Uniaxial Orientation of Columnar Discotic Liquid Crystals

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The present paper explores the possibility of orienting columnar discotic liquid-crystalline (LC) materials and causing a uniaxial "in-plane" orientation of the columns along the orientation direction. The discotic LCs employed were based on 2-hydroxy-3,6,7,10,11-penta-(1-butoxy)triphenylene, which was derivatized with 1-adamantenecarboxylic acid (Ada-PBT) and 10-undecenoic acid (ω-undecenoyl-PBT), respectively. As unequivocally shown by optical microscopy, uniaxial alignment of columnar Ada-PBT structures was readily achieved by spin-coating this material onto a poly(tetrafluoroethylene) orientation layer. Annealing of the films at temperatures at which the Ada-PBT was in its hexagonal plastic or hexagonal ordered mesophase slightly increased the degree of orientation. The optical absorption and photoluminescence spectra of oriented Ada-PBT films were significantly polarized, with absorption and emission dichroic ratios of 6.5 and 3, respectively. The optical anisotropy is unambiguously related to the uniaxial "in-plane" orientation of the cylindrical stacks of the LC molecules rather than an alignment of individual Ada-PBT molecules. Interestingly, this orientational behavior could not be mirrored when attempting to orient blend films of ultrahigh molecular weight polyethylene (UHMW-PE) and Ada-PBT or ω-undecenoyl-PBT by tensile deformation.

Introduction

In recent years discotic liquid crystals (LCs) have attracted considerable interest because their unique structural behavior promises exciting and unusual material characteristics.[1−3] In particular, the optic and electronic properties of this class of materials have been a focal point of substantial research efforts, triggered by the prospect to merge the unique self-organizing propensity of discotic LCs with the exceptional, readily tailored characteristics of functional organic molecules. Moreover, the orientation of columnar discotic phases can often be frozen into an ordered glassy state,[4] which is a most desirable feature from an application point of view. As a result, discotic LC systems are considered for use in devices such as organic light-emitting diodes (LEDs),[5,6] photoconducting layers for xerography,[7,8] and

chemical sensors.[9,10] Columnar discotic LCs in which the disklike molecules spontaneously form one-dimensional molecular stacks that further assemble in a two-dimensional lattice have been shown to exhibit high charge-carrier mobilities (of the order of 10^{-3}−10^{-2} cm²/ V·s) along the column direction.[8,11] As a result, these materials may be particularly useful for applications in which an efficient unidirectional charge transport is desired; examples include the semiconducting layer in organic field-effect transistors[12,13] and the charge-transport or emitting layer in organic LEDs.[14] Because of their particular photophysical characteristics, some columnar discotic LCs are also attractive for use in polymer-dispersed liquid crystals.[15]

Interestingly, however, despite the substantial activities related to the synthesis, processing, and application

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(1) Boden, N.; Movaghar, B. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, p 693.
(2) Chandrasekhar, S. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, p 749.
(3) Kopitzke J.; Wendorff, J. H. *Chem. Unserer Zeit* **2000**, *34*, 4.
(4) Glüsen, B.; Kettner, A.; Kopitzke, J. H.; Wendorff, J. H. *J. Non-Cryst. Solids* **1998**, *241*, 113.
(5) Nagae, I.; Fujimoto, T.; Hizuka, Y., JP 11097176 A2, 1999.
(6) Takimoto, A.; Komori, K.; Sugiura, H.; Nishiyama, K. JP 10282466, 1997.
(7) Haarer, D.; Adam, D.; Simmerer, J.; Closs, F.; Funhoff, D.; Haeussling, L.; Siemensmeyer, K.; Ringsdorf, H.; Schuhmacher, P. *Mol. Cryst. Liq. Cryst. Sci. Technol.* **1994**, *252−253A*, 155.

(8) Simmerer, J.; Glüsen, B.; Paulus, W.; Kettner, A.; Schuhmacher, P.; Adam, A.; Etzbach, K.-H.; Siemensmeyer, K.; Wendorff, J. H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* **1996**, *8*, 815.
(9) Wright, J.; Roisin, P.; Rigby, G. P.; Nolte, R.; Cook, M. J., Thorpe, S. C. *Sensors Actuators B* **1993**, *13−14*, 276.
(10) Cole, A.; McIlroy, R.; Thorpe, S. C.; Cook, M. J.; McMurdo, J.; Ray, A. K. *Sensors Actuators B* **1993**, *13−14*, 416.
(11) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häußlinger, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141.
(12) Dyreklev, P.; Gustafsson, G.; Inganäs, O.; Stubb, H. *Solid State Commun.* **1992**, *82*, 317.
(13) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. *Appl. Phys. Lett.* **2000**, *77*, 406.
(14) Bacher, A.; Bleyl, I.; Erdelen, C. H.; Haarer, D.; Paulus, W.; Schmidt, H. W. *Adv. Mater.* **1997**, *313*, 3148.
(15) Bayer, A.; Kopitzke, J.; Noll, F.; Seifert, A. M.; Wendorff, J. H. *Macromolecules* **2001**, *34*, 3600.
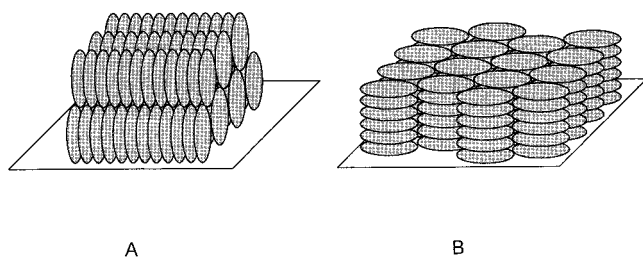
Figure 1. Schematic representation of possible arrangements of a hexagonal columnar discotic phase: (a) uniaxial in-plane orientation; (b) homeotropic orientation.
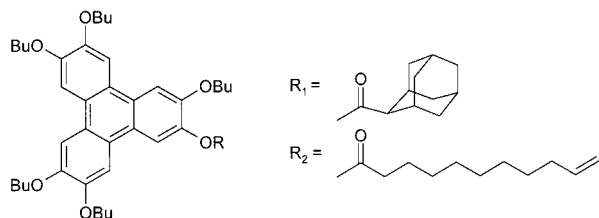

Figure 2. Chemical structure of the 2-hydroxy-3,6,7,10,11-penta(1-butoxy)triphenylene derivatives Ada-PBT (R₁) and ω-undecenoyl-PBT (R₂) investigated in the present study.

of columnar discotic LC materials, the understanding of how such materials can be macroscopically oriented is still rather limited. While a homeotropic orientation of columnar discotic LCs is rather easily induced (Figure 1b),[16] their uniaxial in-plane orientation has been proven difficult to achieve (Figure 1a).[17] In view of the rather favorable driving force for self-organization that is inherent to this class of materials,[18] this situation is somewhat surprising. One may speculate that the problems encountered when attempting to orient discotic LCs are related to the strong intermolecular interactions in these materials, which translate into a comparatively high viscosity and high mesophase temperatures.[1,2] Conventional methods for the uniaxial alignment of discotic LCs include the slow growth in a magnetic field[19] or drawing of freely suspended strands;[20] however, these methods are either rather complex or simply not suited for the fabrication of thin monodomains on planar substrates. In another recent example, a modest degree of uniaxial orientation of columns of a discotic LC has been achieved by mechanically stretching blend films of a ductile host polymer and a discotic guest.[21] Encouraged by these findings, we have embarked on developing and investigating methods for the uniaxial orientation of discotic columnar LC materials and here report our initial results regarding the in-plane alignment of two different 2-hydroxy-3,6,7,10,11-penta(1-butoxy)triphenylene (PBT) derivatives, Ada-PBT and ω-undecenoyl-PBT (Figure 2). These particular materials, created and used by one of us before, are readily available through the esterification of PBT, display interesting electronic properties, and are

employed here because of their convenient phase behavior (vide infra).[22,23] The orientation techniques used in the present study are (i) the spin-coating of the discotic LC on a poly(tetrafluoroethylene) (PTFE) orientation layer[24] and (ii) the tensile deformation of blend films of the discotic LC and ultrahigh molecular weight polyethylene (UHMW−PE), a method which has proven to be highly efficient for the preparation of uniaxially aligned guest−host systems.[25,26] The orientation of the discotics was carefully investigated by means of polarized optical absorption and photoluminescence (PL) emission spectroscopy, as well as by polarized microscopy. As discussed in detail below, the hexagonal plastic columnar (Col$_{hp}$) phase of Ada-PBT was found to uniaxially orient on friction transfer PTFE orientation layers. Glasses of Ada-PBT, produced by quenching the oriented Col$_{hp}$ phase, exhibited a pronounced birefringence and polarized absorption and emission spectra reveal dichroic ratios of more than 6. Interestingly, this orientational behavior could not be mirrored when attempting to orient blend films of UHMW-PE and Ada-PBT or ω-undecenoyl-PBT by tensile deformation.

Experimental Section

The two discotic LC materials used in the present work, Ada-PBT and ω-undecenoyl-PBT, were synthesized according to the procedures published elsewere[22,23] and are characterized by the following phase sequences: Ada-PBT, g 80 °C Col$_{hp}$ 168 °C Col$_{ho}$ 188 °C i; ω-undecenoyl-PBT, g −43 °C Col$_{ho}$ 86 °C i. The abbreviations denote the character of the observed states: g = glass, Col = columnar, hp = hexagonal plastic, ho = hexagonal ordered, and i = isotropic.

To prepare the PTFE orientation layers[24] on glass and Suprasil quartz slides, the respective substrate was heated to 330 °C on a Gel Instrumente AG hotstage in connection with a TC2 temperature controller, and a PTFE bar was manually rubbed at a speed of ca. 5 mm/min over the substrate surface. For the purpose of comparison, PTFE orientation layers were also prepared by using a DACA Instruments Tribotrak instrument at a speed of 1 mm/s and a temperature of 330 °C.

Solutions of Ada-PBT in CHCl₃ (1% w/w) were used for spin-coating thin fims on the PTFE orientation layers. The average thickness of these films, determined with a Detak³ surface profiler, was 40 nm. Unless otherwise noted, experiments were conducted on the pristine films thus produced. Selected samples were annealed under a stream of argon on the above-mentioned hotstage for the time and at the temperature indicated in the text.

Blend films of Ada-PBT and ω-undecenoyl-PBT in UHMW-PE (GUR 412, Hoechst, TICONA) were prepared via gel casting from a *p*-xylene solution as described before,[25] keeping the concentration of the discotic LC between 0.05 and 5% w/w (with respect to the UHMW-PE matrix). The films were stretched on a Wagner&Munz WME hotstage at a temperature of 120 °C to draw ratios of up to 50.

Optical absorption studies were carried out using a Perkin-Elmer Lambda 800 spectrometer equipped with a Glan-Thomson polarizer. Emission studies were performed in front-face mode on a Spex Fluorolog-3 (model no. FL3−12) fluorescence spectrometer equipped with a Glan-Thomson polarizer on the emission side. All spectra were recorded under isotropic excitation and were corrected for the spectral dispersion of the

(16) Christ, T.; Geffarth, F.; Kettner, A.; Lüssem, G.; Schäfer, O.; Stümpflen, V.; Tsukruk, V. V.; Wendorff, J. H. *Thin Solid Films* **1992**, *210/211*, 39.
(17) Vauchier, C.; Zann, A.; Le Barny, P.; Dubois, J. C.; Billard, J. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 103.
(18) Kevenhörster, B.; Kopitzke, J.; Seifert, A. M.; Tsukruk, V. V.; Wendorff, J. H. *Adv. Mater.* **1999**, *11*, 246.
(19) Goldfarb, D.; Luz, Z.; Zimmermann, H. Z. *J. Phys. (France)* **1981**, *70*, 39.
(20) Van Winkle, D. H.; Clark, N. A. *Phys. Rev. Lett.* **1982**, *48*, 1407.
(21) Chénard, Y.; Paiement, N.; Zhao, Y *Liq. Cryst.* **2000**, *27*, 459.

(22) Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *Liq. Cryst.* **1996**, *20*, 627.
(23) Kettner, A.; Ph.D. Thesis, Marburg, 1998.
(24) Wittmann, J. C.; Smith, P. *Nature* **1991**, *352*, 414.
(25) Weder, C.; Sarwa, C.; Bastiaansen, C.; Smith, P. *Adv. Mater.* **1997**, *9*, 1035.
(26) Eglin, M.; Montali, A.; Palmans, A. R. A.; Tervoort, T. A.; Smith, P.; Weder, C. *J. Mater. Chem.* **1999**, *9*, 2221.
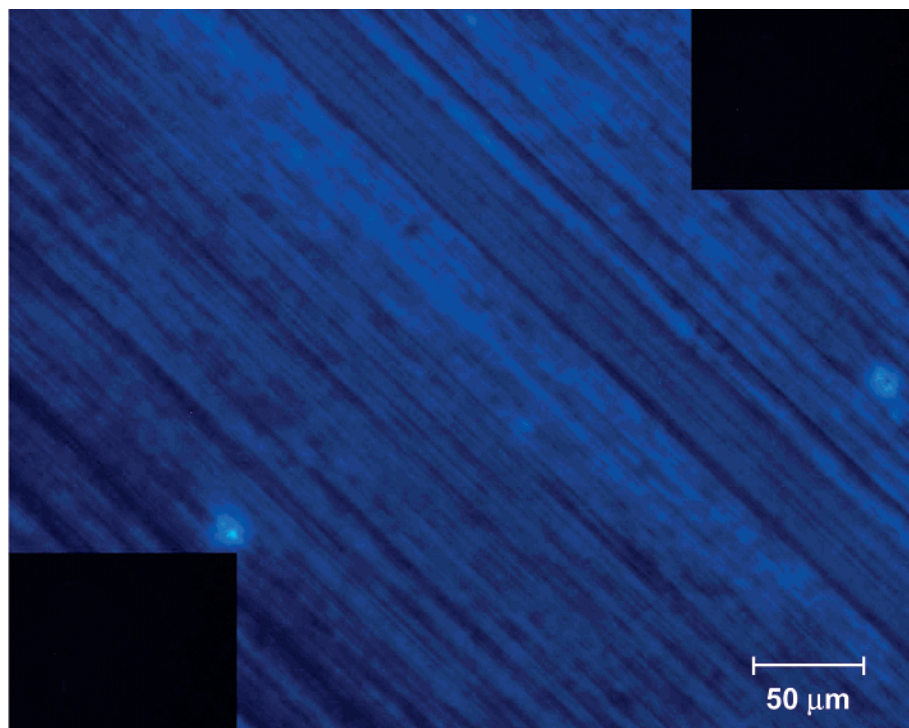
Figure 3. Optical micrograph of an Ada-PBT film, which was produced by spin-casting the LC onto a PTFE orientation layer. The picture was taken immediately after preparation of the film and before any thermal treatment. The sample was positioned between two crossed polarizers and arranged such that the director of the PTFE orientation layer formed a 45° angle with the directors of the polarizers. The top right inset shows the same sample arranged such that the director of the PTFE orientation layer was parallel to the director of the first polarizer. As a reference, the bottom left inset shows only the glass substrate with the PTFE orientation layer (but without the LC) arranged such that the director of the PTFE orientation layer formed a 45° angle with the directors of the polarizers.

Xe lamp, the instrument throughput, and the detector response. A reference detector accounted for fluctuations in lamp intensity. Polarization microscopy was performed on a Leica DMRX light microscope equipped with a Mettler Toledo FP82 HT hotstage.

Wide-angle and small-angle X-ray scattering experiments of the drawn UHMW-PE films have been performed on a Siemens D5000 goniometer and a Huber Laue Camera 802, respectively.

Results and Discussion

Wittman and Smith have demonstrated that a broad variety of materials exhibit highly oriented growth on aligned PTFE orientation layers, which are readily produced by friction transfer of the polymer onto smooth, rigid substrates.[24] Speculating that this process might allow the orientation of the discotic 2-hydroxy-3,6,7,10,11-penta(1-butoxy)triphenylene derivatives investigated here, we have elected to employ this methodology in our present study. Indeed, spin-coating of Ada-PBT/CHCl$_3$ solutions on PTFE orientation layers deposited on glass substrates resulted in Ada-PBT films of a thickness of 40 nm, which exhibit an appreciable degree of uniaxial orientation, as unequivocally demonstrated by means of polarized optical microscopy (Figure 3). This finding is somewhat surprising, given the rather delicate nature of the orientation method employed[24] and considering that the glass transition temperature of Ada-PBT (80 °C) is substantially higher than the processing temperature (≈20 °C). The result seems to suggest that the deposition of Ada-PBT from solution either involves an intermediate lyotropic phase upon evaporation of the solvent or, alternatively, occurs through epitaxial growth. Interestingly, the orientation of Ada-PBT was not equally high and/or homogeneous when comparing different pristine samples. As a matter of fact, some of the samples prepared appeared rather inhomogeneous when investigated by means of polarized optical microscopy, possibly because minor differences in the spin-coating process and/or the uniformity of the orientation layer exert a major influence on the deposition of the LC. Gratifyingly, in all cases, annealing the films at 100 °C (i.e., in the Col$_{hp}$ mesophase of the LC) or at 175 °C (in the Col$_{ho}$ mesophase) for a short time (5−15 min) and quenching the samples into the glassy state resulted in homogeneous samples that were characterized by a comparably high degree of uniaxial orientation, presumably facilitated by the pronounced self-organizing propensity of the LC triphenylenes. (Note that the same orientation and uniformity were found for films deposited on orientation layers produced by manual rubbing and, for the purpose of reference and comparison, under more controlled conditions on a dedicated rubbing machine; cf. Experimental Section for details). Temperature-dependent polarized microscopy further revealed that the orientation of the Ada-PBT films does not change until the isotropization temperature, T_i, at 188 °C is reached, at which point de-wetting takes place and droplets are formed. Interestingly, these droplets do not adopt any appreciable in-plane orientation upon cooling to the LC state, as is also evident from polarized optical micrographs. The fact that T_i of the thin Ada-PBT films is identical to the one of the bulk materials suggests that the phase behavior remains unchanged when processing the LC into thin films.
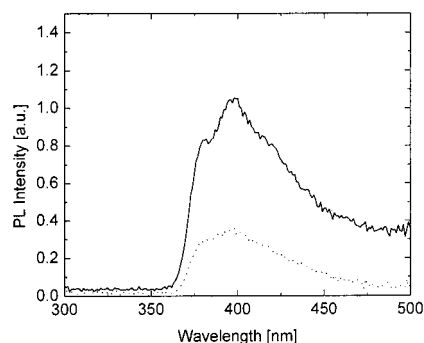
Figure 4. Polarized emission spectra of a film of Ada-PBT on a PTFE orientation layer, recorded after annealing the sample under an inert atmosphere at 100 °C for 15 min. The spectra were acquired under isotropic excitation and detection through a polarizer, which was oriented parallel (dotted line) and perpendicular (straight line), respectively, to the director of the orientation layer.

To investigate the degree of orientation in a more detailed manner, and with the objective to prove the fact that the optical anisotropy observed by polarized microscopy is indeed related to the uniaxial in-plane arrangement of columns of the discotic LCs, polarized absorption and PL emission spectra of the above-discussed Ada-PBT films were measured. Alkoxy-derivatized triphenylenes usually show an absorption band with a peak maximum between 260 and 280 nm and an emission band between 380 and 400 nm, but a shift in the absorption and emission peaks is observed if the LC order is subject to geometrical confinement.[15] The polarized emission spectra of pristine (not shown) and annealed samples of Ada-PBT (Figure 4) were recorded under isotropic exitation at 275 nm, and the emitted light was detected through a linear polarizer, the optical axis of which was oriented parallel (p) and perpendicular (s), respectively, to the director of the PTFE orientation layer. The data reveal that the emission of both pristine and annealed films is linearly polarized, featuring a higher intensity for the s-polarized component than for the p-polarized component. Since the main transition dipole moment of the triphenylene moiety is in the plane of the disk-shaped molecule—and therefore inevitably perpendicular to the director of the columns—this finding is consistent with the uniaxial in-plane orientation as shown in Figure 1a. The discotic molecules form columns, which deposit in an organized arrangement on the orientation layer, such that the column director coincides with the director of the PTFE layer. For a pristine Ada-PBT film, which was measured directly after spin-coating, an emission dichroic ratio, DR_E, (defined as the ratio of the intensity of the s-polarized and the p-polarized components of the emitted light) of about 2.5 was determined at the wavelength of the emission maximum, 400 nm. Upon annealing of the same sample for 15 min at 100 °C (i.e., in the Col_{hp} mesophase of the LC), DR_E was found to slightly increase to a value of ≈ 3 (Figure 4). Polarized optical absorption spectra (Figure 5) of an annealed (5 min at 100 °C) Ada-PBT film on a PTFE orientation layer (which for this experiment was deposited on a quartz substrate that, in contrast to the conventional microscopy slide, is transparent in the UV regime and allows for proper measurement of the PBT absorption) corroborate the structural picture painted by optical mi-
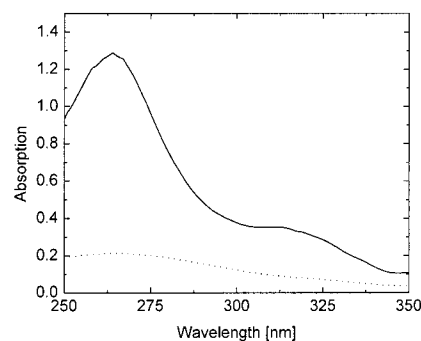

Figure 5. Polarized absorption spectra of a film of Ada-PBT on a PTFE orientation layer, recorded after annealing the sample under an inert atmosphere at 100 °C for 5 min. The spectra were acquired through a polarizer, which was oriented parallel (dotted line) and perpendicular (straight line), respectively, to the director of the orientation layer.

croscopy and polarized emission spectra: the data reveal a significantly polarized absorption, characterized by an absorption dichroic ratio, DR_A (defined as the ratio of the intensity of the s-polarized and the p-polarized components of the absorbed light) of about 6.5 at the wavelength of the absorption maximum, 264 nm. Polarized optical absorption spectroscopy has also been used in a series of further annealing experiments and shown that extending the time of the annealing process (up to 20 min) or annealing the Ada-PBT film in the Col_{ho} phase (175 °C) does not lead to an increase of DR_A. The notable difference between the dichroic ratios observed in emission and absorption is at this time not fully understood and may be explained by a number of reasons, including different directions of the involved electronic transitions and de-polarizing energy transfer processes. Importantly, although the observed optical anisotropy is not extraordinarily high, the present experiments, to the best of our knowledge, represent the first demonstration of polarized PL emission from a uniaxially oriented *columnar* LC material.

In view of Zhao's encouraging finding that columns of a discotic LC in mechanically stretched blend films may adopt some uniaxial orientation,[21] we have also explored the tensile deformation of blends of discotic triphenylene derivatives and UHMW-PE, which we selected because of its uncompared drawability. Blend films of Ada-PBT (1−5% w/w) and UHMW-PE were prepared through solution processing and gel casting as described before[25,26] and the films thus-prepared were mechanically stretched to draw ratios up to 50. The drawing process was conducted at a temperature of ≈ 120 °C, i.e., in the Col_{hp} phase of the triphenylene. The orientational behavior of the triphenylene guest molecules upon deformation was monitored by the PL emission spectra of the films. Unfortunately, in contrast to the observations reported by Zhao et al.,[21] no preferential orientation of the LC guest molecules was observed in the case of the presently investigated system, reflected by a DR_E of close to unity, independent of the draw ratio. The shape of the emission spectrum of the pristine Ada-PBT/UHMW-PE blend films was found to correspond to the characteristic, highly diagnostic spectrum of the bulk Ada-PBT,[15] indicating the phase separation of the two components. The spectral features did also not change upon tensile deformation, implicating that—in contrast to other, previously inves-
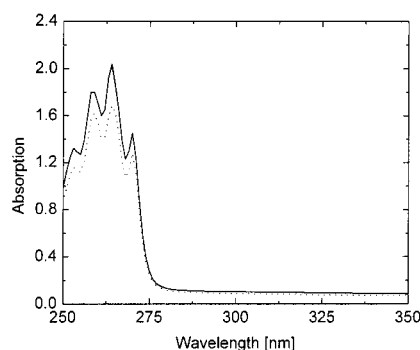
Figure 6. Absorption spectra of stretched blend of ω-undecenoyl-PBT/UHWM-PE (draw ratio 30, film thickness $\approx$1 μm, content of ω-undecenoyl-PBT 0.05% w/w), recorded through a polarizer aligned parallel (straight line) and perpendicular (dotted line), respectively, to the stretching direction of the blend film.

tigated systems[28]—no homogenization takes place upon deformation. Further, the Ada-PBT phase is also not subjected to a significant geometrical confinement during the stretching process, which has been demonstrated to result in a pronounced hypsochromic shift of the emission band.[15] Thus, these findings are consistent with the presence of an unoriented two-phase system at all draw ratios in which the Ada-PBT phase remains essentially unperturbed by the highly oriented matrix polymer. In view of this somewhat surprising result, we opted to conduct the tensile deformation process above the isotropization temperature of the LC guest. Since UHMW-PE can only be drawn in a limited temperature regime, we elected to employ ω-undecenoyl-PBT for these experiments. This discotic LC material features a similar phase behavior to Ada-PBT, but the transition temperatures are considerably lower and the isotropic melt is reached at 86 °C. Thus, blend films of ω-undecenoyl-PBT and UHMW-PE were prepared as described above and the films were mechanically stretched at $\approx$120 °C, i.e., at a temperature at which the triphenylene component forms an isotropic melt. Polarized PL spectroscopy of films comprising 5% w/w of the PBT and featuring draw ratios of between 10 and 50 revealed a modest polarization ($DR_E < 1.5$) of the emitted light. Remarkably, the intensity of the polarization component parallel to the drawing direction was found to be higher than that of the orthogonal component, very much in contrast to the uniaxial orientation of Ada-PBT columns on PTFE orientation layers discussed above. To further investigate the orientation behavior of the ω-undecenoyl-PBT/UHMW-PE blend films, we conducted polarized absorption measurements on the latter. To keep the optical density of the films within the measuring range of the instrument, we investigated ω-undecenoyl-PBT/UHMW-PE blend films with a substantially lower concentration of the PBT (0.05% w/w) than that used before. The polarized absorption data obtained for films of draw ratios between 10 and 30 have revealed DR_A values of the order of 1.25 (Figure 6). The spectra show a high degree of vibronic resolution, which is characteristic for isolated molecules in solution[15] and suggests

a molecular distribution of the triphenylene molecules in the UHMW-PE matrix.[28] Absorption spectra obtained for unstretched films, by contrast, show the typical absorption band of triphenylenes in the bulk LC phase. Hence, we suggest for the present polymer blend that the structure changes upon drawing (at least under the conditions employed here) from a phase-separated system to a structure in which the triphenylene appears to be molecularly dispersed in the UHMW-PE host. This finding is supported by wide- and small-angle X-ray scattering experiments on drawn UHMW-PE/PBT blend films (5% of PBT, draw ratio of 30). The diffraction patterns of these films exclusively revealed *reflections* of the PE matrix. Thus, these observations lead to the conclusion that the orientation behavior in the present PBT/UHMW-PE blend films is not related to the alignment of columns of the discotic PBT guest. Instead, the modest optical anisotropy observed for the present films seems to be associated with the individual orientation of the PBT guest molecules along the stretching direction of the polymer matrix in-line with their individual molecular shape. This situation is conceivable when considering the extended nature of the ω-undecenoyl moiety, which not only seems to adequately compatibilize the PBT derivative with the matrix polymer but also appears to be responsible for the "uniaxial" orientation of the guest molecules within the oriented polyethylene matrix. Assuming that the ω-undecenoyl tail adopts the orientation of the matrix, the aromatic cores of the PBT moieties are likely to be arranged such that the (imaginary) core axis along the direction of the aliphatic tail coincides with the stretching direction of the film. The second imaginary axis of the PBT core (orthogonal to the direction of the aliphatic substituent) does not adopt any preferential orientation, and the cores are statistically arranged around the stretching direction of the film. As a result, light that is polarized parallel to the stretching direction of the film will be absorbed (and possibly re-emitted) by all PBT molecules in an equally efficient manner, while light that is polarized perpendicular to the stretching direction of the film faces a statistical average of the PBT's transition dipole moments due to the "rotation" of the PBT disks about the film axis. Thus, in contrast to Zhao's finding that columns of a discotic LC in mechanically stretched blend films may adopt some uniaxial orientation,[21] no columnar orientation was found for the presently investigated UHMW-PE/PBT blend films. It can be surmised that in the case of the UHMW-PE/Ada-PBT blend films the viscosity Ada-PBT phase is simply too high to allow the LC guest to adopt the orientation of the highly oriented matrix. By contrast, in the case of the of the ω-undecenoyl-PBT/UHMW-PE blend films, the PBT guest molecules seem to molecularly blend with the matrix polymer—at least when deforming the blend at a temperature above T_i of the LC guest and in the case of a low concentration of the latter—preventing the formation of columnar structures. Consequently, the resulting orientation of the PBT guest molecules occurs in-line with their individual molecular shape as opposed to a columnar ensemble.

Conclusions

In summary, we have shown in the example of Ada-PBT that a uniaxial "in-plane" orientation of a columnar

(27) Furumi, S.; Janietz, D.; Kidowaki, M.; Nakagawa, M.; Morino, S.; Stumpe, J.; Ichimura, K. *Chem Mater.* **2001**, *13*, 1434.

(28) Trabesinger, W.; Renn, A.; Hecht, B.; Wild, U. P.; Montali, A.; Smith, P.; Weder, C. *J. Phys. Chem. B* **2000**, *104*, 5221−5224.

discotic LC material can readily be accomplished by spin-casting the LC material onto a PTFE orientation layer. While for the presently investigated triphenylene derivative an appreciable uniaxial orientation of columnar ensembles was observed for pristine, spin-cast films, the highest degree of uniaxial orientation was achieved by annealing the samples above the T_g of the discotic LC for a short period of time. The optical absorption and photoluminescence spectra of oriented Ada-PBT films were significantly polarized, with absorption and emission dichroic ratios of 6.5 and 3, respectively. After Ichimura et al. recently demonstrated for the first time the polarized fluorescence from a *nematic* discotic LC,[27] our present experiments, to the best of our knowledge, represent the first demonstration of polarized PL emission from a uniaxially oriented *columnar* LC material. In view of the ease of the fabrication method employed, these findings are most encouraging, although the modest optical anisotropy observed leaves ample room for further improvement. We further should point out that the question if the orientation behavior of Ada-PBT on PTFE is unique for this particular compound or is a more general behavior of triphenylenes remains to be answered.

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