JOURNAL OF
Materials
CHEMISTRY

Ultra-high performance photoluminescent polarizers based on melt-processed polymer blends

Michael Eglin, Andrea Montali, Anja R. A. Palmans, Theo Tervoort, Paul Smith and Christoph Weder

Department of Materials, Institute of Polymers, ETH Zürich, CH-8092 Zürich, Switzerland

Received 12th April 1999, Accepted 4th June 1999

Photoluminescent polarizers that comprise uniaxially oriented photoluminescent species which absorb and emit light in highly linearly polarized fashion, can efficiently combine the polarization of light and the generation of bright colors. We here report the preparation and characterization of such polarizers by simple melt-processing and solid-state deformation of blends of a photoluminescent guest and a thermoplastic matrix polymer. The orientation behavior of a poly(2,5-dialkoxy-*p*-phenyleneethynylene) derivative (EHO-OPPE), 1,4-bis(phenylethynyl)benzene, and 1,4-bis(4-dodecyloxyphenylethynyl)benzene was systematically compared in different polyethylene grades. Experiments suggest that if phase-separation between the photoluminescent guest and the matrix polymer is reduced during the preparation of the pristine (*i.e.* unstretched) blend films, photoluminescent polarizers can be produced which exhibit unusually high dichroic properties at minimal draw ratios. In connection with this finding, an optimized, melt-processed blend based on 1,4-bis(4-dodecyloxyphenylethynyl)benzene and linear low-density polyethylene was developed that allows efficient manufacturing of photoluminescent polarizers which at draw ratios of only 10 exhibit dichroic ratios exceeding 50.

Introduction

Color liquid-crystal displays (LCDs) suffer from limited brightness and energy efficiency, originating from the use of absorbing polarizers and color filters.[1,2] These limitations have recently triggered, among other advances,[3–8] the development of photoluminescent (PL) polarizers which can efficiently combine the polarization of light and the generation of bright colors,[9,10] concomitant with a substantial increase in brightness and efficiency of PL LCDs based on these elements.[11] These polarizers comprise uniaxially oriented PL polymers, which absorb and emit light in highly linearly polarized fashion. The introduction and use of a polarizing energy transfer effect has led to a second generation of photoluminescent polarizers with further enhanced efficiency.[10] The latter PL polarizers additionally comprise a randomly oriented sensitizer which maximally harvests optical energy by isotropic absorption, efficiently transfers the energy to the oriented, photoluminescent polymer which, subsequently, emits linearly polarized light.[10,12,13]

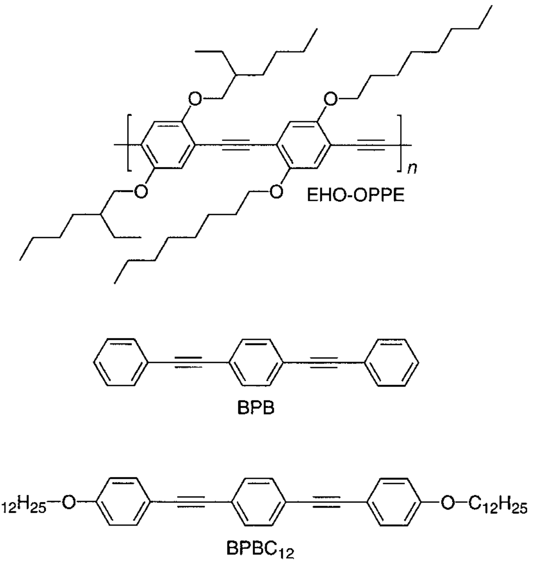

Fig. 1 Molecular structures of the photoluminescent polymer (EHO-OPPE) and small-molecular dyes (BPB, $BPBC_{12}$) employed in this work.

In our previous studies,[9–13] a strongly luminescent, highly form-anisotropic conjugated polymer (EHO-OPPE, a poly(2,5-dialkoxy-*p*-phenyleneethynylene) (PPE) derivative, see Fig. 1) typically was used as the PL emitter, and ultra-high molecular weight polyethylene (UHMW PE) was employed as a highly ductile matrix polymer. Uniaxially oriented blend films which comprised 1 to 2% w/w of the conjugated polymer were prepared by solution casting, drying, and subsequent tensile drawing in the solid state. Uniaxial deformation of these films to draw-ratios of up to 80 resulted in a high degree of orientation of the PL polymer and, consequently, state-of-the-art optical anisotropy. However, the orientation of the PPE molecules in these 'gel-processed' UHMW PE blends[9] did not follow the 'pseudo-affine deformation scheme',[14,15] which is often used to describe the orientation process of small-molecular dichroic (absorbing) chromophores in tensile-deformed polymer matrices.[16–19] Within this theoretical framework, which is based on the aggregate model originally proposed by Ward,[14] the average orientation $\langle\cos^2\phi\rangle$ of initially randomly oriented, statistical chain segments of the macromolecules with respect to the direction of uniaxial deformation depends on a sole parameter, the draw ratio λ, and is given by eqn. (1).[15,20]

$$\langle\cos^2\phi\rangle=\frac{\lambda^3}{\lambda^3-1}-\frac{\lambda^3}{(\lambda^3-1)^{3/2}}\arctan((\lambda^3-1)^{1/2}) \qquad (1)$$

Assuming that dichroic guest molecules adapt the orientation of the host polymer in which they are dispersed or dissolved, and applying Hermans' orientation function (f_h) [eqn. (2)]:[15,20–22]

$$f_h=\frac{3\langle\cos^2\phi\rangle-1}{2}=\frac{DR_A-1}{DR_A+2}\cdot\frac{DR_{A0}+2}{DR_{A0}-1} \qquad (2)$$

the absorption dichroic ratio (DR_A) of an oriented blend film can readily be calculated from the draw ratio and the ultimate absorption dichroic ratio (DR_{A0}). The latter accounts for the parallel and perpendicular components of the extinction coefficient; the fact that the transition dipole moment of the chromophore is not necessarily parallel to its molecular axis; and for a possible misorientation of the guest molecule in the matrix.[18,23] Substitution of DR_A by DR_E (emission dichroic ratio) and DR_{A0} by DR_{E0} (ultimate emission dichroic ratio) leads to an equivalent relation that allows description of the development of anisotropic *photoluminescence*.

As mentioned above, the generation of polarized photoluminescence by tensile deformation of gel-processed EHO-OPPE–UHMW PE blends was found to deviate from an affine orientation mode: only relatively low dichroic ratios were observed at low draw ratios, and draw ratios of more than 50 were required to produce blends with highly dichroic properties.[9] This—from a technological point of view highly undesirable—circumstance is a direct consequence of the particular phase behavior of these blends: due to an initial phase-separation of the system (during gel-casting and drying), a subsequent efficient orientation of the PPE molecules is achieved only after the agglomerates of the latter 'break up' or 'smear out' which requires elevated draw ratios. The transformation of an originally phase-separated blend into a mixture that exhibits the properties of an apparent molecular dispersion or 'solid-solution' was indeed observed upon tensile deformation of the PPE–UHMW PE blends reported before.[9]

Thus, with the above summarized potential relevance of PL polarizers and the general technological advantages of melt-processing in mind; and the notion that phase-separation between the photoluminescent guest and the matrix should be reduced during formation of the pristine (*i.e.*, unstretched) blend films, we embarked on the preparation of PL polarizers based on melt-processed blends. We systematically investigated the orientational behavior of selected polymeric and small-molecular photoluminescent dyes in a variety of polyethylenes of different molecular architecture (*i.e.*, branch type and content, as well as molecular weight). We compared melt-processed materials with gel-processed blends, and also with films in which the photoluminescent guest molecules were incorporated by the frequently used diffusion method.[24,25] Most importantly, we introduce an optimized melt-processable system which exhibits outstanding dichroic PL properties at minimum draw-ratios.

Results and discussion

EHO-OPPE–PE Blends

Our initial experiments were focused on melt-processed blends of EHO-OPPE[26] of a number-average molecular weight ($\bar{M}_n$) of ~10000 g mol^{-1} (Fig. 1) and different polyethylenes (PE). In order to systematically investigate the effect of the molecular architecture of the matrix polymer on the orientation behavior of the PPE guest, we employed low-density polyethylene (LDPE) and several linear low-density polyethylenes (LLDPE) of similar melt-flow index and, thus, approximately comparable molecular weights, but different type and content of branches (reflected in part by the polymers' density ρ). In addition, we utilized high-density polyethylene (HDPE) as a melt-processable model system for UHMW PE (Table 1). Films based on blends of 0.2 and 1% w/w EHO-OPPE in PE were prepared by melt-mixing the two components in a co-rotating twin-screw mini-extruder and subsequent compression molding (see Experimental section for details) at temperatures between 155 and 170 °C, thus, well above the glass transition of the PPE guest (about 100 °C).[27] The films were subsequently drawn at temperatures of 70–120 °C, *i.e.*, around or slightly below the glass transition temperature of the neat PPE. It should be noted, however, that a minute amount of crystallinity might be present in the PPE phase, which, of course, would reduce the mobility of the latter under the drawing conditions employed to some extent. The maximum draw ratios (λ_{max}) and optimum drawing temperatures are summarized in Table 1.

The anisotropic photophysical behavior of the 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.

Fig. 2 displays, as an example, the polarized PL spectra (recorded parallel and perpendicular to the orientation direction) of a 0.2% w/w EHO-OPPE–LLDPE blend film of a draw ratio of 12, which was characterized by a DR_E of 11. The influences of the draw ratio and the architecture of the matrix polymer on the dichroic ratio of the different EHO-OPPE–PE blends are summarized in Fig. 3. For the purpose of comparison, previously published data[9] of gel-processed 2% w/w EHO-OPPE–UHMW PE blend films are also included. Data of the 1% w/w EHO-OPPE–LLDPE blend films were comparable to

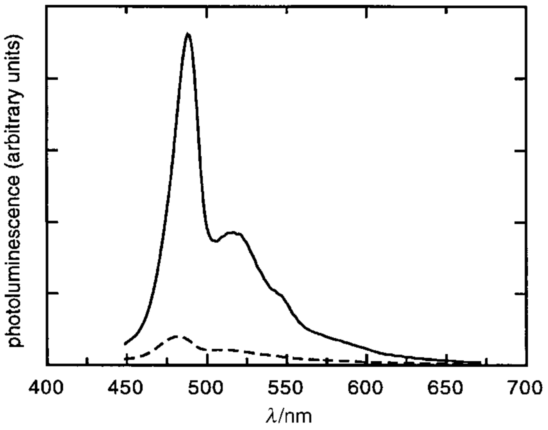

Fig. 2 Polarized photoluminescence spectra of a melt-processed, oriented ($\lambda = 12$) 0.2% w/w EHO-OPPE–LLDPE blend film, recorded under isotropic excitation and polarized detection in p- (solid line) and s- (dashed line) mode.

Table 1 Properties and processing parameters of the polyethylenes used

Polymer	Branches[a]	Melt flow index[b]/ g per 10 min	Density/ g cm^{-3}	Drawing temperature/°C	Maximum draw ratio
LDPE	long-chain (C_4)	1.2	0.922	75	5
LLDPE	short-chain (C_8)	1	0.905	65	7
LLDPE	short-chain (C_8)	1.05	0.919	90	10
LLDPE	short-chain (C_8)	1	0.942	100	12
HDPE	—	0.16	0.958	120	20
UHMW PE	—	n.a.	0.93	120	80

[a]Symbol in brackets indicates the co-monomer (C_8: octene; C_4: butene). [b]Measured at 190 °C/2.16 kg; except HDPE: 190 °C/2.21 kg. n.a.: not applicable.

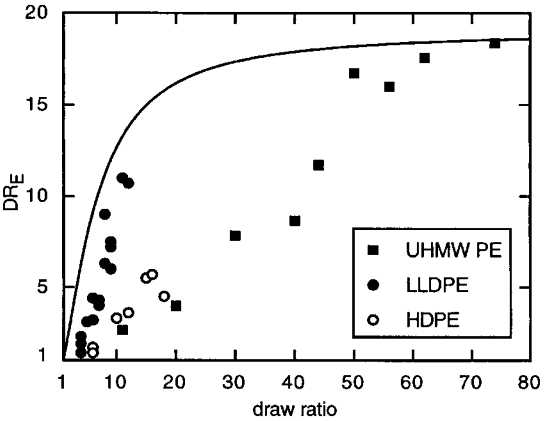

Fig. 3 Emission dichroic ratios of oriented films based on blends of 0.2% w/w EHO-OPPE–LLDPE, 0.2% w/w EHO-OPPE–HDPE, and 2% w/w EHO-OPPE–UHMW PE, as a function of draw ratio. The solid line reflects the theoretical limit, assuming affine deformation and employing an ultimate dichroic ratio of 19 for the EHO-OPPE–PE system [Eqns. (1)–(2)].

those of the 0.2% w/w series but, for the sake of clarity, we omitted these results in Fig. 3. Also, our experiments indicate that the orientational behavior of EHO-OPPE is similar in all LLDPE blends under investigation which therefore have been summarized as one series in Fig. 3. The latter observation suggests that the content of hexyl side chains in these matrix materials only has a minor influence on the development of the guest's orientation behavior; except that it leads to different optimum drawing temperatures and maximum draw ratios. Importantly, the data in Fig. 3 reveal that the orientation behavior of the PPE guest significantly differs when comparing blends with LLDPE, HDPE, and UHMW PE: the slope of the initial linear increase of DR_E with draw ratio is dramatically higher in matrices of LLDPE than UHMW PE. HDPE seems to represent an intermediate between these systems. LDPE—not shown in the graph—yielded similar dichroic ratios to those of comparable HDPE-based films, but exhibited a maximum draw ratio of only about 5. Clearly, at low draw ratios, the EHO-OPPE–LLDPE blends are characterized by a significantly higher orientation of the PPE guest than UHMW PE-based blends of comparable draw ratios. However, due to the lower maximum draw ratio of the present LLDPE-based blends ($\lambda_{max} \sim 12$, see Table 1), and the outstanding drawability of the gel-processed UHMW PE blends ($\lambda_{max} \sim 80$), the maximally achievable DR_E was found to be higher in the latter (18.5 *vs.* 12). The data presented in Fig. 3 suggest that HDPE and LDPE are less suitable matrix materials for the preparation of highly oriented blends with EHO-OPPE, since these polymers seem to combine a limited drawability (particularly LDPE) with a rather unfavorably low orientation efficiency of the PPE guest. Fig. 3 also shows theoretical data for optical anisotropy of EHO-OPPE–PE blends calculated under the assumption of an affine orientation behavior of the luminescent guest molecules [Eqns. (1)–(2)], and employing an ultimate dichroic ratio, DR_{E0}, of 19 for this system (DR_{E0} was semiempirically determined by matching with the highest experimental $DR_E(\lambda_{max})$).

It is evident that in none of the blends under investigation, the conjugated macromolecules exhibit an orientational behavior which precisely follows the pseudo-affine deformation scheme. However, the results unequivocally demonstrate that among the various systems studied EHO-OPPE maximally adopts the orientation of the matrix in LLDPE-based blends. This result is consistent with and explains the different phase behavior of the investigated blends. As discussed above, pristine, gel-processed EHO-OPPE–UHMW PE blends suffer from an initial phase separation of the two polymers. We have shown earlier[9] that in this system a transition into a molecular dispersion or 'solid-solution' can very sensitively be monitored by the shape of the emission spectra of these materials. The emission spectrum of the undrawn gel-processed EHO-OPPE–UHMW PE blend is relatively broad and only poorly resolved; it is comparable to the one of the neat, amorphous or partially crystalline film of the conjugated polymer (Fig. 4A) and indicates that a phase-separation between the PPE and UHMW-PE appears to have occurred. By contrast, the emission spectrum of the drawn EHO-OPPE–UHMW PE blend is fairly narrow, shows well-resolved vibronic features, and virtually matches the spectra of the PPE in solution (Fig. 4B). Thus, in the latter system, the PPE appears to behave as if it was molecularly dispersed or 'dissolved' in the solid polyethylene matrix. Importantly, and very much in contrast to the pristine, undrawn, EHO-OPPE–UHMW PE blends, similar well-defined molecular features were observed for the emission spectra of the *undrawn* melt-processed EHO-OPPE–LLDPE blends. The latter indicates that phase-separation between the luminescent guest and the matrix polymer was—at least to a certain extent—avoided in this system, which explains its favorable orientation behavior, as discussed above. It should be recognized, however, that a truly molecular dispersion or solution in the polymer blends is, of course, highly unlikely for simple thermodynamic reasons,[28] although the photoluminescent characteristics of a true solution appear to be present.

It should be noted that the present melt-processed EHO-OPPE blends show somewhat lower dichroic ratios in absorption than in emission (when calculating DR_A from the ratio of the peak maxima, DR_A was found to be up to a factor of two lower than the respective DR_E). This behavior is in contrast to the previous results obtained for the EHO-OPPE–UHMW PE blends,[9] and also at variance with those of the blends of small-molecular PL dyes and LLDPE pre-

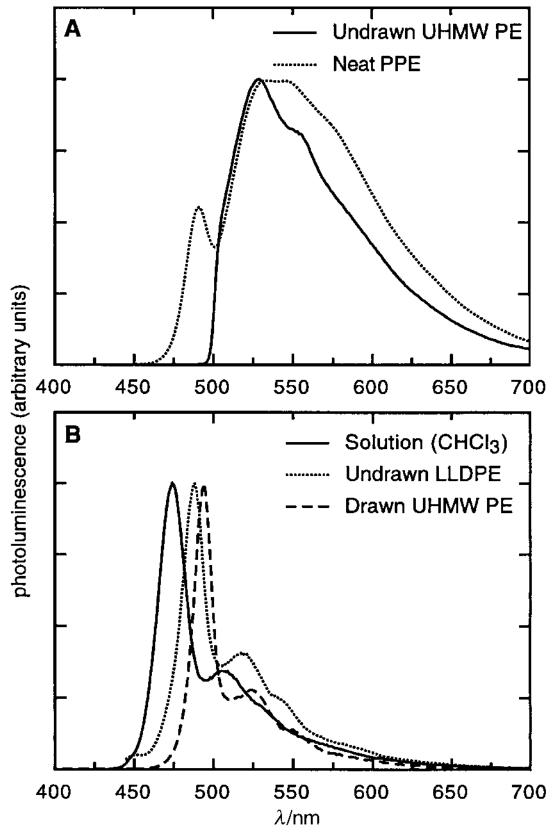

Fig. 4 (A) Photoluminescence spectra of a spin-cast film of neat EHO-OPPE and an *unoriented* EHO-OPPE–UHMW PE blend film. (B) Photoluminescence spectra of EHO-OPPE solution in $CHCl_3$, an *unoriented* EHO-OPPE–LLDPE blend film prepared by melt-extrusion and subsequent molding, and an *oriented* EHO-OPPE–UHMW PE blend film.

sented below, for which similar absorption and emission dichroic ratios were measured. It suggests that the absorption characteristics of the melt-processed EHO-OPPE–LLDPE blends are partially governed by some remaining, hardly oriented and poorly dispersed (and therefore also less luminescent, see refs. 9 and 26), perhaps crosslinked EHO-OPPE-clusters; while the emission characteristics are dominated by highly oriented, well dispersed (and therefore highly luminescent) luminophores.

BPB–PE and BPBC$_{12}$–PE blends

Triggered by the above findings, we have further undertaken to investigate the orientational behavior of melt-processed blends based on LLDPE and two low-molecular weight analogues of PPE (Fig. 1). Very much like EHO-OPPE, these luminophores—based on a 1,4-bis(phenylethynyl)benzene (BPB) moiety—exhibit high aspect ratios and large PL quantum efficiencies,[29] and we surmised that their electronic transition dipole moments could optimally coincide with their geometric long axis. In order to increase the compatibility with the PE matrix, in one instance we derivatized the 1,4-bis(phenylethynyl)benzene moiety with dodecyloxy groups in the *para* positions of the two terminal phenyl rings, resulting in BPBC$_{12}$.[30] Films based on blends of 0.2% and 2%, and in the case of BPBC$_{12}$ also 0.8% w/w of the photoluminescent guest in LLDPE ($\rho = 0.919$ g cm^{-3}) were prepared by melt-processing as described above and were subsequently drawn at 90 °C. For the purpose of comparison, we also have incorporated the BPB and BPBC$_{12}$ guests into unstretched LLDPE films by 'guest-diffusion', *i.e.*, by swelling the latter with a solution containing the photoluminescent dye, prior to tensile deformation.[24,25] Comparative absorption experiments with the melt-processed films indicate concentrations of ~0.05% w/w of the photoluminescent guest in the latter.

Blends containing BPB were processed at 155 or 185 °C, *i.e.*, below or above the melting temperature of the BPB guest (176–178 °C). All BPB–LLDPE blends that were either processed at 155 °C, or comprised 2% w/w BPB, were found to exhibit a large-scale phase-separation between BPB and the LLDPE matrix, as unequivocally visualized with optical microscopy. By contrast, a 0.2% w/w BPB–LLDPE blend film processed at 185 °C had a homogeneous appearance (as determined by polarized optical microscopy). Drawn films of this material were found to exhibit rather strongly polarized absorption and emission, as shown in Fig. 5A for a blend film of a draw ratio of 9, which was characterized by a DR$_E$ of 11 and a DR$_A$ of 14. Interestingly, significantly higher dichroic ratios were measured for the drawn BPB–LLDPE blend films that were prepared by diffusion of the PL guest into a film of the PE matrix. For example, a film of a draw ratio of 10 was characterized by a DR$_E$ of ~44 and an about equally high DR$_A$ (Fig. 5B; additional data for some lower draw ratios are given in Fig. 7). Note that the accurate determination of DR$_A$ in these highly oriented films is stifled by the extremely low absorption of s-polarized light and the comparably large contribution from light scattering of the matrix, resulting in a potentially large experimental error for DR$_A$.

The liquid-crystalline BPBC$_{12}$ displayed a more complex thermal behavior than BPB, with transitions at 112 (solid–solid), 155 (solid–solid), 174 (solid–smectic), 185 (smectic–nematic), and 197 °C (nematic–isotropic melt).[30] Blends containing BPBC$_{12}$ were processed at 155 or 180 °C; all BPBC$_{12}$–LLDPE blends had a homogeneous appearance (as determined by polarized optical microscopy). Drawn films of this material show unexpectedly highly polarized absorption and emission, as demonstrated in Fig. 6 for a 0.2% w/w BPBC$_{12}$–LLDPE blend film of a draw ratio of 10. The latter was characterized by an (integrated) DR$_E$ of about 50 and a similar DR$_A$. Experiments with blends processed at 155 or 180 °C revealed that for this particular composition the orientation of the photoluminescent guest, as reflected by DR$_E$, was independent of the processing temperature. The dichroic ratio of the BPBC$_{12}$–LLDPE systems was found to slightly decrease when the concentration of the photoluminescent guest was increased (0.2% w/w, $\lambda = 9$, DR$_E = 38$; 0.8% w/w, $\lambda = 9$, DR$_E = 37$; 2% w/w, $\lambda = 9$, DR$_E = 24$). We attribute the latter phenomenon to a limited solubility of the dichroic PL dye in the matrix polymer. Oriented BPBC$_{12}$–LLDPE blend films prepared by guest-diffusion exhibited an essentially similar maximum orientation of the photoluminescent guest as the melt-processed 0.2% w/w BPBC$_{12}$–LLDPE blend.

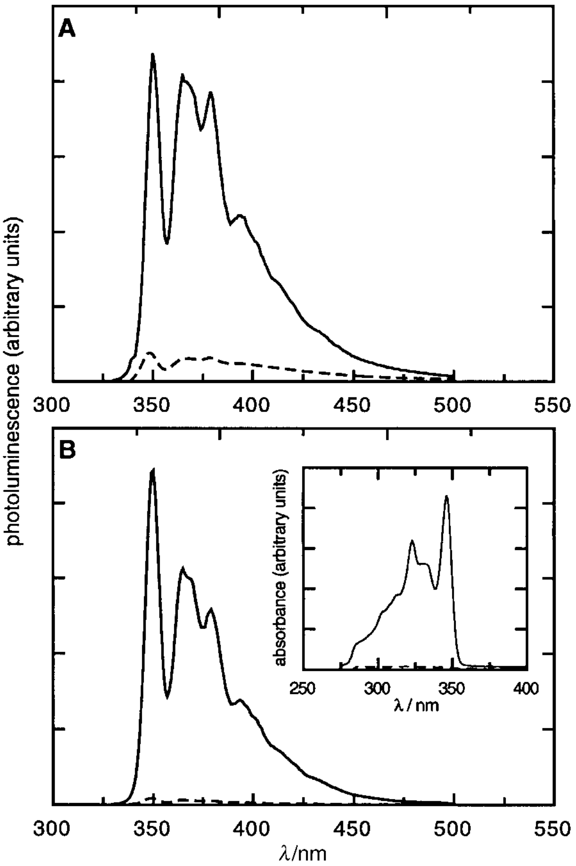

Fig. 5 Polarized photoluminescence spectra of oriented ($\lambda = 9$) BPB–LLDPE blend films, recorded under isotropic excitation and polarized detection in p- (solid line) and s- (dashed line) mode. (A) Blend film comprising 0.2% w/w BPB, prepared by melt-extrusion at 185 °C and subsequent molding. (B) Blend film comprising approximately 0.05% w/w BPB, prepared by diffusing the PL dye into an unstretched film of pure LLDPE and subsequent tensile deformation; the inset shows polarized absorption spectra of the same film, recorded with p- (solid line) and s-polarized (dashed line) light.

In order to compare and rationalize the orientation behavior of the photoluminescent guest molecules in the above described films, the emission dichroic ratios of oriented BPB–LLDPE and BPBC$_{12}$–LLDPE blend films prepared by melt-processing and guest-diffusion are summarized in Fig. 7; together with the theoretical limit, assuming affine deformation, and employing an ultimate dichroic ratio of infinity [Eqns. (1)–(2)]. It is evident that in films prepared by guest-diffusion, the experimentally determined values for DR$_E$ approximately follow the theoretical predictions, demonstrating that the transition dipole moments of the presently employed luminophores indeed coincide with their geometric axis, and perfectly adapt the orientation of the polyethylene matrix. This behavior is consistent with the supposition that the photoluminescent guest molecules are molecularly dispersed in the amorphous fraction of the polyethylene during the diffusion process.[31] By contrast, the optical anisotropy of melt-processed BPB–LLDPE blends is significantly lower than

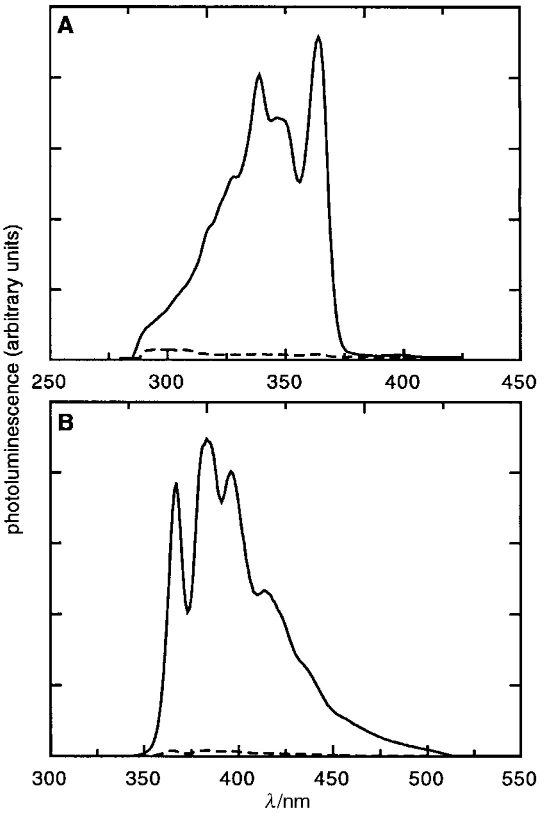

Fig. 6 Polarized absorption and photoluminescence spectra of an oriented ($\lambda = 10$) 0.2% w/w $BPBC_{12}$–LLDPE blend film. (A) Polarized absorption spectra recorded with p- (solid line) and s-polarized (dashed line) light. (B) Polarized photoluminescence spectra, recorded under isotropic excitation and polarized detection in p- (solid line) and s- (dashed line) mode.

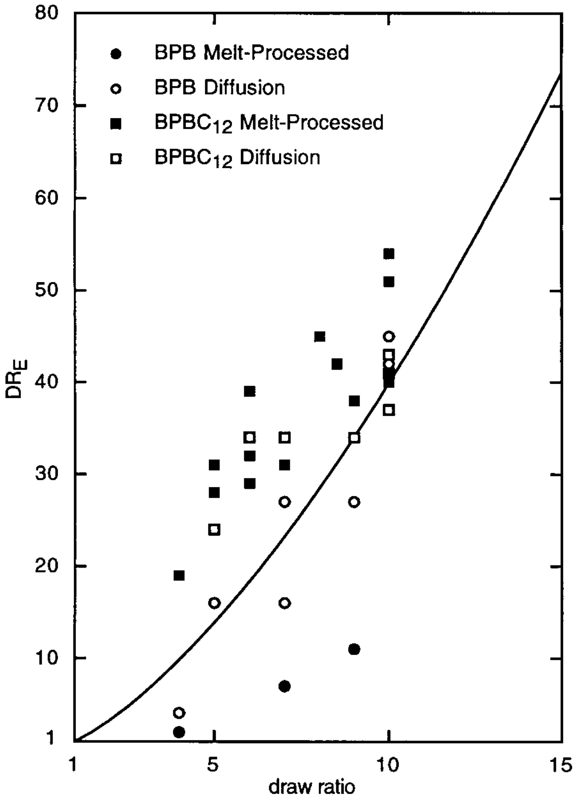

Fig. 7 Emission dichroic ratios of oriented BPB–LLDPE and $BPBC_{12}$–LLDPE blend films prepared by melt-processing (comprising 0.2% w/w of the photoluminescent guest) and diffusion. The solid line reflects the theoretical limit [Eqns. (1)–(2)], assuming affine deformation and employing an ultimate dichroic ratio, DR_{E0}, of infinity.

the predicted values. We attribute the latter observation to phase-separation of this system resulting in an 'immobilization' of the high-melting BPB under the deformation conditions applied. The observed macroscopic phase separation in many of the investigated BPB–LLDPE blends corroborates this view.

Most importantly, melt-processed $BPBC_{12}$–LLDPE films exhibited extraordinary high optical anisotropies that exceed values of the blends prepared by diffusion, as well as those calculated on the basis of affine deformation. This extremely favorable behavior points to a molecular dispersion of the $BPBC_{12}$ luminophores in the polyethylene matrix after thermoplastic processing (at least in a concentration regime of between 0.2–0.8% w/w of the luminescent guest), which ensures a significant orientability of the latter. A slightly 'accelerated' or more efficient orientation of the former, when compared to the affine deformation mode, might be explained by the fact that this model only reliably reflects an average orientation, but fails to adequately separate the components of crystalline and amorphous phases. Thus, it can be speculated that in the case of the present melt-processed $BPBC_{12}$–LLDPE blends the photoluminescent guest molecules do not necessarily adopt an average orientation. However, we should also clearly point out the noticeable scattering of the data presented in Fig. 7. The experimental error in the determination of DR_E (λ) is, in our view, largely related to two factors: first, the value of DR_E is computed by dividing the emission intensity of p-polarized by that of s-polarized light. For the present, highly oriented systems, the latter was an extremely small number and, thus, even relatively small fluctuations in this intensity caused, for example, by scattering from structural defects, reflections, mismatch of angle, quality of the analyzer, *etc.*, may result in a significant experimental error for DR_E. Perhaps an even more important uncertainty arises from the determination of the draw ratio, which in laboratory samples is not necessarily completely homogeneous throughout the whole film, and, particularly in the case of films of low draw ratio, may suffer from some inaccuracy.

Conclusions

In summary, we have shown that melt-processing and subsequent tensile deformation of blends of different photoluminescent guest molecules and polyethylene—in particular LLDPE—can lead to an outstanding orientation of the conjugated polymer guest, resulting in state-of-the-art polarized photoluminescence and absorption of the prepared films. Experiments suggest that maximum orientation and optical anisotropy are obtained if the photoluminescent guest is of high aspect ratio, exhibits electronic transition dipole moments that optimally coincide with its geometric long axis, and if phase-separation between the photoluminescent guest and the matrix polymer is reduced or avoided during the preparation of the pristine blend films. As a result of these findings, an optimized, melt-processable blend based on 1,4-bis(4-dodecyloxyphenylethynyl)benzene and linear low-density polyethylene was developed that allowed production of photoluminescent polarizers which at draw ratios of only 10 exhibited (integrated) dichroic ratios exceeding 50.

Finally, we would like to briefly comment on the implications of the above discussed observations for investigation of orientation processes of polymers with polarized spectroscopy in general. In the past, the orientation development in tensile-deformed polymers has been extensively studied, by monitoring the optical anisotropy caused by dichroic absorbing as well as photoluminescent dyes incorporated in the polymer of interest (see for example refs. 23–25, 31). Here, we clearly demonstrated that the orientation of an incorporated dichroic molecule does not necessarily follow the one of the polymer matrix. Significant variation can be observed for a given material system, depending on, for example, the method of preparation, the concentration of the dichroic guest, the deformation temperature, *etc.* Thus, we urge that great caution should be taken when relating the anisotropic optical properties resulting from incorporated guest molecules to the orientation of the matrix polymer.

Experimental

Materials

EHO-OPPE[26] ($\bar{M}_n$ ~10000 g mol^{-1}) and BPBC$_{12}$[30] were prepared according to procedures published elsewhere. BPB was purchased from GFS Chemicals. All polyethylenes (Table 1) are commercially available and were obtained from Dow (LLDPE: Dowlex NG5056E, $\rho = 0.919$ g cm^{-3}; Dowlex BG2340, $\rho = 0.942$ g cm^{-3}; Attane SL4102, $\rho = 0.905$ g cm^{-3}. LDPE: LDPE 310R) and DSM (HDPE: Stamylan HD8621). All solvents were of analytical grade quality and were purchased from Fluka.

Preparation of blends

PE pellets (5 g) were first coated with the PL dye by casting a solution of the latter (10 or 100 mg) in toluene (EHO-OPPE) or CHCl$_3$ (BPB, BPBC$_{12}$) over the preheated (~60 °C) PE pellets and evaporating the solvent. The coated PE pellets were fed into a recycling, co-rotating twin-screw mini-extruder (commercially available from DACA Instruments, Santa Barbara, CA), mixed for 10 min at 155 °C (all dyes in LLDPE and LDPE), 170 °C (EHO-OPPE in HDPE), 180 °C (BPBC$_{12}$ in LLDPE) or 185 °C (BPB in LLDPE), and subsequently extruded.

Preparation of films

Films were prepared by compression-molding the extruded blends between two Mylar®-foils in a Carver press at 150 °C (all dyes in LLDPE and LDPE), 165 °C (EHO-OPPE in HDPE), 180 °C (BPBC$_{12}$ in LLDPE) or 185 °C (BPB in LLDPE). All resulting blend films had a thickness of about 110–130 μm. The films were drawn at temperatures of 70–120 °C on a thermostatically controlled hot shoe. Draw ratios were calculated from the displacement of distance marks printed on the films prior to drawing.

In addition, blend films were also produced by diffusing the small-molecular PL dyes into unstretched films of pure LLDPE. The LLDPE films were prepared as described above (without the addition of the PL dye) and, subsequently, immersed for 24 h in a solution of the dye (0.5–2% w/w) in CHCl$_3$. In the following, the films were rinsed with CHCl$_3$, dried, and oriented as described above.

Optical characterization

For the photophysical experiments, the polymer films were sandwiched between two quartz slides, applying a minor amount of poly(methylphenylsiloxane) 550® fluid (Aldrich, viscosity 125 centistokes) in order to minimize light scattering at the film surfaces. Polarized UV–VIS spectra were recorded with a Perkin Elmer Lambda 900 instrument, fitted with motor driven Glan-Thomson polarizers. Scattering effects of the matrix were compensated in the absorption measurements by subtracting the spectra of pure PE films of comparable draw ratio and thickness. Absorption dichroic ratios, DR$_A$, were determined by the ratio of the integrals of the main absorption bands (EHO-OPPE: 350–540 nm; BPB and BPBC$_{12}$: 280–370 nm) measured through a polarizer with its optical axis parallel and perpendicular, respectively, to the deformation direction of the film. Corrected PL spectra were recorded in front-face mode on a SPEX Fluorolog 3 (Model FL3–12), using unpolarized light for excitation (excitation at 440 nm for EHO-OPPE-based blends, and 322 nm for BPB and BPBC$_{12}$-based blends) and a Glan-Thomson polarizer on the detector side. In order to compensate for the polarization-sensitivity of the instrument, a depolarizer was placed behind the latter. Emission dichroic ratios, DR$_E$, were determined by the ratio of the integrals of the emission bands (EHO-OPPE: 450–675 nm; BPB and BPBC$_{12}$: 330–520 nm) measured through a polarizer with its optical axis parallel and perpendicular, respectively, to the deformation direction of the film.

Acknowledgements

We wish to thank Dr C. Bastiaansen for many helpful discussions and S. Dellsperger for crucial assistance with the polymer synthesis.

References

1 L. K. M. Chan, in *The Encyclopedia of Advanced Materials*, Vol. 2, ed. D. Bloor, R. J. Brook, M. C. Flemings and S. Mahajan, Elsevier Science Ltd., Oxford, 1994, p. 1294.
2 T. J. Nelson and J. R. Wullert II, in *Electronic Information Display Technologies*, World Scientific Publishing, Singapore, 1997.
3 M. Schadt and J. Fünfschilling, *Jpn. J. Appl. Phys.*, 1990, **29**, 1974.
4 D. J. Broer, J. Lub and G. N. Mol, *Nature*, 1995, **378**, 467.
5 D. Coates, M. J. Goulding, S. Greenfield, J. M. W. Hanmer, E. Jolliffe, S. A. Marden, O. L. Parri and M. Verrall, *SID 96 Applications Digest*, 1996, 67.
6 R. A. M. Hikmet, *Mol. Cryst. Liq. Cryst.*, 1991, **198**, 357.
7 R. A. M. Hikmet, *J. Appl. Phys.*, 1990, **68**, 4406.
8 Y. Dirix, H. Jagt, R. Hikmet and C. Bastiaansen, *J. Appl. Phys.*, 1998, **83**, 2927.
9 C. Weder, C. Sarwa, C. Bastiaansen and P. Smith, *Adv. Mater.*, 1997, **9**, 1035.
10 A. Montali, C. Bastiaansen, P. Smith and C. Weder, *Nature*, 1998, **392**, 261.
11 C. Weder, C. Sarwa, A. Montali, C. Bastiaansen and P. Smith, *Science*, 1998, **279**, 835.
12 A. Montali, P. Smith and C. Weder, *J. Mater. Sci.*, in the press.
13 A. R. A. Palmans, P. Smith and C. Weder, *Macromolecules*, in the press.
14 I. M. Ward, *Proc. Phys. Soc.*, 1962, **80**, 1176.
15 Y. Dirix, T. A. Tervoort, C. Bastiaansen and P. J. Lemstra, *J. Text. Inst.*, 1995, **86**, 314.
16 Y. T. Tang, P. J. Phillips and E. W. Thulstrup, *Chem. Phys. Lett.*, 1982, **93**, 66.
17 P. J. Phillips, *Chem. Rev.*, 1990, **90**, 425.
18 Y. Dirix, T. A. Tervoort and C. Bastiaansen, *Macromolecules*, 1995, **28**, 486.
19 Y. Dirix, T. A. Tervoort and C. Bastiaansen, *Macromolecules*, 1997, **30**, 2175.
20 O. Kratky, *Kolloid Z.*, 1933, **64**, 213.
21 R. B. D. Fraser, *J. Chem. Phys.*, 1953, **21**, 1511.
22 P. H. Hermans and D. Heikens, *Recl. Trav. Chim. Pays-Bas*, 1952, **71**, 49.
23 J. Michl and E. W. Thulstrup, in *Spectroscopy with Polarized Light*, VCH Publishers Inc., New York, 1986.
24 E. W. Thulstrup and J. Michl, *J. Phys. Chem.*, 1980, **84**, 81.
25 E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, 1982, **104**, 5594.
26 C. Weder and M. S. Wrighton, *Macromolecules*, 1996, **29**, 5157.
27 It should be noted that differential scanning calorimetry and dynamic mechanical thermal analysis data of the pure EHO-OPPE indicate an onset of thermal decomposition due to crosslinking at about 130 °C (D. Steiger, P. Smith and C. Weder, *Macromol. Rapid. Commun.*, 1997, **18**, 643). However, the blends prepared here were fully soluble after melt-processing and the absorption and PL emission spectra of these solutions were identical to an untreated reference, indicating that no significant degradation of the PPE occurred.
28 P. J. Flory, *Macromolecules*, 1978, **11**, 1138.
29 S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nakashima, S. Akiyama and W. Fabian, *J. Chem. Soc.*, *Perkin Trans. 1*, 1992, 755.
30 A. R. A. Palmans, M. Eglin, A. Montali, P. Smith and C. Weder, *Chem. Mater.*, submitted.
31 E. W. Thulstrup, J. Michl and J. H. Eggers, *J. Phys. Chem.*, 1970, **74**, 3868.

Paper 9/02864A