Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 10475–10480 **10475**
DOI: 10.1021/ma102137v

"Log-Rolling" Alignment in Friction-Transferred Light-Emitting Conjugated Polymer Thin Films

Xiao-Tao Hao,[†] Nikko Y. Chan,[‡] Claire Heck,[§] Nobutaka Tanigaki,[§] Matthew F. Paige,[⊥] David E. Dunstan,[‡] and Trevor A. Smith*,[†]

[†]School of Chemistry, The University of Melbourne, Victoria 3010, Australia, [‡]Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia, [§]Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-18-31 Midorigaoka, Ikeda 563-8577, Japan, and [⊥]Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan, Canada S7N 5C9

Received September 14, 2010; Revised Manuscript Received November 2, 2010

ABSTRACT: Thin films of a water-soluble poly(phenylenevinylene) (PPV) derivative with sulfonate-containing side chains (DPS-PPV) were formed on silica substrates by a solvent-free friction transfer technique. The films were highly aggregated producing "rods" of polymer aligned *perpendicular* to the drawing direction. This "log rolling" is in contrast with the reported behavior of most comparable polymers, which tend to align along the drawing direction. The photophysical behavior of the friction-transferred film is also different compared with other film formation techniques of the same polymer. Comparison of the steady-state and time-resolved emission characteristics of these films with films coated by the conventional drop-casting method reveals that short-lived fluorescence components are dominant in the highly aggregated friction-transferred polymer films compared to less aggregated drop-cast films in which long-lived emission species are favored. This highlights the importance of the film formation processes on the properties of the film.

1. Introduction

Conjugated polymers that exhibit luminescence under electronic and/or photoexcitation are likely to play an important role in the next generation of light active, nanoassembled materials. They have already been widely used for a number of electronic applications,[1−3] including light-emitting diodes, organic photovoltaic cells, and lasers. Delocalized π-electrons mobilize along the extended one-dimensional backbone of the polymer, resulting in a semiconductor-like electronic structure. The intrinsic characteristics of conjugated polymers originating from the delocalized π-electrons make the conjugated polymers exhibit anisotropic behavior, which can be observed through properties such as polarized luminescence. Electronic characteristics of these systems are based on the arrangement of the polymer backbone and may be tuned or manipulated through either chemical synthesis and/or via the film formation processes. It is known that the photophysical response in solid-state thin films of conjugated polymers relies critically on the polymer film morphology and chain conformations that can be controlled during the film formation processes.[4−6] The ability to create well-characterized thin polymer films on solid substrates with reproducible and optimized physical properties is the missing link in achieving the ultimate performance potential of these advanced materials. However, to date, most polymer films are still prepared using conventional drop-casting or spin-coating. These methods do not induce significant molecular alignment and therefore produce films that exhibit largely isotropic properties. The chain conformation and film morphology influence the energy transfer, interchain interactions, and π-stacking-induced molecular aggregation in such systems.[7−10] To achieve controllable electronic structures in these materials, a variety of solution-based coating methods have been developed in which the deposition parameters can be adjusted, such as film stretching,[11] mechanical rubbing,[12] the Langmuir−Blodgett method,[13] the utilization of the liquid crystallinity of polymers,[14−16] and the application of an external electric field during film formation.[17]

A friction transfer technique first proposed by Makinson and Tabor in the 1960s[18] was demonstrated by Wittmann and Smith[19] in 1991 and has recently attracted much attention because of its unique solution-free processability for polymer thin film fabrication, combined with the reported formation of well-aligned polymer chains in thin films of some conjugated polymers.[20−25] A schematic diagram of the friction transfer technique is shown in Figure 1. A powdered aliquot of the conjugated polymer is compressed into a pellet, which is then pressed and drawn across the surface of the substrate under controlled temperature, pressure, and sliding speed. A solution-free processed film is subsequently deposited on the substrate, with molecular alignment generally in line with the direction of the drawing. Most studies on polymer thin films formed with the friction transfer technique have focused on crystal structure investigations,[21,23] polarized absorption and photoluminescence spectra,[20,23,25] or improvement of device performance.[20,22,26]

It has been reported that asymmetrically side-chain-substituted poly(phenylenevinylene) derivatives (PPVs) (such as MEH-PPV) do not form high-quality, molecularly aligned thin films by the friction transfer technique, and generally the symmetrically substituted polymers more reliably form such films.[23] The reason for this observation is yet to be determined unequivocally. The water-soluble conjugated polymer, poly[2,5-dipropoxysulfonato-*p*-phenylenevinylene] (DPS-PPV),[27,28] has symmetric side chains (inset of Figure 2a) and so may, on the basis of the above observations, be expected to form well-aligned films when cast by the friction transfer (FT) method. In this work we have investigated the use of friction transfer film formation with the aim to produce highly aligned thin films of DPS-PPV. We show that for this particular polymer the film consisted of fibril-type polymer

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*Corresponding author. E-mail: trevoras@unimelb.edu.au.

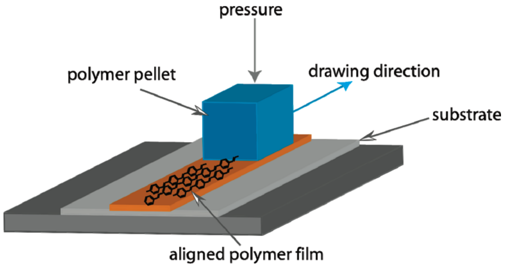

Figure 1. Schematic illustration of the friction transfer process for preparing conjugated polymer films.

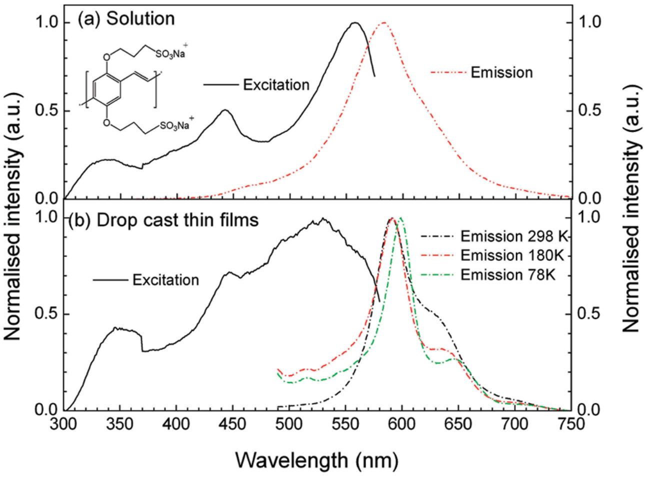

Figure 2. Fluorescence emission (excited at 450 nm) and excitation (detected at 590 nm) spectra of the DPS-PPV (a) solution and (b) drop-cast thin film. The emission spectra of a DPS-PPV film are measured at different temperature from 78 to 298 K.

aggregates aligned perpendicular to the drawing direction. This is related to the observation of compression rather than extension in polymers under certain conditions, which has been reported in our previous work[29,30] along with the observed "log-rolling" phenomenon reported by Romo-Uribe[31] and others. We have performed time-resolved fluorescence studies (to our knowledge, this is the first time these approaches have been applied to friction transfer films) in order to characterize the photophysical behavior and interpret the physical response of this polymer to the friction transfer film formation conditions.

2. Experimental Section

The DPS-PPV was synthesized in our laboratory using approaches described previously.[27,28] DPS-PPV thin films on glass slides were prepared by a friction transfer system (Imoto Machinery Co. Ltd.) at the National Institute of Advanced Industrial Science and Technology, Japan, or by conventional drop-casting from aqueous solution. The friction transfer process was performed under the following conditions: substrate temperature of 300 °C, the squeezing pressure of 3.9 MPa, and the drawing speed of 50 cm/min. A Varian Cary Eclipse fluorescence spectrophotometer was used to record the excitation and emission spectra of the conjugated polymer thin films, and an Oxford Optistat DN liquid nitrogen cryostat was used for the temperature-dependent measurements. The emission spectrum of the friction transfer cast DPS-PPV film was recorded on an inverted microscope (Nikon TE2000) using a high numerical aperture (1.49) objective lens and coupled with a high-resolution fiber-optic spectrophotometer (Ocean Optics model HR2000). A Becker & Hickl SPC-830 FLIM module coupled to an Olympus confocal scanning microscope (FV300/IX71) was employed for the fluorescence lifetime imaging measurements. The pulsed excitation (400 nm) source was the frequency-doubled output of a mode-locked titanium sapphire laser (Coherent Mira 900f, ~120 fs) pumped by ~4 W from a DPSS laser (Coherent Verdi 10). This excitation source (repetition rate of 76 MHz corresponding to 13.2 ns of pulse separation) was delivered via a single-mode optical fiber to the microscope. Confocally isolated emission was acquired by a SPC830 single photon counting unit and controlled using the SPCM TCSPC operating software. The fluorescence decay data were analyzed using "SPCImage" FLIM data analysis software. Atomic force microscope images were recorded on a Digital Instruments Dimension 3100 (Veeco Instruments Inc., Santa Barbara, CA) measuring under tapping mode at a scan rate of 0.35 Hz.

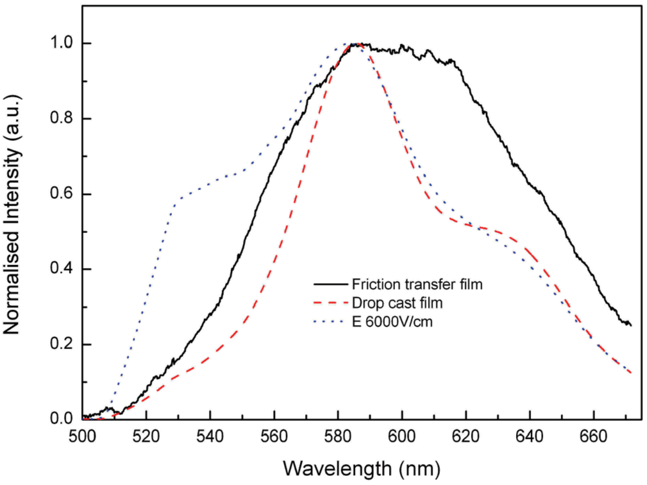

Figure 3. Fluorescence emission spectra of a friction-transferred DPS-PPV film, a drop-cast DPS-PPV film, and a high electric field (6000 V/cm) induced DPS-PPV film.

3. Results and Discussion

Steady-state excitation and emission spectra provide general information relating to the conformational structure of conjugated polymers.[32] Figure 2 shows the excitation (detected at 590 nm) and emission (excited at 450 nm) spectra of an aqueous DPS-PPV solution and a conventional DPS-PPV drop-cast film. Also included is the emission spectrum of the drop-cast film at low temperatures. The excitation spectra are generally similar for both solution and the drop-cast films although the main visible excitation peak is broader and blue-shifted relative to the polymer in solution. In contrast, the emission band from the DPS-PPV film is generally sharper and slightly red-shifted compared to the DPS-PPV in solution. As the temperature of the film is decreased, the expected enhancement in the structure of the emission bands is observed, but the general structure is maintained and there is a further clear but small red shift of the emission spectrum with decreasing temperature. This is attributed to a concomitant decrease in electron−phonon interactions and increased effective conjugation lengths compared to room temperature.[17,33]

For the friction-transferred DPS-PPV thin films, the very weak emission was not readily detectable using a conventional fluorimeter, presumably due to fluorescence quenching processes or an effective "dilution" of the polymer due to nonuniform coating of the film, reducing the emission collected. Instead, a high numerical aperture objective lens on an inverted microscope coupled with a high-resolution fiber-optic-based spectrophotometer was used to record the emission spectrum of the friction transfer cast film. The emission spectra of DPS-PPV films formed by friction transfer, drop-casting, and casting under a high electric field are compared in Figure 3. Distinct spectral shapes can be seen for the films formed under the different conditions, reflecting different polymer conformations. The spectral behavior of DPS-PPV cast

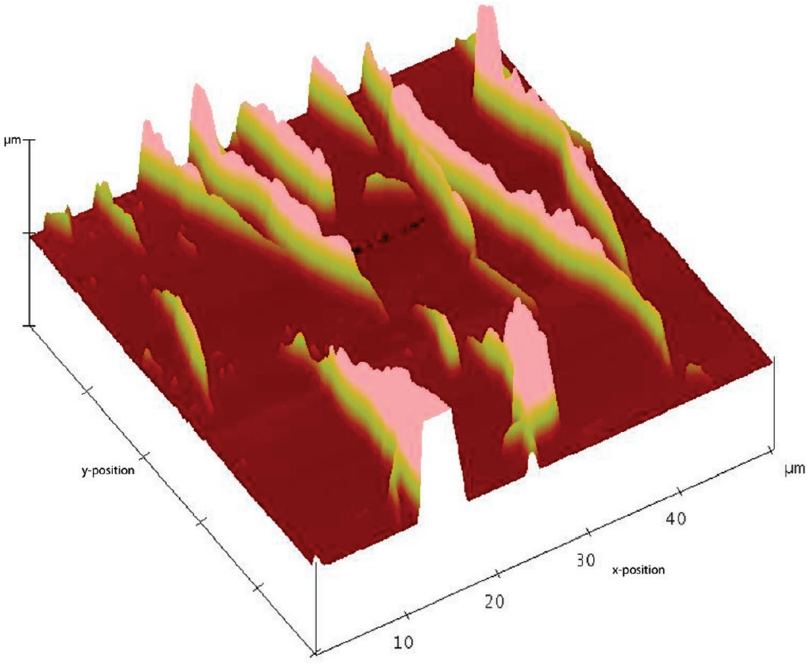

Figure 4. AFM image of the friction-transferred DPS-PPV film.

under the electric field is similar to that observed from a related conjugated polymer, MEH-PPV, reported in our previous work,[17] which was attributed to decreased aggregate formation and improved chain alignment in thin films of MEH-PPV cast under a high electric field.

The peak emission wavelength for the drop-cast film is centered at 590 nm, while it is shifted to 585 nm for the electric-field-influenced film, and at the same time the emission shoulder around 620 nm becomes marginally less pronounced in the latter. The slight blue shift of the emission spectrum indicates a propensity for the polymer to adopt conformational configurations favoring higher energy shorter conjugation length segments, and the reduced shoulder on the red side of the emission suggests a less aggregated state for the polymer in the electric-field-induced films compared with the other films. We assume that polymers with charged side chains are more highly aligned than their uncharged counterparts during the process of self-assembly, even in the absence of an electric field. This is supported by the polarization ratio changes in these solid-state polymer films: An emission polarization ratio ($I_{\parallel}:I_{\perp}$) of 4.64 can be achieved for the DPS-PPV film cast with high electric field of 6000 V/cm, which is higher than the value in the reported MEH-PPV films under similar casting conditions (3.55).[17]

The less aggregated film prepared under the influence of the electric field has a strong emission shoulder from the isolated blue-emitting chromophores (around 530 nm) that is absent in either of the other two spectra. The reduction in the prominence of the emission shoulder in the red and the increase in emission in the blue is interpreted as being due to reduced energy migration from the shorter, higher energy segments to the longer, low energy segments in the less aggregated films, resulting from the reduced intermolecular chain–chain contacts. The film prepared with the friction transfer technique, however, has a very broad emission peak, which is assumed to be related to the increased prevalence of the species giving rise to the emission shoulder at 620 nm. Lemmer et al.[34] assigned the low energy fluorescence to aggregated states in closely packed solid conjugated polymer films. Thus, the observed behavior may result from the strong chain–chain interaction and aggregation states in friction-transferred films. Since the less aggregated film was also reported to show higher luminescence intensity as compared to that with more π-aggregated chains,[7,17] the lower emission intensity may indicate the presence of more highly aggregated clusters in the friction-transferred DPS-PPV thin films. It therefore appears that the specific solid state of conjugated polymers formed via the friction transfer process is influenced by enhanced strong interchain interactions, resulting in highly aggregated polymer clusters, and that these interchain interactions significantly reduce the luminescence efficiency of the film.[35]

Atomic force microscopy of the friction-transferred film (Figure 4) reveals the behavior of the polymer under these conditions. Aligned stick- or rodlike clusters are evident in the friction-transferred films, and film coverage is sparse. The rodlike formations are rough and up to ~1 μm in height, making more quantitative AFM measurements problematic.

Optical (fluorescence) microscopy (Figure 5) confirms the aligned stick- or rodlike cluster morphology of the friction-transferred film (Figure 5a) and illustrates the obvious difference between this and a drop-cast DPS-PPV film which exhibits more random, globular aggregates (Figure 5b). Counter to initial expectations, the alignment direction of the polymer "rods" in the friction-transferred film is *perpendicular* to the drawing direction rather than parallel to it, in a manner somewhat similar to the residue resulting when one uses a pencil eraser. This behavior differs from the previous reports of other polymers in friction-transferred films being completely aligned along the drawing direction of the friction transfer.[23,25] However, similar behavior, sometimes referred to as "log rolling", has been reported from other macromolecular systems under various conditions. Arya et al.[36] reported the "log-rolling" phenomena of self-assembled cylindrical micelles experiencing extreme confinement in shear conditions. Their work indicated that the wormlike micelles aligned perpendicular to the direction of the shearing plates when the distance between the shearing plates is comparable to the micelle diameter. Masselon et al.[37] recently further described the influence of confinement by geometric and boundary constraints on wormlike micellar systems that behave like entangled flexible polymers. Romo-Uribe et al. have also observed "log-rolling" behavior for a specially synthesized series of thermotropic copolyester melts under shear.[31] In that work the

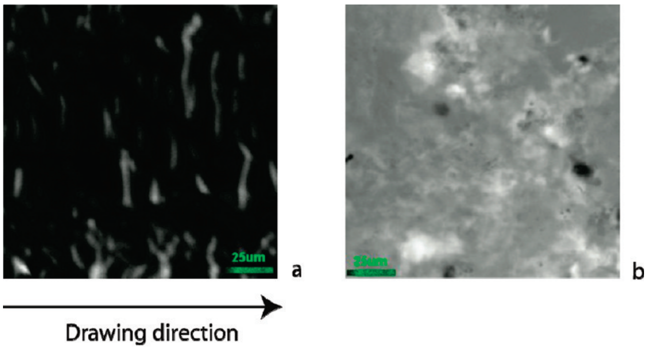

Figure 5. Fluorescence microscope images of (a) friction-transferred and (b) drop-cast DPS-PPV films.

transition from the in-flow-aligning to the "log-rolling" regime was observed to occur in a comparatively narrow band of temperatures above the crystal melting point. The observed behavior is also consistent with our findings on related polymers which undergo molecular alignment under the influence of shear flow at high shear rates.[29,30] The polymer molecules of diacetylene 4-butoxycarbonylmethylurethane (4BCMU) were found to align parallel to the shear direction at shear rates below 500 s^{-1} but aligned perpendicular to the shear direction at higher shear rates. Our observation of the polymer "rods" aligning *perpendicular* to the drawing direction, therefore, is believed to result from strongly coupling of the polymer with the confining surfaces on the substrates under high pressure during the friction transfer process.[23,25] The observation of the "log-rolling" phenomenon, while being somewhat disappointing from the viewpoint of attempts to form well-aligned and uniform polymer films, highlights that caution must be used when employing friction transfer methods to achieve well-aligned polymer films and that not all polymers behave identically under specific conditions used.

In the friction-transferred DPS-PPV thin films, we estimate that each polymer rod (with diameter of 2 or 3 μm) contains tens or hundreds of single polymer chains. Li et al.[22] have investigated similar effects in a friction-transferred poly(9,9-dioctylfluorene-*co*-bithiophene) thin film and reported that the influence of the molecular interaction strength (including van der Waals interactions and molecule side-chain entanglements) is much higher than the surface energy of the polymer, with the system tending to form "wires" or "rods".[22] The strong intermolecular interactions among the individual polymer chains and interactions between the polymer and the substrate can both result in fluorescence quenching in the films, as is observed. These factors combine to produce the aggregated rods oriented perpendicularly to the drawing direction, which exhibit a reduction in fluorescence intensity in these films compared with films formed by other techniques.

Polarized fluorescence spectra were recorded for the friction-transferred DPS-PPV film (Figure 6). The experimental restrictions imposed by the use of the homemade microscope-based fluorescence spectrophotometer limit our ability to determine the polarization ratio quantitatively (e.g., determination of the polarization bias (G factor)[38] correction is inherently difficult in high numerical aperture microscopes). We therefore report simply the ratio of the emission intensity collected with polarization parallel ($I_{\|}$) and perpendicular ($I_{\perp}$) to the plane of the incident excitation light. The $I_{\|}:I_{\perp}$ ratio is about 1.83, which is larger than the 1.4 observed from the drop-cast films under the same conditions, although lower in magnitude than expected for highly aligned samples. This reduction in the degree of polarization is possibly due to efficient energy migration within the aggregated "rods" in the friction-transferred film. In polymer films, energy transfer induced by excitons migrating rapidly from higher energy, shorter conjugated segments to longer conjugated segments with lower energy results in

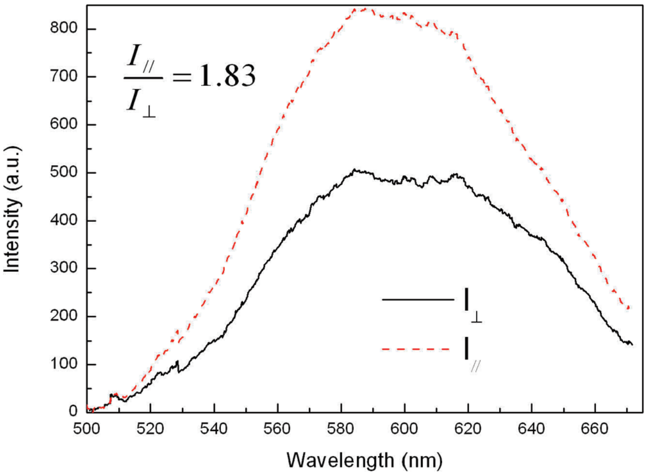

Figure 6. Polarized fluorescence spectra for a friction-transferred DPS-PPV film.

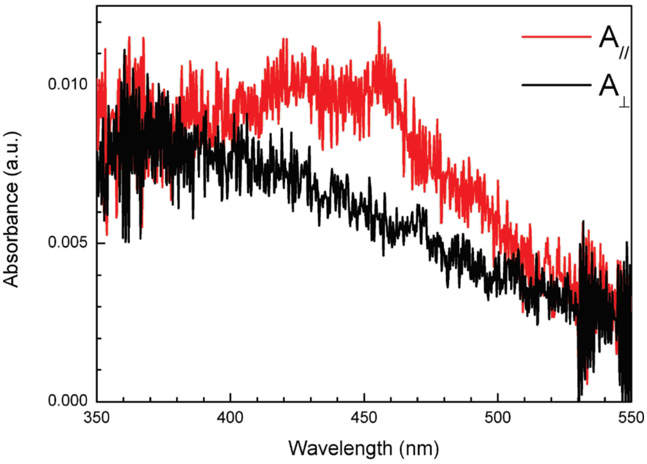

Figure 7. Polarized UV/vis absorption spectra of a friction-transferred film.

scrambling of the emission polarization.[39] The isolated polymer "rods" formed in the friction-transferred thin film had a relatively large separation distance of order tens of micrometers, thus excluding inter-rod resonance energy transfer. However, the high degree of packing of the polymer chains within the clusters may favor the transfer of energy among chromophoric segments within the macroscopic aligned "rods" and therefore reduced the emission polarization ratio of the film. The degree of uniformity of the film might also play a role in determining the overall level of emission polarization observed.

We have also performed polarized UV/vis absorption measurements on the friction-transferred DPS-PPV film (Figure 7). The low absorbance, which can be compared with the significantly higher absorbance values achieved in measurements performed on other friction-transferred conjugated polymer films,[23,26,40] makes it difficult to determine an accurate polarization ratio, but at ~450 nm this ratio is approximately 1.8, which is in good agreement with the value determined from the fluorescence spectral measurements. The low level of absorbance is also indicative of the sparse coverage of the film in the present case, providing evidence that the low level of emission from these films is in fact primarily due to low polymer coverage and less to do with emission quenching processes.

The reduced overall coverage of the film due to these rodlike clusters may account for the difficulty in recording emission spectra from these films in the conventional spectrometer as discussed above. However, low signal levels may also be due to

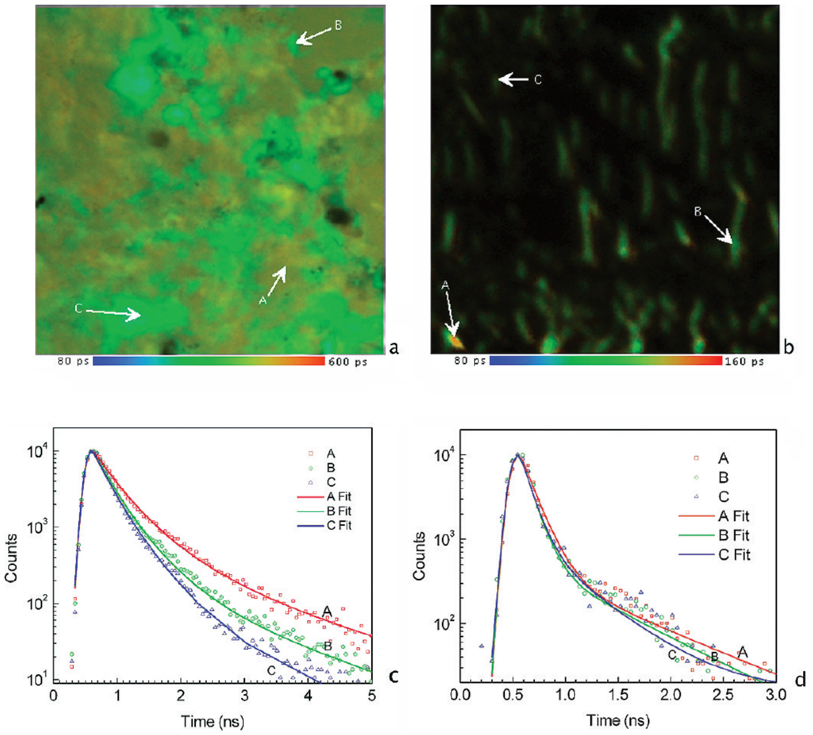

Figure 8. Fluorescence lifetime images of (a) drop-cast and (b) friction-transferred DPS-PPV thin films and fitted decay profiles of typical points at (c) drop-cast and (d) friction-transferred DPS-PPV thin films.

emission quenching processes, as mentioned above. Steady-state spectroscopy and imaging cannot differentiate between these two possibilities, and so time-resolved fluorescence imaging measurements were also performed on the drop-cast and friction-transferred DPS-PPV thin films. Such methods are useful in discriminating between static processes that result merely in reduced emission intensity (such as low surface coverage) from those that result from dynamic processes or distributions of species with different quantum yields/decay times. In the method used here (time-resolved confocal fluorescence imaging based on a commercial time-correlated single photon counting system (Becker & Hickl)),[41,42] a complete fluorescence decay profile is collected in each pixel of a scanned confocal emission image. The emission decay time for each pixel can then be used to map the variation in the time-resolved emission behavior of the sample as a function of spatial location. The same sized area was scanned for both the drop-cast and friction-transferred DPS-PPV films and emission lifetime images generated, as shown in Figure 8.

Fluorescence decay profiles for three typical positions on each film are shown in parts c and d of Figure 8 for the drop-cast and friction-transferred films, respectively. The emission is clearly shorter lived and more homogeneous in terms of time-resolved behavior for the friction transfer film. The fitted decay times and their relative contribution for each specific position of these polymer films are recorded in Table 1. We have not attempted to assign any individual decay component to any specific species in the films. In the case of the drop-cast film, the relatively uniform area (A in Figure 8a) appears to contain less aggregated chromophoric segments since it exhibits a longer average fluorescence lifetime with two major decay components ($\tau_1 = 300$ ps and $\tau_2 = 578$ ps) and a third residual component ($\tau_3 = 1609$ ps). The area B in Figure 8a suggests a more aggregated region in the drop-cast film, which also exhibits triple-exponential behavior in the decay profile with slightly shorter fluorescence decay times (two major decay components ($\tau_1 = 243$ ps and $\tau_2 = 452$ ps) and a third residual component ($\tau_3 = 1392$ ps)). Region C in Figure 8a exhibits different behavior, again being fit adequately with a two decay component model ($\tau_1 = 238$ ps and $\tau_2 = 537$ ps). However, the fitted decay times in the friction transfer film (Figure 8b,d) are much shorter, most likely due to the high degree of aggregation within the "rods". For an area showing bright fluorescence intensity (A in Figure 8b), which may be a less aggregated position in the friction transfer thin film, the corresponding decay profiles are double-exponential with fitted decay times of $\tau_1 = 130$ ps and a residual component of $\tau_2 = 802$ ps. The area in the "rod" with highly packed polymer chains, such as B and C in Figure 8b, exhibits even shorter fluorescence lifetimes with $\tau_1 = 105$ ps and $\tau_2 = 671$ ps and $\tau_1 = 100$ ps and $\tau_2 = 441$ ps, respectively.

Table 1. Fitted Decay Times of the Drop-Cast DPS-PPV Thin Film and the Friction-Transferred Thin Film[a]

		fitted decay times (ps)		
		τ_1	τ_2	τ_3
drop-cast	A	300 (70.1%)	580 (26%)	1609 (3.9%)
	B	243 (72.9%)	452 (25.1%)	1392 (2%)
	C	238 (84.1%)	537 (15.9%)	
friction-transferred	A	130 (97.1%)	802 (2.9%)	
	B	105 (96.8%)	671 (3.2%)	
	C	100 (93.9%)	441 (6.1%)	

[a] Figures in parentheses are the relative contributions to the decay.

The results of fitting the fluorescence decay profiles (deconvoluted decays) of typical points in DPS-PPV thin films prepared with the various coating methods are compared in Figure 9. It is clearly seen that the fluorescence decays much faster in the friction-transferred films than in either the electric-field-induced or drop-cast films. We concluded in a previous work[17] that the PPV film coated under a high electric field of 6000 V/cm has less aggregated chain conformation than the commonly deposited drop-casting PPV films. Compared to the long-lived components with $\tau_1 = 338$ ps, $\tau_2 = 1044$ ps, and $\tau_3 = 2501$ ps in the electric-field-induced film, a typical aggregated point (B in Figure 8b) in the friction-transferred film has very short fluorescence lifetime of $\tau_1 = 105$ ps and $\tau_2 = 671$ ps as discussed above. We attribute the short decay components, dominant in the friction transfer film as

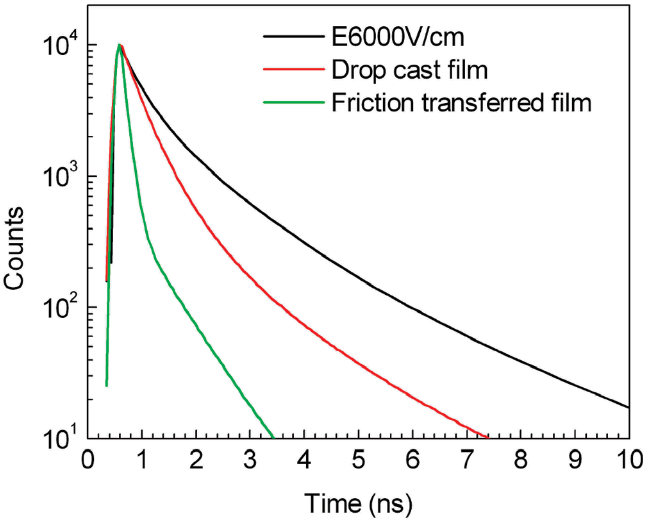

Figure 9. Fluorescence decay profiles of typical points in conjugated polymer DPS-PPV thin films prepared with high electric field, drop-casting, and friction transfer technique.

shown in Figure 9, to the fluorescence decay of highly packed chromophores or chains in the polymer "rod".[43] The relatively "isolated" chromophores in less aggregated electric-field-induced films or even drop-cast films under excitation are dominated with long-lived fluorescence species. Friction transfer films would be expected to be more favorable to aggregate formation within the polymer "rods" and therefore contain more short-lived fluorescence species that enhance the fluorescence quenching, resulting in weaker emission in the films.

4. Conclusions

We have recorded steady-state fluorescence spectral information and time-resolved emission images of conjugated polymer thin films formed with both drop-casting and a friction transfer technique. The friction transfer method is able to create thin films of conjugated polymers with defined conformation and morphology, with corresponding spectroscopic properties that differ from films created using other techniques. For the polymer used in this work, the friction transfer method produces films that are highly aggregated into "rods" of polymer that are aligned *perpendicular* to the draw direction. This is in contrast to the behavior reported for other polymers that produce thin films in which the polymer chains are aligned in the direction of drawing. The rods formed through this process exhibit a higher emission polarization ratio due to this alignment and reduced emission quantum yield (as reported by the shorter fluorescence decay behavior), presumably as a result of enhanced interchain interactions.

Acknowledgment. Funding through the ARC grant DP-0663889 is acknowledged.

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