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Highly Oriented Langmuir−Blodgett Films of Poly(*p*-phenylenevinylene) Using a Long Chain Sulfonic Counterion

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ABSTRACT: Langmuir−Blodgett (LB) films of a poly(*p*-phenylenevinylene) (PPV) precursor were prepared using an amphiphilic precursor, poly(xylylidenetetrahydrothiophenium chloride) (PTHT), where the counterion chloride was replaced by a long chain dodecylbenzenesulfonate (DBS) ion. Stable PTHT−DBS monolayers were transferred onto quartz substrates in the form of LB films. Using DBS allowed PPV films to be converted under atmospheric pressure at temperatures as low as 80 °C, with conjugation length and optical properties better than for standard films converted at temperatures above 200 °C under controlled atmospheres. These LB−PPV films are highly anisotropic as demonstrated by linear dichroism experiments using linearly polarized optical absorption and emission. The dichroic ratio between the intensity of the emitted light parallel and perpendicular to the dipping direction was ca. 17, which is much higher than the dichroic ratio of 3.6 found in the polarized absorption experiment. This difference indicates an efficient excitation transfer between the low conjugated segments (disordered) and the highly conjugated (ordered) ones after excitation.

Introduction

After considerable progress in methods for synthesis and processability, conjugated polymers are now employed as active components of organic electroluminescent devices.[1] In specific applications, such as polarized light-emitting diodes (LEDs), where a higher degree of control is required, structural disorder remains a severe limitation.[2] Highly anisotropic optical properties have been obtained in stretched layers,[3] as in LEDs with polarized emission with an intensity ratio up to 3.1 between light emitted parallel and perpendicular to the stretching direction.[4] Such films can also be strongly birefringent with different refractive indexes taken at the preferential directions.[5] Control over the molecular and supramolecular organization may therefore have great influence on the optical and electrical properties of a device, which may be achieved with the Langmuir−Blodgett (LB) technique to produce ultrathin films with controllable thickness, molecular ordering, and low number of defects.[2] LB films from luminescent poly(*p*-phenylenevinylene) (PPV) and derivatives have been produced for which soluble precursor polyelectrolytes were generally used.[6,7] Such a fabrication process is by no means straightforward because soluble precursors normally do not possess well-defined hydrophobic and hydrophilic groups that make a material ideally suitable for the LB technique.

Here we have adopted an alternative approach consisting of substituting the chloride counterion of a water-soluble precursor, poly(xylylidenetetrahydrothiophenium chloride) (PTHT), by a long chain sulfonic counterion (DBS) using a sodium salt of dodecylbenzenesulfonic acid. The advantage of this precursor polymer lies in the possibility of converting spin-cast PPV films with a high conjugation length at 115 °C within only 3 min.[8] Monolayers made from solutions of PTHT with DBS were spread onto aqueous subphases and then transferred onto suitable substrates in the form of LB films. It will be shown that these LB films converted at lower temperatures (∼80 °C) display anisotropic optical absorption and photoluminescence reflecting the high degree of order and polarizability of the emitted light when compared to conventional cast films.

Experimental Section

The precursor PTHT was synthesized using the same procedure described in the literature.[7,9] Langmuir and LB films were obtained using a KSV LB-5000 system in a class 10 000 clean room. The spreading solution was prepared by mixing PTHT and DBS at a 1:20 mol/mol in 1,2-dichloromethane−ethanol (1:1 v/v) composition. Langmuir monolayers were spread onto ultrapure water subphases by dispensing 800 μL of the spreading solution. Having allowed ca. 60 min for evaporation of the solvent and monolayer stability, the monolayer was compressed at a 10 mm/min barrier speed and characterized by performing surface pressure−area isotherms. These monolayers could be transferred using the vertical dipping Langmuir−Blodgett method. LB films of PTHT−DBS (LB−PTHT) with 20 and 40 monolayers were deposited onto quartz substrates at a fixed pressure of 25 mN m^{-1}, with a barrier speed of 5 mm min^{-1} and a dipping vertical speed of 2−4 mm min^{-1}. LB−PTHT films were converted into PPV (LB−PPV) for 2 h at various temperatures: at 80 and 90 °C under atmospheric pressure and at 110, 200, and 230 °C under vacuum. For the sake of comparison, cast PTHT films deposited on quartz were thermally converted under vacuum for 2 h at 230 °C.

Converted PPV films were optically characterized using a spectrophotometer Cary 17 equipped with a helium cryostat in which the temperature could be varied from 4 to 300 K. Photoluminescence (PL) measurements were performed upon exciting the sample with the 458 nm line of an Ar$^+$ laser (average excitation density of about 25 mW cm^{-2}) within a closed-cycle helium cryostat where the temperature was varied from 15 to 300 K. The PL signal was detected with a photomultiplier mounted on a 0.5 m monochromator (for detection in the lock-in mode) in the 480−700 nm range. Anisotropy in the LB and cast films was probed by employing polarized UV−vis absorption (Hitachi U-2001), polarized fluorescence (Digital ISS K2 time-resolved fluorimeter), and PL measurements.

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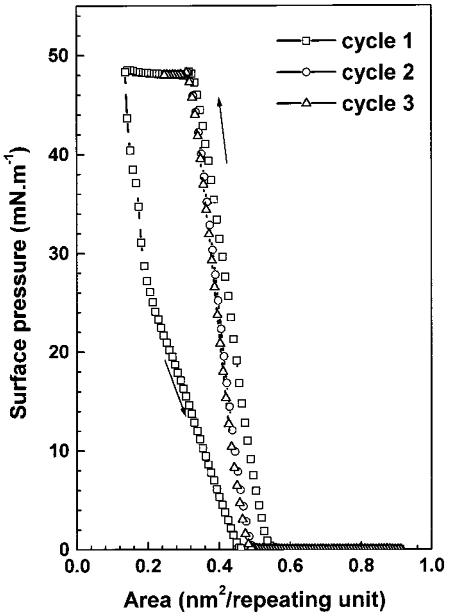

Figure 1. Surface pressure vs area per molecule isotherm of a Langmuir monolayer from a 1:20 mol/mol PTHT−DBS mixture spread on pure water. Three compression−decompression cycles are shown. The curves for decompression in the hysteresis cycles coincide provided that compression was effected to the same area per repeat unit in each case.

Results and Discussion

A systematic investigation of monolayer properties showed that the PTHT−DBS mixture as spreading solution led to stable successive compression−decompression cycles of surface pressure vs mean molecular area (Π*A*) isotherms. Monolayer stability at the air/water interface was checked by maintaining a fixed surface pressure of ca. 25 mN m^{-1} for 1 h. The area per repeat unit decreased by approximately 5−10% during the stabilization time prior to the monolayer compression. For obtaining stable films, the monolayer spread was left to rest for at least 1 h, before compression started. Figure 1 displays the isotherm of a PTHT−DBS mixture spread on pure water, featuring a high collapse pressure (ca. 48 mN m^{-1}) and a well-defined condensed phase. Collapse is denoted by a sharp decrease in area per repeat unit at the collapse pressure. Interestingly, even after collapse in the first compression−decompression cycle, subsequent compression−decompression cycles display isotherms that are very similar to the first cycle, as shown in Figure 1. This indicates that the formation of polymer stacks during collapse may be reverted upon decompression, which is not the case of traditional amphiphilic compounds. The monolayer transfer onto solid substrates was possible by a Z-type-like transfer process at a fixed pressure of around 25 mN m^{-1}, with transfer ratios between 0.8 and 1.0 for the upstrokes and less than 0.3 in the downstrokes. Monolayer transfer was always carried out with monolayers that had not reached collapse, and LB of films of tens of layers could be deposited.

Thermal conversion of PTHT−DBS into PPV was followed by absorption spectroscopy and the film properties were probed by photoluminescence measurements (PL). Figure 2a shows the absorption spectra for LB films converted for 2 h at 80 and 90 °C under atmospheric pressure and at 230 °C under vacuum. Infrared measurements[8] revealed that PPV films can be obtained without carbonyl groups using such low-temperature conversion procedure. The broad band extending from 300 to ca. 520 nm coincides with the $\pi-\pi^*$ absorption transitions between delocalized states coupled with the vibronic states of PPV. Essentially, the three absorption spectra in Figure 2a exhibit similar characteristics in this spectral region and the same band-edge position (510 nm), indicating a similar degree of final conjugation length after the conversion procedure for both low- and high-temperature conversions. Such characteristics can be found in high-quality PPV films prepared under standard high-temperature procedures.[10,11] Since the thickness of the LB films did not influence the conversion process or the optical properties, we shall henceforth present results only for the 40-layer LB sample.

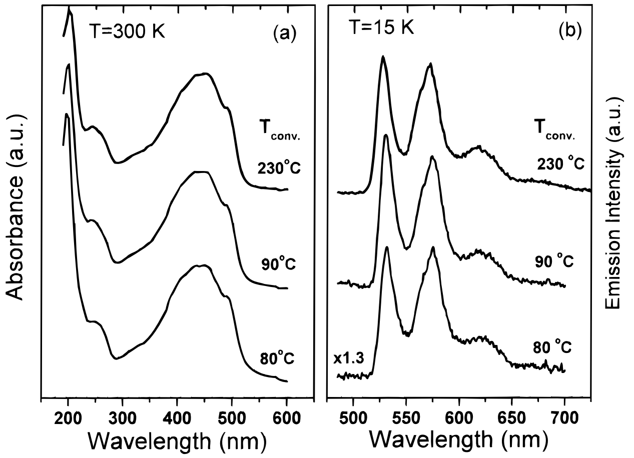

Figure 2. Absorption (a) and photoluminescence (b) spectra for 40-layer LB films converted for 2 h at 80 and 90 °C under atmospheric conditions and at 230 °C under vacuum.

The quality of the PPV films and the efficacy of the conversion procedure at low temperatures are corroborated by photoluminescence measurements. Figure 2b compares the PL spectra of the corresponding samples displayed in Figure 2a, in which the spectra display the same overall behavior, including peak intensity and position of the zero-phonon line at 530 nm. The similar intensity of the well-resolved vibronic structures and the absence of a shift in the spectrum of the sample converted at 80 and 90 °C indicate that no significant amount of defects was generated during the low-temperature conversion of the LB films.

These results allow one to conclude that the degree of conjugation length is practically unaltered by changing the conversion temperature, thus demonstrating that the amount of DBS used is sufficient to achieve the amphiphilic character necessary to produce reproducible LB films with a high effective conjugation length. This occurs because the sulfonium group in DBS is a better leaving molecule for thermal conversion at low conversion temperatures as compared with the chloride counterion. However, the conjugation length does depend on the amount of DBS employed, as demonstrated in ref 8 for spin-cast PPV films. For the LB films produced in this work, a fixed amount of DBS was used to prepare the PTHT−DBS spreading solution, thus leading to identical features in the absorption and PL spectra. Moreover, such good optical properties are obtained even for conversion temperatures of 80 °C, whereas a temperature of 100 °C is necessary for converting good-quality spin-coating films.[8]

The absorption and photoluminescence spectra taken at various temperatures for an LB PTHT−DBS film

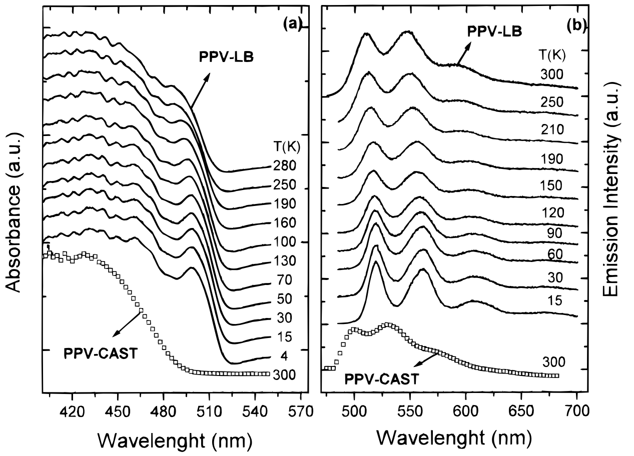

Figure 3. Absorption and photoluminescence spectra at different temperatures for a PPV-cast and 40-layer LB−PPV films converted under vacuum at 230 °C for 2 h.

converted at 230 °C for 2 h under vacuum are shown in Figure 3. Also shown for comparison are the spectra at 300 K of a cast PPV film using the PTHT precursor without DBS and converted under identical conditions. Figure 3a shows that a better definition of the vibronic structures in the absorption edge is achieved at lower temperatures, even though the line shape was almost the same for all temperatures. The spectra of LB films are also red-shifted compared to that of a cast film, which indicates a higher conjugation degree of the polymer chains. The smaller effective conjugation length of spin-cast PPV is probably caused by structural defects, such as chain bends and twists which introduce disorder in the final polymer structure.[12] Small conjugation lengths also favor the coupling of the electronic states to the vibrational modes of the polymer chain which broadens the energy levels and promotes redistribution in intensity of the spectral weight of lowest energy vibronic features.[13] This effect is also observed in the photoluminescence spectra (Figure 3b), where a PPV cast film displays a structureless spectrum with line width of 250 meV at 300 K, while the LB−PPV film displays well-resolved vibronic structures with line widths of 65 meV at 15 K and 124 meV at 300 K.

The temperature dependence of the PL intensity can provide information about nonradiative processes in films converted at different conversion temperatures (Figure 4). For instance, the integrated photoluminescence intensity of a LB−PPV film converted at 230 °C decreased by 68% when the temperature was raised from 30 to 260 K. This quenching effect was reduced by 20% for the same temperature range for an LB−PPV film converted at 110 °C, which may be explained by the absence of extrinsic defects such as carbonyl groups,[8] as discussed before. Furthermore, the above results obtained for the PPV film converted at low temperature are comparable to spin-cast films obtained from a PPV oligomer[14] that had its radiative efficiency decreased by 68% when the temperature was raised from 4 to 300 K. This quenching effect was reduced when the PPV oligomer was diluted in blends formed with poly(methyl methacrylate) (PMMA). In the latter case, the emission efficiency decreased by only 20% upon increasing the temperature from 4 to 300 K,[14] since intrinsic intermolecular processes of nonradiative recombination are ruled out in the blends. Owing to the preferential orientation of the polymer chains in LB−PPV films with DBS, the external quantum efficiency is expected to be higher when compared to an isotropic polymer.[1,21] Further experiments with spin-cast films are being conducted to confirm such expectation.

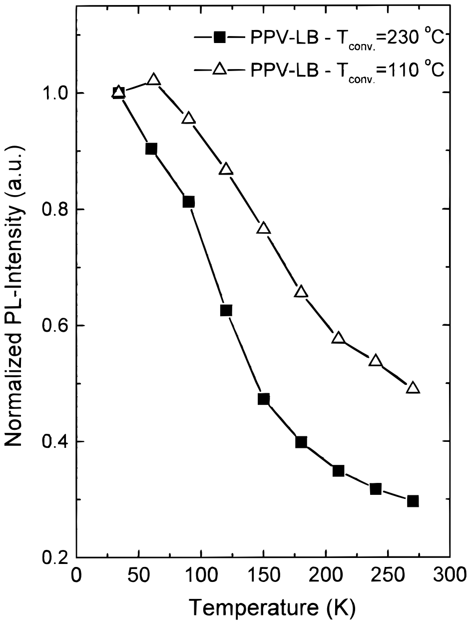

Figure 4. Dependence of the integrated photoluminescence intensity on the temperature of the measurement for LB−PPV films converted at 110 °C under atmospheric pressure and 230 °C under vacuum.

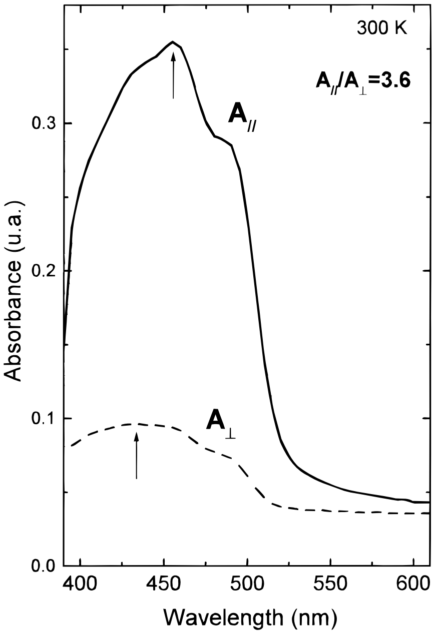

Figure 5. Polarized absorption measurement at 300 K of a 40-layer LB−PPV film converted at 90 °C for two polarizations of the incident light: parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the dipping direction.

LB−PPV films prepared with DBS are highly anisotropic as demonstrated by linear dichroism experiments using linearly polarized optical absorption and emission at 300 K. The absorption spectra of a 40-layer LB film converted at 90 °C are displayed in Figure 5 in the energy range near the band edge for two polarizations of the incident light: parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the dipping direction. The dichroic ratio $A_{\perp}/A_{\parallel}$ between the two values of absorbance at the maximum of the $\pi-\pi^*$ band is 3.6. Since the $\pi-\pi^*$ absorption of PPV

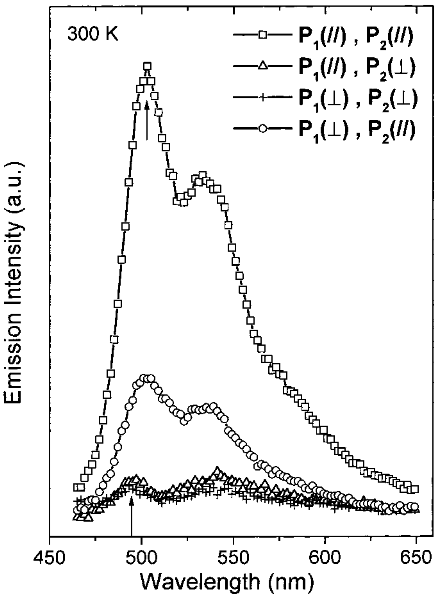

Figure 6. Polarized photoluminescence at 300 K of the same 40-layer LB–PPV film shown in Figure 5, where the polarization directions of the exciting light, P_1 ($\lambda_{ex} = 400$ nm), and of the emitting light, P_2, were either parallel (||) or perpendicular (⊥) to the dipping direction.

is polarized parallel to the molecular backbone, the corresponding in-plane order parameter, $S = (A_{\|} - A_{\perp})/(A_{\|} + A_{\perp})$,[15] is about 0.6. This order parameter compares well with that typically achieved for oriented LB films[2] and liquid crystals,[16,17] and its value is preserved after conversion regardless of the conversion temperature employed (90 up to 230 °C), which demonstrates the structural stability of the LB–PPV films prepared with DBS. It seems that the attachment of the DBS molecule to the soluble PTHT precursor via Cl^- substitution may lead to well-aligned chains in the Langmuir film, with the subsequent LB deposition producing an impressive in-plane orientation along the dipping direction. Both absorption spectra in Figure 5 have maxima at 455 and 432 nm (arrows) for the parallel and perpendicular orientations, respectively, which have been attributed to the conjugation length distribution of polymer chains in LB films due to disorder.[1] One expects, therefore, aligned chains to have a higher conjugation length, whereas randomly oriented chains should have shorter conjugation lengths.

Polarized photoluminescence at 300 K of the same 40-layer LB film is shown in Figure 6 where the directions of the polarization of the exciting light, P_1 ($\lambda_{ex} = 400$ nm), and emitting light, P_2, were varied. The configuration (P_1(||), P_2(||)), in which both directions are parallel to the dipping direction, has the highest PL intensity, while the cross-polarized (P_1(||), P_2(⊥)) and the perpendicular (P_1(⊥), P_2(⊥)) configurations present very low and almost equal intensities. The intensity ratio between the parallel and these configurations measured at the zero-phonon line (509 nm) is ca. 17, which is much higher than the dichroic ratio found in the polarized absorption experiment. This value is higher than for liquid crystals, which have shown large polarization anisotropy of 1 order of magnitude.[16,17] The high intensity ratio observed in the present work might indicate a strong charge transfer via energy transfer and/or carrier diffusion between low conjugated segments (disordered) and highly conjugated (ordered) ones after excitation.[3,18] This assumption is corroborated by the other polarization experiment shown in Figure 6, when the exciting light was aligned perpendicular (P_1(⊥)) and the emitting light was parallel (P_2(||)) to the dipping direction. Surprisingly, one observes a luminescence intensity only 3.4 times lower than that in the parallel (P_1(||), P_2(||)) configuration. This means that even when shorter conjugated chains (oriented randomly) are excited, the carriers are efficiently transferred to long conjugated (oriented) chains prior to their radiative decay and consequent emission.

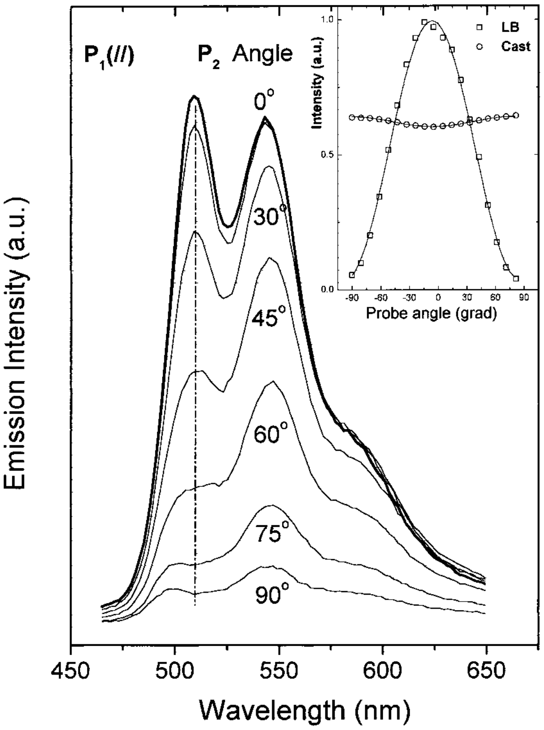

Figure 7. Polarized photoluminescence measurements at room temperature for a 40-layer LB–PPV film as a function of the angle θ between the direction of the analyzer polarization and the dipping direction. The inset compares the polarization dependence of the emission intensity for the LB film and cast PPV films. The excitation was polarized parallel to the dipping direction.

Figure 6 also shows a spectral blue shift of the zero phonon line (arrows) and an increase in the relative intensity of the vibronic structures when the polarization of the emitting light changes from parallel to perpendicular. This is consistent with an increasing disorder in the residual nonoriented PPV chains perpendicular to the dipping direction. Further details on the vibronic progression have been obtained in Figure 7, where the emission spectra at room temperature are shown for another 40-layer LB film as a function of the angle θ between the direction of the analyzer polarization and the dipping direction. Excitation was polarized parallel to the dipping direction in this experiment. In contrast to the LB film in Figure 6, this sample presents more pronounced vibronic structures. The anisotropy given by the ratio between the parallel (0°) and perpendicular (90°) emission intensity measured at the zero-phonon line (510 nm) was again 17. Also evident is a monotonic increase of the vibronic structures as the perpendicular component of the emission increases, thus demonstrating the existence of an angular distribution of polymer chain segments in the sample. As the chains are aligned, this distribution reflects mainly the in-plane angular dependence of the segment lengths given by disorder. The inset compares the polarization dependence of the emission intensity for the LB film and cast PPV films. As expected, the measured angular distribution for an LB−PPV film differs from that in an isotropic film as the latter shows almost no dependence with polarization. The relative amplitudes of the vibronic structures are directly related to the coupling between the electronic transitions and vibrational modes, in which its magnitude can be characterized by the Huang−Rhys factor.[13] Experimental studies[13,19,20] reveal that the Huang−Rhys factor is correlated with disorder; that is, the more localized the electronic states are, the more pronounced the vibronic progression is. Since disorder causes the conjugation length of PPV to decrease, one expects the Huang−Rhys factor to increase for chain orientations other than that of the dipping direction.

Conclusions

The results presented here have several implications for the analysis of light-emitting diodes with a conjugated polymer as the emitting layer. In the case of the preferential orientation of the polymer chains, the external quantum efficiency is expected to be higher when compared to that of an isotropic polymer.[1,21] For conductivity, in particular, Gagnon et al.[22] showed that doped, stretched-oriented PPV has a conductivity 10^3 times larger in the direction parallel to the chains than perpendicular to them. The addition of DBS into PTHT to facilitate the Langmuir−Blodgett processability has other important consequences, as we have recently found that the substitution of chloride anions by DBS makes it possible to convert the system into PPV at lower temperatures and much faster than with conventional methods. Indeed, spin-coated films from PTHT−DBS could be converted into PPV within an astonishingly short period of 3 min,[8] with the advantage of improved optical properties. Here we showed that LB films from PTHT−DBS may also be converted at relatively low temperatures, with their luminescence behaving in much the same way as the PPV film converted at 230 °C. The order induced by the LB deposition was reflected in a high conjugation length, with the vibronic structure being clearly identified in both absorption and photoluminescence spectra, which was not the case for a PPV cast film. In addition, the LB films were highly anisotropic, since the absorption and PL were more intense when the polarization direction was parallel to the dipping direction. One may envisage that new supramolecular structures, suitable for polarized LEDs applications, may be achieved with the layer-by-layer deposition and the chain orientation allowed by the LB technique together with the low-temperature conversion process allowed by the presence of DBS. Furthermore, such control may help in understanding basic phenomena, such as energy and charge transfer in polymer materials.

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References and Notes

(1) Kalinowski, J. *J. Phys. D: Appl. Phys.* **1999**, *32*, R179−R250.
(2) Cimrová, V.; Remmers, M.; Neher, D.; Wegner, G. *Adv. Mater.* **1996**, *8*, 146−149.
(3) Montali, A.; Bastiaansen, C.; Smith, P.; Weder, C. *Nature* **1998**, *392*, 261−264.
(4) Dyreklev, P.; Berggren, M.; Inganäs, O.; Andersson, M. R.; Wennerström, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43.
(5) Wan, W. M. V.; Greenham, N. C.; Friend, R. H. *Synth. Met.* **1999**, *102*, 1055−1056.
(6) Kim, Y. K.; Kim, K. S.; Kang, W. H.; Yang, S. S.; Sohn, B. C. *Thin Solid Films* **1998**, *312*, 291−294.
(7) Nishikata, Y.; Kakimoto, M.-A.; Imai, Y. *Thin Solid Films* **1989**, *179*, 191−197.
(8) Marletta, A.; Gonçalves, D.; Oliveira, O. N., Jr.; Faria, R. M.; Guimarães, F. E. G. *Adv. Mater.* **2000**, *12*, 69−74.
(9) Halliday, D. A.; Burn, P. L.; Friend, R. H.; Holmes, A. B. *J. Chem. Soc., Chem. Commun.* **1992**, 1685−1687.
(10) Halliday, D. A.; Burn, P. L.; Friend, R. H.; Bradley, D. D. C.; Holmes, A. B.; Kraft, A. *Synth. Met.* **1993**, *954*, 55−57.
(11) Zhang, C.; Braun, D.; Heeger, A. J. *J. Appl. Phys.* **1993**, *73*, 5177−5180.
(12) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, 376−378.
(13) Heeger, A. J. In *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundström, I., Ranby, B., Eds.; Oxford University Press: Oxford, 1993; p 27.
(14) Heller, C. M.; Campbell, I. H.; Laurich, B. K.; Smith, D. L.; Burn, D. D. C.; Feraris, J. P.; Müller, K. *Phys. Rev. B* **1996**, *54*, 5516−5522.
(15) Schwiegk, S.; Vahlenkamp, T.; Xu, Y.; Wegner, G. *Macromolecules* **1992**, *25*, 2513−2525.
(16) Bradley, D. D. D.; Grell, M.; Grice, A.; Tajbakhsh, A. R.; O'Brien, D. F.; Bleyer, A. *Opt. Mater.* **1998**, *9*, 1−11.
(17) Sariciftci, N. S.; Lemmer, U.; Vacar, D.; Heeger, A. J.; Janssen, R. A. J. *Adv. Mater.* **1996**, *8*, 651−654.
(18) Kaito, A.; Tanigaki, N.; Hajiheidari, D.; Yatabe, T.; Tanabe, Y. *J. Phys. Chem. B* **1999**, *103*, 8467−8473.
(19) Pichler, K.; Halliday, D. A.; Bradley, D. D. C.; Burn, P. L.; Friend, R. H.; Holmes, A. B. *J. Phys.: Condens. Matter* **1993**, *5*, 7155−7172.
(20) Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652−8666.
(21) McBranch, D.; Campbell, I. H.; Smith, D. L. *Appl. Phys. Lett.* **1995**, *66*, 1175−1177.
(22) Gagnon, D. R.; Karasz, F. E.; Thomas, E. L.; Lenz, R. W. *Synth. Met.* **1987**, *20*, 85−95.

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