472 *Chem. Mater.* **2000,** *12,* 472−480

Tensile Orientation Behavior of Alkoxy-Substituted Bis(phenylethynyl)benzene Derivatives in Polyolefin Blend Films

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Received August 27, 1999. Revised Manuscript Received November 2, 1999

A series of new dichroic, photoluminescent alkoxy-substituted bis(phenylethynyl)benzene derivatives **1a**−**e**, have been synthesized and characterized. All dyes are highly emissive and show bright-blue photoluminescence with quantum yields in solution ranging from 0.63 to 0.72. Oriented blend films comprising these dyes were prepared with ultrahigh-molecular-weight polyethylene (UHMW PE) as the matrix material by solution-casting, and with linear low-density polyethylene (LLDPE) by melt-processing as well as guest diffusion. Despite the introduction of alkoxy substituents, not all dyes are compatible with UHMW PE and large-scale phase segregation was observed during the preparation of a number of UHMW PE blend films. In the case of the latter, films with relatively good dichroic properties are only obtained if the melting point of the dye is lower than or equal to the deformation temperature. On the other hand, melt-processing of **1a**−**e** with LLDPE produces homogeneous blends that, after tensile deformation, give rise to highly dichroic photoluminescent films. In this case, the melting temperature of the dye was found to be less relevant for the orientation process. In view of a future application of these PL blends as photoluminescent polarizer, melt-processed blends based on octyloxy- and dodecyloxy-substituted bis(phenylethynyl)benzene derivatives (**1c**,**d**) and LLDPE embody the optimal combination of good accessibility, excellent luminescence characteristics and high polarization of the emitted light.

Introduction

Solid-state drawing of ductile polymer films, comprising absorbing[1−8] or photoluminescent[9−11] organic guest molecules, is a widely used procedure to provide oriented structures that allow one to investigate the anisotropic photophysical characteristics of these guest molecules as well as the orientation behavior of the polymer host.[1−11] The anisotropic properties of oriented guest−host systems have been successfully exploited for half a century in, e.g., polymeric sheet polarizers.[12−14] Typically, guest diffusion is the prime method for the commercial preparation of these (often poly(vinyl alcohol)-based) absorbance polarizers.

Recently, absorbance polarizers were developed in which highly dichroic dyes were embedded in a polyolefin matrix using either solution-casting or melt-processing techniques; subsequent tensile deformation of the resulting blend films led to highly dichroic films.[15−19] Such hydrophobic polarizers are of considerable interest due to their high humidity resistance, excellent optical performance, and simple manufacturing conditions. Detailed studies on the orientation mechanism of these guest−host systems indicated that in order to achieve efficient orientation of the guest dye during tensile deformation, the latter should have a high molecular aspect ratio, a transition dipole moment that coincides with the orientation direction, and a melting point close to the drawing temperature.[16−18]

We have recently concentrated on the development of a new generation of photoluminescent (PL) polarizers based on a poly(*p*-phenylene ethynylene) derivative

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(1) (a) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers Inc.: New York, 1986. (b) Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 5594.

(2) Phillips, P. J. *Chem. Rev.* **1990**, *90*, 425.

(3) Natarajan, L. V.; Stein, F. M.; Blankenship, R. E.; Chang, R. *Chem. Phys. Lett.* **1983**, *95*, 525.

(4) Dekkers, J. J.; Hoornweg, G. Ph.; Maclean, C.; Velthorst, N. H. *Chem. Phys. Lett.* **1973**, *19*, 517.

(5) (a) Springer, H.; Neuert, R.; Müller, F. D.; Hinrichsen, G. *Colloid Polym. Sci.* **1984**, *262*, 46. (b) Neuert, R.; Springer, H.; Hinrichsen, G. *Colloid Polym. Sci.* **1985**, *263*, 392.

(6) van Gerp, M.; van Ginkel, G.; Levine, Y. K. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 1613.

(7) Hagler, T. W.; Pakbaz, K.; Moulton, J.; Wudl, F.; Smith, P.; Heeger, A. J. *Polym. Commun.* **1991**, *32*, 339.

(8) Luzzati, S.; Elmino, P.; Bolognesi, A. *Synth. Met.* **1996**, *76*, 23.

(9) Talhavani, M.; Atvars, T. D. Z.; Schurr, O.; Weiss, R. G. *Polymer* **1998**, *39*, 3221.

(10) Everall, N.; Chalmers, J.; Mills, P. *Appl. Spectrosc.* **1996**, *50*, 1229.

(11) (a) Hennecke, M.; Fuhrmann, J. *Colloid Polym. Sci.* **1980**, *258*, 219. (b) Fuhrmann, J.; Hennecke, M. *Macromol. Chem.* **1980**, *181*, 1685.

(12) (a) Land, E. H.; West, C. D. *Colloid Chemistry*; Alexander, J., Ed.; Reinhold Publishing Corporation, 1946; Vol. 6. (b) Land, E. H. *J. Opt. Soc. Am.* **1940**, *30*, 230.

(13) Mizogushi, R.; Kobayashi, K.; Shimomura, T. Kobayashi, S. *Displays* **1983**, 201.

(14) Miyasaka, K. *Adv. Polym. Sci.* **1992**, *108*, 91.

(15) (a) Bastiaansen, C. W. M.; Schmidt, H.-W.; Nishino, T.; Smith, P. *Polymer* **1993**, *34*, 3951. (b) Bastiaansen, C. W. M. U.S. Patent No. 5312568, 1994.

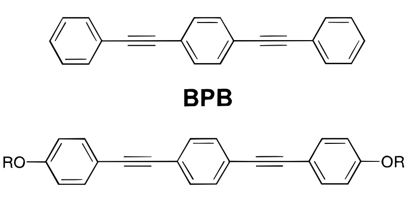
(16) Dirix, Y.; Tervoort, T. A.; Bastiaansen, C. W. M.; Lemstra, P. J. *J. Text. Inst.* **1995**, *86*, 314.

(17) Dirix, Y.; Tervoort, T. A.; Bastiaansen, C. W. M. *Macromolecules* **1995**, *28*, 486.

(18) Dirix, Y.; Tervoort, T. A.; Bastiaansen, C. W. M. *Macromolecules* **1997**, *30*, 2175.

(19) Toda, H.; Ishibashi, T.; Itsubo, A. European Patent No. 348964 1990.

10.1021/cm990558+ CCC: $19.00



BPB

1a-e

Figure 1. Molecular structures of bis(phenylethynyl)benzene (BPB) and its alkoxy-substituted derivatives **1a**−**e**. **1a** (MeO−BPB): R = CH_3. **1b** (EHO−BPB): R = 2-ethylhexyl. **1c** (C_8O−BPB): R = n-C_8H_{17}. **1d** ($C_{12}O$−BPB): R = n-$C_{12}H_{25}$. **1e** ($C_{30}O$−BPB): R = n-$C_{30}H_{61}$.

(EHO−OPPE) in ultrahigh-molecular-weight polyethylene (UHMW PE).[20,21] In these polarizers, the polarization of light is efficiently combined with the generation of bright colors.[21] To facilitate their manufacturing, efforts were undertaken to produce PL polarizers based on EHO−OPPE/polyethylene blends with melt-processing/drawing techniques as they were introduced for absorbance polarizers.[15−19] Oriented PL films with moderate-to-good dichroic properties were obtained, and the results unequivocally showed that if homogeneous blends can be produced, the orientation of the guest in the EHO−OPPE/PE blends follows reasonably well the pseudo-affine deformation scheme.[22]

To further improve the dichroic properties of dye/PE polarizers, we designed a low-molecular-weight analogue of PPE, i.e. a bis(phenylethynyl)benzene (BPB) derivative **1**, in which alkoxy substituents are introduced with the aim to improve the compatibility with the PE matrix and to manipulate the thermal properties of the dye. The BPB fragment is interesting because of its high aspect ratio, a transition dipole moment that likely is parallel to the molecular axis of the chromophore, and a high luminescence quantum yield.[23−25] In addition, preliminary studies showed that the parent BPB and a dodecyloxy−BPB derivative could be highly oriented in linear low-density polyethylene (LLDPE)-based blends, and dichroic ratios of up to 50 were obtained.[22]

With the aim to systematically study the orientation behavior of BPB derivatives in polyolefin matrices, a series of PL dyes **1a**−**e** (Figure 1) was synthesized in which the number of methylene units (n) in the alkoxy substituent is varied (n = 1, 8, 12, 30) and branching is introduced (R = 2-ethylhexyl). Blend films were prepared with UHMW PE, LLDPE, and isotactic polypropylene as the matrix material and via different processing methods: solution-casting, melt-processing, and guest diffusion.

We here report on the efficiency of orienting **1a**−**e** in blend films and its dependence on the matrix material and the processing technique employed. Furthermore, we evaluate the effect of melting temperature of the dye and the nature of the alkoxy substituent on the development of orientation of PL dyes **1a**−**e** during tensile deformation. Finally, the importance of the phase behavior of the dye and the polyethylene matrix during the preparation of the pristine blend films is addressed.

Experimental Section

Materials. All reagents and solvents were purchased from Aldrich Chemical Co., Fluka, or Acros. 1,4-Diethynylbenzene was purchased from Tokyo Kasei Organic Chemicals. 1,4-Bis(phenylethynyl)-benzene was obtained from GFS Chemicals. LLDPE (Dowlex BG 2340, $\rho = 0.942$ g/cm^3) and UHMW PE (Hostalen Gur 412) were obtained from Dow and Hoechst, respectively. Isotactic polypropylene (i-PP, $M_w = 220\,000$, $M_n = 40\,000$) was purchased from Polysciences, Inc. Spectroscopic grade $CHCl_3$ (Aldrich, stabilized with EtOH) was used for all absorption and emission experiments. Diisopropylamine was dried over KOH, and toluene was dried over CaH; both solvents were subsequently distilled under argon atmosphere and deoxygenated by sparging with argon for 1 h. Preparations for the Heck-type cross-coupling reactions were carried out in a glovebox, and all reactions were conducted using standard vacuum-line techniques.

Film Preparation. Blend films comprising UHMW PE and 0.2−2% w/w of the respective PL dye were prepared and oriented as previously published.[20] Binary blends based on LLDPE were prepared by melt-mixing one of the new PL dyes **1a**−**e** (6−10 mg) and LLDPE (5 g) in a recycling, corotating twin-screw mini-extruder (DACA Instruments, Santa Barbara, CA), for 10 min at 180 °C, and subsequent extrusion. The composition of the blends was selected such that all blend films had approximately the same molar concentration of emitting species (except in the case of $C_{30}O$−BPB); the exact concentrations in the blends were as follows: MeO−BPB, 0.13% w/w (3.7×10^{-6} mol/g); EHO−BPB, 0.17% w/w (3.2×10^{-6} mol/g); C_8O−BPB, 0.17% w/w (3.2×10^{-6} mol/g); $C_{12}O$−BPB, 0.20% w/w (3.1×10^{-6} mol/g); $C_{30}O$−BPB: 0.20% w/w (1.7×10^{-6} mol/g). Films were prepared by compression-molding the extruded blends between two Mylar foils in a Carver press at 180 °C for approximately 5 min. All resulting blend films had a homogeneous thickness of about 0.1 mm. The films were drawn at 90 °C on a thermostatically controlled hot-shoe to draw ratios of up to 10. Melt-processed blend films based on i-PP and EHO−BPB or C_8O−BPB (0.2% w/w) were prepared analogously as described for the LLDPE blends, but with extrusion and compression-molding temperatures of 220 °C instead of 180 °C. The i-PP blend films that had an initial thickness of ~0.3 mm were drawn at 135 °C to draw ratios of approximately 14. In addition, blend films based on LLDPE and selected PL dyes were also produced by guest diffusion. The films were prepared by immersing an unstretched LLDPE film, prepared as described above, in a solution of one of the PL dyes **1a**−**d** in $CHCl_3$ (approximately 2% w/w) under stirring at 50 °C for 48 h. The films were subsequently rinsed with CH_2Cl_2 and acetone, dried, and oriented as described above. The concentration of the dyes in the films prepared by guest diffusion could be estimated from the absorbance spectra and was determined to be between 0.02 and 0.05% w/w.

Methods. ^{1}H NMR and ^{13}C NMR spectra were obtained on various Bruker spectrometers (300 or 500 MHz for ^{1}H NMR and 75 or 125 MHz for ^{13}C NMR). All chemical shifts are expressed in ppm relative to an internal TMS standard. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC 7 under N_2 atmosphere at heating and cooling rates of 10 K/min. All melting points (mp)

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(20) Weder, Ch.; Sarwa, C.; Bastiaansen, C.; Smith, P. *Adv. Mater.* **1997**, *9*, 1035.

(21) Weder, Ch.; Sarwa, C.; Montali, A.; Bastiaansen, C.; Smith, P. *Science* **1998**, *279*, 835.

(22) Eglin, M.; Montali, A.; Palmans, A. R. A.; Tervoort, T.; Smith, P.; Weder, Ch. *J. Mater. Chem.* **1999**, *9* (9), 2221.

(23) Previously, fluorinated BPB derivatives have been prepared in order to investigate their liquid crystalline properties. See: (a) Wen, J.; Tian, M.; Chen, Q. *J. Fluorine Chem.* **1994**, *68*, 117. (b) Pugh, C.; Andersson, S. K.; Percec, V. *Liq. Cryst.* **1991**, *10* (2), 229. BPB derivatives with dialkoxy substitution at the central benzene ring have been prepared as well. See: (c) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52. (d) Davey, A. P.; Howard, R. G. Blau, W. J. *J. Mater. Chem.* **1997**, *7* (3), 417. (e) Swager, T. M.; Gill, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886. (f) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12539.

(24) Biswas, M.; Nguyen, P.; Marder, T. B.; Khundkar, L. R. *J. Phys. Chem.* **1997**, *101*, 1689.

(25) Nakatsuji, S.; Matsuda, K.; Uesugi, Y.; Nakashima, K.; Akiyama, S.; Fabian, W. *J. Chem. Soc., Perkin Trans. 1* **1992**, 755.

and other transition temperatures (except those observed by polarization microscopy) were obtained using DSC, taking the peak maximum measured in the second heating scan as the transition temperature. Polarization microscopy studies were conducted on a Leica DMRX equipped with a Linkam hot stage with the sample between crossed polarizers. Elemental analyses were carried out by the Microanalysis Laboratory of the Department of Chemistry of ETH Zürich. UV–vis spectra were measured on a Perkin-Elmer Lambda 900 UV–vis spectrophotometer. Steady-state PL spectra were recorded on a SPEX Fluorolog 3 (model FL3–12). All spectra were corrected for the spectral dispersion of the 450 W Xe lamp that was used for excitation, the instrument throughput, and the detector response. PL spectra of solutions were measured in a standard 90° cuvette geometry. Quantum yields were determined according to methods previously published[26–28] and were obtained after sparging the $CHCl_3$ solutions with argon for 1 h and using quinine sulfate in 1 N H_2SO_4 as a reference for which an absolute quantum yield of 54.6% at an excitation wavelength of 365 nm was taken.[26,27] All solutions employed had an optical density of $\sim$0.1 at the excitation wavelength, the optical path length was 1 cm, and the concentration of the solutions of the PL dyes was around 1.5×10^{-6} mol/L. Polarized PL spectra of oriented films were recorded in front-face mode at an angle of 22.5° from the excitation beam, using unpolarized light for excitation (338 nm) and a motor-driven Glan-Thompson polarizer on the detector side. To compensate for the polarization sensitivity of the instrument, a depolarizer was placed between the sample and the detection system. All films were sandwiched between two quartz slides, and a small amount of silicon oil was added to minimize scattering effects at the film surfaces. The dichroic ratios in emission (DR_E) were obtained by dividing the integrated areas of the spectra measured under p-polarized and s-polarized detection, respectively.

General Procedure for the Preparation of 2b–d. A suspension of K_2CO_3 (8.0 g, 58 mmol) and dimethylformamide (30 mL) was purged with Ar for 15 min and heated to 70 °C, and 4-iodophenol (5.0 g, 23 mmol) was added. After 10 min, the respective alkyl bromide (26 mmol) was slowly added via a syringe, and the suspension was stirred at 70 °C under Ar sparging for 4 h. The reaction was subsequently terminated by pouring the suspension into ice–water (300 mL).

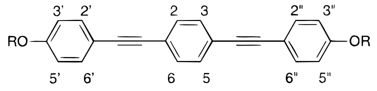
*4-(2-Ethylhexyloxy)-1-iodobenzene (**2b**).* The reaction was conducted according to the general procedure described above using 2-ethylhexyl bromide. The aqueous phase was extracted with CH_2Cl_2. The collected organic layers were washed with H_2O, aqueous NaOH (1 M), H_2O, and saturated aqueous NaCl. The organic layer was dried with $MgSO_4$, filtered, and evaporated in vacuo. Column chromatography (SiO_2; eluent, heptane) of the resulting crude oil afforded pure **2b** as a colorless liquid (4.6 g, 61%). ^1H NMR ($CDCl_3$): δ 7.55 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–I)); 6.67 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–OR)); 3.80 (d, 2H, OCH_2); 1.70 (qui, 1H, OCH_2CH); 1.3 (m, 8H, $CHCH_2CH_3$ and $CH(CH_2)_3CH_3$); 0.91 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.3 (C–OCH_2), 138.1, 116.9, 82.3 (C–I) (aromatic carbons); 70.6 (OCH_2), 39.3, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1 (aliphatic carbons). Anal. Calcd for $C_{14}H_{21}IO$ (332.22): C, 50.61; H, 6.37; I, 38.20. Found: C, 50.68; H, 6.17; I, 38.12.

*4-Octyloxy-1-iodobenzene (**2c**).* The reaction was conducted according to the general procedure described above using octyl bromide. The aqueous phase was extracted with diethyl ether. The collected organic layers were washed with H_2O, aqueous NaOH (1 M), and H_2O. The organic layer was dried with $MgSO_4$, filtered, and evaporated in vacuo. Column chromatography (SiO_2; eluent, heptane) of the resulting crude product, followed by distillation under reduced pressure afforded pure **2c** as a colorless liquid (6.0 g, 79%). Bp: 118 °C/0.38 mbar. ^1H NMR ($CDCl_3$): δ 7.53 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–I)); 6.67 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–OR)); 3.87 (t, 2H, OCH_2); 1.75 (qui, 2H, OCH_2CH_2); 1.5–1.2 (m, 10H, $(CH_2)_5$); 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.1 (C–OCH_2), 138.2, 117.0, 82.5 (C–I) (aromatic carbons); 68.2 (OCH_2), 31.9, 29.4, 29.3, 29.2, 26.1, 22.7, 14.2 (aliphatic carbons). Anal. Calcd for $C_{14}H_{21}IO$ (332.22): C, 50.61; H, 6.37; I, 38.20. Found: C, 50.61; H, 6.26; I, 38.25.

*4-Dodecyloxy-1-iodobenzene (**2d**).* The reaction was conducted according to the general procedure described above using dodecyl bromide. The resulting white precipitate in the aqueous phase was filtered off, washed with aqueous NaOH (5%) and water, and dried in vacuo. The crude product was purified by column chromatography (SiO_2; eluent, heptane). Subsequent recrystallization from EtOH (100 mL) afforded pure **2d** as a white powder (6.3 g, 72%). Mp: 42.1 °C. ^1H NMR ($CDCl_3$): δ 7.55 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–I)); 6.68 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–OR)); 3.90 (t, 2H, OCH_2); 1.76 (qui, 2H, OCH_2CH_2); 1.30 (bs, 18H, $(CH_2)_9$); 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.1 (C–OCH_2), 138.2, 117.0, 82.4 (C–I) (aromatic carbons); 68.2 (OCH_2), 32.0, 29.7, 29.7–29.2 ($7 \times CH_2$), 26.0, 22.7, 14.2 (aliphatic carbons). Anal. Calcd for $C_{18}H_{29}OI$ (388.33): C, 55.67; H, 7.53. Found: C, 55.89; H, 7.25.

*4-Triacontanyloxy-1-iodobenzene (**2e**).* Under Ar atmosphere, 1-triacontanol (500 mg, 1.14 mmol), 4-iodophenol (270 mg, 1.23 mmol), and PPh_3 (460 mg, 1.75 mmol) were dissolved in dry THF (16 mL) under gentle heating. Diethyl azodicarboxylate (250 mg, 1.75 mmol) was slowly added via a syringe. The solution was stirred at room temperature for 16 h. Diethyl ether (50 mL) and H_2O (50 mL) were added, and the organic layer (a suspension) was extracted with aqueous NaOH (1 M, 2×50 mL), H_2O (50 mL), and saturated aqueous NaCl (50 mL). The organic layer was evaporated in vacuo, and the resulting crude product was recrystallized from diethyl ether to afford pure **2e** as a white powder (405 mg, 70%). Mp: 87.2 °C. ^1H NMR ($CDCl_3$): δ 7.53 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–I)); 6.66 (d, 2H, $J = 9.0$ Hz, H_{ortho}(C–OR)); 3.90 (t, 2H, OCH_2); 1.75 (qui, 2H, OCH_2CH_2); 1.43 (qui, 2H, OCH_2 CH_2CH_2); 1.25 (bs, 52H, $(CH_2)_{26}$); 0.87 (t, 3H, CH_3). Anal. Calcd for $C_{36}H_{65}IO$ (640.81): C, 67.48; H, 10.22. Found: C, 67.56; H, 10.06.

General Procedure for the Synthesis of 1a–e. Under inert atmosphere, 1,4-diethynylbenzene (300 mg, 2.38 mmol), 4-alkoxy-1-iodobenzene (5.24 mmol), $Pd(PPh_3)_4$ (30 mg), and CuI (5 mg) were added to a 3/1 v/v mixture of toluene/diisopropylamine (40 mL). After the mixture was heated to 75 °C, a precipitate started to appear. The mixture was stirred for 18 h at 75 °C under Ar atmosphere. The resulting, strongly luminescent suspension was subsequently slowly dropped into an excess of MeOH (300 mL), and the precipitate was filtered over a glass filter (P4).



1a-e

*MeO–BPB (**1a**).* The crude product was recrystallized, first from CH_2Cl_2 and then from THF to afford pure **1a** as off-white needles (355 mg, 44%). Mp: 216.7 °C (lit.:[25] 216–218 °C). ^1H NMR ($CDCl_3$): δ 7.46 (m, 8H, H-2, H-3, H-5, H-6, H-2′, H-6′, H-2″, and H-6″); 6.89 (d, $J = 8.8$ Hz, 4H, H-3′, H-5′, H-3″, and H-5″); 3.83 (s, 6H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 159.9 (C–OCH_3), 133.1, 131.3, 123.2 (C_{ipso}), 115.4 (C_{ipso}), 114.1 (aromatic carbons); 91.1, 88.0 (acetylenic carbons); 55.3 (CH_3). Anal. Calcd for $C_{24}H_{18}O_2$ (338.41): C, 85.18; H, 5.36; O, 9.46. Found: C, 85.13; H, 5.58; O, 9.36.

*EHO–BPB (**1b**).* The crude product was purified by column chromatography (SiO_2; eluent, heptane/CH_2Cl_2 95/5 v/v) to afford pure **1b** as a white powder (1.25 g, 80%). Mp: 95.6 °C. ^1H NMR ($CDCl_3$): δ 7.46 (m, 8H, H-2, H-3, H-5, H-6, H-2′, H-6′, H-2″, and H-6″); 6.89 (d, $J = 8.8$ Hz, 4H, H-3′, H-5′, H-3″, and H-5″); 3.80 (d, 4H, OCH_2); 1.70 (qui, 2H, OCH_2CH); 1.3 (m, 16H, $CHCH_2CH_3$ and $CH(CH_2)_3CH_3$); 0.91 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.7 (C–OCH_2), 133.0, 131.3, 123.3 (C_{ipso}), 115.1 (C_{ipso}), 114.7 (aromatic carbons); 91.3, 87.8 (acetylenic carbons); 70.9 (OCH_2), 39.5, 30.6, 29.1, 24.0, 22.9, 13.8, 11.0 (aliphatic carbons). Anal. Calcd for $C_{38}H_{46}O_2$ (534.78): C, 85.35; H, 8.67; O, 5.98. Found: C, 85.16; H, 8.65; O, 6.01.

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(26) Melhuis, W. H. *J. Phys. Chem.* **1961**, *65*, 229.
(27) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
(28) Weder, Ch.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157.

C_8O−BPB (**1c**). The crude product was recrystallized first from EtOH/THF 1/1 v/v and then from THF to afford pure **1c** as white plate-shaped crystals (0.90 g, 50%). K_1 74 °C K_2 128.3 °C S_1 165.2 °C S_2 182.0 °C N 217.7 °C I. ^1H NMR ($CDCl_3$): δ 7.43 (m, 8H, H-2, H-3, H-5, H-6, H-2′, H-6′, H-2″ and H-6″); 6.85 (d, J = 8.8 Hz, 4H, H-3′, H-5′, H-3″ and H-5″); 3.96 (t, 4H, OCH_2); 1.79 (qui, 4H, OCH_2CH_2); 1.30 (m, 20H, $(CH_2)_5$); 0.89 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.5 (C−OCH_2), 133.0, 131.3, 123.3 (C_{ipso}), 115.2 (C_{ipso}), 114.7 (aromatic carbons); 91.3, 87.9 (acetylenic carbons); 68.3 (OCH_2), 31.7, 29.3, 29.2, 19.1, 26.0, 22.5, 13.9 (aliphatic carbons). Anal. Calcd for $C_{38}H_{46}O_2$ (534.78): C, 85.35; H, 8.67; O, 5.98. Found: C, 85.39; H, 8.66; O, 5.92.

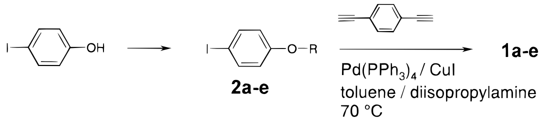
$C_{12}O$−BPB (**1d**). The crude product was recrystallized first from heptane and then from THF to afford pure **1d** as off-white small needles (0.90 g, 64%). K_1 112.3 °C K_2 118.9 °C S_1 161.6 °C S_2 165.4 °C S_3 173.2 °C S_4 183.4 °C N 188.9 °C I. ^1H NMR ($CDCl_3$): δ 7.45 (m, 8H, H-2, H-3, H-5, H-6, H-2′, H-6′, H-2″, and H-6″); 6.85 (d, J = 8.8 Hz, 4H, H-3′, H-5′, H-3′, and H-5″); 3.97 (t, 4H, OCH_2); 1.82 (qui, 4H, OCH_2CH_2); 1.3 (m, 36H, $(CH_2)_9$); 0.88 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.5 (C-OCH_2), 133.0, 131.3, 123.3 (C_{ipso}), 115.2 (C_{ipso}), 114.7 (aromatic carbons); 91.3, 87.9 (acetylenic carbons); 68.3 (OCH_2), 31.8, 29.6−29.2 (7 × CH_2), 26.0, 22.6, 13.9 (aliphatic carbons). Anal. Calcd for $C_{46}H_{62}O_2$ (646.99): C, 85.40; H, 9.66; O, 4.95. Found: C, 85.44; H, 9.60; O, 5.07.

$C_{30}O$−BPB (**1e**). The crude product was washed with MeOH, CH_2Cl_2, and diethyl ether. Recrystallization from THF afforded pure **1e** as an off-white powder (105 mg, 59%). K 126.3 °C S 141.4 °C I. ^1H NMR ($CDCl_3$): δ 7.43 (m, 8H, H-2, H-3, H-5, H-6, H-2′, H-6′, H-2″, and H-6″); 6.87 (d, J = 8.8 Hz, 4H, H-3′, H-5′, H-3″, and H-5″); 3.97 (t, 4H, OCH_2); 1.75 (qui, 4H, OCH_2CH_2); 1.3 (m, 108H, $(CH_2)_{27}$); 0.88 (t, 6H, CH_3). Anal. Calcd for $C_{82}H_{134}O_2$ (1151.96): C, 85.50; H, 11.72. Found: C, 84.71; H, 11.14.

Results and Discussion

Synthesis of 1a−e. The PL dyes **1a**−**e** have been synthesized via Heck-type cross-coupling reactions of the corresponding 4-alkoxy-1-iodobenzene with commercially available 1,4-diethynylbenzene using standard procedures[23f,28] (Scheme 1). The crude products were thoroughly purified and afforded pure **1a**−**e** in reasonable-to-good yields (44−80%). Despite the presence of alkoxy substituents, the solubility of the new PL dyes proved to be limited in common organic solvents at ambient temperature. In fact, the solubility was found to be less favorable than in the case of the unsubstituted 1,4-bis(phenylethynyl)benzene, BPB. Only EHO−BPB (**1b**) was highly soluble in solvents such as hexane, xylene, chloroform, and THF.

Scheme 1. Synthesis of the PL Dyes 1a−e

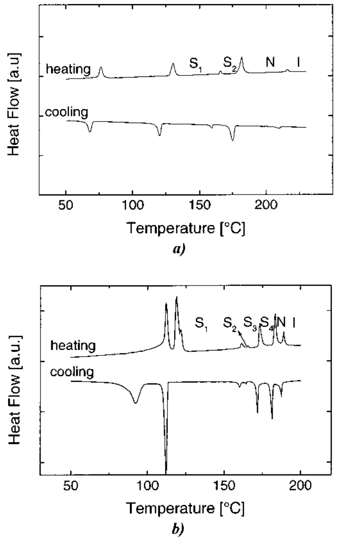


Thermal Behavior of 1a−e. The thermal behavior of **1a**−**e** was studied using DSC at heating and cooling rates of 10 K/min, as well as polarization microscopy. The phase transition temperatures (T) and corresponding enthalpies (ΔH) measured in the second DSC heating scans are summarized in Table 1.

Table 1. Transition Temperatures, T, and Enthalpies, ΔH, for the PL dyes 1a−e As Determined by DSC[a]

PL dye	K	T (ΔH)[b]	S	T (ΔH)[b]	N	T (ΔH)[b]	I
MeO−BPB (1a)	•	216.7 (40.5)	−	−	−	−	•
EHO−BPB (1b)	•	95.6 (35.1)	−	−	−	−	•
C_8O−BPB (1c)	•[c]	128.3 (15.3)	•[e]	182.0 (19.6)	•	217.7 (2.1)	•
$C_{12}O$−BPB (1d)	•[d]	118.9 (24.1)	•[f]	183.4 (7.3)	•	188.9 (2.0)	•
$C_{30}O$−BPB (1e)	•	126.3 (136.0)	•[g]	−	−	141.4 (34.1)	•

[a] All phases are assigned by means of optical microscopy. •: phase is observed. −: phase is not observed. K = crystalline phase. [b] Transition temperatures are in degrees Celsius. Values in parentheses are enthalpies in kilojoules per moles. [c] Two crystalline phases present with transition at 74.0 °C. [d] Two crystalline phases present with transition at 112.3 °C. S = unidentified smectic mesophase. [e] Two different smectic phases with transition at 165.2 °C. [f] Four different smectic phases with transitions at 161.6, 165.4, and 173.2 °C. [g] One smectic phase. N = nematic mesophase. I = isotropic phase.



a)

b)

Figure 2. DSC traces of (a) C_8O−BPB and (b) $C_{12}O$−BPB second heating and cooling runs recorded at 10 K/min.

The DSC traces of MeO−BPB and EHO−BPB both showed one well-defined transition at 216.7 °C for MeO−BPB and 95.6 °C for EHO−BPB, respectively, which by means of polarization microscopy could be assigned to crystalline-to-isotropic transitions. By contrast, C_8O−BPB and $C_{12}O$−BPB showed several reversible transitions upon heating and cooling in DSC traces, as visualized in Figure 2. For C_8O−BPB, the DSC heating scan revealed transitions at 74.0, 128.3, 165.2, 182.0, and 217.7 °C (see Figure 2),[29] and for $C_{12}O$−BPB, transitions were found at 112.3, 118.9, 161.6, 165.4, 173.2, 183.4, and 188.9 °C (see Figure 2b). A detailed investigation with polarization microscopy revealed that upon heating C_8O−BPB entered a birefringent, highly viscous, mobile state around 128 °C. Two additional transitions were observed around 167 and 182 °C before the isotropic melt was entered at around 218 °C. The transition temperatures observed with polarization microscopy perfectly matched those determined with DSC. The low viscosity and the Schlieren texture of the phase between 182 and 218 °C suggested the presence of a nematic phase, whereas the textures of the two phases between 128 and 182 °C suggested the presence of smectic phases in this temperature regime.[30] Polarization microscopy showed that $C_{12}O$−BPB entered a birefringent, viscous, mobile phase around 118 °C. This transition was followed by several other transitions at

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(29) The DSC trace of C_7O−BPB has been published and shows several transitions as well. See: Pugh, C.; Percec, V. *Polym. Bull.* **1990**, *23*, 177.

(30) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals: Textures and Structures*; Leonard Hill: Glasgow, 1984.

Table 2. Photophysical Characteristics of the PL Dyes BPB and 1a−e in $CHCl_3$

PL dye	$\lambda_{max,abs}$ [nm]	ϵ [L/mol cm]	$\lambda_{max,em}$ [nm]	Φ^a [−]
BPB	324.4 (322^b)	−(4.98E4^{b,c})	347.4 (370^b)	0.56 (0.56^b)
MeO-BPB (**1a**)	335.4 (332^b)	6.34E4 (5.82E4^b)	364.1 (368^b)	0.72 (0.59^b)
EHO-BPB (**1b**)	337.8	6.38E4	367.0	0.65
C_8O-BPB (**1c**)	337.8	6.26E4	366.3	0.66
C_{12}O-BPB (**1d**)	337.8	6.28E4	366.4	0.63
C_{30}O-BPB (**1e**)	337.0^d	^{e}	366.4^d	^{e}

[a] Excitation at 338 nm for **1a**−**e** and 322 nm for BPB. [b] Nakatsuji et al.[25] [c] E represents ×10. [d] Measured at 50 °C. [e] Not available due to insolubility of **1e** at ambient temperature.

163, 175, and 184 °C before the compound turned into an isotropic melt at 189 °C. In addition, for this dye, the phase between 184 and 189 °C exhibited a low viscosity and showed a Schlieren texture, characteristic of a nematic phase. The textures grown for the other phases suggested the presence of a number of different smectic phases between 184 and 118 °C.[30] The precise nature of the smectic phases present in C_8O−BPB and C_{12}O−BPB could not be unambiguously assigned. With both compounds, C_8O−BPB and C_{12}O−BPB, the first transition upon heating observed in DSC at 74.0 and 112.3 °C, respectively, could no not be observed with polarization microscopy, suggesting that this transition is most likely a crystal−crystal transition. The DSC trace of C_{30}O−BPB showed two reversible transitions at 126.3 and 141.4 °C. Polarization microscopy showed a transition from a crystalline to a mobile, birefringent phase around 126 °C and a transition into an isotropic liquid at 142 °C. The mesophase between 126 and 142 °C displayed a relatively high viscosity, and the spherulitic growth pattern observed upon cooling from the isotropic melt suggested the presence of a smectic phase, which is consistent with the relatively large ΔH accompanying this transition.[30]

Spectroscopic Characterization of 1a−e. The molar extinction coefficient (ϵ) and the maxima of absorption ($\lambda_{max,abs}$) and emission ($\lambda_{max,em}$) of the new PL dyes are summarized in Table 2. For the purpose of comparison, we also measured the optical characteristics of the commercially available BPB, and the results compare well to previously published data.[25]

All alkoxy−BPBs show similar absorption and emission maxima, and their molar extinction coefficients ϵ are essentially the same, consistent with the fact that their conjugated system is identical. The optical characterization of C_{30}O−BPB was hampered due to its poor solubility in $CHCl_3$ and other organic solvents at room temperature. All compounds are highly emissive in solution, as evidenced by their quantum yields that range from 0.63 to 0.72, and emit light of an intense, bright-blue color. The quantum yield of MeO−BPB was found to be slightly higher than that previously published (0.59,[25] in contrast to 0.72 reported here), which, most likely, can be attributed to differences in the purity of the present MeO−BPB. All new PL dyes were also found to be highly emissive in the solid state; however, no quantitative results for the latter were obtained yet.

Blends of 1a−e and UHMW PE. Binary blend films based on a UHMW PE matrix and 0.2−2% w/w of **1a**−**e** were prepared by solution-casting from *p*-xylene, according to previously described procedures.[20] The pristine blend films were examined by optical microscopy in order to qualitatively evaluate homogeneity of the blends. The application of other standard analytical techniques that are usually employed for the investigation of phase behavior and could provide complementary insights (e.g., diffraction techniques, DSC, evaluation of UV- or PL-spectral shapes) would be desirable. However, these techniques are often stifled for blends comprising minute amounts of guest molecules and as a consequence are rarely employed.[1−11,16−18,20,22,31]

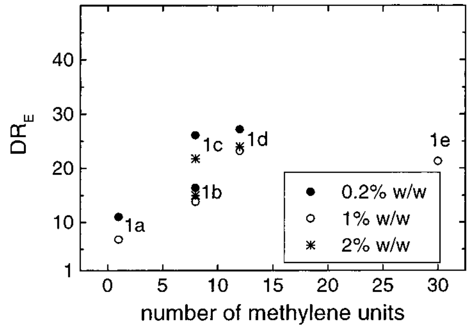

Figure 3. Emission dichroic ratio, DR$_E$, as a function of PL dye concentration and nature of the alkoxy substituent for **1a**−**e**/UHMW PE-oriented blend films at constant draw ratio $l/l_0 \approx 80$.

The films were uniaxially oriented by tensile deformation at 120 °C to draw ratios of 70−80. The results of polarized PL experiments are summarized in Figure 3.

Optical microscopy revealed that several pristine blends were inhomogeneous due to the formation of relatively large crystals of the guest molecule during the drying process; MeO−BPB, C_8O−BPB, and C_{12}O−BPB at least partially crystallized during drying if the concentration of the dye was above 1% w/w. By contrast, all blend films comprising only 0.2% w/w of the PL dye appeared homogeneous on the micrometer level after drying. However, the below results suggest that also in the case of the latter a substantial fraction of guest molecules may be present in (apparently rather small) crystalline domains, well-segregated from the PE matrix. As evidenced by polarization microscopy, the inhomogeneities present in the pristine blends were retained after tensile deformation, as shown, for example, for a 1% w/w MeO−BPB/UHMW PE blend film before and after orientation in Figure 4. A routine DSC experiment of the unstretched 1% w/w MeO−BPB/UHMW PE blend film could not reveal the melting of the unequivocally present MeO−BPB crystals (Figure 4 left), providing an illustrative example for the limitation of this technique in the context of the present investigation.

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(31) Montali, A.; Palmans, A. R. A.; Eglin, M.; Weder, Ch.; Smith, P.; Trabesinger, W.; Renn, A.; Hecht, B.; Wild, U. P. *Macromol. Symp.*, in press.

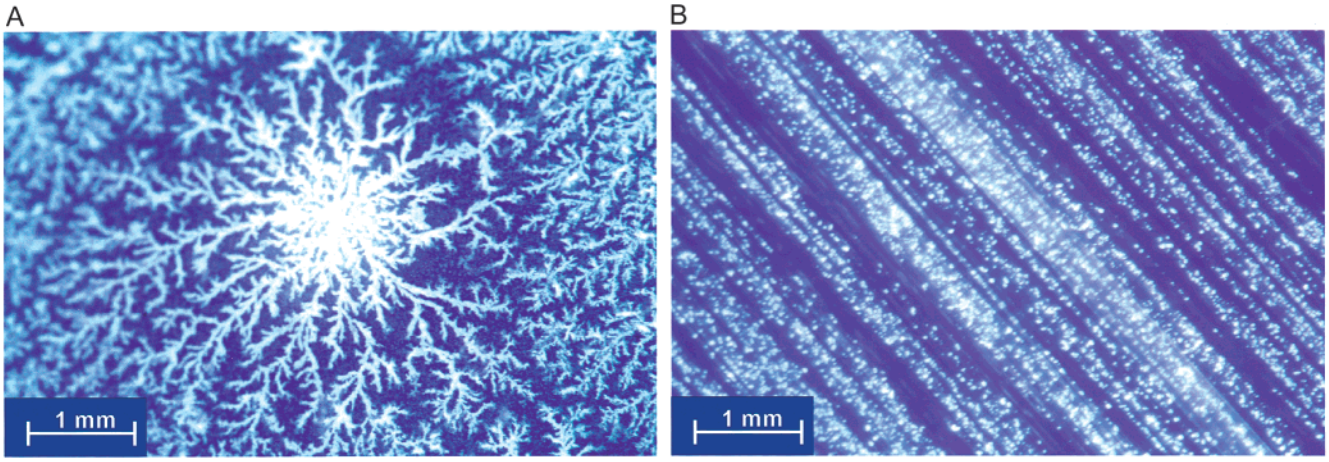

Figure 4. Polarized optical microscopy image of a 1% w/w MeO−BPB/UHMW PE blend before (a) and after (b) orientation ($l/l_0 \approx 25$).

Interestingly, despite the above-noted phase segregation, DR_E was found to be relatively insensitive with respect to the concentration of the dye in the oriented blend films, as evidenced by the data shown in Figure 3. MeO−BPB was found to orient rather poorly in UHMW PE-based blends (1% w/w, $DR_E = 7$, $l/l_0 = 80$) and in films comprising low concentrations of the PL guest (0.2% w/w, $DR_E = 11$, $l/l_0 = 80$). The relatively poor orientation of the guest molecules in MeO−BPB/UHMW PE blends, even at draw ratios of 80, can be understood in view of the previous finding that a melting temperature of the guest dye close to the drawing temperature is required in order to obtain highly dichroic guest−host systems.[18] In addition, in previous studies regarding the orientation behavior of conjugated polymer/UHMW PE-based blends, the mobility of the guest polymer at the drawing temperature proved to be a deciding factor in order to obtain high dichroic ratios.[32,33] Because MeO−BPB exhibits a high melting temperature (217.7 °C) and at least partially crystallized during drying of the MeO−BPB/UHMW PE blend (see Figure 4), it is rather unlikely that MeO−BPB is in a mobile state at the drawing temperature of 120 °C. Thus, these results imply that a large fraction of the PL guest molecules indeed is present as crystallites (see Figure 4), and because the melting temperature of MeO−BPB significantly exceeds the drawing temperature, these crystallites will not or only hardly orient. The slightly higher DR_E for blend films in which the concentration of MeO−BPB in UHMW PE was decreased from 1 to 0.2% w/w may be explained by a somewhat more homogeneous system in which a smaller fraction of phase-segregated crystallites remain unoriented after solid-state drawing.

Blend films based on C_8O−BPB or $C_{12}O$−BPB and UHMW PE, on the other hand, display a higher optical anisotropy, characterized by dichroic ratios of 22−27. As these compounds are almost identical in chemical structure (only four methylene units difference in the alkoxy substituent) and exhibit similar solubility characteristics and thermal behavior, it is not surprising that the orientation behavior of C_8O−BPB and $C_{12}O$−BPB is also essentially the same. Both compounds attain a mobile, smectic phase at 128.3 and 118.9 °C, respectively. As a result (taking a transition-temperature depression in the binary system into account),[16] C_8O−BPB and $C_{12}O$−BPB are expected to be in a mobile phase at the drawing temperature of 120 °C, which, in view of previous results,[16] may account for their relatively good orientation. Thus, in this system, it seems that the dyes are oriented by shearing the LC domains of the dyes in the UHMW PE matrix as well as the (grapho-)epitaxial influence of the latter.[2] As can be expected from the fact that a smectic phase is present for pure $C_{30}O$−BPB above 126.3 °C, blends based on $C_{30}O$−BPB were observed to behave similarly to blends based on C_8O−BPB or $C_{12}O$−BPB and UHMW PE. Phase segregation is in this case less visible due to a significantly lower tendency of $C_{30}O$−BPB to crystallize during the drying of the blend film.

EHO−BPB, containing a branched alkoxy substituent, exhibits a most preferred thermal behavior for the preparation of UHMW PE-based blends, exhibiting a melting temperature of 95.6 °C. In addition, optically homogeneous blends were obtained for all compositions investigated. Nevertheless, the degree of orientation of this dye in UHMW PE blends is only modest ($DR_E \sim 15$). Apparently, the introduction of branching negatively influences the orientation behavior during tensile deformation, as revealed by the differences in the dichroic ratios found for PE blends comprising EHO−BPB when compared to those with its linear analogue C_8O−BPB ($DR_E = 26$ for C_8O−BPB/UHMW PE and $DR_E = 16$ for EHO−BPB/UHMW PE, both 0.2% w/w and drawn to the same draw ratios).

Blends of 1a−e and LLDPE. Binary blends based on a LLDPE matrix and **1a−e** were prepared by melt-processing at 180 °C (see Experimental Section for details). All films produced by this method appeared homogeneous when examined by polarization microscopy. In addition, blend films based on LLDPE and the PL dyes **1a−e** were prepared through guest diffusion[1] by swelling an unstretched LLDPE film in a solution containing one of the PL dyes, drying, and subsequent drawing at 90 °C to draw ratios l/l_0 of up to 10. The latter technique has been employed in a plethora of studies to investigate the orientation behavior of sem-

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(32) Montali, A.; Smith, P.; Weder, Ch. *J. Mater. Sci.*, in press.

(33) Palmans, A. R. A.; Smith, P.; Weder, Ch. *Macromolecules* **1999**, *32*, 4677.

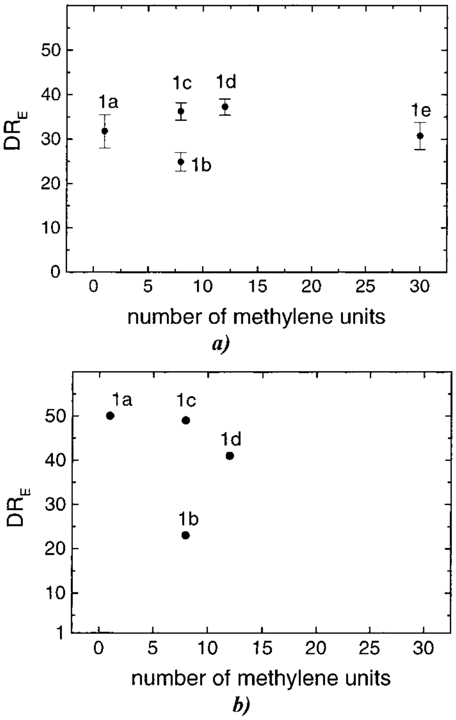

Figure 5. (a) Emission dichroic ratio, DR$_E$, as a function of the nature of the alkoxy substituent in oriented ($l/l_0 = 10$) melt-processed dye/LLDPE blend films. Concentration of the dyes: MeO–BPB, 0.13% w/w; EHO–BPB, 0.17% w/w; C$_8$O–BPB, 0.17% w/w; C$_{12}$O–BPB, 0.20% w/w; and C$_{30}$O–BPB, 0.20% w/w. DR$_E$ was averaged over two different measured sections of two independently stretched pieces of film; error bars are included. (b) Emission dichroic ratio, DR$_E$, as a function of the nature of the alkoxy substituent in dye/LLDPE blend films prepared by guest diffusion. The dye concentration, as estimated from absorbance spectra, was between 0.02 and 0.05% w/w.

icrystalline polymer systems.[1–11] Detailed structural investigations[2] suggest that during the swelling step the guest molecules are (in rather low concentration) incorporated in the amorphous phase of the matrix in molecularly dissolved or dispersed fashion, leading to ultimate orientability of the guest molecules. The results of polarized PL experiments of these films, the draw ratio of which is limited to about 10 due to the nature of the PE host material employed, are summarized in Figure 5.

Figure 5a shows that very high dichroic ratios (DR$_E$ = 30–36) were observed for all melt-processed LLDPE blends, except for EHO–BPB-based blends that exhibited a lower optical anisotropy (DR$_E$ ~ 24). Figure 5b demonstrates that films prepared by guest diffusion exhibit even higher values for DR$_E$ for all derivatives (DR$_E$ = 41–50) except again the EHO–BPB-based blend. In the latter case, the DR$_E$ was found to be comparable with that of the melt-processed film.

Most interestingly, application of melt-processing techniques in combination with LLDPE as the matrix material significantly enhances the orientation of MeO–BPB blends (DR$_E$ ~ 30, $l/l_0 = 10$ in 0.2% w/w MeO–BPB /LLDPE blend) when compared to UHMW PE-based blends comprising this dye (DR$_E$ = 11, $l/l_0 = 80$ in 0.2% w/w MeO–BPB/UHMW PE blend) despite the significantly lower draw ratios achieved with LLDPE. The MeO–BPB/LLDPE blend film appears to be homogeneous before and after tensile deformation; potentially, a significant fraction of the MeO–BPB molecules is quasimolecularly dispersed in the amorphous domains of the matrix material and orients according to the pseudo-affine deformation scheme.[16–18,34,35] This finding seems to be in contradiction with earlier statements that the melting temperature of the guest molecule should be near the drawing temperature.[16] However, as was shown previously for BPB/LLDPE blend films[22] and many organic guest molecules studied in stretched polyethylene,[1–4] the inclusion of the guest molecule in a molecularly dissolved or dispersed form may lead to a very high degree of orientation, regardless of the melting temperature of their crystalline form. Indeed, diminishing the concentration of MeO–BPB, which reduces the fraction of “non-dissolved” dye, was found to increase DR$_E$ even further (DR$_E$ = 50, l/l_0 = 10 in 0.03% w/w MeO–BPB/LLDPE blend prepared by guest diffusion).

The dichroic ratios of melt-processed blend based on C$_8$O–BPB/LLDPE and C$_{12}$O–BPB/LLDPE are similar, as evidenced by Figure 5a, and both were found to be higher when compared to corresponding ratios of blend films obtained by solution-casting. DR$_E$ was increased from around 25 to around 35 for the former. All C$_8$O–BPB/LLDPE and C$_{12}$O–BPB/LLDPE blends appeared homogeneous, and the high optical anisotropy found for the oriented films indicate, as already discussed for MeO–BPB, that a larger fraction of the guest molecules appeared to be in a quasimolecularly dissolved form and oriented according to the pseudo-affine deformation scheme.[16–18,34,35] Again, as observed above, diminishing the concentration leads to very high dichroic ratios (DR$_E$ ~ 45). It must be noted that the concentration of the dye in the PE matrix in the case of melt-processed blends plays a crucial factor for the dichroic ratios achieved: for example, upon increasing the concentration of C$_{12}$O–BPB in LLDPE from 0.2 to 2% w/w, the dichroic ratio actually decreased to 24,[22] indicating that the solubility of C$_{12}$O–BPB in the LLDPE matrix is a limiting factor.

It should be noted that dichroic ratios of up to 50 have been reported previously for melt-processed C$_{12}$O–BPB/LLDPE blend films.[22] The values presented here are somewhat lower (DR$_E$ ~ 36). This can most likely be attributed to differences in the LLDPE matrix materials used, because the determinations of the dichroic ratios reported here were reproducible, as evidenced by the limited error bars given in Figure 5a. In the latter case, we averaged the dichroic ratios obtained from stretching two different parts of the pristine film and measuring the stretched film at two different places. Nevertheless, we should clearly point out that a significant error may occur in the determination of DR$_E$, as discussed in detail in Eglin et al.[22]

The dichroic ratios of oriented C$_{30}$O–BPB/LLDPE blend films prepared by melt-processing are similar to those discussed for the other alkoxy-substituted BPB-based blends. Although a further increase of the dichroic ratio due to the introduction of an alkoxy substituent

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(34) (a) Ward, I. M. *J. Polym. Sci., Polym. Symp.* **1977**, *58*, 1. (b) Ward, I. M. *Proc. Phys. Soc.* **1962**, *80*, 1176.

(35) Hermans, P. H.; Heikens, D. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 49.

with increased alkane length could be anticipated, the latter appeared not to substantially influence the orientation behavior of the PL dye, as evidenced by the data given in Figure 5a.

The introduction of branching in the alkoxy substituent, on the other hand, does play a role in the orientation of the guest in melt-processed LLDPE blends, as evidenced by the lower DR_E found for blends based on EHO−BPB compared to its linear analogue C_8O−BPB (DR_E = 23 vs 36, for EHO−BPB and C_8O−BPB-based blends, respectively). In addition, the preparation of blend films by guest diffusion did not improve the dichroic ratio (DR_E = 22) of this system.

The impact of branching in the alkoxy substituent was further investigated by evaluating the dichroic ratio of melt-processed blend films of EHO−BPB or C_8O−BPB and LLDPE as a function of the draw ratio l/l_0. From these data, the order parameter of the PL guest, S_{dye}, was calculated as follows:[5a,15]

$$S_{dye} = \frac{DR_E - 1}{DR_E + 2} \tag{1}$$

The orientation behavior of the tensile deformed matrix polymer can be described by the pseudo-affine deformation scheme.[34] Here, the average orientation $\langle \cos^2 \phi \rangle$ of initially randomly oriented statistical chain segments of the macromolecule with respect to the direction of uniaxial deformation can be given as a function of the draw ratio:

$$\langle \cos^2 \phi \rangle = \frac{(l/l_0)^3}{(l/l_0)^3 - 1} - \frac{(l/l_0)^3}{\sqrt{((l/l_0)^3 - 1)^3}} \arctan\sqrt{(l/l_0)^3 - 1} \tag{2}$$

in which l/l_0 is the draw ratio, i.e., the ratio between the length of a deformed and undeformed sample, and ϕ is the angle between a statistical chain segment and the drawing direction. By assuming that dichroic guest molecules adapt the orientation of the host polymer and applying Hermans' orientation function (f_H), the orientation behavior of the guest molecules and the anisotropic absorption of the blends can be described as follows:[16−18,35]

$$f_H = \frac{3\langle \cos^2 \phi \rangle - 1}{2} = \frac{DR_A - 1}{DR_A + 2}\,\frac{DR_{A_0} + 2}{DR_{A_0} - 1} \tag{3a}$$

in which the dichroic ratio in absorption (DR_A) can easily be calculated from the polarized absorption spectra recorded parallel ($A_{//}$) and perpendicular ($A_\perp$) to the orientation direction ($DR_A = A_{//}/A_\perp$). DR_{A_0} represents the ultimate dichroic ratio in absorption, which is obtained for a perfectly aligned dye in the polymer matrix. Substitution of DR_A by the dichroic ratio in emission (DR_E) leads to an equivalent relationship that allows one to describe the development of anisotropic photoluminescence:[5a,22]

$$f_H = \frac{3\langle \cos^2 \phi \rangle - 1}{2} = \frac{DR_E - 1}{DR_E + 2}\,\frac{DR_{E_0} + 2}{DR_{E_0} - 1} \tag{3b}$$

in which DR_E can be calculated by integration of the emission detected parallel ($E_{//}$) and perpendicular ($E_\perp$) to the orientation direction ($DR_E = E_{//}/E_\perp$), and the ultimate dichroic ratio in emission DR_{E_0} expresses the limit for perfect alignment of the dye in the polymer matrix. Of course, S and $\langle \cos^2 \phi \rangle$ reflect the average orientation of the ensemble, to which aggregated and isolated guest molecules (if present in the respective form) will contribute.

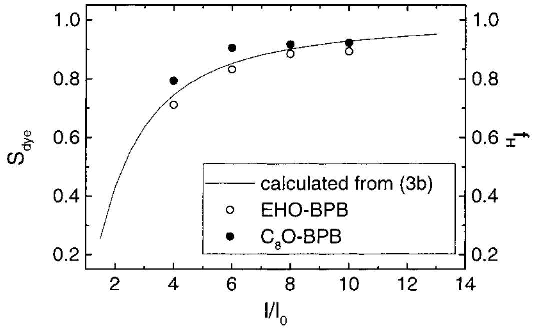

Figure 6. Order parameter of the PL dyes, S_{dye}, and the theoretical orientation of the PE matrix, f_H, as a function of draw ratio, l/l_0, for EHO−BPB/LLDPE and C_8O−BPB/LLDPE blend films. Compositions are as in Figure 5.

The evolution of the order parameter S_{dye} with l/l_0 is shown in Figure 6 and is compared to the theoretically expected orientation of the matrix material, f_H, which was calculated according to eqs 2 and 3b.

Figure 6 demonstrates that the order parameter S_{dye} is higher for all draw ratios in the case of the C_8O−BPB/LLDPE blend films when compared to those of the EHO−BPB/LLDPE blend films. As a consequence, we conclude that the deviating DR_E found for EHO−BPB-based PE blends is inherent to the molecular structure of this dye. The above-described behavior is consistent with the notion that the branched alkoxy substituent in fact hampers orientation of the dye along the crystalline PE domains, and therefore, EHO−BPB appears to preferentially reside in the amorphous domains of PE. The fact that Figure 6 shows a good match between theory and observation for C_8O−BPB indicates the presence of isolated guest molecules. Interestingly, the values for the order parameter of C_8O−BPB in the LLDPE blend films were found to be slightly higher than the orientation of the matrix itself (Figure 6), implying that the C_8O−BPB guest molecules actually appear to orient more efficiently than the matrix material. This finding is in agreement with the behavior of melt-processed $C_{12}O$−BPB/LLDPE blend films reported earlier.[22] Slightly accelerated orientation of C_8O−BPB compared to that of the affine deformation scheme might be explained by the fact that the model reflects an average orientation of the chain segments but fails to separate the components of the crystalline and amorphous phase. Certain dyes in LLDPE blends do not necessarily adopt an average orientation. It may very well be that the linear alkoxy substituent in C_8O−BPB preferentially crystallizes on the developing PE crystal faces during deformation, and as a result, the average orientation can become higher than predicted.[2]

To briefly explore the influence of the matrix polymer on the orientation behavior of EHO−BPB and C_8O−BPB, we also prepared blends with *i*-PP. The concentration of the PL dyes was similar to that in the LLDPE-based blends (0.2% w/w); films were produced by melt-processing and oriented at 135 °C to draw ratios of about 14. The blends were characterized by dichroic ratios of 15 (EHO−BPB/*i*-PP) and 29 (C_8O−BPB/*i*-PP), respectively, and, thus, exhibit only slightly lower optical anisotropy when compared to that of their respective LLDPE-based blends. Importantly, these experiments demonstrate the suitability of *i*-PP for the production of highly dichroic PL polarizers.

Conclusions

A new series of photoluminescent dichroic dyes has been synthesized via a simple and accessible route. All dyes show excellent luminescence properties and can be easily incorporated and oriented in polyolefin matrices. From the above-discussed results, it is evident that several parameters determine the orientation behavior of the guest molecules in oriented blends based on **1a**−**e** and the matrix. The melting temperature of the dye plays an important role if the initial, unoriented pristine blend is phase-separated.[15−18,20,22,31−33] In this case, molecular mobility of the dye is required in order to efficiently orient the dye during tensile deformation and achieve highly dichroic blend films. If, on the other hand, more homogeneous pristine blends can be produced (for example, by the use of melt-processing or guest-diffusion methods) from guest−host systems with tailored compatibility, excellent dichroic ratios can be obtained even in films of low draw ratio and independent of the melting temperature of the dye. Finally, small changes in the *molecular* structure of the PL dye play a substantial role in the orientation process as is exemplified by introducing branching in the alkoxy substituent. The latter was found to consistently lower the dichroic ratios. This finding may be attributed to the fact that such a dye is more prone to reside in truly amorphous regions of the PE matrix and as such has a lower tendency to adopt the orientation of the PE crystal faces. In view of future applications of these PL blends as photoluminescent polarizers, melt-processed blends based on **1c**,**d** and LLDPE embody an optimal combination of excellent luminescence characteristics, simple processing, and high polarization of the emitted light.

Acknowledgment. The authors thank Drs. Y. Dirix, T. Tervoort, and C. Bastiaansen, ETH, Zürich, for elaborate discussions.

CM990558+