

# 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

## 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  $\mu\text{m}$  and 18  $\mu\text{m}$ ) free-standing PPV samples oriented by tensile drawing with an elongation ratio of 5. The parallel ( $\parallel$ ) reflectance spectrum shows the electronic transition (the  $\pi$ - $\pi^*$  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).

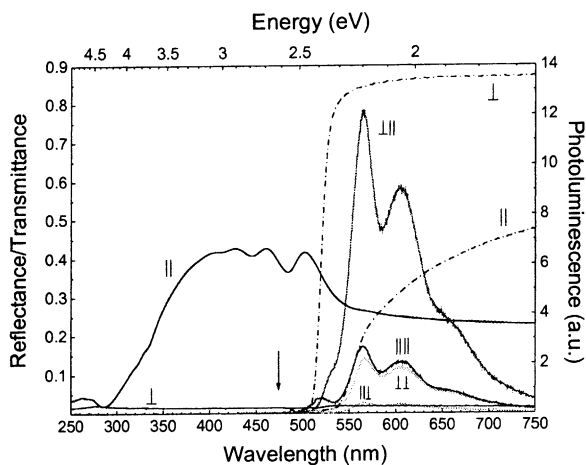


Fig. 1. Polarized reflectance (continuous lines) and transmittance (dash lines) and PL (in the low energy region) spectra of highly oriented PPV. The arrow indicates the excitation wavelength ( $\lambda_{exc}=458$  nm).

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  $\sin\phi$ ,  $\phi$  being the misalignment angle [4]. Even though  $\phi$  is estimated in high quality samples to be very low (about  $3^\circ$ ), 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  $\pi-\pi^*$  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.

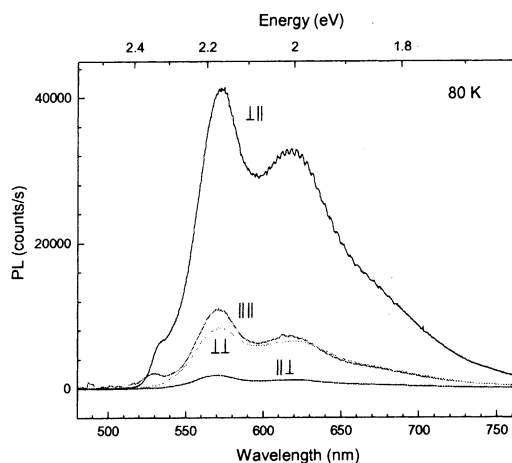


Fig. 2. Polarized PL spectra of highly stretch oriented PPV. Excitation at 458 nm,  $T=80$  K.

Upon lowering the temperature down to 80 K the signal intensity increases and the PL spectra shift to longer wavelength ( $560 \Rightarrow 570$  nm;  $602 \Rightarrow 620$  nm for the main peaks) indicating an extension of  $\pi$ -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

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