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Deformation-Induced Color Changes in Melt-Processed Photoluminescent Polymer Blends

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Binary blends of linear low-density polyethylene (LLDPE) and a series of highly photoluminescent (PL) 1,4-bis(α-cyano-4-alkoxystyryl)benzenes were prepared using melt-processing techniques. It was shown that the phase behavior of these blends, which comprised 0.01−3% w/w of the PL guest, could be controlled via the molecular structure of the dye, its concentration, and the processing conditions. Because of the dyes' strong tendencies to form excimers, the emission characteristics of the blends strongly depended on the extent of molecular aggregation of the PL guest molecules. Bathochromic shifts of up to 147 nm were observed when comparing the PL emission spectra of molecularly mixed blends with samples that comprise aggregates of the dyes. Phase-separated blends with apparently very small dye aggregates could be produced by rapidly quenching the samples after melt processing and subsequent plasticization with a hydrocarbon solvent. The mechanical deformation of the blends thus produced led to a pronounced change of the materials PL characteristics. When the films were stretched to a draw ratio $\lambda = (l - l_0)/l_0 = 500\%$, the monomer to excimer emission ratios I_M/I_E were increased by a factor of up to 10. This effect appears to bear significant potential for the use of such dyes as internal strain sensors in polymer objects.

Introduction

A number of research groups have studied the electronic characteristics of oligo(*p*-phenylene vinylene) (OPV) derivatives, which comprise electron-withdrawing cyano groups as part of the conjugated system.[1−4] Many of these cyano-OPVs have served as model compounds for the corresponding poly(*p*-phenylene vinylene) (PPV) derivatives, which are under consideration for use in polymer light-emitting diodes.[5] Expanding on this work, we recently described the synthesis of a family of new photoluminescent (PL) dyes, which exhibit bathochromic shifts of up to 138 nm when comparing the PL emission spectrum of a dilute solution with that of the crystalline dye (Figures 1 and 2, Table 1).[6] This remarkable change is related to the pronounced $\pi-\pi$ interactions encountered in the crystalline lattice of these planar, conjugated molecules, which facilitate the formation of excimers.[7] As a result, the emission characteristics of these molecules in the solid state strongly depend on their supramolecular architecture. Intrigued by the possibility to control the emission color of a given PL dye over a wide range by merely tuning the extent of π-stacking, we embarked to explore the possibility of accessing structures between the limiting states of crystalline solid and molecular liquid solution.[8−10] It has long been recognized that the formation of excimers in polymeric hosts, which comprise a fluorescent marker or probe—often covalently bound to the polymer—can be used to extract information about a polymer's architecture,[11] on the molecular[12] (e.g., conformation of macromolecules in solution) as well as macroscopic (e.g., morphology,[13] miscibility of polymer blends,[14] and distribution of

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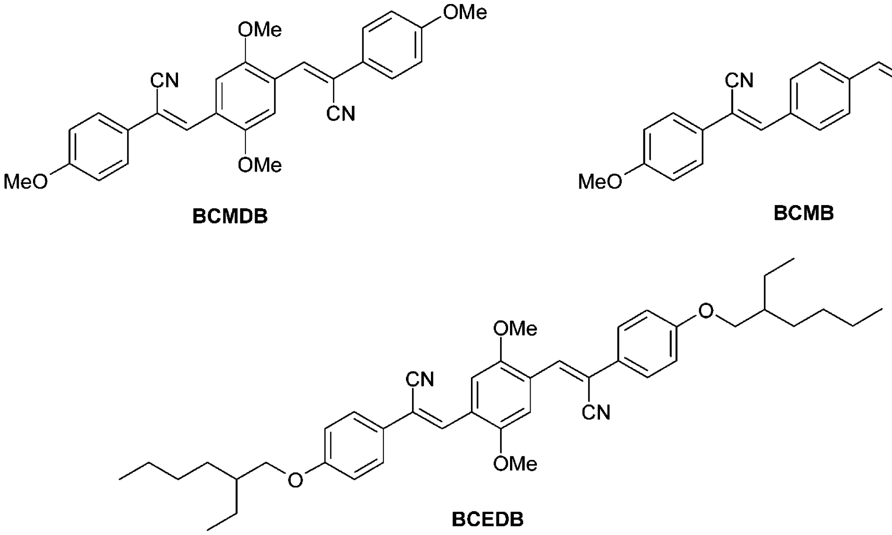

Figure 1. Chemical structures of 1,4-bis(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (BCMDB), 1,4-bis(α-cyano-4-methoxystyryl)benzene (BCMB), and 1,4-bis(α-cyano-4-(2-ethylhexyloxystyryl))-2,5-dimethoxybenzene (BCEDB).

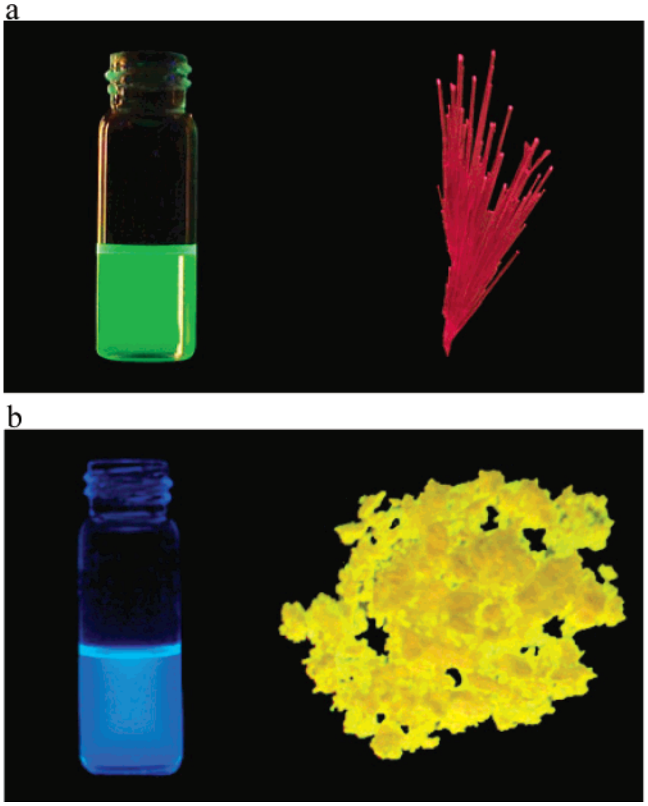

Figure 2. Pictures of photoluminescent chloroform solutions and crystals of (a) BCMDB and (b) BCMB, taken under excitation with UV light of a wavelength of 365 nm.

dopant site sizes[15]) level. The spectroscopic detection of excimers has also extensively been employed to detect the aggregation of guest molecules in polymeric host materials. For example, a number of research groups have investigated the concentration dependence of pyrene[16] excimer formation in various polymer hosts, including poly(methyl methacrylate),[17] polystyrene,[18] and polyethylene.[19] In qualitative agreement with the concentration dependence reported for these systems, we observed a pronounced variation of the PL emission when diffusing cyano-OPVs from dilute solutions into semicrystalline polyolefin host polymers, such as linear low-density polyethylene (LLDPE) or polypropylene.[6,8] Our initial experiments suggest that literally any combination of monomer and excimer emission can be achieved by tuning the phase behavior of the blends via composition, processing conditions, or temperature. We have also demonstrated that mechanical deformation can lead to a substantial change of the emission characteristics of such blends, which allows exploiting the framework of excimer (de)formation as “molecular” strain sensors.[8] This effect appears to bear significant potential for technological applications, in particular, the use of such dyes as integrated deformation sensors in polymer objects.[20] Most of our earlier work on this subject has been limited to blends that were prepared by diffusing a solution of 1,4-bis(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (BCMDB, Figure 1) into a polyolefin host polymer.[8] To answer the fundamental question of how appropriate polymer/dye blends can be prepared by conventional melt-processing schemes and expanding upon preliminary experiments,[9,10] we here present a detailed investigation of the phase behavior of binary blends of LLDPE and various OPVs and

Table 1. Optical Absorption and PL Emission Characteristics of the Photoluminescent Dyes Employed in the Present Study

dye	Abs. λ_{max} solution[a] [nm]	PL λ_{max} solution[a] [nm]	PL λ_{max} solid[b] [nm]	PL $\lambda_{monomer}$ LLDPE[c] [nm]	PL $\lambda_{excimer}$ LLDPE[c] [nm]
BCMDB	365, 436	506, 538	644	497, 535	644
BCMB	389	461, 486	550	448, 478	573
BCEDB	371, 440	508, 541	619	500, 540	605

[a] Measured in $CHCl_3$ with a dye concentration of ca. 2–2.5 10^{-3} mol·L^{-1}. [b] Semicrystalline powder as-synthesized. [c] Measured on melt-processed blend films. The values slightly depended on the dye concentration ($\lambda \pm 2$ nm).

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demonstrate that desirable supramolecular architectures are accessible by rapidly quenching the samples after melt processing and subsequent plasticization.

Experimental Section

Materials. 1,4-Bis(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (BCMDB) and 1,4-bis(α-cyano-4-methoxystyryl)benzene (BCMB) were prepared as described before.[6] All solvents employed were of analytical grade. For spectroscopic experiments, spectroscopy-grade chloroform (stabilized with 0.8% v/v ethanol) was used. All chemicals were of highest commercial quality and were used as received. 2,5-Dimethoxy terephthaldicarboxyaldehyde was purchased from Ryan Scientific Inc., Isle of Palms, SC. For the preparation of polymer blend films, a commercial-grade linear low-density polyethylene (LLDPE) from Dow containing 1.2% octene as a comonomer was used (Dowlex BG 2340, $\rho = 0.942$ g/cm^3).

Synthesis of (4-(2-ethylhexyloxy)phenyl)acetonitrile. A suspension of K_2CO_3 (4.05 g, 29.2 mmol) and dimethylformamide (15 mL) was purged with Ar for 15 min and heated to 70 °C, and $HOPhCH_2CN$ (1.47 g, 11.0 mmol) was added. After 10 min, 2-ethylhexyl bromide (2.75 g, 14.2 mmol) was slowly added via a syringe, and the suspension was stirred at 70 °C under Ar for 4 h. The reaction was subsequently terminated by pouring the suspension into ice water (150 mL). The aqueous phase was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with H_2O and saturated aqueous NaCl. The organic phase was dried with $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. Column chromatography of the resulting crude oil (1.94 g) afforded pure (4-(2-ethylhexyloxy)phenyl)acetonitrile as a slightly yellow oil (0.55 g, 20.4%). ^{1}H NMR: δ 7.17 Hz (d, 2 H, ArH), 6.83 Hz (d, 2 H, ArH), 3.85 Hz (d, 2 H, CH_2−O), 3.65 Hz (s, 2 H, CH_2−CN), 1.7 Hz (m, 1 H, CH), 1.6−1.2 Hz (m, 8 H, CH_2), 0.91 Hz (m, 6 H, $2 \times CH_3$).

Synthesis of 1,4-bis(α-cyano-4-(2-ethylhexyloxystyryl))-2,5-dimethoxybenzene (BCEDB). 2,5-Dimethoxyterephthaldehyde (120 mg, 0.62 mmol) and (4-(2-ethylhexyloxy)phenyl)-acetonitrile (380 mg, 1.55 mmol) were dissolved in a mixture of *t*-BuOH (11 mL) and THF (3.5 mL) and the mixture was heated to 50 °C. *t*-BuOK (9.8 mg, 0.09 mmol) and *n*-Bu_4NH_4OH (1 mL of a 1 M solution in methanol) were added quickly, and an orange precipitate started to form immediately. The mixture was stirred for 15 min at 50 °C, cooled to RT, and poured into acidified methanol (50 mL containing 1 drop of concentrated acetic acid). The precipitate was filtered off, excessively washed with MeOH, and dried in vacuo at 50 °C to yield BCEDB (280 mg, 70%) in the form of orange crystals; mp (DSC) 131 and 141 °C. ^{1}H NMR: δ 7.88 ($2 \times$ s, 2×2 H, Ar*H* + C*H* = CCN), 7.63 (d, $^3J_{(H,H)} = 8.6$ Hz, 4 H, Ar*H*), 6.96 (d, $^3J_{(H,H)} = 8.6$ Hz, 4 H, Ar*H*), 3.95 (s, 6 H, O−CH_3), 3.89 (d, 4 H, $^3J_{(H,H)} = 5.3$ Hz, O−CH_2) 1.7 Hz (m, 2 H, CH), 1.57−1.33 Hz (m, 16 H, CH_2), 0.91 Hz (m, 12 H, $4 \times CH_3$).

General Methods. ^{1}H NMR spectral data are expressed in ppm relative to internal TMS and were obtained in $CDCl_3$ on a Varian Gemini 200-MHz NMR spectrometer. DSC traces were recorded under a nitrogen atmosphere on a Perkin-Elmer DSC Pyris 1 at heating and cooling rates of 5 °C/min.

Film Preparation. Binary blends of LLDPE and BCMDB or BCMB with a dye concentration of more than 0.18% w/w were prepared by feeding the appropriate amount of dye and 4.0 g of LLDPE into a recycling, co-rotating twin-screw mini-extruder (DACA Instruments, Santa Barbara, CA), mixing for 5 min at 180 °C, and subsequent extrusion. Blends comprising less than 0.18% w/w of BCMDB or BCMB were prepared by diluting a concentrated blend (prepared as described above) with neat LLDPE and extruding this material in the same manner. Blends comprising between ca. 0.40 and 3.0% w/w BCEDB were prepared by manually mixing 500 mg of LLDPE with 2−15 mg of BCEDB for 10 min in an aluminum dish on a hot stage at ca. 180 °C. Films were prepared by compression-molding the blends between two aluminum foils and using four 110-μm spacers in a Carver press at 180 °C for approximately 3 min. Unless otherwise noted, the samples were immediately quenched after removal from the hot press by immersion in an ice water bath. The resulting blend films had a homogeneous thickness of ca. 100 μm.

Optical Spectroscopy. UV−vis absorption spectra were obtained on a Perkin-Elmer Lambda 800. Steady-state PL spectra were acquired on a SPEX Fluorolog FL3-12. Spectra were collected under excitation at 435 nm (BCMDB and BCEDB) and 375 nm (BCMB) and corrected for the instrument throughput and the detector response. At room temperature, PL experiments were conducted on free-standing films. For the temperature-dependent PL experiments, samples were heated between a microscopy slide and a glass cover slip on a Gel Instrumente AG hot stage in connection with a TC2 temperature controller and the PL spectra were measured with the above-mentioned spectrometer by making use of a Y-shaped optical fiber. PL spectra of films referred to as “freshly prepared” were obtained within 4 h of quenching. Lifetime measurements were conducted with a PTI Laser Strobe model C720 fluorescence spectrometer, under excitation with a N_2-pumped dye laser at 481 nm and detection at 495 and 650 nm, respectively. The repetition rate of the laser was 10 Hz, with a pulse length of 800 ps and a primary pulse energy of 1.47 mJ.

Optical Microscopy. Polarization microscopy studies were conducted on an Olympus BX60 equipped with a Mettler FP82 hot stage and a Mettler FP80 controller with samples placed between crossed polarizers.

Results and Discussion

1,4-Bis(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (BCMDB) and 1,4-bis(α-cyano-4-methoxystyryl)-benzene (BCMB) were prepared as described before.[6] 1,4-Bis(α-cyano-4-(2-ethylhexyloxystyryl))-2,5-dimethoxybenzene (BCEDB) was obtained in good yield through the Knoevenagel reaction of (4-(2-ethylhexyloxy)phenyl)-acetonitrile with 2,5-dimethoxy terephthaldicarboxyaldehyde (see Experimental Section for details). Binary blends of LLDPE and between ca. 0.01 and 0.8% w/w of these PL dyes were prepared by melt-mixing the components at 180 °C in a co-rotating twin-screw mini-extruder. In the case of BCEDB, blends comprising up to 3% w/w of the dye were prepared by manually mixing the components on a hot stage. The materials were subsequently compression-molded at a temperature of 180 °C to produce films of a thickness of ca. 100 μm. It should be noted that after melt-pressing, the samples were rapidly quenched to 0 °C, to prevent large-scale phase separation between dye and polymer host (vide infra). In the case of BCMDB and BCMB, the processing temperature was well below the melting temperature (248 °C, BCMDB) or solid-smectic transition (245 °C, BCMB) of the dye. Due to the extended alkyloxy substituents, BCEDB displays a significantly lower melting temperature than the other two cyano-OPVs investigated here (131 °C), and thus LLDPE blends comprising this dye were processed with the dye in its molten state.

Upon excitation with ultraviolet (UV) light, freshly prepared blend films comprising 0.01% w/w of BCMDB fluoresce green. Similar to dilute blends prepared by guest diffusion,[8] these samples display an emission spectrum that features well-resolved vibronic structures with maxima at 497 and 535 nm (Figure 3a, Table 1). The spectrum displays a modest (∼10 nm) hypsochromic shift when compared to the one of a $CHCl_3$ solution of the dye,[6] but otherwise matches the latter well. Thus, these spectroscopic data suggest that at low concentration the BCMDB molecules are incorporated in the

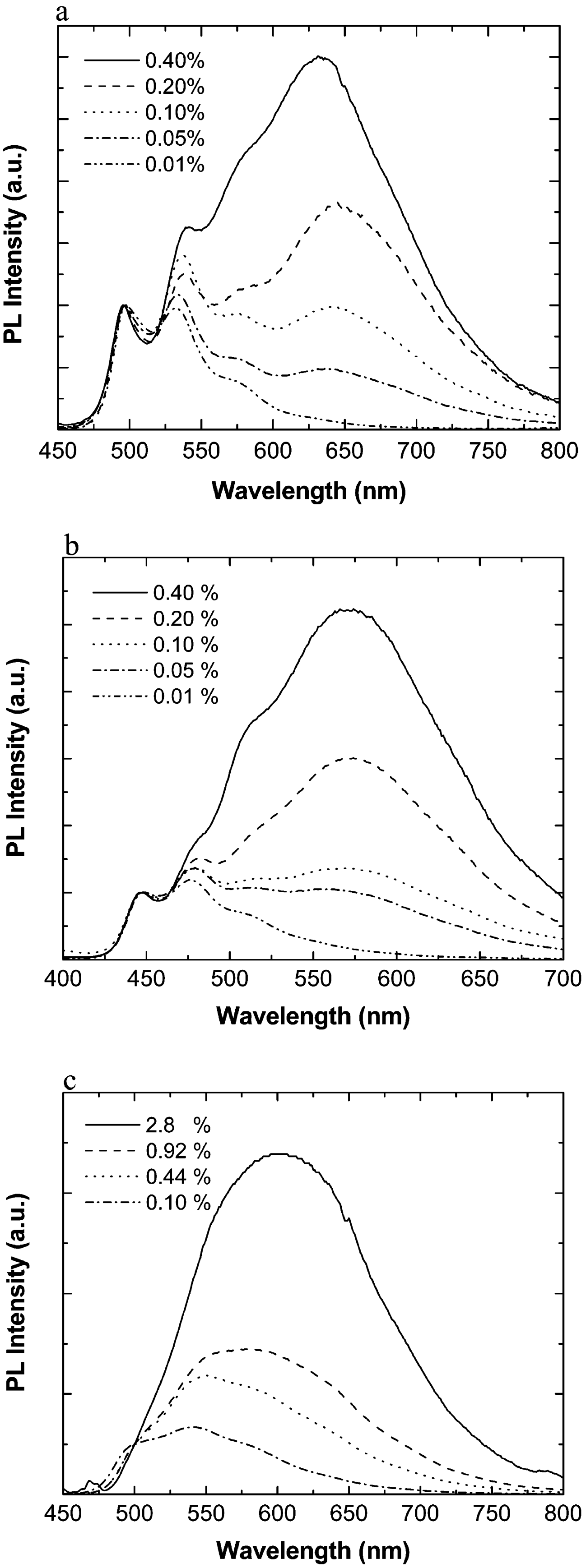

Figure 3. PL emission spectra of freshly prepared blend films of LLDPE and (a) BCMDB, (b) BCMB, and (c) BCEDB as a function of dye concentration (given in % w/w). The blend films had rapidly been cooled to 0 °C after processing. All spectra were normalized to the intensity of the monomer peak.

amorphous fraction of the LLDPE in an apparently molecularly dispersed or dissolved fashion; we have observed this behavior for the same polymer and similar mixing conditions, but different PL dyes before.[21] The situation changes significantly if the concentration of the PL dye is increased. LLDPE/BCMDB blends of a dye concentration of ~0.02% w/w or more were found to develop a broad, unstructured red emission band centered around 644 nm, which increased with increasing dye concentration. This red portion of the spectrum matches the one of the dye in its crystalline form[6] and is characteristic of excimer emission. In solution, excimer formation is frequently a diffusion-controlled process, where the encounter of an excited molecule and a second molecule in the ground state is the rate-determining step.[22] By contrast, diffusion of the dye molecules in a solid polyethylene matrix is usually slow compared to the lifetime of the excited states.[23] Thus, we conclude that higher dye concentrations lead to the aggregation of multiple dye molecules and that conformations which facilitate excimers (i.e., sandwich-type structures of at least two dye molecules) are formed during sample preparation. Figure 3b and Table 1 show that the behavior of LLDPE/BCMB mixtures is quite similar to that of the LLDPE/BCMDB blends, except for a hypsochromic shift, which is consistent with the different substitution pattern on the central phenyl ring.[6] Thus, LLDPE films comprising BCMB in low concentration fluoresce blue and display an emission spectrum with maxima at 448 and 478 nm that matches the one of a molecular solution well (Figure 3b). At higher dye concentration the samples develop a yellow emission band with maximum around 573 nm, which is again the result of excimer formation. BCEDB also displays a similar behavior, but due to the extended alkyloxy substituents, the solubility of this dye in the LLDPE matrix is substantially higher than that of the other dyes investigated here (vide infra). As a result, the onset of aggregation and excimer formation is observed only at much higher concentrations (Figure 3c, Table 1), that is, above ca. 0.1% w/w. It should also be noted that the "contrast" between monomer and excimer emission is somewhat less pronounced in the case of this dye when compared to BCMDB or BCMB.

As mentioned heretofore, the above-discussed samples were produced by rapidly quenching the corresponding melts after melt pressing the films. Not surprisingly, we observed that above a certain threshold concentration (ca. 0.02% w/w in case of BCMDB) the intensity of the excimer emission bands increased upon storage under ambient conditions, as exemplarily shown in Figure 4 for a 0.18% w/w LLDPE/BCMDB blend film. As can be seen from the figure, the rate of this process decreases sharply as a function of time and appears to approach zero after a time frame of a few months. This behavior seems to be a direct consequence of the quenching step and reflects a changing phase behavior of the system upon cooling and storage under ambient

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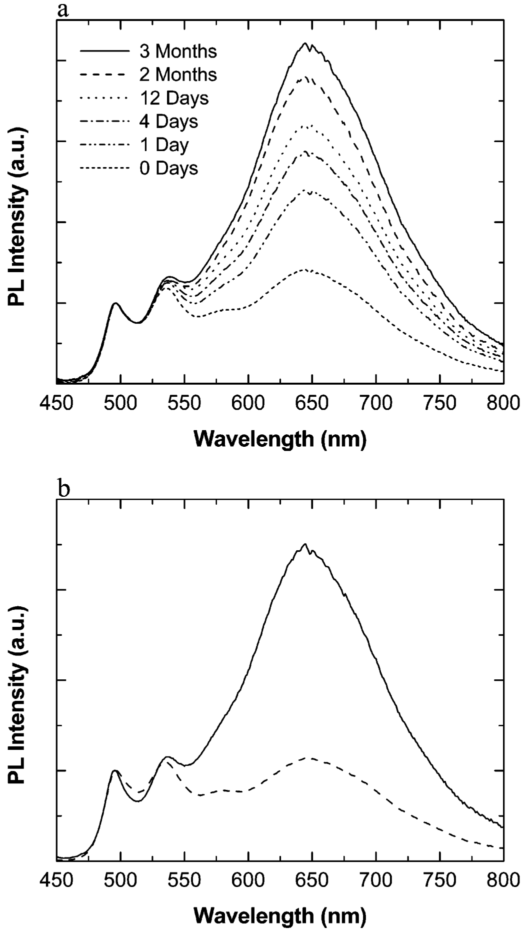

Figure 4. (a) PL emission spectra of a blend film of LLDPE and 0.18% w/w BCMDB as function of storage time under ambient conditions. (b) PL emission spectra of a blend film of LLDPE and 0.18% w/w BCMDB freshly prepared (dashed line) and after swelling the film for 15 min in hexane and subsequent drying (solid line). All spectra were normalized to the intensity of the monomer peak.

conditions. It appears that during melt processing most, if not all, of the dye is molecularly dispersed or dissolved in the molten polyethylene, at least in the case of the more dilute compositions investigated here. This interpretation is consistent with the fact that if heated to 180 °C, all blends displayed virtually exclusively the emission characteristic of molecular emission. Thus, rapid quenching apparently allows kinetic “trapping” of the system such that a substantial fraction of the dye molecules remains molecularly dispersed in the LLDPE. However, the resulting blends are thermodynamically unstable under ambient conditions, and the low glass transition temperature of the LLDPE matrix allows for slow demixing and aggregation of the dye molecules. Apparently, the dye aggregates formed in this process are very small and as a result the mechanically deformed samples feature a vastly different behavior when compared to blends with similar dye content but large-scale phase separation (vide infra).

To develop a better understanding for the phase behavior of the systems at hand, we investigated the solubility of the OPVs in LLDPE in the temperature regime between 20 and 180 °C using polarized optical microscopy (Figure 5) and PL spectroscopy (Figure 6). The phase behavior of blends with a dye content of $\geq$0.20% w/w was characterized by polarized optical microscopy. For this study, the blends were first *slowly* (i.e., at a rate of approximately 5 °C/min) cooled, in contrast to the quenched samples, large-scale phase separation between the dye and the PE matrix was achieved under these conditions, and dye crystals of a size between a few and a few dozen micrometers formed well above the melting temperature of the LLDPE matrix (Figure 5b). The temperature was subsequently increased in increments of 10 °C, and the samples were kept at each temperature for 20 min. The temperature at which the dye crystals had completely dissolved corresponded to the dissolution temperature. We verified for samples with the lowest concentration of BCMDB (cf. Figure 7) that the dissolution temperature was independent of the heating rate. For this experiment a sample was cooled from the melt to 10 °C below the determined dissolution temperature, and the dye crystallized immediately. The sample was kept under these conditions for 15 min; the temperature was subsequently increased by 10 °C and the dye completely redissolved. Thus, the data presented in Figure 7 appear to be little influenced by kinetic effects. The phase behavior of blends of lower concentration was difficult to study by optical microscopy. Either the dye crystals were too small to be unequivocally discerned by microscopy or light scattering from the LLDPE matrix impeded a careful microscopy study because the dye crystals dissolved at a temperature below the melting temperature of the LLDPE matrix. Thus, PL spectroscopy was employed as a complementary “indirect” tool to study the phase behavior. The temperature of the films was usually increased in increments of 10 °C, and the samples were kept at each temperature for 20 min (in the case of BCEDB, samples were additionally kept 10 °C below the dissolution temperature for up to 5 h, without noticeable effect). In this case the dissolution of the dye was reflected by the disappearance of the characteristic signal of the excimer band (Figure 6). It is well-established that soluble additives dissolve essentially exclusively in the amorphous fraction of the polyethylene.[24] Consequently, solid-state concentrations were corrected for a crystallinity of 51% (determined by DSC) and were normalized for a (hypothetical) completely amorphous material. Gratifyingly, the two methods employed provided consistent data (cf. high-concentration data for BCMDB in Figure 7). Logarithmic plots of the solubility of the various dyes (in % w/w) against $1/T$ display linear relations, in the case of BCMDB even through the melting transition of the LLDPE matrix (cf. Figure 7). The behavior of the present LLDPE/OPV blends appears to be consistent with the theoretical description of the dissolution of crystalline additives in an amorphous polymer[25] and follows the trend observed for the dissolution of conventional stabilizers in polyolefins.[26] As can be seen from Figure 7, the absolute solubility of the dyes significantly varies with their molecular structure (cf. Figure 1) and sharply increases with the number and length of the aliphatic substituents, which allow for favorable van der Waals interac-

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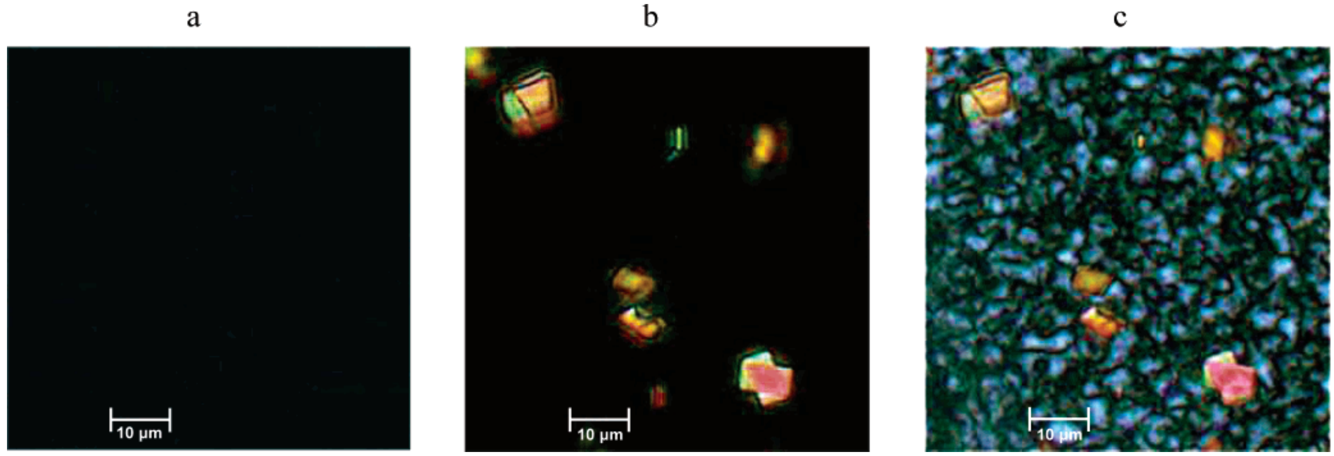

Figure 5. Cross-polarized optical micrographs documenting the cooling process of a blend of LLDPE and 0.46% w/w BCMDB at (a) 180 °C, (b) 135 °C, and (c) 100 °C.

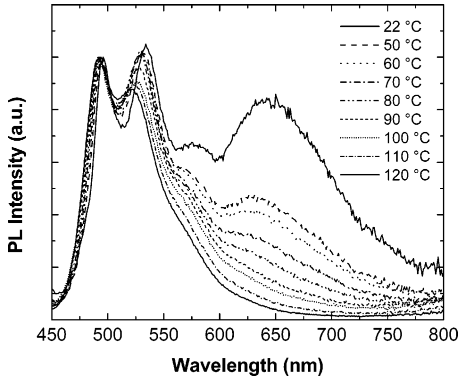

Figure 6. PL emission spectra of a blend film of LLDPE and 0.05% w/w BCMDB as a function of temperature. All spectra were normalized to the intensity of the monomer peak.

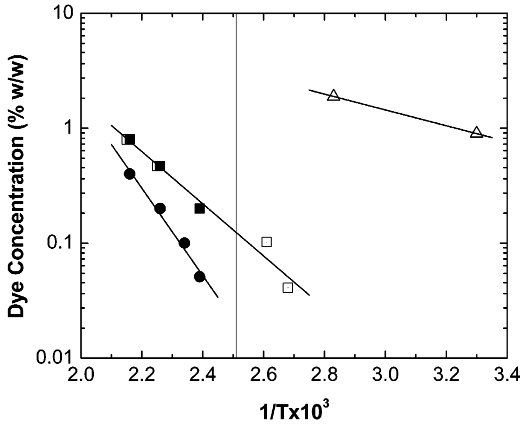

Figure 7. Solubility of BCEDB (△), BCMDB (■, □), and BCMB (●) in LLDPE. Empty symbols represent data obtained by PL spectroscopy and filled symbols are used for data obtained by optical microscopy. At temperatures below the melting temperature of LLDPE, which is indicated by the vertical solid line, concentrations were corrected for a crystallinity of 51%, assuming that the dyes were dissolved exclusively in the amorphous fraction of the polyethylene.

tions with the polymer matrix and reduce the dyes' heat of fusion. The comparison of the three different OPVs (BCMB, BCMDB, and BCEDB) indicates that the temperature dependence of the solubility becomes less pronounced as the molar heat of fusion of the dye decreases (109, 101, and 54 J/g for BCMDB, BCMB, and BCEDB, respectively). This finding appears to be consistent with a comparably weak temperature dependence of the Flory−Huggins parameter χ.[26] It should be noted that in the case of BCMDB and BCMB our attempts to extend the solubility studies to lower temperatures were stifled by kinetic effects. As can be seen from the data presented for a (rather concentrated) BCMDB sample in Figure 4, aggregation of the dye molecules continued to occur over a period of a couple of months, suggesting that at room temperature the diffusion of the dye is extremely slow. This may explain the fact that samples comprising 0.01% w/w of either BCMDB or BCMB did not develop the characteristic excimer bands over a period of weeks, while extrapolations of the solubility data suggest phase-separated systems at room temperature.

As discussed above based on the example of quenched blends of LLDPE and BCMDB, phase-separated blends with apparently very small dye aggregates can be produced by rapidly quenching the samples after melt processing, while large-scale phase separation is observed when slowly cooling the blends from the melt (cf. Figure 5b). Small dye aggregates are important, if the dye molecules are to be used as integral strain sensors, since large-scale phase separation usually prevents an efficient breakup of the aggregates.[27] However, as shown by the data in Figure 4a, the relative intensity of the excimer emission band is rather small in freshly quenched blends and only slowly increases upon storage under ambient conditions due to slow demixing and aggregation of the dye molecules. To increase the speed of the demixing process, blend films were briefly (15 min, longer immersion times had no further effect) immersed in hexane, which is a poor solvent for the OPVs but swells LLDPE well. Gratifyingly, due to the plasticizing effect of the solvent, the BCMDB molecules aggregated virtually instantaneously, and the PL spectra of the films thus treated were dominated by excimer emission (Figure 4b). The PL spectra of blend films of LLDPE and 0.18% w/w BCMDB that were either stored at ambient conditions for 3 months (Figure 4a) or plasticized with hexane (Figure 4b) show essentially identical features and monomer to excimer emission ratios I_M/I_E, suggesting that both systems had essentially fully relaxed to the thermodynamic equilibri-

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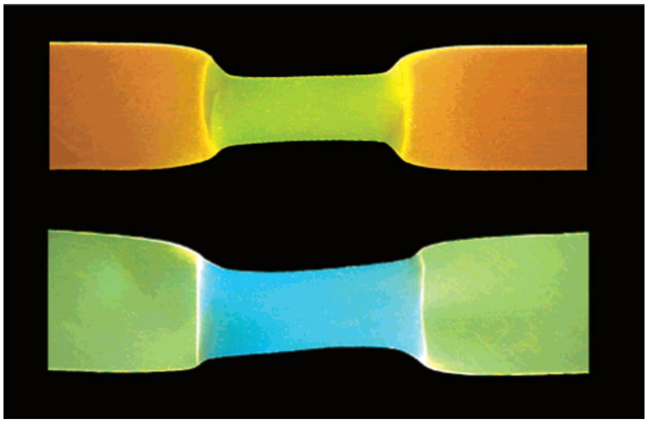

Figure 8. Pictures of blend films of LLDPE and 0.18% w/w BCMDB (top) and 0.20% w/w BCMB (bottom) stretched at room temperature to a draw ratio of 500%. The pictures were taken under excitation with UV light of a wavelength of 365 nm.

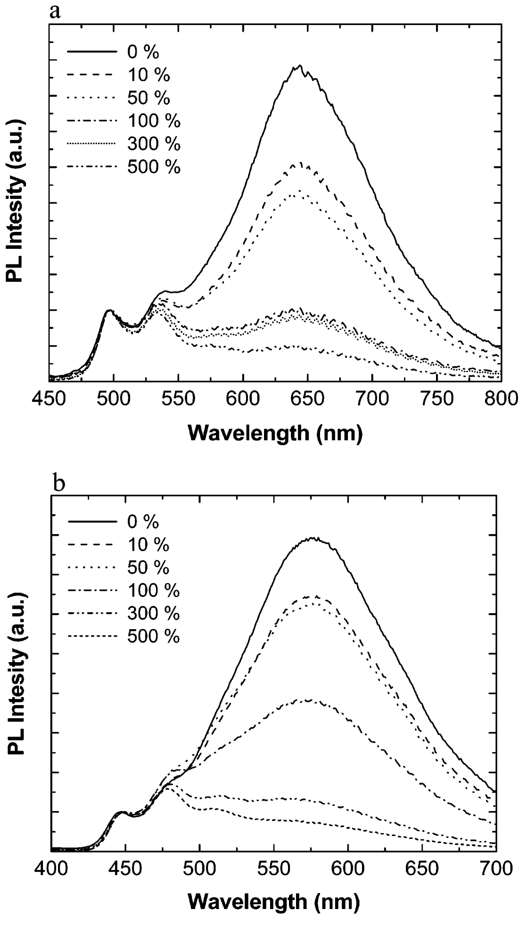

Figure 9. PL emission spectra of blend films of LLDPE and 0.20% w/w BCMDB (a) and 0.20% w/w BCMB (b) as a function of draw ratio. All spectra were normalized to the intensity of the monomer peak.

um. Similar results were obtained for LLDPE/BCMB blends, while plasticization with hexane was not an option for BCEDB because of the higher solubility of this dye in hydrocarbon solvents.

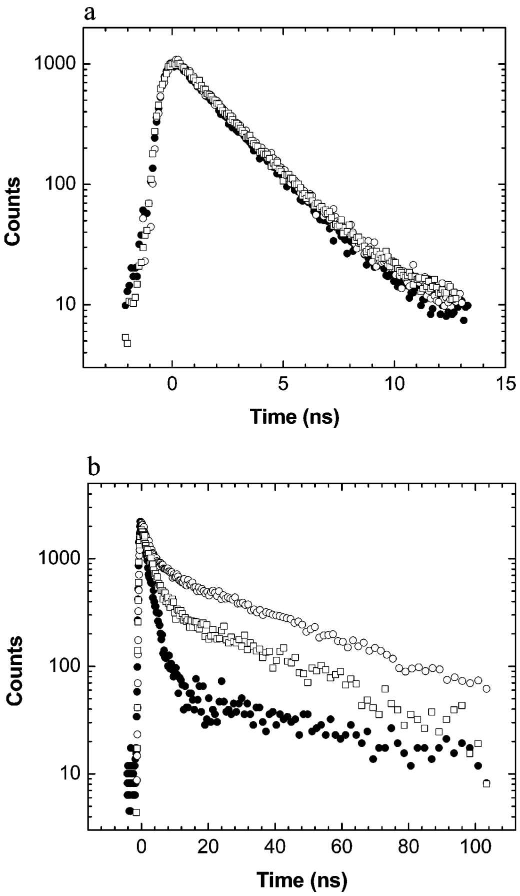

Figure 10. PL decay curves of blend films of LLDPE and BCMDB measured under excitation at 481 nm at 495 (a) and 650 (b) nm. The films contained the dye in concentrations of 0.01 (●) and 0.15% w/w (○). The latter film was also measured after being stretched at room temperature to $\lambda = 350\%$ (□).

Finally, we have also investigated the influence of solid-state tensile deformation on the emission characteristics of the blend films. Figures 8 and 9 unequivocally demonstrate that solid-state tensile deformation has a pronounced effect on the emission characteristics of blends of LLDPE and BCMDB or BCMB. When the films are stretched to a draw ratio $\lambda = (l - l_0)/l_0 = 500\%$, samples that have been quenched and conditioned by immersion in hexane as described above and comprised either of the dyes at a concentration of ca. 0.2% w/w display good visual contrast between stretched and unstretched portions (Figure 8). Concomitantly, PL emission spectra show a substantial reduction in the relative intensity of the excimer band, which scales with the draw ratio (Figure 9). The monomer to excimer emission ratios I_M/I_E are increased by a factor of about 10 (0.23 to 2.00 and 0.13 to 1.33 for LLDPE/BCMDB and LLDPE/BCMB, respectively) when comparing unstretched and stretched ($\lambda = 500\%$) samples. These findings are consistent with our previous experiments,[8,21,27] which have shown that tensile deformation can indeed cause the transformation of a phase-separated polymer blend into an apparent molecular dispersion or solution. The results are also in good qualitative agreement with the experiments of Weiss and Naciri,[15] who have investigated the influence of mechanical deformation on the emission characteristics of pyrene molecules that were covalently attached to low-density polyethylene. Although much less pronounced, these systems also displayed an increase of I_M/I_E upon stretching, which led the authors to conclude that deformation decreased the average size of dopant sites. It should be noted that the emission spectra of the drawn portions of the high-draw-ratio films investigated here were stable with time, at least over a period of 5 months, which is concomitant with a considerably reduced mobility upon stretching. Not surprisingly, mechanical deformation had a comparably small effect on the emission characteristics and visual appearance of slowly cooled films comprising ca. 0.2% w/w of BCMDB or BCMB, which showed large-scale phase separation. To provide evidence of excimer formation and confirm the postulated molecular architectures of the materials investigated, we have conducted PL lifetime measurements on blends of LLDPE and 0.15 and 0.01% w/w BCMDB. The steady-state PL spectra of these films follow the trends depicted in Figure 3 and are dominated by monomer (0.01% w/w) and excimer (0.15% w/w) emission, respectively. The PL decay curves of these films, measured at 495 and 650 nm, are shown in Figure 10, together with the data of the high-concentration sample, collected after stretching the film at room temperature to $\lambda = 350\%$. The PL decay curves show multiexponential dependencies, with lifetimes of about 2.25 and 35 ns for the dominant processes. Gratifyingly, these values are typical for the monomer and excimer emission of small organic dyes, respectively.[7] The contribution of the fast decay dominates the measurements conducted at 495 nm (Figure 10a), while the long-lived excited states contribute predominantly to the decay curves recorded at 650 nm (Figure 10b). Consistent with the proposed molecular architectures, the contribution of the long-lived excited states is only substantial in the case of the high-concentration sample, while the decay behavior of the low-concentration sample as well as the stretched film are dominated by monomer decay.

Conclusions

In summary, we have demonstrated that binary blends of LLDPE and cyano-OPVs can readily be produced via conventional melt-processing techniques. The phase behavior of these materials can be controlled via the molecular structure of the dye, the blend's composition, and the detailed processing conditions. While homogeneous blends display emission spectra that are characteristic of the dyes' monomer emission, demixing leads to the formation of excimers, which emit at lower energies. Phase-separated blends with apparently very small OPV aggregates can readily be produced by rapidly quenching the samples from the corresponding homogeneous melts and subsequent plasticization. Mechanical deformation of the materials thus produced leads to a pronounced change of the materials emission characteristics. This effect appears to bear significant potential for technological applications, in particular, the use of such dyes as internal strain sensors in polymer objects.

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