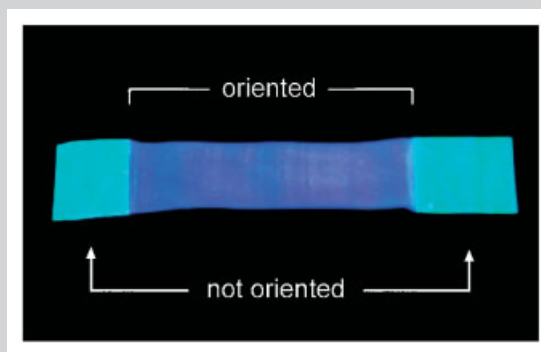


Summary: Poly(propylene) (PP) films containing different concentrations of bis(benzoxazolyl)stilbene (BBS) have been prepared by melt processing. We demonstrate that the emission characteristics of PP films depend on BBS concentration and polymer deformation. A well-defined excimer band is observed with more than 0.2 wt.-% of BBS, conferring to the film a green luminescence. During drawing (130 °C) the PP reorganisation breaks the BBS excimer-type arrangement, leading to the prevalence of the blue emission of the single molecules. We have efficiently applied the photophysics of this commercial stilbene derivative to the production of powerful tools acting as an internal probe for PP deformation.



Picture of oriented PP/BBS-0.5 film taken under excitation with a long-range UV lamp ($\lambda = 366$ nm). During drawing, the macromolecular chains reorganisation is able to break the BBS excimer-type arrangement leading to the prevalence of the blue emission of the single molecules.

Luminescent Bis(benzoxazolyl)stilbene as a Molecular Probe for Poly(propylene) Film Deformation

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Introduction

In recent years, the incorporation of luminescent aromatic molecules in polymers as covalently attached chromophores or dispersed dyes has been extensively investigated to obtain accurate information on polymer conformations,^[1–6] polymer blend compatibility,^[5,7,8] polymer chain deformation and alignment.^[9–13] The fluorescence response usually depends on the luminescence of the isolated chromophores, or on the formation of an excimer-type emission band.^[14–18]

The possibility to tune the emission of the luminescent molecules chemically linked to a macromolecule backbone or physically dispersed in the polymers, simply by changing the supramolecular architecture, stimulated new potential technological applications, such as molecular probes for

polymer films deformation. Indeed, oligo(*p*-phenylene vinylene) excimers have recently been shown to act as internal strain sensors for polymer films, as their emission characteristics change after polymer matrix deformation due to the disruption of the excimers and consequent prevalence of the emission from the isolated molecules excited states.^[10,11,19,20]

Captured by the possibility of using fluorescence as a powerful tool for monitoring the polymer deformation caused by the film production or by any structure modification of the plastic material, we have explored the photophysics of low cost, commercial bis(benzoxazolyl)stilbene (BBS, structure shown in Figure 1) dispersed in poly(propylene) (PP) films.

BBS chromophores belong to a well-known class of stilbene derivatives generally employed as optical brighteners

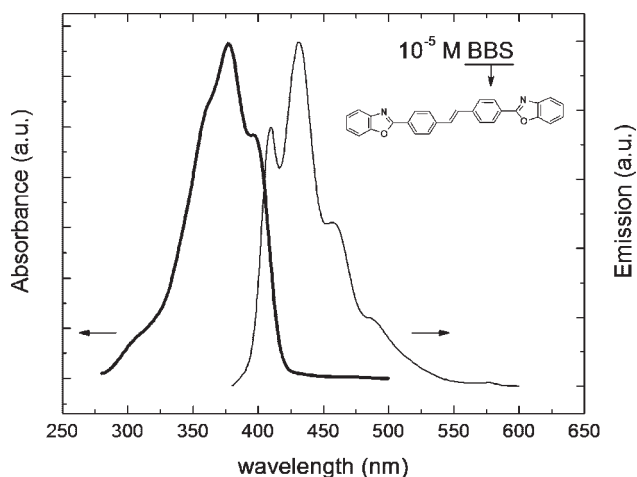


Figure 1. Absorption and emission curves ($\lambda_{\text{exc}} = 277 \text{ nm}$) for 10^{-5} M BBS in TCE solution.

in many polymer objects and textiles.^[21,22] BBS is a very good additive for thermoplastic materials (such as, polyethylene (PE), PP, poly(vinylchloride) (PVC)) due to the excellent dispersibility in the molten polymer. Moreover, the high resistance of such molecules to solvent extraction, the very high melting point (360°C) and degradation temperature (380°C) comply with the US Food and Drug Administration (FDA) regulations, making it ideal as an additive for indirect food and consumer packaging materials.^[23]

In the present paper, melt-processed PP/BBS films, prepared starting from different dye concentrations, have been studied by UV-vis and fluorescence spectroscopy, and the results are discussed in terms of their use as PP deformation sensors.

Experimental Part

Materials

4,4'-Bis(2-benzoxazolyl)-stilbene (BBS, 97%) was purchased from Aldrich. 1,1,2,2-Tetrachloroethane (TCE, 99%) was supplied by Carlo Erba. All the chemicals were used without further purification. Poly(propylene) (PP, BB213CF, melt flow rate (MFR, $230^\circ\text{C} \cdot (2.16 \text{ kg})^{-1}$) = 1.2, density = $0.90\text{--}0.91 \text{ g} \cdot \text{cm}^{-3}$, melting temperature (DSC) = $158\text{--}162^\circ\text{C}$, flexural modulus (ISO 178) = 1100 MPa, supplied by Borealis, Denmark) was used as the polymer host matrix.

Apparatus and Methods

UV-vis spectra of BBS solutions in TCE and of PP/BBS films were acquired on a Perkin-Elmer Lambda 650. Fluorescence spectra were recorded at room temperature with the help of a Perkin-Elmer Luminescence spectrometer LS50B. PP blends were prepared in a Brabender plastograph mixer (mod. OHG47055, 30 cm^3) under nitrogen atmosphere by introducing about 20 g of the polymer and 0.02–0.5 wt.-% of BBS in the

mixer at 260°C with a rotor speed of 50 rpm. After 10 min, the mixing was stopped and the recovered materials were moulded between two aluminium foils under compression in a press (Campana PM20/200) at 210°C for approximately 5 min. After removal from the press, the films were allowed to slowly reach room temperature ($\sim 5^\circ\text{C} \cdot \text{min}^{-1}$). The films were generally analysed after 2–3 d. The thickness of the obtained films was in the range of 80–100 μm . The scanning electron microscopy (SEM) analysis was performed with a Jeol 5600-LV microscope, equipped with an Oxford X-rays EDS microprobe. Solid-state drawings of the binary films were performed on a thermostatically controlled hot stage at 130°C . The drawing ratio (D_r), defined as the ratio between the final and the initial length of the samples, was determined by measuring the displacement of ink-marks printed onto the films before stretching. Digital images were obtained by using a Nikon Coolpix 2000 camera exposing the films under a Camag UV-Cabinet II equipped with Sylvania 8W long-range lamps (366 nm). Fluorescence spectra of the PP films were recorded at room temperature under isotropic excitation with the help of a Perkin-Elmer Luminescence spectrometer LS50B equipped with a motor-driven linear polarizer on the detection side. The position of the sample was adjusted in the direction of the excitation beam in such a way that the optical axis of excitation and emission crossed in the film plane. The films roughness was diminished by using ultra-pure silicon oil (Poly(methylphenylsiloxane), 710[®] fluid, Aldrich) to reduce surface scattering between the polymeric films and the Suprasil quartz slides, and to keep them planar. Origin 7.5, software by Microcal Origin[®], was used in the analysis of the absorption and emission data.

Results and Discussion

Solubility tests reveal that BBS is insoluble in most organic solvents, with the exception of high boiling point chlorinated solvents.

The opto-electronic properties of BBS in tetrachloroethane (TCE) solutions are reported in Figure 1.

BBS shows an absorption band centred at 377 nm ($\epsilon = 62\,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), mostly located in the near-UV region of the electromagnetic spectrum of light. The emission spectrum of the same solution displays, when excited at 277 nm, an emission feature characterized by a well-defined vibronic structure attributed to the 0–0, 0–1, and 0–2 radiative transitions, appearing at 410, 425, and 450 nm, respectively. In addition, no detectable bands attributed to aggregation phenomena between the chromophores are visible in both absorption and emission spectra with increasing BBS concentration. Moreover, UV-vis and fluorescence experiments performed on the supernatant portion of partially soluble BBS/hydrocarbon solvent mixtures (i.e., heptane, toluene, and xylene) show absorption and emission features comparable to that observed from TCE solutions.

Poly(propylene) (PP) films containing different concentrations of BBS have been prepared by compression

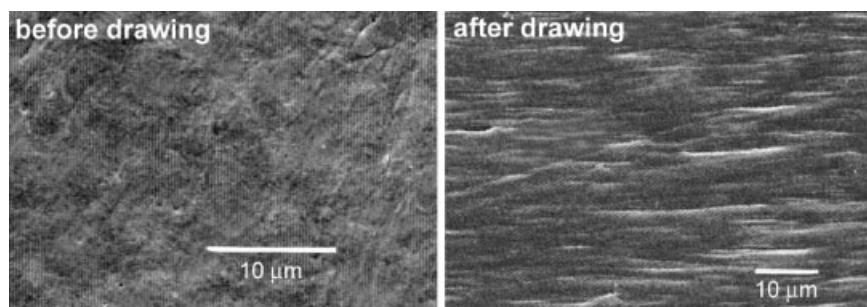


Figure 2. SEM micrographs of a PP/BBS-0.5 film, before (left) and after (right) uniaxial orientation.

moulding of the respective PP/BBS mixtures, obtained by blending the components at 260 °C in a Brabender-type mixer. Three different PP films containing 0.02, 0.2, and 0.5 wt.-% BBS (PP/BBS-0.02, PP/BBS-0.2, and PP/BBS-0.5, respectively) have been analyzed by UV-vis absorption and emission spectroscopies.

The molecular dispersion of BBS in PP has been evaluated by scanning electron micrographs, which evidence the absence of micro-sized aggregates of the luminescent molecules (Figure 2). Therefore, BBS was well dispersed in the amorphous phase of the polymer matrix down to the SEM resolution.

As in solution, the UV-vis spectra of the PP/BBS films show absorption bands centred at about 375 and 400 nm, with an increasing intensity with increasing BBS concentration (Figure 3a). In particular, despite the high scattering contribution of the 100 µm thick PP matrix, the films do not display any absorption band attributed to the formation of BBS aggregates.

However, different from the UV-vis absorption spectra, the emission characteristics of PP/BBS films change with BBS concentration (Figure 3b). Indeed the PP/BBS-0.02 film shows an emission feature similar to that reported for isolated BBS chromophores dissolved in TCE solutions (Figure 1), with emission peaks centred at 410, 430, and 455 nm.

On the contrary, with increasing in BBS concentration from 0.02 to 0.2–0.5 wt.-% in the PP blends, a new emission band emerges in the green region of the electromagnetic spectrum (500 nm), the intensity of which tends to overcome the emission contribution of the isolated BBS chromophores (400–450 nm). The occurrence of this broad, unstructured emission, which is red-shifted relative to the transitions by the BBS isolated molecule, and the presence of an absorption behaviour independent of concentration, may suggest that the new luminescence contribution comes from excimer-type arrangements in the solid state.^[17,18,24] Actually, this phenomenon, caused by the presence of dimers with associated excited electronic states, is favoured by the π – π stacking interactions between the BBS molecules and is probably promoted by the more planar chromophore conformation in the solid state.^[25] In TCE solutions,

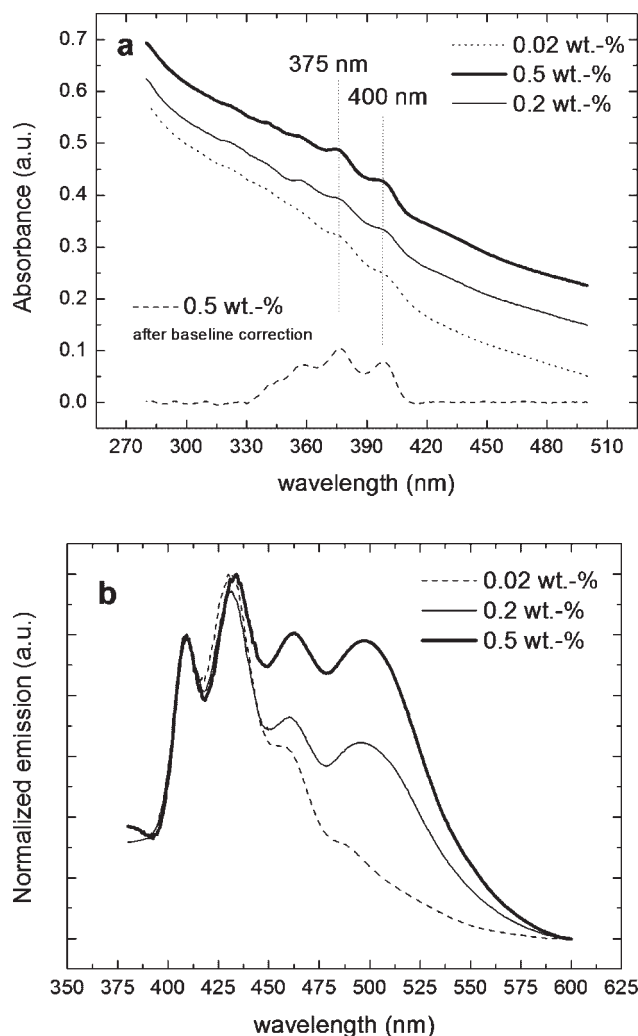


Figure 3. a) UV-vis absorption spectra of PP/BBS films as a function of dye concentration, expressed as the weight-% of BBS molecules with respect to the polymer matrix. The spectrum of the PP/BBS-0.5 film is also reported after depuration from most of the scattering components by subtraction of the spectrum of a neat PP film with the same thickness; b) Fluorescence emission spectra ($\lambda_{\text{exc}} = 277$ nm) of PP/BBS films as a function of dye concentration, expressed as the weight-% of BBS molecules with respect to the polymer matrix. The spectra are normalized to the intensity of the isolated BBS molecules peak (409 nm).

the formation of BBS excimers is avoided due to the high chromophore diffusion rate with respect to the excited state lifetime.^[18,26] In contrast, the low diffusion rate and low solubility of BBS dyes in the PP matrix facilitates the aggregation of at least two dyes (with inter-planar distance between their conjugated structure of about 3–4 Å),^[16,27] and a planar sandwich-type conformation provides the formation of excimers.

The thermal stability of the BBS supramolecular structure in PP has been qualitatively investigated by placing the film containing the 0.5 wt.-% of BBS chromophores in contact with a hot plate at the temperature of 130 °C for more than 10 min. The films maintain their green excimer emission under the excitation of a long-range UV lamp (366 nm) differently to the recently investigated oligo(*p*-phenylene vinylene) derivatives dispersed in linear low-density polyethylene (LLDPE), in which the excimer emission was sensitive to heating.^[10] In our case, the different preparation procedure of the PP films (slow cooling to room temperature) with respect to the LLDPE samples (rapid quenching of the films at 0 °C after removal from the hot press),^[10] may probably lead to the formation of more thermodynamically stable aggregates of dye molecules. The combination of the preparation procedure with the type of dye molecules (low solubility in PP and a melting point of approx. 360 °C) and with the polymer properties (PP instead of LLDPE) renders BBS aggregates more stable to thermal stress even at high temperature (up to 130 °C). However, this is true for PP films with a BBS concentration ≥ 0.5 wt.-%. PP/BBS-0.2 films, characterized by a low concentration of BBS aggregates, displayed sensitivity to thermal stress showing at 130 °C under the excitation of the long-range UV lamp, by the suppression of the green emission and the emersion of the blue colour. This behaviour suggests a particular thermal stability of BBS aggregates responsible of the excimer emission when the concentration of the luminescent molecules is higher than 0.5 wt.-%. On the other hand, decreasing the BBS concentration from 0.5 to 0.2 wt.-%, the BBS aggregates are less thermally stable due to the higher solubility of BBS molecules in the polymer matrix. Indeed, at lower additive concentration (~ 0.2 wt.-%) the de-aggregation process was favoured with increasing temperature.

The luminescence behaviour of PP/BBS films have also been investigated after solid-state drawing. The films have been uniaxially stretched at different draw ratios (D_r , defined as the ratio between the final and the initial length of the sample) at the temperature of 130 °C. The effect produced by the mechanical deformation is depicted in Figure 4a for a PP/BBS-0.5 tape excited at 366 nm: the oriented portion of the film changes its emission from green to blue, which is the typical luminescence of the isolated BBS molecules.

This interesting behaviour is confirmed using fluorescence spectroscopy by analysing a PP/BBS-0.5 film before

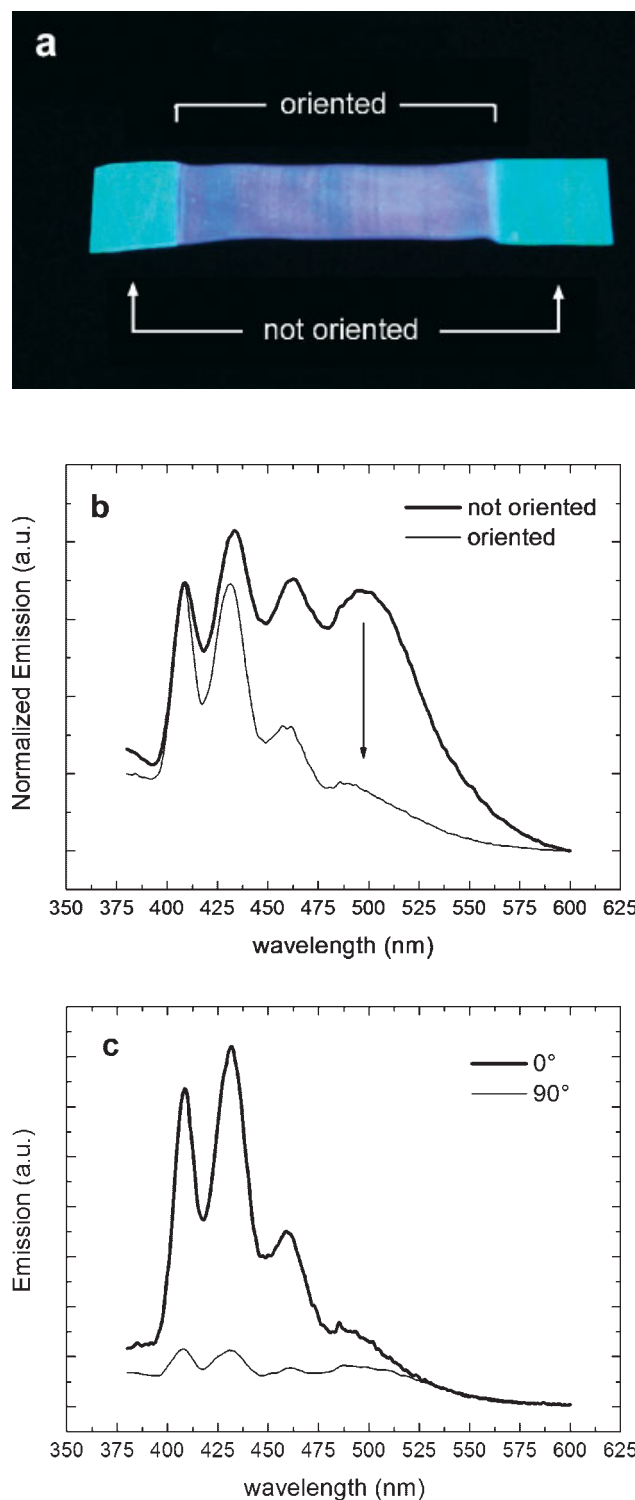


Figure 4. a) Digital image of the uniaxially oriented PP/BBS-0.5 film taken under excitation with a long-range UV lamp ($\lambda = 366$ nm). b) Fluorescence emission spectra ($\lambda_{\text{exc}} = 277$ nm) of a PP/BBS-0.5 film containing 0.5 wt.-% of BBS molecules, before and after solid-state drawing ($D_r = 8$). The spectra are normalized to the intensity of the isolated BBS molecules peak (409 nm). c) Fluorescence emission spectra ($\lambda_{\text{exc}} = 277$ nm) of the uniaxially oriented PP/BBS-0.5 film recorded with polarisation parallel (0°) and perpendicular (90°) to the drawing direction, respectively.

and after tensile drawing ($D_r = 8$, Figure 4b). The oriented tape only shows the emission bands characteristic of the radiative transitions of the BBS monomers, whereas the excimer band at 500 nm was almost completely suppressed. This behaviour suggests the collapse of the molecular BBS arrangements, which are responsible for the excimer emission as a consequence of the PP matrix orientation achieved by tensile drawing. It is well established that during polymer deformation, the mechanical forces are able to unfold the macromolecular chains leading to microfibrils in oriented crystalline and amorphous regions.^[21] At the same time, the dyes dispersed in the polymer as isolated molecules or aggregates, and exclusively located in the amorphous phase, undergo an alignment along the stretching direction. Dyes aggregates are generally destroyed during polymer deformation, which favours the uniaxial orientation of the single molecules.^[13] This is not completely true for micro-sized aggregates, whose phase separation from the polymer matrix hampers their breakup and limits the anisotropic arrangements of the dyes.^[13,28,29] The dispersion degree of the BBS supramolecular structures, therefore, plays a crucial role in the effectiveness of the strain effect. BBS molecules dispersed in PP at a concentration higher than 0.2 wt.-% were arranged in well-dispersed few-molecule aggregates where π - π interactions between the conjugated planar structures leads to the generation of excimers. These small (down to SEM resolution) well-dispersed luminescent aggregates were easily broken by mechanical stretching of the host PP matrix. The oriented films show the same emission features after two months, confirming the low diffusion rate of BBS dyes into the PP matrix.

The effective anisotropic distribution of BBS molecules along the oriented macromolecular PP fibres after solid-state drawing is confirmed by fluorescence spectroscopy measurements in polarized light. These have been performed by exciting the stretched tape with an unpolarised radiation and monitoring the dichroism of the emission through a linear polarizer. By rotating the direction of the polarizer from 0° (parallel to the stretching direction of the film) to 90° (perpendicular to the stretching direction), the emission contribution of the single BBS molecules strongly decreases with a dichroic emission ratio of about 10 (evaluated as the ratio between the emission at 0° and the emission at 90°) (Figure 4c). This phenomenon indicates the very high dichroic distribution of the isolated BBS chromophores after PP deformation.^[30]

Conclusion

In summary, we have prepared PP films with modulated emission properties by the very fine molecular dispersion of moderate (≤ 0.5 wt.-%) amounts of commercial BBS optical brighteners via melt processing. When the concen-

tration of BBS is increased to over 0.2 wt.-%, the emission of the film changes from blue to green. This suggests the formation of excimers, which is promoted by the π - π interaction between the conjugated planar structure of the dyes. The original blue colour of the film that is provided by the radiative transitions of the isolated BBS molecules, may be restored after polymer stretching, which promotes the breakup of the aggregates and the alignment of the single chromophore molecules along the stretching direction. The possibility of tuning the luminescence properties of PP films simply by adjusting the supramolecular structure of the BBS chromophores dispersed in the polymer matrix and its dependence on macromolecular organisation provides a very sensitive tool for determining the polymer orientation in extruded films. To the best of our knowledge, this is the first example of a low-cost commercial optical brightener being efficiently employed for the detection of tensile deformation in PP films. In the future, time-resolved fluorescence spectroscopy will be performed on the PP/BBS films before and after solid-state deformation for a deeper and more complete understanding of the investigated phenomenon.

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