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Enhanced Optical Properties of Layer-by-Layer Films of Poly(*p*-phenylenevinylene) Alternated with a Long Chain Counterion and Converted at Low Temperatures

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ABSTRACT: Layer-by-layer (LBL) thin films of a poly(*p*-phenylenevinylene) (PPV) precursor have been processed using the long chain dodecylbenzenesulfonate anion (DBS). We adopted the alternative approach with controlled substitution of the chloride counterion of the water-soluble PPV precursor by DBS. The internal layer structure of these films is likely to be different from conventional LBL films, since DBS is incorporated into the PPV precursor chain. In addition to the fast adsorption of the sulfonic salt, introducing DBS allows the films to be converted at 110 °C within 12 min with a high conjugation length. By varying the amount of DBS in the solution, the conjugation length of the PPV segments can be controlled. The luminescence and absorption spectra show intense vibronic structures that are better resolved than for cast and Langmuir−Blodgett films of PPV. LBL films converted at lower temperatures display higher quantum efficiency, owing to the absence of carbonyl groups arising from high-temperature conversion procedures.

Introduction

The electrostatic layer-by-layer (LBL) (or self-assembly) method has been widely used to assemble ultrathin polymer multilayer films controlled at the molecular level,[1−3] with the alternate adsorption of anionic and cationic layers on a solid substrate. It has been used to fabricate polymeric electroluminescent and photovoltaic devices,[4,5] in which poly(*p*-phenylenevinylene) (PPV) acts as the electronic active layer. The recent discovery of extremely rapid (3 min) thermal conversion for PPV at low temperatures (<100 °C),[6,7] under ambient conditions, has opened up new possibilities to get molecularly engineered superstructures with improved PPV properties. This has been accomplished by substituting the chloride counterions of a water-soluble PPV precursor, the poly(xylyliden tetrahydrothiophenium chloride) (PTHT), by a long chain dodecylbenzenesulfonate ion (DBS). Incorporation of DBS in the polymeric chain was originally conceived to facilitate deposition of PPV precursors as Langmuir−Blodgett (LB) multilayers.[7,8] These PPV-LB films feature additional characteristics such as strongly ordered PPV chains, which resulted in polarization-dependent optical absorption and high definition of luminescence peaks.[7] The exchange of Cl for DBS counterions is carried out directly in the precursor solution, owing to the different basicity degree of such ions.[6] Sulfonium groups, such as tetrahydrothiophenium, are more stable when counterbalanced by counterions, which are conjugated bases of strong acids. Since halides form stronger acids than DBS, precursors with leaving groups counterbalanced by halides are thermally more stable. Such properties explain the different thermal behavior in the low-temperature conversion kinetics for the PPV precursor containing halides and DBS.

In earlier reports,[9] we employed DBS to produce LBL-PPV multilayers, by alternating adsorption of a PPV polyelectrolyte precursor and DBS in aqueous solutions. Here we extend these studies with a fuller characterization of morphological and optical properties of these LBL films, in addition to investigating the adsorption characteristics of the films and the kinetics of thermal conversion. The internal layer structure of PTHT-DBS films is likely to be different from conventional LBL films,[1−3] since DBS is incorporated into the PTHT chain.[6] Such incorporation probably leads to some degree of charge overcompensation, thus allowing multilayers to be assembled. Recent works in the literature have indeed demonstrated that alternate adsorption occurs even with a small degree of overcompensation.[11] The chloride counterion in the PTHT layers is substituted by the long chain sulfonic counterion DBS instead of forming polycationic/polyanionic multilayers. The advantages of using DBS in the LBL process are demonstrated, among which is included the possibility of converting the precursor film into PPV at lower temperatures and controlling the conjugation length of the chains. Furthermore, an extremely fast adsorption takes place with PTHT/DBS LBL films. These features make LBL films from PPV promising for device applications where control of the HOMO−LUMO band gap is desirable.

Experimental Section

Synthesis of the PPV Films. PPV films were obtained by thermal conversion of LBL films prepared from poly(xylyliden tetrahydrothiophenium chloride) (PTHT) and dodecylbenzenesulfonate (DBS) as cationic and anionic solutions, respectively. The PTHT−DBS films were adsorbed on hydrophilic quartz substrates which were treated in a H_2SO_4/H_2O_2 (7:3) bath for 30 min and in a $H_2O/H_2O_2/NH_3$ (5:1:1) bath for 30 min. After each of such procedures, the substrates were washed with Milli-Q water. PTHT (PPV precursor) was synthesized using the precursor route described in the literature.[12] The concentration of the polycationic PTHT solution was 0.16 mg/mL, and the anionic DBS solution was prepared with 10^{-2} M concentration. The solutions were diluted in pure water at pH = 5.0. LBL layers (PTHT/DBS) were deposited

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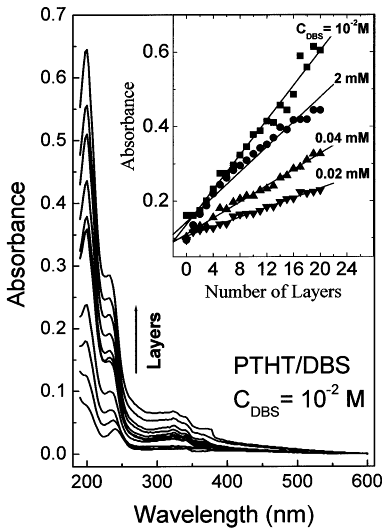

Figure 1. Absorbance spectra of a LBL PTHT/DBS film for various numbers of layers ($C_{DBS} = 10^{-2}$ M). The inset shows the absorbance at 200 nm against the number of layers for various DBS concentrations (10^{-2} M to 0.02 mM).

through alternate immersion in the polycation solution and in the anion solution, for periods of times referred to as t_1 and t_2, respectively, and finally dried with N_2. Here, PTHT/DBS films were obtained for different DBS concentrations (from 10^{-2} to 10^{-5} M) and converted to PPV films at low temperatures (80−120 °C) for 30 min under ambient conditions. Films converted at 230 °C under vacuum were used for comparison.

Conversion Procedure. The conversion process at low temperature was followed by in loco optical absorption measurements using a homemade heater cavity coupled to a Hitachi U-2001 spectrometer, where the heat exchange was achieved by mechanical contact between the sample and the internal wall of the heater cavity. Absorption spectra were measured at intervals of 2 min over 120 min.

Optical Measurements. UV−vis absorption spectroscopy was carried out with a closed helium cryostat coupled to a Hitachi U-2001, which enabled us to vary the temperature from 10 to 300 K. Photoluminescence (PL) measurements in the visible region (480−700 nm) were performed with the sample excited by a 458 nm line of an Ar^+ laser with an average excitation of 5 mW cm^{-2}. We used a photomultiplier mounted on a 0.5 m monochromator for detection in the lock-in mode. Infrared (IR) measurements were obtained with a Nicolet Magna-IR 560 spectrometer for cast-PPV/DBS films treated under vacuum at various temperatures (from room temperature to 230 °C). For comparison, we carried out absorption measurements at low temperatures of cast-PPV films and Langmuir−Blodgett PPV (LB−PPV) films prepared as in ref 7 and thermally converted under the same conditions of LBL−PPV films.

Surface Analysis. Atomic force microscopy (AFM) images were obtained with a Digital Nanoscope III in the tapping mode.

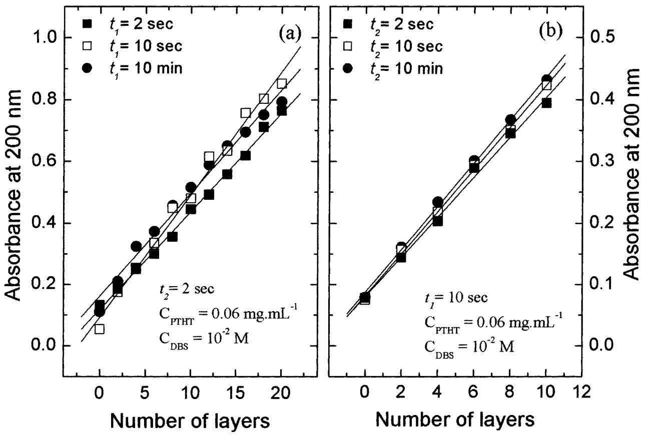

Figure 2. Absorbance intensity at 200 nm vs number of PTHT/DBS layers for various immersion times: (a) t_1 in PTHT solution and (b) t_2 in DBS solution varying between 2 s and 10 min. For case (a) the immersion time t_2 was fixed at 2 s, while for case (b) t_1 was fixed at 10 s.

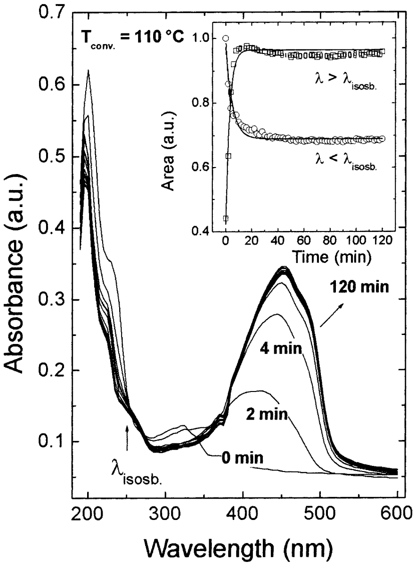

Figure 3. Low-temperature conversion process of 20-bilayer PTHT/DBS films into PPV monitored by optical absorption. In the inset is displayed the normalized integrated intensity as a function of the conversion time for $\lambda < \lambda_{isosb}$ (circles) and $\lambda > \lambda_{isosb}$ (squares).

Results and Discussion

Figure 1 shows UV−vis absorption spectra of LBL PTHT/DBS films for increasing numbers of bilayers deposited on quartz substrates. The optical characteristics do not depend on the number of layers deposited. Two regions can be distinguished in the spectra. Below 270 nm absorption is due to intramolecular transitions between localized energetic states. These transitions are related to arylsulfonium from the PPV precursor and from benzene rings that exist in the precursor and in the DBS molecule.[13−16] The other spectral region, between 270 and 390 nm, corresponds to transitions involving nonlocalized states, probably situated in conjugated stilbene units from PTHT.[16] The absorption intensities of both regions increase linearly with the number of deposited layers (see inset of Figure 1). Therefore, both PTHT and DBS are adsorbed in each dipping cycle. The inset in Figure 1 also shows that the adsorption rate (slope of the absorbance at 200 nm as a function of numbers of layers) increases with increasing DBS concentration (from 0.02 mM to 10^{-2} M), probably because more DBS molecules replace chloride ions. The adsorption rate of each layer is almost independent of the times of immersion in PTHT (t_1) and DBS (t_2) solutions, in the range from 2 s to 10 min, as shown in Figure 2. Saturation in the adsorption process therefore occurs at extremely short times. This may have important technological implications, with the low cost involved in such rapid adsorption processes.

The thermal conversion process into PPV was monitored by UV−vis absorption spectroscopy. Figure 3 shows results for a 20-bilayer PTHT/DBS film, adsorbed with t_1 = 1 min and t_2 = 1 min, thermally treated at 110 °C, following procedures described by Marletta et al.[6,9] Measurements were taken every 2 min, for a total period of 120 min, under ambient conditions since no significant difference was observed if nitrogen was purged in the sample chamber. Earlier experiments[6] revealed that PPV films converted through this procedure are free from carbonyl groups. As the conversion reaction proceeds, a large band related to PPV segments appears between 300 and ca. 510 nm. With approximately 12 min of thermal treatment this band saturates; i.e., the PPV segments are completely formed. Essentially, a final absorption edge at 503 nm indicates a high effective conjugation length of the chains after the conversion procedure. Such characteristics can be found in high-quality PPV films prepared under standard high-temperature procedures.[17,18]

For the region associated with localized transitions, located below an isosbestic point (λ_{isos}) at 253 nm, the spectral intensity decreases during the conversion process. The inset of Figure 3 shows the total normalized absorption (intensity integrated in wavelength) as a function of the conversion time for two complementary regions: below and above the isosbestic point. The intensity of the peaks below λ_{isos} decreases because they are associated with localized transitions of tetrahydrothiophenium rings that are eliminated during the thermal treatment. The results in Figure 3 demonstrate that the amount of DBS (10^{-2} M) used is sufficient to produce PPV films with a high effective conjugation length and consequently with excellent optical characteristics. In addition, the tetrahydrothiophenium group, when stabilized with DBS, is a better leaving moiety for thermal conversion at temperatures considerably lower than the conventional procedures (i.e., >200 °C).[17,18] This explains the rapid and effective conversion process at low temperatures achieved in this work.

Figure 4a shows an atomic force microscopy (AFM) image of a two-bilayer LBL PTHT/DBS film deposited on quartz substrate ($t_1 = 10$ s and $t_2 = 2$ s), which was converted to PPV at 110 °C under ambient conditions. The substrate was fully covered, and the film exhibits a reasonable homogeneity. The thickness of the sample was measured through AFM, following the procedure suggested by Lobo et al.,[19] in which a furrow is created in the sample with the AFM tip until reaching the substrate. The film thickness is then estimated from the height profile across the furrow. Figure 4b shows that the film thickness (0.5 nm per layer) increases linearly with the number of layers, consistent with the data in the inset of Figures 1 and 2.

Figure 5 shows the evolution of the optical absorption for 20-bilayer films built using distinct concentrations of DBS solution, from 10^{-5} to 10^{-2} M, and with t_1 and t_2 fixed at 10 and 2 s, respectively. The films were all converted at 110 °C for 30 min in a vacuum, which is sufficient for conversion of PTHT segments containing DBS. In the figure, the C_0* curve is a spectrum, used for comparison, of a nonconverted film which was dipped in a 10^{-2} M solution of DBS. The absorption band edge (defined by λ_{edge}) is shifted to higher wavelengths (red shift) with increasing DBS concentration, and the shift saturates for films prepared with DBS concentrations at about C_0/50 (Figure 5). This red shift, which depends on the size of conjugated sequences along the PPV chain, results from the gradual DBS incorporation as counterion in the PTHT molecule.

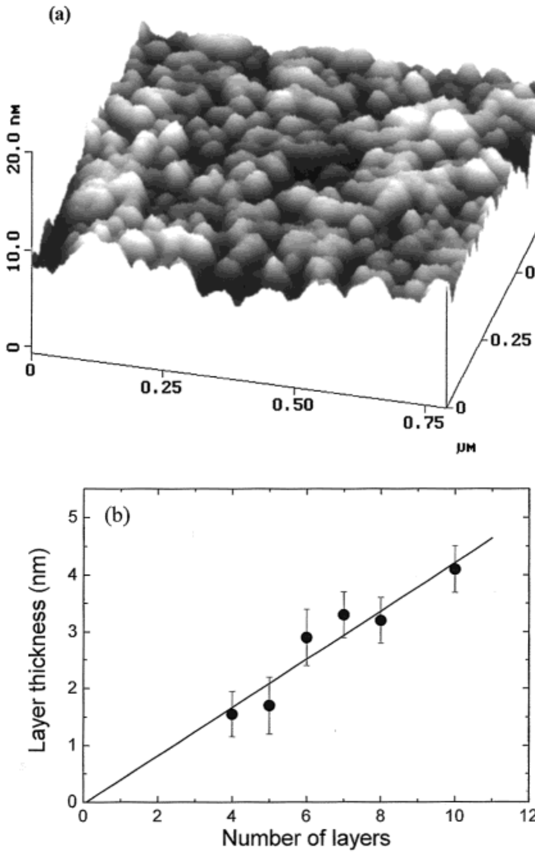

Figure 4. (a) AFM image of a 2-bilayer LBL PPV film on quartz substrate which was converted at 110 °C under atmospheric conditions. (b) Thickness dependence for LBL−PPV films on quartz substrates from 4 to 12 bilayers.

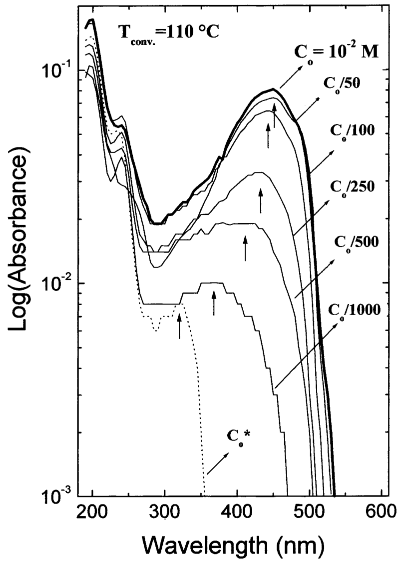

Figure 5. Absorption spectra of a PPV film converted at 110 °C for 30 min as a function of DBS concentration, from $C_0 = 10^{-2}$ M to C_0/1000. The spectrum C_0* corresponds to a nonconverted film with a DBS concentration of C_0.

Figure 6a shows absorption spectra carried out at 30 K for LBL films of PPV and for conventional cast-PPV films, both converted at 230 °C for 2 h in a vacuum. Figure 6b shows similar curves for LBL and LB PPV films, converted at 110 °C for 30 min in a vacuum. In the case of LBL samples, we use the same preparation conditions as those used for the sample with DBS concentration $C_0 = 10^{-2}$ M in Figure 5, whereas DBS concentrations used in the LB- and cast-films were published elsewhere.[7] All curves were normalized in

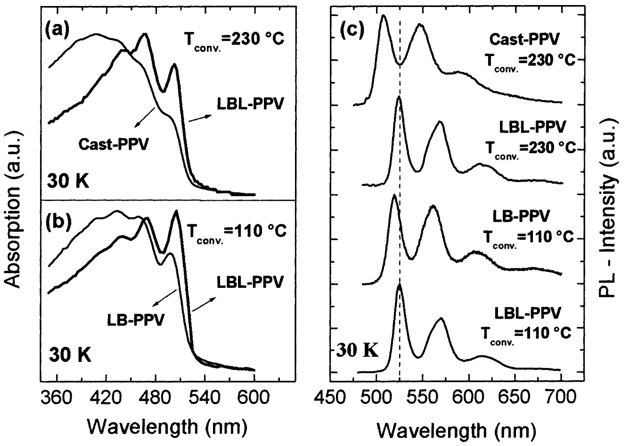

Figure 6. (a) and (b) Absorption spectra at 30 K for LBL PPV, cast-PPV, and LB−PPV films converted at 110 and 230 °C under vacuum. (c) Corresponding emission spectra at 30 K for the films presented in part (a) and (b). All curves were normalized to have the same intensity in the figure.

order to have the same intensity in the figure and have a direct comparison of line shape. The absorption spectra of the LBL film, regardless of the conversion temperature, showed highly defined vibronic structures near the band edge when compared to cast and LB PPV films. The spectra of the LBL film are also less intense in the lower wavelength region (see Figure 6), probably compensated by the increase in the vibronic peaks located above 450 nm. This may indicate that the molecules of LBL−PPV films contain longer conjugated segments than those of cast and LB films. We may also infer that the interchain exciton generation is facilitated by the length of the conjugated segment,[20,21] which explains the increase, and high definition, of the peak at 510 nm. These improvements in the spectra resolution can also be explained by a weaker interchain interaction in the LBL films,[21] which provides the formation of larger conjugated segments. We cannot estimate quantitatively the effective conjugation length from the band energetic position as the latter depends strongly on the conformational properties of the chains. In addition, the band edge is sensitive to changes in conjugation only for conjugation length $N < 15$ or even less.[20]

The photoluminescence (PL) spectra of LBL films are more resolved than for the cast and LB films, as shown in Figure 6c for measurements taken at 30 K. These curves are again normalized in the figure to have better comparison. Note, however, that as shown in Figure 7 the luminescence intensity is higher for LBL films converted at lower temperatures. The emission of LBL−PPV films is also red-shifted in comparison with the other films. Since the vibronic peaks in the absorption spectra are approximately at the same position for all films (see Figure 6a,b), the red shift in emission should be associated with a change in the Stokes shift, which depends on the degree of order of the film.[20] The high resolution in absorption and emission spectra are unprecedented for the PPV. This is strong evidence of the relatively low amount of incorporated defects when DBS is used to build the LBL−PPV films. It may also indicate a highly ordered structure for LBL and LB films, consistent with a low electron−phonon coupling, as verified by the increase in the zero-phonon line around 525 nm for such samples (Figure 6c).

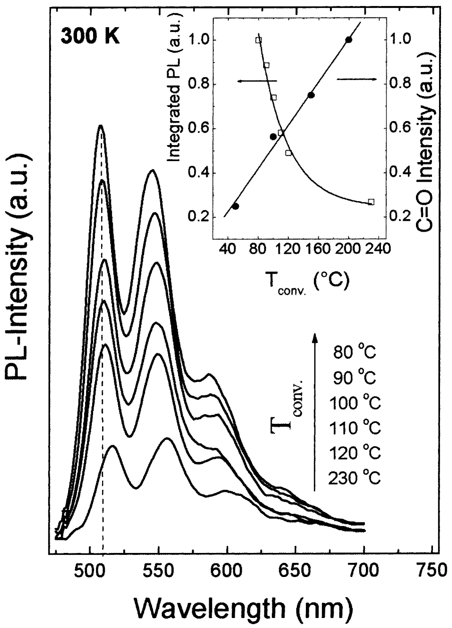

Figure 7. Emission spectra of PPV films converted at 80, 90, 100, and 120 °C in air and 230 °C under vacuum. The inset compares the intensities of integrated luminescence and IR carbonyl peak as a function of the conversion temperature.

Figure 7 shows PL spectra carried out at 300 K with films converted at 80, 90, 100, 110, 120 °C in air, and 230 °C under vacuum. These samples were prepared with DBS-10^{-2} M and under identical conditions to those for the samples used in Figure 5. Essentially, the spectra exhibit the same peak positions and similar well-resolved vibronic structures for samples converted at low temperatures. For the sample converted at 230 °C, the spectrum presents a small red shift. This is explained by further elimination of Cl^- at high temperatures, since the DBS amount used for such samples was not enough to obtain conjugated PPV segments with high effective conjugation length. However, the major difference in the PL spectra appears when the emission intensity is considered. A dramatic improvement in quantum efficiency of PPV is observed when the conversion temperature is decreased from 230 to 80 °C. This effect is in agreement with previous findings[22,23] and may be explained by the decrease of extrinsic defect incorporation, such as carbonyl groups, when films were converted at low temperatures. The inset of Figure 6 shows that the enhancement of the luminescence intensity at low conversion temperatures is correlated with the decrease of carbonyl stretch band intensity (1690 cm^{-1}) measured by infrared spectroscopy. In addition, the electron−phonon coupling decreases (indicating less structural disorder) and more resolved peaks are obtained at lower conversion temperatures. Therefore, converting the films at lower temperatures leads to less extrinsic defects that originate from for example thermal oxidation.

Conversion at lower temperatures has a particularly positive effect on the integrated PL. Figure 8 shows the temperature dependence of integrated PL for LBL films converted at different temperatures. The curves were normalized to coincide at 30 K. The PL intensity of a film converted at 230 °C decreases 60% from 30 to 300 K, but this decrease is only 18% for a sample converted at 80 °C. Therefore, the luminescence quenching due

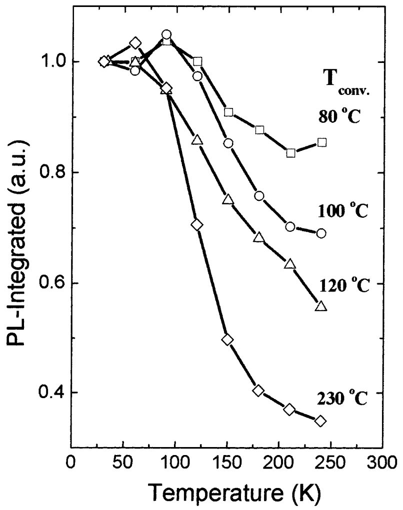

Figure 8. Luminescence integrated intensity as a function of sample temperature for PPV films converted at 80, 100, 120, and 230 °C. The curves were normalized to coincide at 30 K.

to temperature increases is less significant for LBL films converted at lower temperatures.

We have not as yet investigated the supramolecular structure of the LBL films. From elemental analysis of PPV prepared with DBS after conversion at different temperatures,[6] we observed that DBS is not eliminated even at 230 °C. On the other hand, the absorption measurements in Figures 5 and 6b and the luminescence results in Figures 6b, 7, and 8 indicate that highly conjugated PPV films can be obtained with the LBL procedure employed here. Therefore, the optical properties of PPV are unaffected by residual DBS in the film, suggesting that DBS salt does not form a chemical complex with the PPV structure and the films with DBS behave as a blend. The PTHT/DBS multilayers are certainly different from traditional LBL films involving ionic attraction of oppositely charged polymer layers. To build a PTHT/DBS multilayer, a PTHT layer is initially adsorbed on the substrate, driven by ionic attraction. Immersion of this film in a DBS solution causes DBS moieties to incorporate into PTHT as counterions. The bilayer PTHT/DBS is thicker than a single layer of PTHT, probably because the alkyl tails of DBS protrude from the PTHT-covered surface. This is shown in Figure 4 where the thickness of the films increases as successive PTHT or DBS layers are deposited. For an additional PTHT layer to be adsorbed on a PTHT/DBS structure, one must assume that the exposed surface contains excess DBS ions that attract the oppositely charged PTHT molecules.

Conclusions

In conclusion, using DBS in the LBL process is advantageous for several reasons: (i) Extremely fast adsorption of the LBL films. (ii) The possibility of converting PPV films with a high average conjugation length at low temperatures (110 °C) for only 12 min, with enhanced optical properties. (iii) The resulting PPV films display fewer defects compared to films converted at high temperatures, owing to the absence of carbonyl-related defects, thus leading to higher quantum yields in the luminescence processes. Light emission of the films exhibited highly resolved patterns, with an energy bandwidth of about 65 meV for the zero-phonon peak. (iv) The control of different amounts of DBS, together with the rapid low-temperature conversion process, provides an accurate selectivity on the conjugation length of PPV segments and consequently control of the HOMO−LUMO band gap.

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