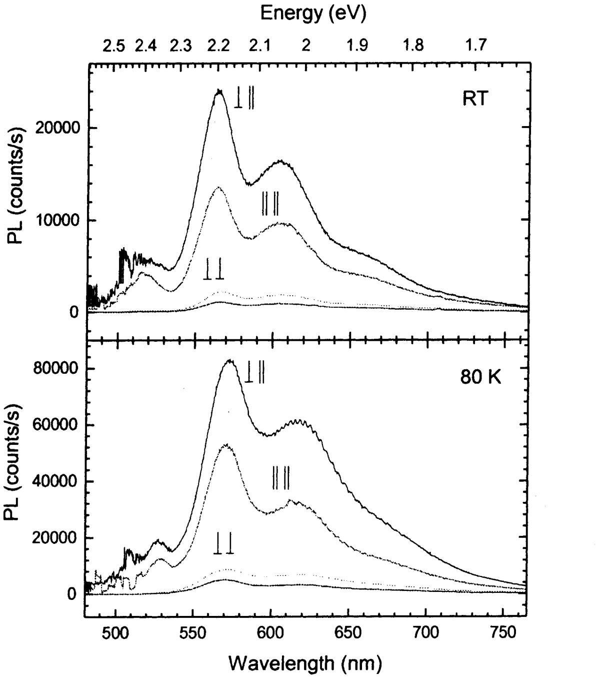

Fig. 3. Room temperature (upper panel) and 80 K (lower panel) polarized PL spectra of highly stretch oriented PPV corrected for the same number of absorbed photons and for self-absorption effects.

The main consequence of the correction of 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 adopted the following approach: first we fit with a Frank-Condon progression the oscillator strength for the absorption process ($\int \omega\varepsilon_2(\omega)d\omega$) for parallel polarization. Then the fitting is extended to the PL spectra and the Huang-Rhys parameters obtained for absorption and emission processes are compared. This work is done both for spectra recorded at room temperature and 80 K.

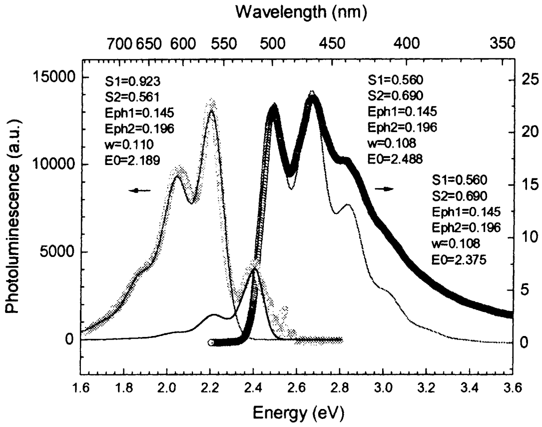

Fig. 4 Frank-Condon fitting of $\parallel$ absorption and $(\parallel,\parallel)$ PL spectra at room temperature. Fitting parameters are reported in the insets.

Ingredients of the Frank-Condon progression are the energies of phonons coupled to the electronic transition (E_{phj}), the linewidth (w, identical for all transitions) and the Huang-Rhys parameters (S_j), which are related to the displacement of the ground and excited states along the coordinate describing the normal modes involved. In the emission process, phonons involved in the transition are those detected in the resonant Raman spectrum. Raman spectra with excitation at 1064 nm (632.8 nm) (not reported here) show that five modes are excited at 1170 (1172), 1328 (1330), 1546 (1548), 1582 (1584), and 1624 (1626) cm^{-1}. For the fitting of the vibronic progression, we used the two strongest Raman modes at 1170 (0.145 eV) and 1582 cm^{-1} (0.196 eV). It is much more difficult to independently determine the phonon frequencies for the absorption process. For this reason, as a first approximation, we use here the same phonon frequencies as for the ground state.

The oscillator strength for the absorption process (Fig. 4) cannot be fully reproduced within the Frank-Condon progression neither at room temperature or 80 K as a broad transition at about 400 nm ('ghost' band) must be added to obtain a satisfactory fit. This additional band must not be confused with peak II or peak III.

The fitting of the emission spectra require to take also into account the strongly dispersive $n^3(\omega)(\hbar\omega)^3$ terms, which provides the influence of the environment on the emission rate [10]. It is not possible to fit the PL spectra with a unique vibronic progression originating from the 517 nm band. This fact indicates that two distinct emitting states are involved in the process. We then tried to fit the PL spectra by fixing arbitrarily the 0-0 transition on the 568 nm band

and by using the same parameters obtained from the absorption fit. Even in this case the fit was poor. Only without constraints on S_j and w a satisfactory result could be obtained (Fig. 4). In the same figure, we also reported a fit with parameters deduced by absorption and by assuming the 0-0 transition at 517 nm. The difference observed for the S_j in the emission (0-0 at 568 nm) and absorption process suggests the two processes are not correlated. This is also confirmed by the large apparent Stokes shift observed (if the band at 517 nm is neglected). The large apparent Stokes shift could be assigned to spectral diffusion of the photoexcited states to lower energy sites, represented by very long conjugated segments [11].

The existence of two emitting and absorbing states in highly oriented PPV films needs a careful analysis. Data may be interpreted either within a one-dimensional single chain model or a three-dimensional model in which effects of intermolecular interactions have to be considered.

Assuming the single molecule approach with extended π-electron delocalization along a one-dimensional system [2], the following interpretation is possible. Main peak in $\varepsilon_2 \parallel$ spectrum at 500 nm is due to an inter-band transition for a one-dimensional system. Its asymmetric lineshape is in agreement with previous findings [12]. An excitonic transition can be tentatively assigned to a very weak spectral feature observed in the transmission spectra [7], corresponding to the field-dependent peak observed in photoconductivity measurements and assigned to field-induced exciton dissociation [2]. Emission at 517 nm arises from the exciton while emission at 568 nm from the "ghost" absorption band at about 400 nm.

Assuming the three dimensional coupled chain model, the two emitting/absorbing states may be correlated to the amorphous and crystalline phases co-existing in the oriented PPV samples [13]. In the amorphous phase, the electronic transitions stem mainly from isolated macromolecules, while in the crystalline phase intermolecular interactions must be considered. Recently, a similar observation has been reported for PPV-silica nanoparticles composites where PL spectra could be understood only by assuming the emission arising from two distinct states, one of which was attributed to aggregates [6]. 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. In the crystalline regions, the inter-chain interaction perturbation split the single molecule states into an allowed-high-energy (H) and forbidden-low-energy (L) transitions. The L transition is weakly allowed due to disorder. The H transition is the "ghost" absorption band at about 400 nm needed to reproduce the $\varepsilon_2 \parallel$ spectrum in addition to the molecular state. We tentatively suggest that L may be underneath the 0-0 transition [7]. According to this interpretation, emission at 517 nm arises from a molecular state occupied through spectral migration while weak emission at 568 nm arises from weakly allowed L state.

In order to definitively determine the correct interpretation, further measurements such as site-selective or time-resolved PL are needed (currently in progress).

4. Conclusions

We present a detailed characterization of the polarized optical and emission properties of highly oriented PPV at various temperatures. Polarized transmission, reflectance, and PL spectra indicate the presence of additional states in the HOMO-LUMO energy gap. The emerging spectral structure is complicated, and its analysis requires full account of the PL self-absorption losses as well as an exact determination of the number of absorbed phonons in the different polarization configurations.

Acknowledgments

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