Dichroic Properties of Bis(benzoxazolyl)stilbene and Bis(benzoxazolyl)thiophene Dispersed into Oriented Polyethylene Films: A Combined Experimental and Density Functional Theory Approach

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In this work, a combination of experimental and quantum mechanical investigations is performed for the study of dichroic absorption properties of melt-processed linear low-density polyethylene (LLDPE) oriented films containing ≤0.5 wt % of either 4,4′-bis(2-benzoxazolyl)stilbene (BBS) or 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene (BTBBT). The data acquired reveal that the film optical anisotropy and the performances as linear polarizer are strongly dependent on the molecular structure of the chromophore. In particular, the rodlike structure of BBS favors the alignment of the dye along the drawing direction of the PE film, providing dichroic ratios as high as 100 and optical performances as linear polarizer close to the pseudo-affine deformation scheme. On the contrary BTBBT, although characterized by huge anisotropic potentialities, confers the oriented film very poor dichroism and is unsuitable for linear polarizer applications. This behavior is attributed to the more complex banana-shaped structure of BTBBT dye caused by the thiophene 2,5-functionalization that limits the molecule parallel orientation to the drawing direction.

Introduction

Considerable research has been devoted in recent years to study of the optical properties of systems based on dichroic dyes dispersed in oriented macromolecular matrixes. The resulting macroscopic absorption anisotropy can be used to study the chromophores orientation and to produce polarized light thanks to the transfer of the axial orientation of the host to the low molecular weight guest.[1–6]

On the other side, the polarized absorption and/or emission provide detailed information on the distribution of the orientations of macromolecules in the polymer matrixes labeled by the probe dye.[7–13]

The optical properties of chromophores employed as dispersed additives for the preparation of polymer linear polarizers, colored filters, and molecular probes for polymer deformation are strongly affected by the chromophore tendency to anisotropically distribute along the oriented macromolecular chains of the host matrix. Actually, during polymer matrix deformation, the dye molecules are forced by the mechanical stress toward the macromolecular chain axis.[14]

With polymers as host, some key features must guide in the design of appropriate dichroic dyes such as (a) dispersibility in the polymer matrix, (b) presence of a rigid rodlike absorbing core (for orientation), and (c) high molar absorption, generally related to a high dipole moment. Depending on the structure complexity of the dye molecules, the transition dipole is not necessarily parallel to the molecular axis and the dye, after polymer deformation, may not be necessarily aligned to the

oriented polymer chains, thus resulting in a clear mismatch angle.[14,15] All these factors tend to limit the anisotropic behavior of the dispersed dye molecules and the global dichroic performances of the oriented polymeric devices.

Very recently, terthiophene-based molecules, whose key feature is a rigid rod shaped central part, dispersed into oriented polyethylenes (PE) have shown remarkable dichroic properties both in absorption and in emission.[5,6] Analogously, rod-shaped bis(benzoxazolyl)stilbene (BBS) molecules have been efficiently incorporated into polymer films providing, after uniaxial matrix deformation, a clear dichroic response in emission.[7,8,14]

BBS and the similar UV–vis absorbing dye 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene (BTBBT) are attracting high attention due to use as optical brighteners in many polymer objects and textiles.[14,16] However, the UV–vis absorption anisotropy of this class of dyes dispersed into oriented semi-crystalline polymer matrixes has not accurately investigated yet from a quantitative viewpoint.[17,18]

In this work, the dichroic behavior of BBS and BTBBT (Figure 1) is studied and compared by analyzing their dispersions (0.02–0.5 wt %) in linear low-density polyethylene (LLDPE) oriented films by UV–vis spectroscopy in linearly polarized light.

The results are discussed in terms of the different anisotropic behavior shown by the two dyes in the light of their potential use as low-cost commercial dyes for the production of near-UV dichroic filters.

The application of linear dichroism permits also detailed structural information to be obtained, such as the determination of transition moment directions and order parameters. To this end, experimental linear dichroism spectra are usually interpreted by means of well-established models, such as those due to Eggers, Thulstrup, and Michl,[19,20] Tanizaki et al.,[21] Popov,[22]

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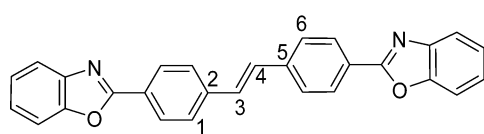
4,4'-Bis(2-benzoxazolyl)-stilbene
(BBS)
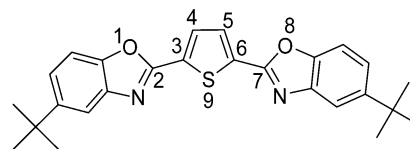
2,5-Bis(5-tert-butyl-2-benzoxazolyl)-thiophene
(BTBBT)

Figure 1. Molecular structures of BBS and BTBBT with atom numbering.

Yogev et al.,[23] and Norden et al.[24] Such models rely on simplifying assumptions so that, depending on how complex the molecular system is and on whether it is planar or not, a number of cases, each appropriate to a specific application, are obtained (for more details and a discussion on this topic see also ref 25).

In this paper, a different analysis leading to investigations about the preferred orientation of the two dyes is proposed, using state-of-the-art quantum mechanical investigations at the density functional theory (TD-DFT) level, which has been proven to be able to give reliable structural and spectroscopic properties of organic molecules and complex molecular systems at a low computational cost.[26]

The use of calculations undertakes most of the assumptions exploited in the treatment of experimental data and thus permits an effective methodology to be obtained that is able to correlate dichroic parameters with the preferential orientation direction of the chromophores toward the polymer matrix deformation axis. The combination of experimental linear dichroism data (both the in UV and infrared spectral regions) and quantum mechanical calculations at various levels has been widely exploited in the literature to obtain structural information on various molecular systems (see for example refs 27−30).

Experimental Section

Materials. 4,4′-Bis(2-benzoxazolyl)stilbene (BBS, 97%) and 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene (BTBBT, 99%) were purchased from Aldrich and used without further purification. Linear low-density polyethylene (LLDPE, Dowlex SC 2107, melt flow index, 190 °C/2.16 kg = 2.3 g/10 min, d = 0.917 g/cm^3, supplied by Dow Plastics, USA) was used as polymer host matrix. Samples were named by listing polymer (abbreviated as LL), guest molecule, and concentration, e.g. LLBBS-0.02.

Apparatus and Methods. LLDPE blends were prepared in a Brabender plastograph mixer (model OHG47055, 30 cm^3) under nitrogen atmosphere by introducing about 20 g of the polymer and 0.02−0.5 wt % of BBS or BTBBT in the mixer at 180 °C with a rotor speed of 50 rpm. After 10 min, the mixing was stopped and the recovered materials were molded between two sheets of aluminum foil under compression in a press (Campana PM20/200) at 180 °C for approximately 5 min. After removal from the press, the films were allowed to reach slowly room temperature (∼5 °C min^{-1}). The films were generally analyzed after 2−3 days. The thickness of the obtained films was in the range of 80−100 μm. Solid-state drawings of the binary films were performed on a thermostatically controlled hot stage at 90 °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. The scanning electron microscopy (SEM) analysis was performed with a JEOL 5600-LV microscope, equipped with Oxford X-rays EDS microprobe. UV−vis spectra of LLDPE films were recorded at room

temperature in polarized light with the help of a Perkin-Elmer Lambda 650 spectrophotometer equipped with motor-driven Glan-Taylor linear polarizers. Fluorescence spectra of PE films were recorded at room temperature under isotropic excitation with the help of a Perkin-Elmer LS55 luminescence spectrometer 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 fluorescence anisotropy has been quantitatively evaluated by calculating the dichroic emission ratio R_E (defined as $R_E = E_{||}/E_\perp$) of the emission intensities (E).[5]

The film's roughness was diminished, using ultrapure silicon oil (poly(methylphenylsiloxane), 710 fluid, Aldrich) to reduce surface scattering between the polymeric films and the Suprasil quartz slides, used to keep them planar. Origin 7.5, software by Microcal Origin, was used in the analysis of the absorption and emission data.

Computational Methodology. The structures of the stable conformations of BBS and BTBBT were obtained at the DFT level by using the B3LYP hybrid functional[26,31] and the 6-31+G* basis set.[32] UV and linear dichroism (LD) spectra were calculated for each stable conformation by using the time-dependent DFT (TDDFT) methodology.[33,34] Simulated spectra reported in the figures were obtained by summing oscillator strengths weighted Gaussian curves with a full width of 0.15 eV at the 1/e of the maximum for each calculated electronic transition. Thirty electronic transitions were considered.

The reported structures and spectra were obtained by considering effects of a medium polarity dielectric environment surrounding the dyes, so to simulate effects of the LLDPE polymeric matrix. Medium effects were accounted for by exploiting the polarizable continuum model (PCM).[35−37] Such a model, if tailored to reproduce solvent effects, has been also successfully applied to the prediction of structural and spectroscopic properties of molecules in polymeric environments.[38]

All the calculations were performed with the Gaussian03 code.[39]

Results and Discussion

(a) Experimental Evidence. *Absorption.* BBS and BTBBT are very good additives for thermoplastic materials (such as PE, PP, and poly(vinyl chloride) (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 and 200 °C, respectively), and degradation temperature (380 and 340 °C, respectively) comply with the U.S. Food and Drug Administration (FDA) regulations, making them ideal as additives for indirect food and consumer packaging materials.[40]

Solubility tests reveal that BBS is insoluble in most organic solvents, with the exception of high-boiling chlorinated solvents, and is different from BTBBT, which is soluble in both chlorinated and some polar organic solvents. BBS and BTBBT

show in tetrachloroethane (TCE) solutions absorption bands centered at 401 nm (ϵ = 62 000 L mol^{-1} cm^{-1}) for the former and 405 nm (ϵ = 25 000 L mol^{-1} cm^{-1}) for the latter, mostly located in the near-UV region of the electromagnetic spectrum of light and attributed to a $\pi-\pi^*$ transition.

In this study, linear low-density polyethylene (LLDPE) films containing different concentrations of BBS and BTBBT were prepared by compression molding of the respective LLDPE-based mixtures, which were obtained by blending the components at 180 °C in a Brabender type mixer.

The molecular dispersion of the two molecules into LLDPE was evaluated by scanning electron micrographs (see Supporting Information), which showed the absence of microsized aggregates of the guest molecules. Therefore, both BBS and BTBBT are well dispersed in the amorphous phase of the polymer matrix down to the SEM resolution as similarly reported for the stilbene derivative into polypropylene.[8]

The UV−vis spectra of BBS and BTBBT molecules dissolved into LLDPE matrix show absorption maxima centered at 378 and 376 nm, respectively, i.e., about 20−30 nm blue shifted with respect to TCE solution. Moreover, the overall vibronic pattern of the absorption bands is also different from the solution spectrum, perhaps due to increased rigidity provided by the polymeric environment.

The binary LLDPE-based films were successively oriented by uniaxial tensile drawing at different draw ratios (D_r, defined as the ratio between the final and the initial length of the sample) at a temperature of 90 °C, and the anisotropic behavior of the stretched films was evaluated by UV−vis spectroscopy in polarized light.

The key parameter to characterize the molecular orientation of dyes and the optical performances of oriented devices as linear polarizers are the dichroic ratio R, the order parameter S, the polarizing efficiency PE, and the single piece transmittance T_{sp}. These parameters are defined as follows:[1]

$$R = A_{\parallel}/A_{\perp}$$

$$S = (R - 1)/(R + 2)$$

$$PE = (T_{\perp} - T_{\parallel})/(T_{\perp} + T_{\parallel})$$

$$T_{\mathrm{sp}} = (T_{\perp} + T_{\parallel})/2$$

The transmissions parallel ($T_{\parallel}$) and perpendicular ($T_{\perp}$) to the orientation direction are calculated ($T = 10^{-A}$) from absorbances parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the drawing direction of the film.[41]

The absorption spectrum in polarized light of the LLBBS-0.5 film, with a draw ratio of 10, is reported in Figure 2a for different values of the angle θ between the light polarization direction and the film orientation. When the polarization of the incident light is parallel to the stretching direction, the film shows an absorption maximum pointed at 378 nm. On the contrary, in the perpendicular configuration the absorption band results completely suppressed, thus clearly indicating a pronounced anisotropic behavior.

The dichroism increases with D_r from 6 to 10 and is substantially independent of composition (Table 1).

The best dichroic ratios as high as 100 and order parameter values close to the unity suggest a striking alignment (on average) of the BBS molecules along the deformation direction of the polymer matrix.
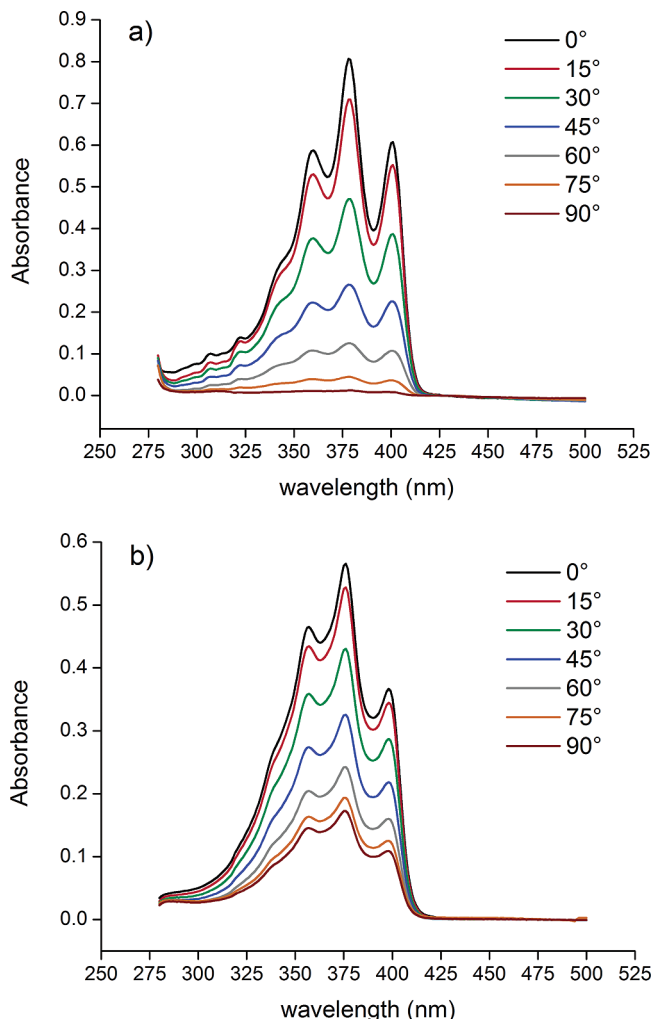

Figure 2. UV−vis absorption spectra as a function of the polarization angle θ for LLBBS-0.5 (a) and LLBTBBT-0.5 (b) oriented films (D_r = 10 in both cases). Absorbances are given in arbitrary units.

TABLE 1: Experimental Polarizer Performance on Varying Chromophore Load and Drawing Ratio

sample	dye	wt %	D_r	R	S	PE	T_{sp}
LLBBS-0.02	BBS	0.02	6	31	0.91	0.33	0.73
LLBBS-0.02	BBS	0.02	8	48	0.94	0.21	0.82
LLBBS-0.02	BBS	0.02	10	99	0.97	0.33	0.75
LLBBS-0.2	BBS	0.2	6	36	0.92	0.73	0.55
LLBBS-0.2	BBS	0.2	8	67	0.96	0.69	0.58
LLBBS-0.2	BBS	0.2	10	81	0.96	0.72	0.57
LLBBS-0.5	BBS	0.5	6	40	0.93	0.71	0.56
LLBBS-0.5	BBS	0.5	8	69	0.96	0.30	0.76
LLBBS-0.5	BBS	0.5	10	96	0.97	0.32	0.75
LLBTBBT-0.02	BTBBT	0.02	6	1.8	0.21	0.04	0.86
LLBTBBT-0.02	BTBBT	0.02	10	3.2	0.42	0.06	0.89
LLBTBBT-0.2	BTBBT	0.2	6	2.2	0.29	0.37	0.37
LLBTBBT-0.2	BTBBT	0.2	8	2.3	0.30	0.47	0.31
LLBTBBT-0.2	BTBBT	0.2	10	3.3	0.43	0.42	0.47
LLBTBBT-0.5	BTBBT	0.5	6	1.5	0.14	0.11	0.52
LLBTBBT-0.5	BTBBT	0.5	8	2	0.25	0.18	0.58
LLBTBBT-0.5	BTBBT	0.5	10	3	0.32	0.80	0.12

Conversely, BTBBT shows a much lower anisotropic behavior (D_r = 10, Figure 2b) with low values of the dichroic ratio (ranging from 1.5 to 3.3) and the order parameter (from 0.21 to 0.43) (Table 1). In addition, R and S values are completely independent from draw ratio extent and dye concentration.

The different tendency of BBS and BTBBT molecules to give anisotropic behavior in stretched LLDPE films is also shown
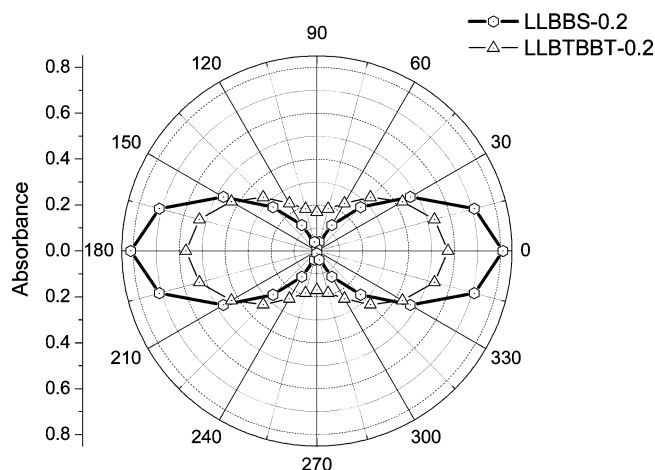
Figure 3. Distribution of the $A_{\parallel}$ values as a function of the polarization angle θ for LLBBS-0.2 (○) and LLBTBBT-0.2 (△) oriented films. Absorbances are given in arbitrary units.
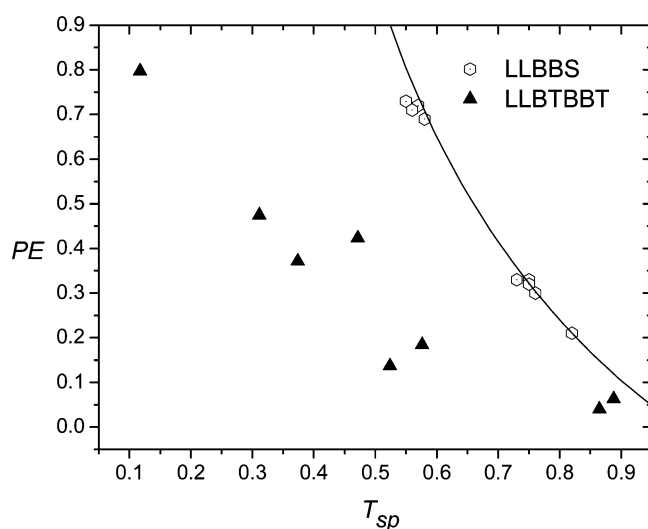

Figure 4. Polarizing efficiency as a function of single piece transmittance for LLBBS (○) and LLBTBBT (▲) oriented films and theoretical prediction (solid line), infinite draw ratio ($D_r \rightarrow \infty$), and infinite anisotropy of the dye ($\epsilon_{\parallel}/\epsilon_{\perp} \rightarrow \infty$).

by the plot of the distribution of the polarized components of the absorbance $A_{\parallel}$ (radial) as a function of the angle θ (Figure 3).

Indeed, oriented LLBBS-0.2 and LLBTBBT-0.2 films ($D_r = 10$ in both cases) clearly show different shapes of the polar plots and the complete ∞-shaped angular distribution displayed by the former film demonstrates once again a much more effective orientation of BBS molecules.

Polarizing efficiency (*PE*) plotted as a function of the single piece transmittance (T_{sp}) shows (Figure 4) that BBS chromophore has a dependence of *PE* versus T_{sp} close to the ultimate properties calculated for molecularly dispersed dyes with *R* and extinction coefficient ratio $\epsilon_{\parallel}/\epsilon_{\perp} \rightarrow \infty$ (solid line), according to the pseudo-affine deformation scheme.[2]

Thus oriented LLBBS-0.2 and LLBBS-0.5 films fit very well the theoretical prediction according to the values of PE and T_{sp} reported for a perfect linear polarizer, i.e., 1 and 0.5, respectively,[1,3] whereas LLBTBBT-oriented films do not fit the scheme at all.

Emission. The dichroism of oriented LLBBS and LLBTBBT films has been analyzed in fluorescence to show the different anisotropic behavior of the two chromophores also in emission. The luminescent dichroic behavior reported in Figure 5 for
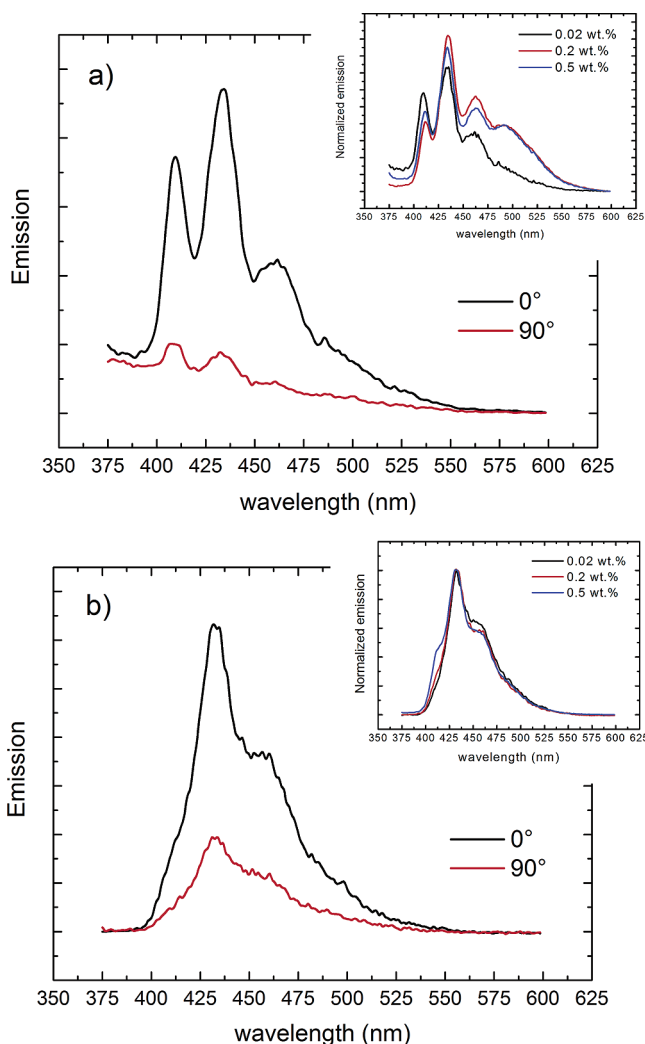

Figure 5. Fluorescence spectra recorded with emission polarization parallel (0°) and perpendicular (90°) to the drawing direction of oriented (a) LLBBS-0.02 ($\lambda_{exc} = 277$ nm, $D_r = 8$) and (b) LLBTBBT-0.2 ($\lambda_{exc} = 280$ nm, $D_r = 8$) films and emission spectra of (a, inset) LLBBS and (b, inset) LLBTBBT films as a function of chromophore load.

oriented LLBBS-0.02 (a) and LLBTBBT-0.2 (b) films ($D_r = 8$, in both cases) confirms the results obtained in absorption suggesting a higher anisotropic emission (R_E)[5] of the rodlike BBS chromophore ($R_E = 9.7$ for LLBBS-0.02, 6.0 for LLBBS-0.2, and 7.2 for LLBBS-0.5 oriented films; $D_r = 8$) with respect to the banana-shaped BTBBT dye ($R_E = 2.3$ for LLBTBBT-0.02, 3.2 for LLBTBBT-0.2, and 2.0 for LLBTBBT-0.5 oriented films; $D_r = 8$). As recently reported for highly miscible dyes dispersed into PE,[6] the dichroism in emission is often lower than that in absorption probably due to depolarization phenomena and the existence of different electronic chromophore conformations in the excited state.

Insets in Figure 5 report also the normalized luminescent behavior of the two dyes dispersed into LLDPE as a function of chromophore concentration. With respect to polypropylene (PP) films, BBS does not generate strong excimer emission[8] at about 500 nm suggesting different nanoscale morphology of PE/BBS blends with respect to PP/BBS mixtures, probably associated to a better dispersion behavior of the stilbene derivative obtained during melt processing with PE.

On the contrary, for PE/BTBBT blends no emission band attributed to the chromophores aggregates emerges with dye concentration (at least for the investigated range of concentra-
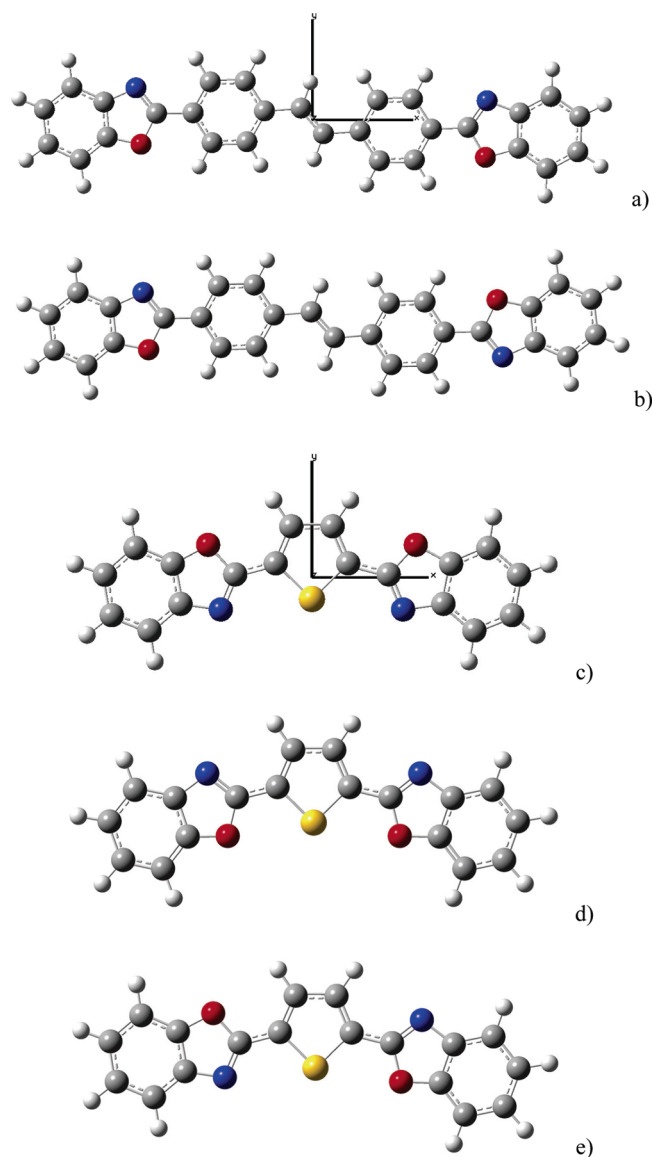
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Figure 6. Calculated B3LYP/6-31+G* structures of BBS and BTBBT conformers: (a) BBS-A; (b) BBS−B; (c) BTBBT-A; (d) BTBBT-B; (e) BTBBT-C. For BBS-A and BTBBT-A the orientation of the inertial coordinate system is shown: gray, carbon; white, hydrogen; red, oxygen; blue, nitrogen; yellow, sulfur.

tion, i.e., from 0.02 to 0.5 wt %) indicating an excellent phase dispersion behavior of the banana-shaped chromophore into the PE matrix.

(b) Quantum Mechanical Investigations. It has been well established by both experimental investigations[15] and theoretical predictions[41] that a lower dichroism may be ascribed to (a) a low instrinsic dichroism of the dye, i.e., similar transition moment components for the parallel and the perpendicular directions and (b) a scarce orientation of the guest chromophores inside the polymer matrix.

By assuming for both BBS and BTBBT guests a similar homogeneous distribution inside the polyethylene matrix, i.e., by discarding the formation of hardly orienting large dye crystals, the obtained results can be ascribed to the greater structural complexity of BTBBT with respect to BBS.

Indeed, the molecular complexity hampers the attainment of high dichroic ratios owing to two fundamental aspects: (a) the electric transition dipole moment associated to the electronic transition responsible for the band is not parallel to the molecular

TABLE 2: Dihedral Angles and Normalized Boltzmann Statistical Weights of the BBS and BTBBT Conformers As Calculated at the B3LYP/6-31+G* Level[a]

	γ	δ	statistical weight
BBS-A	0	0	0.54
BBS−B	0	180	0.46
BTBBT-A	0	0	0.56
BTBBT-B	180	180	0.13
BTBBT-C	0	180	0.31

[a] BBS: γ = C4, C3, C2, C1; δ = C3, C4, C5, C6. BTBBT: γ = C4, C3, C2, O1; δ = C5, C6, C7, O8 (see Figure 1 for atom numbering).

TABLE 3: Calculated B3LYP/6-31+G* Dichroic Ratio R for the Various Conformations of BBS as a Function of the Orientation[a]

orientation (atom−atom)	BBS-A	BBS−B	average
inertial	480.62	1025.52	731.27
C3−C5	8.83	8.43	8.65
C3−C4	1.10	1.13	1.11
C2−C3	75.96	77.24	76.55
C4−C5	68.00	77.24	72.25
C2−C4	8.84	8.43	8.65

[a] Boltzmann average is also reported.

axis of the dye; (b) this last does not adopt a molecular orientation parallel to the polymer uniaxially oriented chains.

To verify these issues, quantum mechanical calculations have been performed, thus investigating both the structure of the molecules and their transition dipole moments orientation associated to UV electronic transitions.

In Figure 6, the calculated structures of the two minimum energy possible conformations of BBS (A and B) are depicted; in Table 2, relevant dihedral angles and normalized Boltzmann statistical weights of the two conformations are reported. A slight preference for the "symmetric" conformation (BBS-A), having both the oxygens on the same side with respect to the delocalized π-system is observed. However, due to the low difference in the calculated statistical weight, and to the error associated to calculated weights (mostly due to the fact that effects due to the solid polymeric matrix are only partially accounted for), it can be assumed roughly a 50:50 mixture of the two conformers.

In Figure 7 simulated LD spectra for a selection of possible orientations of BBS (conformer A) in the film are considered. The corresponding spectra for conformer B are very similar to those of A, and for this reason they are not reported. Note that calculated and experimental UV maxima do not coincide: this is not surprising, because of only a partial account of environmental effects and the choice of a medium-quality quantum mechanical level. Also, calculated data lack any introduction of electronic−vibrational coupling, so that the vibrational structure experimentally detected is not reproduced in the simulated spectra. However, here interest will be focused on the comparison between spectra obtained for different orientations of the dyes more than on a quantitative calculated− experimental comparison. In addition, only ratios between the parallel and perpendicular components of the calculated spectra (and not absolute values) will be considered; for all these reasons, computed quantities should be reasonably reliable.

Calculated spectra (Figure 7) show that the potential dichroism of BBS varies as a function of its orientation on the film, ranging from high (in the case of the orientation along the inertial coordinate system—see Figure 6) to very low, such as when BBS is oriented along the C3−C4 axis. To compare calculated data with experiments, in Table 3 calculated dichroic
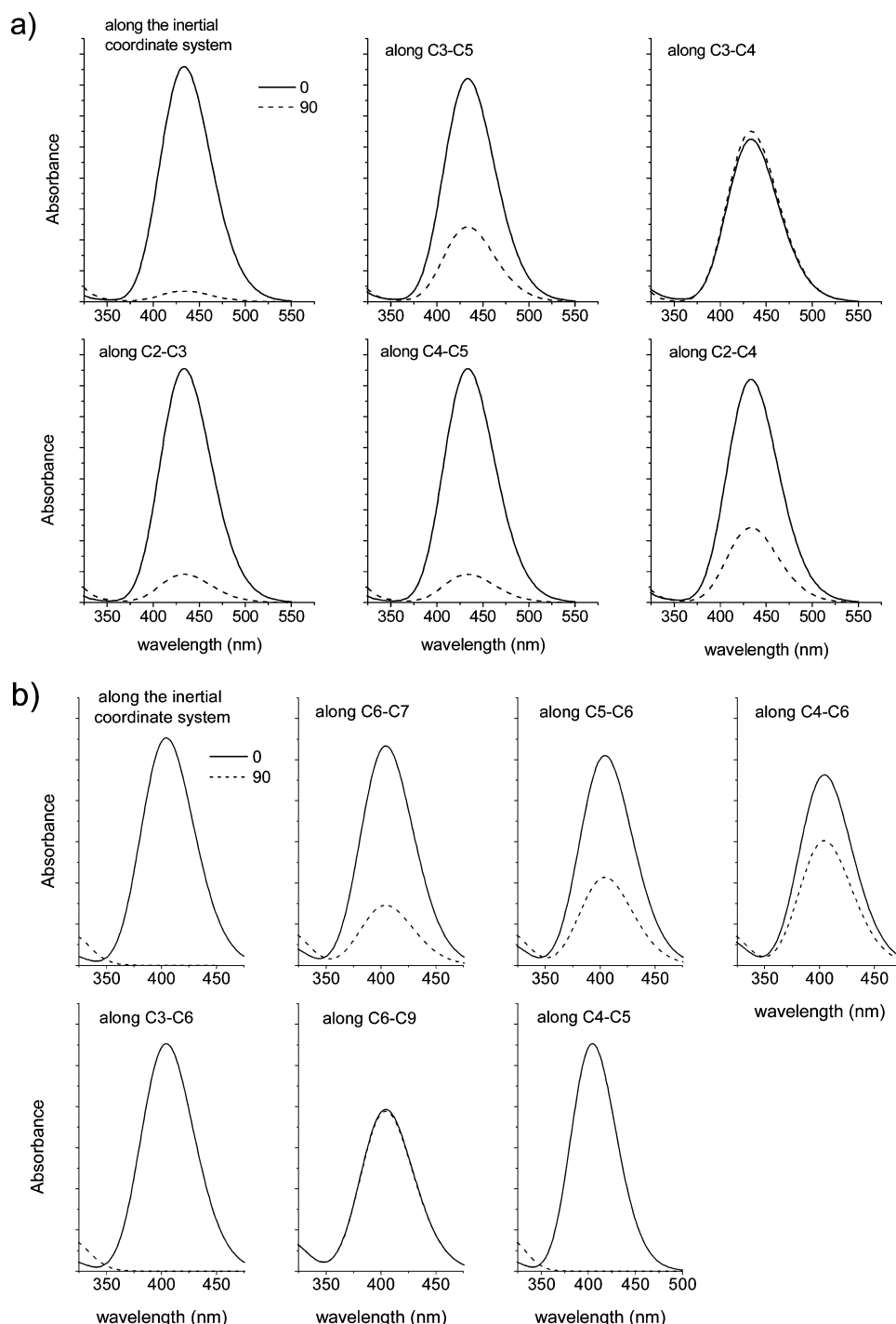
Figure 7. Calculated B3LYP/6-31+G* polarized spectra of (a) BBS-A and (b) BTBBT-A for selected orientations. Absorbances are given in arbitrary units.

ratios R for selected orientations of BBS are reported. The comparison of calculated and experimental values (Table 1) shows that in the LLDPE matrix BBS is reasonably oriented along one of the C2−C3 or C4−C5 axes, which, as expected, are almost equivalent; higher R values would be obtained if BBS were oriented along the inertial coordinate system.

To speed the quantum mechanical calculations, in the model structures of BTBBT the *tert*-butyl groups were replaced by hydrogen atoms. Such an approximation should not be very strict, because *tert*-butyl groups are commonly exploited in experimental research to enhance the compound solubility in organic solvents and the miscibility into polyolefins. Also, the lack of the two *tert*-butyl groups in the model structures should

not affect the electronic structure of the delocalized π-system, which is responsible for the absorption properties.

The calculated Boltzmann statistical weights (Table 2) for the three minimum energy conformers of BTBBT (Figure 6) indicate that the most stable conformation (BTBBT-A) is the one with both the oxygen atoms on the same side with respect to the thiophene ring, pointing toward the thiophene ring hydrogens. The least stable conformer (BTBBT-B) has, instead, both nitrogen atoms pointing toward the thiophene ring, whereas a population of around 30% corresponds to the asymmetric structure BTBBT-C, having only one oxygen atom pointing toward one thiophene ring hydrogen. This energy hierarchy is

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TABLE 4: Calculated B3LYP/6-31+G* Dichroic Ratio *R* for the Various Conformations of BTBBT as a Function of the Orientation[a]

orientation (atom−atom)	BTBBT-A	BTBBT-B	BTBBT-C	average
inertial	≫1000	≫1000	≫1000	≫1000
C6− C7	13.36	16.40	19.40	15.63
C5− C6	5.70	5.62	5.11	5.50
C4− C6	2.34	2.34	2.54	2.40
C3− C6	≫1000	≫1000	>1000	≫1000
C6− S9	1.02	1.03	1.05	1.03
C4− C5	≫1000	≫1000	>1000	≫1000

[a] Boltzmann average is also reported.

not surprising, because it reflects the number of stabilizing hydrogen bonding like O···H interactions present in the structures.

Calculated polarized UV spectra for the parallel and perpendicular components are reported (Figure 7) for the most stable conformer, BTBBT-A, along selected orientations. Also in this case, the corresponding spectra for the B and C conformations are very similar to those of A, and they are not reported. Inspection of calculated dichroic ratios *R* (Table 4) shows only little differences in the dichroism of the three conformers, which behave almost in the same way.

The comparison between calculated and experimental findings shows that the very low dichroism observed when BTBBT is dispersed in LLDPE matrix (see previous section) is not due to an intrinsic lack of dichroism but to orientation in the stretched polymeric matrix which minimizes its dichroic behavior. In particular, calculated data for the inertial orientation (see Figure 5 for the definition), as well as for the orientation along the C3−C6 (or C4−C5) axes, show huge dichroic potentialities of BTBBT, which, however, are not exploited as a result of the dispersion−orientation in LLDPE. On the contrary, still resorting to Table 4 and comparison of the data with experiments in Table 1, it appears reasonable to infer an actual orientation of the dye along the C4−C6 axis, which is, among the selected, the one giving calculated data most similar to the average experimental results.

In summary, the observed high dichroism of BBS results from a "good" orientation of the dye in the stretched polymeric matrix, i.e., a orientation exploiting its dichroic potentiality, whereas in the case of BTBBT, which could potentially show dichroic properties even more marked than BBS, the direction of orientation in the stretched films causes a decrement in the dichroism.

Summary and Conclusions

LLDPE films containing different concentrations (0.02−0.5 wt %) of two chromophores 4,4′-bis(2-benzoxazolyl)stilbene (BBS) or 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene (BT-BBT) were prepared by melt processing. After uniaxial stretching, the films containing BBS show excellent dichroic properties in absorption and optical performances as linear polarizer close to the pseudo-affine deformation scheme. On the contrary, oriented polyethylene films based on BTBBT dye display very poor anisotropic behavior and the results are completely unsuitable for linear polarizer applications. Luminescent anisotropic experiments confirm the different dichroic behavior of the two dyes also in emission. Quantum mechanical calculations at the DFT level predict for both chromophores huge anisotropic potentialities, thus attributing the poor experimental dichroic response of BTBBT to its scarce orientation with respect to the rodlike BBS dye along the drawing film direction.

The combination of experimental and theoretical investigations proposed in this work, provides effective and informative methodologies able to correlate the measured anisotropy of the composite films with the preferential orientation direction of the dispersed chromophores toward the deformation axis. The approach appears very suitable for modulating optical response of dye-doped polymer films.

Supporting Information Available: A scanning electron micrograph of a LLBBS-0.5 film. This material is available free of charge via the Internet at http://pubs.acs.org.

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