

Highly polarized luminescence from oriented conjugated polymer/ polyethylene blend films

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Highly Polarized Luminescence from Oriented Conjugated Polymer/Polyethylene Blend Films**

By Christoph Weder,* Christian Sarwa, Cees Bastiaansen, and Paul Smith

Since the early 1990s, much research has focused on the photoluminescence (PL) and electroluminescence (EL) properties of conjugated polymers, because of their potential application as an emitting layer in EL devices.^[1] The introduction of uniaxial molecular orientation into films of luminescent polymers was naturally found to yield structures that emit polarized light.^[2–13] Such polarized light-emitting devices (LEDs) are of particular practical interest if the current limitations of these devices with respect to lifetime and stability can be resolved, since polarized light sources may facilitate the fabrication of brighter liquid-crystal displays (LCDs).

Rather surprisingly, the photoluminescence properties of oriented, conjugated polymers have attracted substantially less attention, especially from an application point of view in polymeric sheet polarizers. Polarized PL has mainly been used to characterize the orientation of the polymer and/or to elucidate its electronic structure. Isotropic luminescent layers were previously used to enhance the visual performance of LCDs, especially with respect to brightness.^[14] Anisotropic luminescent films may combine two separate features (i.e., polarization of light and bright color) that in current LCDs are performed by separate optical components. A substantial improvement in the brightness of such devices is expected even in a very simple device in which one polarizer (analyzer) and the color filter are replaced by a single, oriented photoluminescent film. Moreover, more sophisticated devices with further enhanced brightness and light efficiency can readily be envisaged.

Oriented films of conjugated polymers have been prepared by various techniques, including the Langmuir–Blodgett (LB) deposition technique,^[2,3] mechanical deformation^[4,5] or rubbing^[6] of the pure conjugated-polymer layer, and the deposition of the latter onto a highly aligned orientation layer, such as poly(tetrafluoroethylene)^[7,8] or poly(imide).^[9] However, the degree of orientation and, hence, the dichroic ratios obtained with these methods are usually only modest, typically well below 10 and, therefore, limit the device characteristics with respect to contrast and resolution.

A different, promising technique is the tensile deformation of host-guest systems, in which the guest molecules

Tables of Contents
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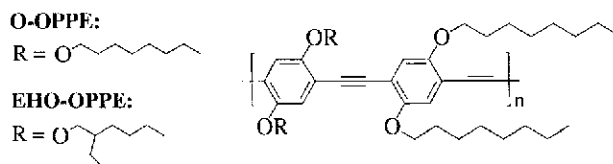
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adopt the orientation of the host. This concept has been used in the past for the preparation of polarized luminescent films based on blends of poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) and ultra-high molecular weight polyethylene (UHMW-PE),^[10,11] and for blends of poly(*p*-phenylphenylenevinylene) and various oligomeric model compounds and polystyrene or polyethylene.^[12,13] While the latter systems only revealed relatively modest anisotropies due to low draw ratios,^[12,13] absorption experiments on the MEH-PPV/UHMW-PE blends revealed high dichroic ratios.^[10,11] Polarized emission experiments were also reported for this system but, unfortunately, linear polarized light was used for excitation and, consequently, the performance of these drawn, photoluminescent films when excited with unpolarized light (i.e., the most relevant situation from a technological point of view) cannot be deduced from these experimental data. In fact, it can be argued that the polarized luminescence from these films, at least to some extent, reflects rotational mobility of the excited molecules and energy transfer processes,^[12,13] rather than the orientation of the conjugated polymer. This latter hypothesis appears consistent with the observation of higher dichroic ratios measured for emission, when compared to absorption.^[10,11]

With the above described relevance of photoluminescence for LCD applications, and in order to explore and advance materials properties to the limits of polarized luminescence, we have undertaken a systematic investigation of the structure-property relationships in oriented films based on blends of different poly(2,5-dialkoxy-*p*-phenyleneethynylene)s^[15,16] (PPEs) and UHMW-PE. In this study, the influence of the various parameters, such as the molecular weight of the conjugated polymer, the structure of the side chains, the composition of the blends, and the draw ratio of the blend films, were investigated, resulting in materials with extremely high polarization anisotropies in excess of 1:70.^[17] In addition, our experimental results suggest a new model for the orientation of the PPE/UHMW-PE blends, which contrasts the mesoepitaxial crystal growth process that has previously been proposed for the orientation of MEH-PPV/UHMW-PE blends.^[10]

PPEs exhibit an ideal matrix of properties with respect to the preparation of oriented blends:^[15-20] i) PPEs have been shown to exhibit large PL quantum efficiencies both in solution and the solid state, and were successfully used as the emission layer in EL devices; ii) the extremely stiff, linear polymer backbone enables maximum orientation, while high solubility and, therefore, ease of processibility can be induced by substitution with, e.g., alkyloxy side chains. Thus, we elected to use two different PPE derivatives for this work: O-OPPE, substituted with linear alkyloxy side chains only, and EHO-OPPE, derivatized with linear and sterically hindered alkyloxy groups in an alternating pattern (Scheme 1). The O-OPPE sample had an \bar{M}_n of 10 000 g mol⁻¹, and two different EHO-OPPE samples with \bar{M}_n of 10 000 and 84 000 g mol⁻¹ were used. The synthesis of



Scheme 1. Molecular structure of the poly(2,5-dialkoxy-*p*-phenyleneethynylene)s under investigation.

these polymers is described elsewhere.^[15,18] Films based on blends with contents of 1, 2, and 25 % w/w of PPE in UHMW-PE were prepared as described in the experimental section. The pristine, solution-cast films were subsequently drawn at temperatures of 90–120 °C, i.e., in the narrow temperature window above the glass transition of the PPE guest, and below the melting point of the polyethylene, to a series of different draw ratios ($\lambda = \text{final length/initial length}$) ranging from 10 to 80. The thickness of drawn films with the maximum draw ratio of 80 was in the order of 2 μm and, depending on the concentration of the PPE, the optical densities of these films related to the absorption of the conjugated polymer were in the range 0.6–1.7 for the polarization direction parallel to the drawing direction.

The anisotropic photophysical behavior of these drawn films was studied employing polarized UV-vis absorption and steady-state PL spectroscopy. In all PL experiments unpolarized light was used for excitation. In order to quantify the anisotropic optical characteristics of the drawn films, we determined the dichroic ratios, defined for absorption (DR_A) and emission (DR_E) as the ratio between the respective spectra measured with polarization parallel and perpendicular to the drawing direction. In our evaluations, we integrated the spectra because the integrals are directly related to the energy of the relevant electronic transitions and, hence, reflect the underlying physical processes best. However, from the physiological point of view (c.g., brightness of a device as perceived by the human eye) the absolute maxima are also of interest and therefore we have also included some values for the dichroic ratio expressed as the ratio of the absolute maxima of the respective spectra (of course the fundamental reason why different dichroic ratios are obtained for the two evaluation methods is the difference in spectral shape for the two polarizations, as seen from the inset in Fig. 1c).

Most noteworthy, highly polarized absorption and emission were observed for the drawn films, as visualized for PL in Figure 1 for a film containing 2 % EHO-PPE ($\bar{M}_n = 84\,000 \text{ g mol}^{-1}$) with a draw ratio of 80. The polarized emission spectra of this film, shown in Figure 1c, reflect state of the art optical anisotropy, characterized by dichroic ratios of 22 (integrals) and 72 (maxima). The influences of the draw ratio, the molecular weight of the PPE, the structure of the side chains, and the composition of the blends on the dichroic ratio are summarized in Figure 2. Similar dichroic ratios were determined for absorption and emission experiments, suggesting that no molecular reorientation, and no

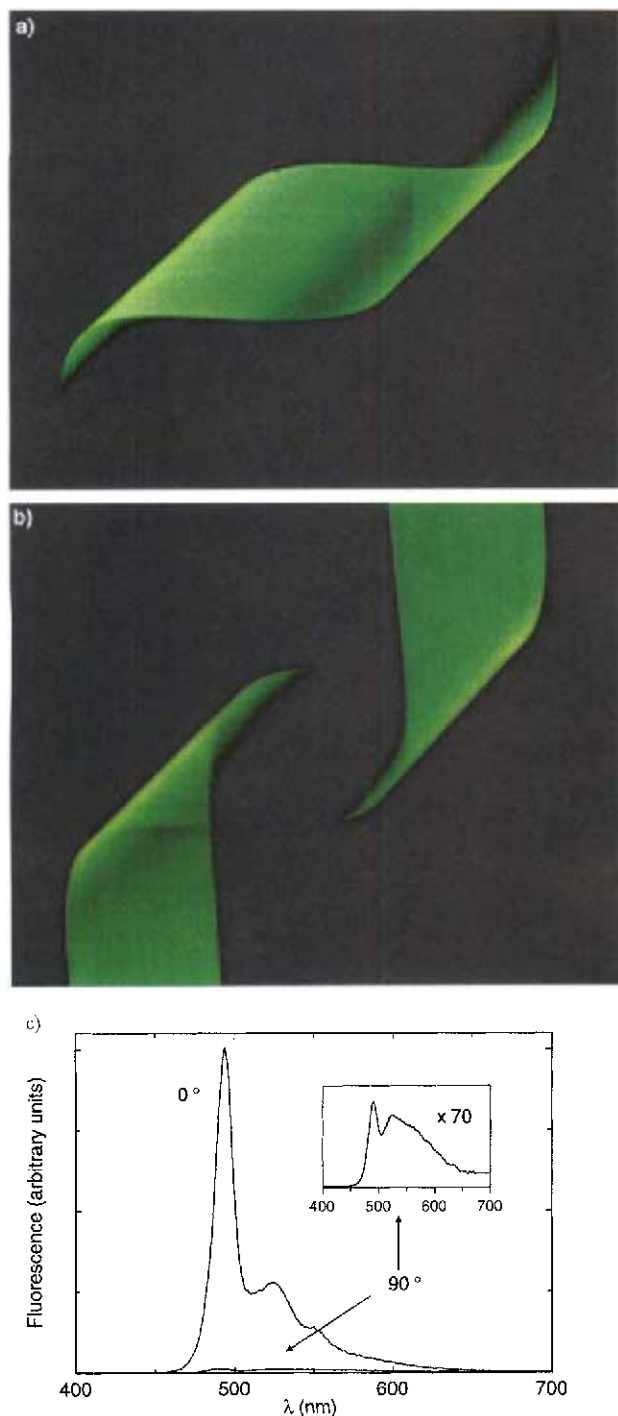


Fig. 1. Polarized photoluminescence from an oriented film ($\lambda = 80$) of 2% EHO-OPPE/UHMW-PE blends. a) Twisted film shown through a linear polarizer with its polarization axis oriented horizontally. b) Twisted film shown through a linear polarizer with its polarization axis oriented vertically. c) PL spectra recorded for light emission parallel (0°) and perpendicular (90°) to the drawing direction.

energy transfer processes, which could eventually limit the dichroic ratio, are present.^[13,21] The significant influence of the draw ratio on the dichroic ratio in all systems under investigation is characterized by an initial linear increase of

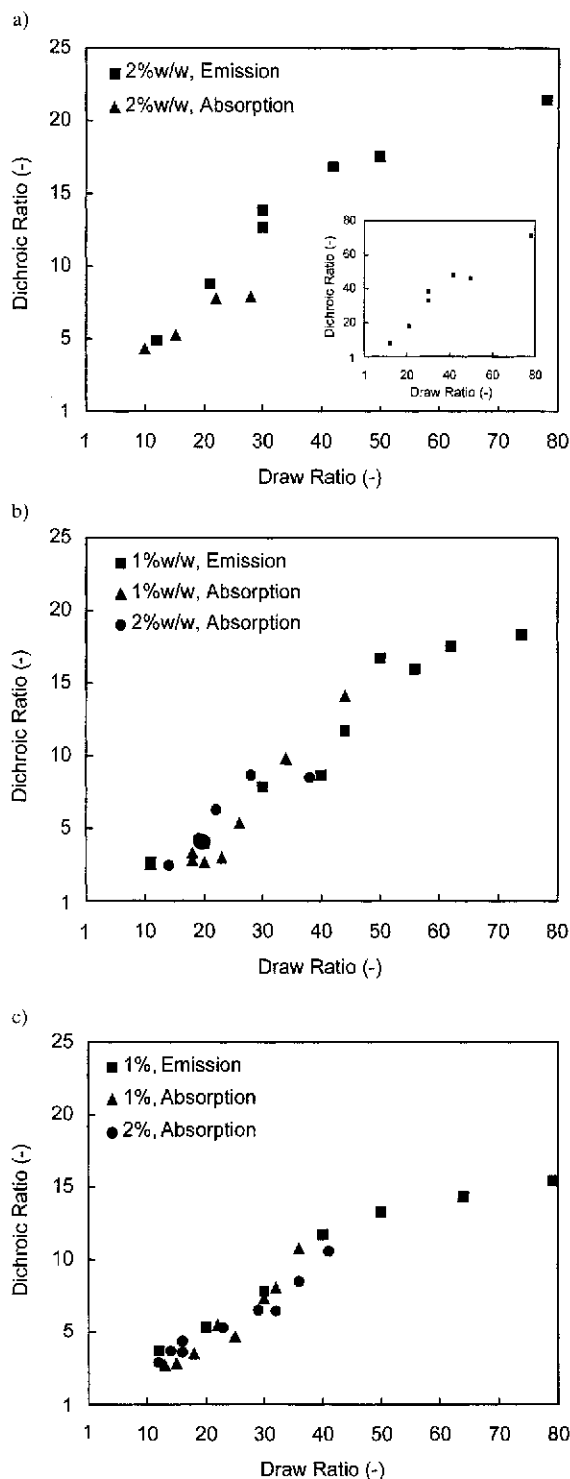


Fig. 2. Dichroic ratio (measured in absorption and emission), calculated from the integrals of the respective spectra, as a function of draw ratio, for films containing 1 or 2% PPE. a) EHO-OPPE with an \bar{M}_n of $84\,000\text{ g mol}^{-1}$; as a comparison, the inset shows the peak maxima of the respective spectra. b) EHO-OPPE with an \bar{M}_n of $10\,000\text{ g mol}^{-1}$. c) O-OPPE of a \bar{M}_n of $10\,000\text{ g mol}^{-1}$.

dichroic ratio, with a tendency to level off at $\lambda > 50$. Comparing the properties of blends based on EHO-OPPE with \bar{M}_n of $10\,000\text{ g mol}^{-1}$ and $84\,000\text{ g mol}^{-1}$ (Figs. 2a and 2b),

we find that the molecular weight of the conjugated polymer has a significant influence on the orientation. The high molecular weight material exhibits maximum orientability, which is understood in terms of its more favorable molecular aspect ratio. It was observed that the orientation of the PPE was not influenced by the blend composition in the concentration regime of 1–2 % (w/w) of the PPE. However, preliminary experiments with films containing 25 % (w/w) EHO-OPPE, showed a good drawability ($\lambda_{\text{max}} = 60$), but a lower dichroic ratio compared to the more diluted blends. When comparing EHO-OPPE and O-OPPE (Figs. 2b and 2c), the nature of the side chains was found to influence the orientation only at high draw ratios. Because higher orientations were obtained for PPEs derivatized with sterically hindered side chains, we conclude, that *linear* side chains might strongly interact with the PE matrix, leading—due to the PPE molecular structure—to a somewhat limited alignment.

In order to investigate the phenomena occurring during the orientation process in more detail, we have compared the emission spectra of the PPEs in various states of matter, i.e., undrawn and drawn films of the PPE/UHMW-PE blends, pure amorphous PPEs spincoated from CHCl_3 , and a dilute solution of the pure PPEs in CHCl_3 .^[15] Representative spectra for EHO-OPPE (\overline{M}_n of 10 000 g mol^{-1}) are shown in Figure 3. The emission spectrum of the *undrawn* blend is relatively broad and only poorly resolved; it is comparable to the one of the pure, amorphous or partially crystalline film of the conjugated polymer (see Fig. 3a). By contrast, the emission spectrum for the *drawn* blend is fairly narrow, shows well resolved vibronic features, and virtually matches the spectra of the pure PPE in solution (Fig. 3b). This most remarkable behavior suggests different structures for the pristine and the drawn blends. In pristine blends, a phase separation between the PPE and UHMW-PE appears to occur, and consequently their photophysical properties are similar to those of the pure PPE. In drawn films, however, the PPE behaves as if it was molecularly dispersed or dissolved in a hydrocarbon matrix, and, therefore, the photophysical properties are comparable to those of a dilute solution (note, however, that a *true* molecular dispersion or solution is, of course, highly unlikely for thermodynamic reasons, although the photoluminescent characteristics of a true solution are mimicked at least to some extent). The fact that we observed a significantly enhanced brightness for the PL of oriented PPE/UHMW-PE films, when compared to the pristine films, corroborates this view, since the PL quantum efficiency of the PPE in solution was found to be more than twice the efficiency of an amorphous film.^[15]

Consistent with the above spectroscopic observations, we found in wide angle X-ray and electron diffraction experiments on films containing 25 % w/w EHO-OPPE that undrawn blends display reflections of both PPE and PE crystal structures, whereas the drawn blends revealed solely those associated with the polyethylene crystalline unit cell.

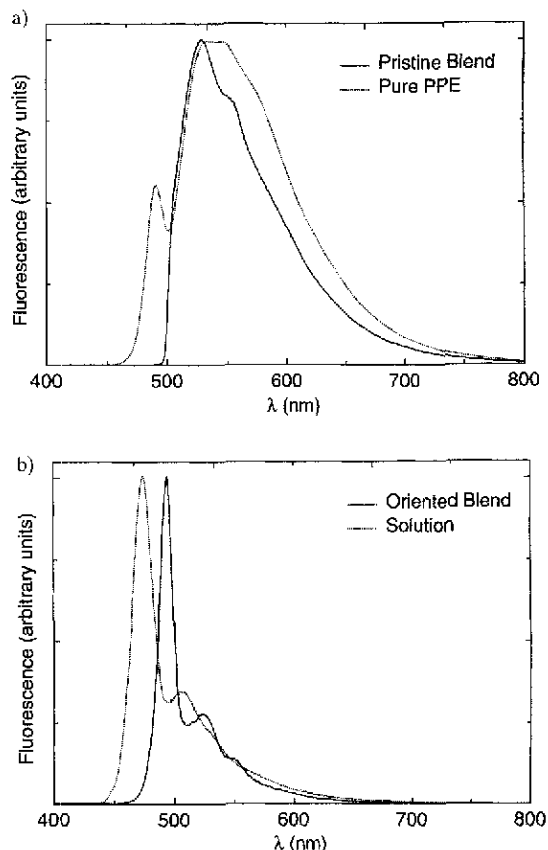


Fig. 3. a) Comparison between the PL spectra of a film of pure EHO-OPPE and an *unoriented* EHO-OPPE/UHMW-PE film. b) Comparison between the PL spectra of an EHO-OPPE solution in CHCl_3 and an *oriented* EHO-OPPE/UHMW-PE film.

Hence, we suggest for the present polymer blend that the structure changes upon drawing from a phase-separated system to a structure in which the PPE phase contains crystals which are extremely small or contain defects or, in fact, that the dispersed PPE is amorphous. Nevertheless, irrespective of the exact structure of the PPE phase, the conclusion remains valid; the blends behave like an *apparent* molecular dispersion of the PPE guest within the PE host. The exact structure of the PPE phase in the drawn blends is currently being investigated and will be reported in a future publication. Thus, it appears that phase separation cannot be avoided during the processing of the pristine blends from solution, but tensile deformation may be employed to optimally disperse and orient the conjugated polymer in the UHMW-PE host. The structural change observed in this work is clearly in contrast to the mesoepitaxial crystal growth process that has previously been proposed for the orientation of MEH-PPV/UHMW-PE blends,^[10] but is, apart from a different orientation mechanism, widely consistent with the results obtained for tensile deformed blends of polypropylene and dichroic dyes, the use of which as new absorption polarizers has recently been proposed.^[22–24]

Finally, it is worth noting that the oriented films were found to be extremely stable: the films could be stored under ambient conditions (exposure to air and light) for months without any noticeable change to their properties. We attribute the latter, most relevant, phenomenon to the encapsulation of the conjugated polymer in the highly crystalline PE matrix.

In conclusion, we have shown that gel processing and subsequent tensile deformation of blends of different PPEs and ultra-high molecular weight polyethylene leads to an outstanding orientation of the conjugated polymer guest, resulting in state of the art polarized photoluminescence and absorption of the prepared films. Maximum orientation and polarization is obtained when the conjugated guest is of high molecular weight and derivatized with sterically hindered, rather than only linear, side chains. The orientation process used appears to induce a transformation of an initially phase-separated system into an apparent molecular dispersion of the conjugated polymer guest in the PE host.

Experimental

O-OPPE, EHO-OPPE, and HMW EHO-OPPE used in this work were prepared according to previously published procedures [15,18]. UHMW-PE (Hostalun Gur 412) was obtained from Hoechst AG.

Thin films were prepared by casting a solution of the PPE (5–125 mg) and UHMW-PE (0.5 g) in xylene (50 mL) (dissolution at 130 °C after degassing the mixture in vacuum at 25 °C for 15 min) into a petri dish 11 cm in diameter. The gels were dried under ambient conditions for 24 h. All resulting blend films had a homogeneous thickness of about 70 μm. The films were drawn at temperatures of 90–120 °C on a thermostatically controlled hot shoe. Draw ratios were calculated from the displacement of distance marks printed on the films prior to drawing.

Polarized UV-vis spectra were recorded with a Perkin Elmer Lambda 900 instrument, fitted with motor driven Glan-Thomson polarizers. PL spectra were recorded on a SPEX Fluorolog 2 (Model F212), using unpolarized light (350 nm) for excitation and a Glan-Thomson polarizer on the detector side. For the photophysical experiments, the polymer films were sandwiched between two quartz slides, applying a silicon oil fluid in order to minimize light scattering at the film surfaces. The remaining scattering effects were compensated in the absorption measurements by subtracting the spectra of pure UHMW-PE films of comparable draw ratio and thickness.

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Imaging Polymers with Supercritical Carbon Dioxide**

By Christopher K. Ober,* Allen H. Gabor,
Paula Gallagher-Wetmore, and Robert D. Allen

The ability to quickly and reproducibly form nanostructures in surfaces and polymer thin films has been made possible by the invention of new lithographic techniques. Motivating the development of these new, more efficient processes is the need to create ever smaller structures for integrated microelectronic devices, micromachines, and biotechnology, including processes for combinatorial chemistry. Three recent examples of new lithographic techniques include:

1. stamping of self-assembled monolayers on gold surfaces;^[1a]
2. compression molding of PMMA films, which after an anisotropic etch leads to features 25 nm in size;^[1b]
3. 193 nm wavelength lithography.^[2]

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