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Phase Behavior and Anisotropic Optical Properties of Photoluminescent Polarizers

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SUMMARY: The phase behavior and anisotropic optical properties of tensile deformed blends of a photoluminescent polymer guest in an ultra-high molecular weight polyethylene matrix were studied on the level of single molecules by means of scanning confocal optical microscopy. It is shown that upon tensile deformation of the blends, the system transforms from a phase-separated system into a quasi-molecular solid solution. The influence of this phase transition on the anisotropic optical properties of oriented blend films was also investigated with polarized steady-state photoluminescence spectroscopy. We show that well-dissolved guest molecules tend to reach higher degrees of orientation at lower draw ratios of the blend films compared to guests that phase-separate from the matrix polymer. Dichroic ratios in emission in the range of 50 were observed in optimized blend films based on photoluminescent oligomers and linear low density polyethylene.

Introduction

Color liquid-crystal displays (LCDs) suffer from limited brightness and energy efficiency, originating from the use of absorbing polarizers and color filters1). Photoluminescent (PL) polarizers consisting of uniaxially oriented blends of a PL polymer and ultra-high molecular weight polyethylene (UHMW-PE) which, after photoexcitation, absorb and emit light in a highly linearly polarized fashion, have been presented as a possibility to increase the efficiency, brightness and viewing angle of LCDs2). In our previous studies, a highly luminescent and form-anisotropic conjugated polymer (EHO-OPPE, a poly(2,5-dialkoxy-*p*-phenylene ethynylene) derivative) was typically used as the PL emitter, embedded in UHMW-PE2,3). The PL polarizers were prepared by the earlier described gel-casting process3),

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and uniaxially oriented through tensile deformation to draw ratios, λ, in excess of 70. Due to the thermodynamically unfavorable mixing behavior of polymers[4)], a phase-separated system was observed in the pristine, i.e. unstretched PL films[3)]. Based on the interpretation of properties of large multimolecular ensembles (i.e., luminescence and diffraction spectra) it was previously suggested that the phase-separated PL polymer domains are deformed during tensile deformation in order to yield an *apparent* molecular dispersion of EHO-OPPE in UHMW-PE[3)]. We now present investigations carried out on the level of single-molecules with scanning confocal optical microscopy (SCOM)[5)], which confirm this view. The influence of the initial domain size on the anisotropic emission properties of the PL polarizers was investigated by characterizing UHMW-PE blends with EHO-OPPE concentrations of 0.05, 0.2, 1, 2, 5 and 25% w/w. The importance of using PL dyes which are "soluble" in the matrix polymer was shown by comparing blends based on 1,4-bis(4-dodecyloxy phenyl ethynyl)benzene ($BPBC_{12}$) and EHO-OPPE, respectively, of similar concentrations; in the former blend, the optical anisotropy was found to be substantially higher compared to the latter. Finally, an optimized, melt-processed blend based on $BPBC_{12}$ and linear low-density polyethylene (LLDPE) was developed that allows efficient manufacturing of PL polarizers which at draw ratios of only 10 exhibit emission dichroic ratios exceeding 50.

Experimental

EHO-OPPE[6)] (M_n ~ 10'000 $gmol^{-1}$) and $BPBC_{12}$[7)] (Fig. 1) were prepared according to procedures described elsewhere. The polyethylenes employed are commercially available and were obtained from Hoechst (UHMW-PE: GUR 412, M_w ~ $3.5 \cdot 10^6$) and Dow (LLDPE: Dowlex NG5056E, $\rho = 0.919 gcm^{-3}$).

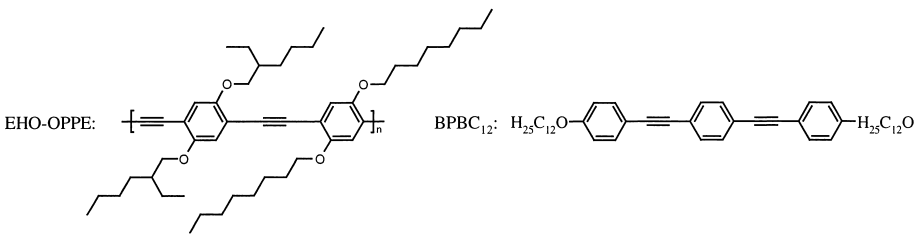

Fig. 1: Chemical structure of the photoluminescent dyes employed in this work.

Film Preparation. Blend films of EHO-OPPE and UHMW-PE with EHO-OPPE concentrations of 0.05, 0.2, 1, 2, 5 and 25% w/w were prepared according to procedures described elsewhere$^{3)}$. Similarly, a film with a nominal concentration of 10^{-4} % w/w EHO-OPPE in UHMW-PE was prepared through gel-casting for the SCOM measurements, and the same procedures were also employed for the preparation of a blend film of 0.2% w/w $BPBC_{12}$ in UHMW-PE. Films of $BPBC_{12}$ and LLDPE with $BPBC_{12}$ concentrations of 0.2, 0.8 and 2% w/w were prepared by feeding PE pellets, which had previously been coated with the PL dye, into a recycling, co-rotating twin-screw mini-extruder (DACA instruments, Santa Barbara, CA). The pellets were mixed for 10 min at 155°C and subsequently extruded. The extrudate was compression-molded in a Carver press at 150°C to yield films of around 100 μm thickness. All films were drawn at temperatures of 70°C (LLDPE) or 120°C (UHMW-PE) on a thermostatically controlled hot shoe. Draw ratios were calculated from the displacement of distance marks printed on the films prior to drawing.

Optical Characterization. PL spectra were recorded on a SPEX Fluorolog 3 (Model FL3-12), fitted with motor driven Glan-Thompson polarizers, and with a 450W Xe-lamp for excitation. The films were sandwiched between two quartz slides, applying a minor amount of silicon oil in order to minimize light scattering at the film surfaces. We quantified the anisotropic optical characteristics of the drawn films by the dichroic ratio, defined for emission (DR_{em}) as the ratio between the respective spectra measured with polarization parallel (*p*-) and perpendicular (*s*-) to the drawing direction. In our determination of the dichroic ratio in emission, 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. SCOM measurements were performed under excitation from an Ar-laser at 488 nm; the setup for the measurements was described by Fleury et al.$^{8)}$

Results and Discussion

SCOM images of an EHO-OPPE / UHMW-PE blend film with a nominal EHO-OPPE concentration of 10^{-4} % w/w which was drawn to a draw ratio of 80 (Fig. 2a), recorded by detecting the polarization component parallel to the drawing direction (vertical in the Fig.) appear to reveal single fluorescent spots of variable intensity aligned along the drawing direction. Many of these spots can be attributed to single EHO-OPPE molecules because of their characteristic blinking and stepwise photobleaching apparent from fluorescence time traces$^{9)}$. The insets in Figs. 2a and 2b show the fluorescence signal recorded simultaneously for the perpendicular polarization component at the corresponding positions. The high contrast in intensity between the polarization directions in Fig. 2a clearly demonstrates on a molecular level the high degree of orientation of the conjugated molecules. The above observations are in sharp contrast to the corresponding confocal images of the unoriented film (Fig. 2b and inset). For the latter, the absence of blinking and stepwise photobleaching are fully consistent with the presence of EHO-PPE clusters that are phase-separated from the UHMW-PE matrix; and it is obvious that the PL molecules are, as expected, fully disordered. These images, although obtained on films of a significantly lower dye concentration than employed in earlier experiments, confirm previous findings$^{3)}$, demonstrating that an efficient orientation of the EHO-OPPE molecules is achieved only after the clusters of the latter are deformed and successively dispersed in the UHMW-PE matrix, finally yielding an apparent molecular dispersion or solid solution.

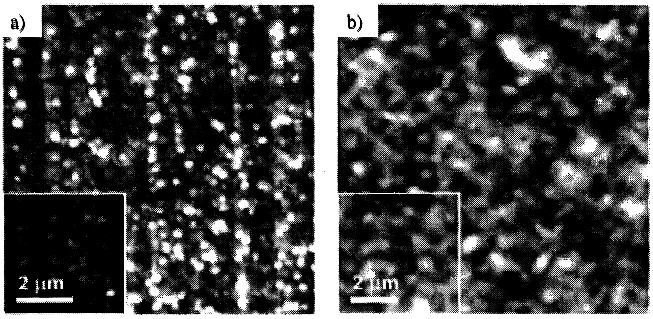

Fig. 2: a) SCOM image of an EHO-OPPE / UHMW-PE blend film oriented to a draw ratio of 80 and b) of the same film in the pristine, undrawn state. Insets: images of the perpendicular polarization component recorded simultaneously at the respective positions (same scale).

In order to obtain more quantitative information on the degree of clustering and orientation of single EHO-OPPE molecules as a function of draw ratio, ~25x25 μm^2 squares of oriented dilute films (10^{-4} % w/w EHO-OPPE) of different draw ratios (20, 30, 40, 70) were imaged. For each draw ratio, at least two images were taken at different locations of the sample in order to minimize effects of inhomogeneous distribution of EHO-OPPE in the matrix. A non-linear least-square fit of fluorescence spots appearing in the images to two-dimensional

Gaussians was performed using the Levenberg-Marquard algorithm[10)]. In addition to accurately determining the center of the fluorescence spots, the fitting procedure yields the integrated intensity, the local background, as well as the respective errors on all parameters. All subsequent statistical evaluations were based on fluorescent spots only with a peak height exceeding the local background by a factor of at least three, and which met the additional requirement that the error of the intensity parameter[10)] does not exceed 20% of the integrated intensity of a peak. By applying these two empirical criteria, fits of poor quality in areas with large background signal or erroneous fits due to e.g. photobleaching during the measurement are discarded without introducing a bias for any particular size of clusters. Each individually fitted fluorescence spot permits the construction of a probability density function (pdf) that specifies the probability for possible results of repeated integrated intensity measurements[11)]. Combining all individual pdf's for accepted fluorescence spots (typically about 100 for a given draw ratio, λ) results in pdf's that characterize the probability distribution for measuring a certain integrated intensity on a randomly selected fluorescent spot. Fig. 3 shows such combined pdf's for films of various draw ratios. The combined pdf's show well-defined maxima at smaller integrated intensities. The peaks occur at equidistant integrated intensity values, independent of λ, as is obvious from the inset of Fig 3. This finding is clear evidence for the presence of an integer number of chromophores in each cluster.

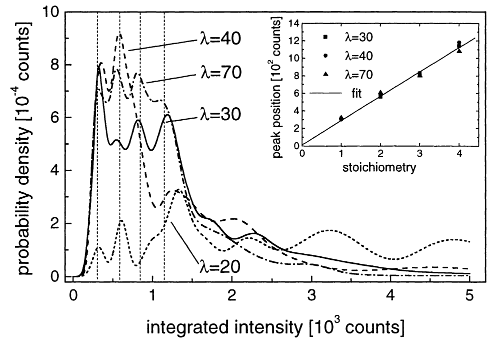

Fig. 3: Intensity probability density functions (pdf's) of oriented binary EHO-OPPE / UHMW-PE blend films comprising 10^{-4} % w/w of the EHO-OPPE guest, as a function of the draw ratio λ.

The probability for measuring a given stoichiometry (i.e. the number of chromophores comprised in a cluster) can be deduced from such combined pdf's by fitting a sum of Gaussians to the distributions to determine peak positions and relative weight of the first peaks[11)]. Peaks with stoichiometries larger than 4 can hardly be observed in our experiments. This is probably due to the strongly increased probability of photobleaching in larger clusters; an increasing influence of energy transfer effects and an intrinsic increase in the width of individual pdf's due to shot noise[11)]. We monitored the relative weight of the different stoichiometries in order to study cluster dissolution as a result of tensile deformation. The obvious increase in the occurrence of single chromophores and bi-chromophoric clusters with increasing draw ratio (Fig. 3) at the expense of a decrease in the number of ter-chromophoric and larger clusters illustrates the increased degree of molecular dispersion of initially phase-separated domains. This effect is nicely illustrated by comparing, for example, the pdf for λ=30 with the pdf for λ=40. The probability to find single chromophores and bi-chromophoric clusters is strongly increased for the latter. For films of relatively low draw ratio (λ=20), only single fluorescence spots contribute to the uni- and bichromophoric peaks in the pdf, respectively, while the ter-chromophoric peak, in fact, happens to be completely absent. The pdf for λ=20 is, therefore, not included in the inset. For films of λ=70, a strong decrease of larger clusters is observed in the pdf, while the weight of the first three peaks is approximately equal. For single and bichromophoric clusters in the latter film the weight actually is slightly smaller than for the film of λ=40. We attribute this finding to inhomogeneities in the films that could not completely be averaged out although images were recorded at different locations. Alternatively, it might be argued that single conjugated molecules may actually represent two or more indistinguishable chromophores[12,13)]. Nevertheless, Fig. 3 provides clear quantitative evidence for a deformation-induced molecular dispersion of small clusters, ultimately leading to isolated single chromophores. Finally, in order to address the issue of deformation-induced orientation of the molecules, the average dichroic ratio of isolated fluorescence spots was determined as a function of the draw ratio. To this end, the ratios of the integrated intensities of fluorescence spots in both polarization directions were calculated for the same set of fluorescence spots as used for the clustering analysis. For each value of the draw ratio λ, the average of the dichroic ratios of individual spots was calculated. The results are plotted in Fig. 4a. Gratifyingly, the dichroic ratio increases with increasing draw ratio and reaches saturation around λ=40. This behavior is in well accord with the results presented and discussed below (Fig. 4b) as well as with previous findings[3)], both obtained in macroscopic studies.

In order to more clearly unveil the influence of a transition from a phase-separated to an apparently dissolved system on the macroscopic emission properties of the polymer blends, we prepared and characterized UHMW-PE blends of different EHO-OPPE concentration. The draw ratio required to obtain an optimal dissolution or dispersion of the guest polymer domains in the host material, and an optimal orientation of the latter, should strongly depend on the initial phase behavior of the pristine blends. In homogeneous blends or blends with smaller PPE clusters highly polarized emission can be expected at smaller draw ratios than in phase separated blends; and it is assumed that the phase behavior of the present EHO-OPPE / UHMW-PE system -at least to a certain extent- can be governed by the composition of the blend.

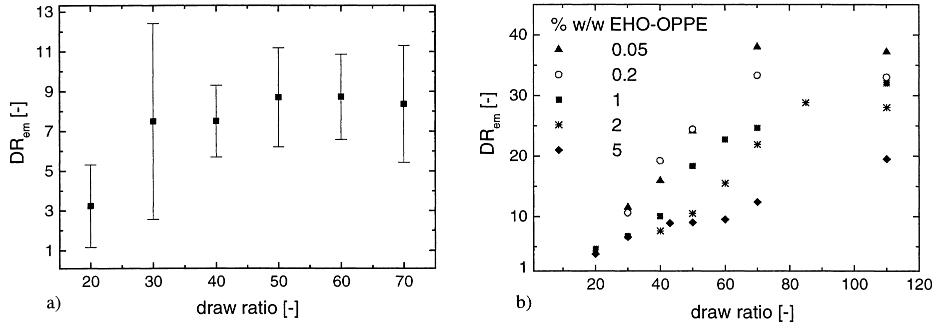

Fig. 4: a) DR_{em} of individual EHO-OPPE clusters and/or single molecules in oriented binary EHO-OPPE / UHMW-PE blend films comprising 10^{-4} % w/w of the EHO-OPPE guest, as a function of draw ratio. b) Macroscopic DR_{em} vs. draw ratio for EHO-OPPE / UHMW-PE blends with different EHO-OPPE concentrations. The absolute values of the maximum dichroic ratio determined by single molecule microscopy of about 9 are significantly lower than the values determined in the macroscopic experiments due to the significant contribution of background luminescence in the former.

The determination of DR_{em} of samples of a draw ratio of 70 confirms this expected behavior, showing a decrease of DR_{em} with increasing EHO-OPPE concentration from 38 in a 0.05% EHO-OPPE blend, to 13 in a blend comprising 5% EHO-OPPE (cf. Fig. 4b). For a blend comprising 25% w/w EHO-OPPE, a DR_{em} of only 5 at a maximal draw ratio of 60 could be measured[3]. The proposed deformation and orientation mechanism for the embedded PPE molecules is further demonstrated by the fact that at even higher draw ratios (λ ~110) all films with concentrations up to 2% w/w of EHO-OPPE reach very high values of around 30 and more. It appears from Fig. 4b that the dichroic ratios of these samples level off at draw ratios of 70-80, and a further increase of the draw ratio does not cause an increase of the optical anisotropy, consistent with the fact that in these samples the EHO-OPPE molecules are optimally dispersed and oriented. On the other hand, when considering films comprising 5% w/w EHO-OPPE, DR_{em} does not seem to reach saturation even at a draw ratio of 110, indicating that - in contrast to the above described diluted samples - in the latter the dispersion and orientation of originally phase-separated EHO-OPPE is significantly stifled. It can be assumed that a further deformation and orientation of the EHO-OPPE clusters and, thus, a further increase in DR_{em}, could be obtained at even higher draw ratios; however, such draw ratios ($\lambda > 110$) could not be obtained in the present films. The same discussion applies to samples with 25% EHO-OPPE, for which such high draw ratios could not be obtained, and, therefore, the maximum value for DR_{em} was found to be limited to only 5 (Fig. 4b, Table 1).

Table 1. Influence of the composition on the dichroic ratio of PL polarizers

composition [a]			DR_{em} @ λ =70	λ_{max}	DR_{em} @ λ_{max}
0.05%	EHO-OPPE	UHMW-PE	38	110	37
0.2%	EHO-OPPE	UHMW-PE	33	110	33
1%	EHO-OPPE	UHMW-PE	25	110	32
2%	EHO-OPPE	UHMW-PE	22	110	28
5%	EHO-OPPE	UHMW-PE	13	110	20
25%	EHO-OPPE	UHMW-PE	n.a.[b]	60	5
0.2%	$BPBC_{12}$	UHMW-PE	45	80	>50
0.2%	$BPBC_{12}$	LLDPE	n.a.	10	>50
0.8%	$BPBC_{12}$	LLDPE	n.a.	9	37
2%	$BPBC_{12}$	LLDPE	n.a.	9	24

[a] All compositions in % w/w.

[b] Not applicable.

We have shown earlier that PL emission spectra of undrawn films allow further insights regarding the relations between the EHO-OPPE concentration and the extent of phase separation. As can be seen from Fig. 5, in the case of a low EHO-OPPE concentration of 0.05% w/w the spectra of unoriented blend films show the characteristics of a (molecular) solution, i.e. a strong predominance of the vibronic band associated to the transition from the lowest vibrational energy level of the excited state to the corresponding ground state. With increasing concentration of the PL polymer, the fraction of well-dispersed EHO-OPPE molecules decreases in favor of aggregated molecules, which at higher concentrations account for the major part of photoluminescence emission. Therefore, with more and larger aggregates present in the films the form of the emission spectrum gradually approaches that of a pure EHO-OPPE film (Fig. 5). A similar effect was observed earlier, when comparing the emission spectra of an undrawn and of an oriented film[3].

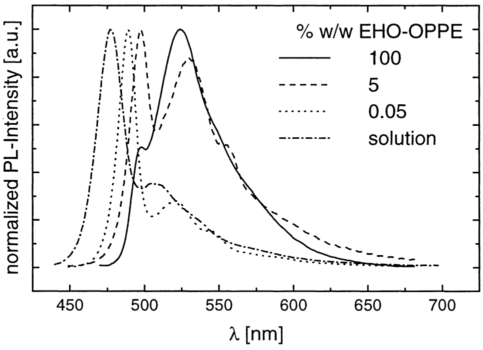

Fig. 5: Steady-state emission spectra of unoriented EHO-OPPE / UHMW-PE blend films with different EHO-OPPE concentrations, and of an EHO-OPPE solution in chloroform. All spectra were recorded under isotropic excitation at 440 nm.

The finding that at a low EHO-OPPE concentration the emission spectrum has the characteristics of a molecular solution apparently stands in contradiction to the SCOM measurements, which indicate that in undrawn films even at extreme dilutions, such as 10^{-4} % w/w, the EHO-OPPE is present in clusters. However, these results suggest that in dilute samples well-dispersed EHO-OPPE molecules dominate the emission, and, therefore, the emission spectra exhibit the characteristics of an apparent solution. Although some clustering can be encountered in films of these concentrations, the emission from these seems to be of rather low intensity due to possible luminescence-quenching in the aggregates[14,15].

In addition, one might speculate that the emission characteristics of clusters of only a few EHO-OPPE molecules are essentially similar to those of a "true" molecular solution.

From the above results we conclude that, in order to obtain highly dichroic emission at moderate draw ratios, a system is required in which the PL dyes are already optimally dispersed prior to the orientation process. Based on these findings, a blend film was prepared, in which EHO-OPPE was substituted by a phenylene ethynylene derivative oligomer, $BPBC_{12}$, based on the assumption that a low-molecular dye might be more compatible with the UHMW-PE matrix. It could, therefore, be expected, that higher dichroic ratios would be obtained at lower draw ratios than in the case of EHO-OPPE-based blends. In Fig. 6, the emission dichroic ratios are shown as a function of draw ratio for dilute 0.2% w/w EHO-OPPE / UHMW-PE and 0.2% w/w $BPBC_{12}$ / UHMW-PE blend films. It is evident that the orientation of the guest occurs much more efficiently in the low molecular weight $BPBC_{12}$-based blend films compared to the EHO-OPPE-based films. High values of DR_{em} (>30) were obtained at draw ratios of only 35. This compares favorably to PL polarizers containing EHO-OPPE as the PL dye, for which draw ratios of more than 70 were necessary to obtain a comparable DR_{em} (cf. Fig. 4 and Fig. 6).

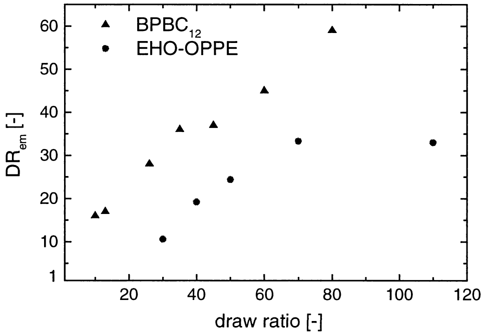

Fig. 6: DR_{em} vs. draw ratio of $BPBC_{12}$ / UHMW-PE and of EHO-OPPE / UHMW-PE blend films, the PL dye concentration in both blends was 0.2% w/w. All values were determined under isotropic excitation at 325 nm ($BPBC_{12}$) and 440 nm (EHO-OPPE).

Triggered by the above findings, we have further undertaken to investigate the orientational behavior of melt-processed blends based on LLDPE and $BPBC_{12}$ [16)]. Films based on blends of 0.2 %, 0.8 % and 2 % w/w of the photoluminescent guest in LLDPE were prepared by melt-processing as described above and were subsequently drawn at 90 °C to draw ratios of around 10. These comparably low draw ratios were limited by the nature of the matrix polymer.

Drawn films of these blends show unexpectedly highly polarized emission, as demonstrated in Figure 7 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_{em} of about 50. 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, $\lambda = 9$, $DR_{em} = 38$; 0.8 % w/w, $\lambda = 9$, $DR_{em} = 37$; 2 % w/w, $\lambda = 9$, $DR_{em} = 24$). The latter results reflect an analogous behavior as was found for the EHO-OPPE / UHMW-PE blends, namely that also in the case of $BPBC_{12}$ / LLDPE blend films higher dye concentrations may lead to a phase separation of the dye in the LLDPE matrix. A thorough investigation of the orientational- and of the phase-behavior of melt-processible PL polarizers based on low molecular weight dyes will be published elsewhere[16].

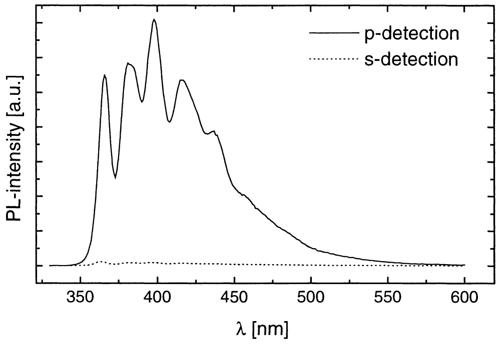

Fig. 7: Emission spectra of an oriented (λ = 10) 0.2% w/w $BPBC_{12}$ / LLDPE blend under isotropic excitation at 322 nm.

Conclusions

In summary, we have demonstrated that control of the phase behavior of blends used for the production of PL polarizers is essential for obtaining maximal orientation of the PL dyes and, consequently, high polarization of the emitted light. In the case of the presently investigated blends comprising polymeric PL dyes, the latter are present in clusters in the pristine polyethylene matrix. These clusters are deformed and elongated upon tensile deformation of the blend films, eventually leading to a quasi-molecular "solid solution". The initial size of such clusters determines the draw ratio which is needed to obtain high optical anisotropy.

Phase-separation between the PL dye and the matrix material is observed for large concentrations of the PL dye, and leads to comparably low optical anisotropies at low draw ratios as well as a limited maximal orientation of the dye molecules at maximum draw ratios. Due to a high compatibility with the polymeric matrix, low molecularweight dyes have been demonstrated to yield PL polarizers with extremely high emission dichroic ratios. Furthermore, the latter allow the use of melt-processible matrix materials, such as LLDPE.

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