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Solution processing of conjugated polymers: the effects of polymer solubility on the morphology and electronic properties of semiconducting polymer films

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Abstract

It is becoming increasingly clear that the electronic properties of conjugated polymers are controlled by the way the films are cast: changing the solvent, spin speed or concentration changes the film morphology and thus the performance of devices based on these materials. In this paper, we show that the way a conjugated polymer is dissolved into solution also affects the interchain interactions and electronic behavior in the resulting film. Light scattering shows that even low molecular weight samples of poly(2,5-bis[*N*-methyl-*N*-hexylamino]phenylene vinylene) (BAMH-PPV) do not completely dissolve in the good solvent *o*-xylene, even after stirring for 2 days. The solutions behave more as a suspension of small pieces of polymer film, showing solid-state effects such as exciton–exciton annihilation; the corresponding cast films have a rough, agglomerated morphology. Complete dissolution of the polymer can be achieved either by heating the solutions while stirring for 2 days, or by stirring at room temperature for 2 weeks. In addition to aiding dissolution, heating is found to promote interactions between conjugated polymer chains, leading to films with a higher degree of exciton–exciton annihilation and devices with higher operating currents but lower electroluminescence quantum efficiencies than films cast from solutions that were fully dissolved but not heated. All the results suggest that understanding the details of how a conjugated polymer is dissolved into solution is critical to being able to reproducibly fabricate and optimize conjugated polymer-based devices.

Keywords: Conjugated polymers; Exciton–exciton annihilation; Light-emitting diode (LED)

1. Introduction

Conjugated polymers are remarkable materials because they are both plastic and semiconducting [1–3]. The bandgaps of most conjugated polymers occur in the visible region of the spectrum, and the emission color can be tuned to essentially any desired wavelength region by altering the chemical nature of either the polymer backbone or the side groups [4]. Perhaps more importantly, semiconducting polymers can be dissolved in common organic solvents, making it straightforward to prepare uniform, large area, and flexible thin films of these materials by spin-casting or dip-coating. It is this ease of processing that makes conjugated polymers so attractive as the active medium for novel optoelectronic devices such as plastic light-emitting diodes (LEDs) or photovoltaic cells [1–3]. Fabrication of a typical sandwich-structure polymer device is quite simple: a sample of the polymer is dissolved in a solvent, a few drops of the solution are spun onto an electrode-coated substrate, and after the solvent is removed the second electrode is evaporated on top. Given the number of steps involved in manufacturing a comparable device from inorganic semiconductors like GaAs, it is difficult to imagine a simpler device construction process than that afforded by conjugated polymers.

Although it is easy to construct conjugated polymer-based devices, optimizing the performance characteristics of such devices is complicated by the molecular nature of these materials. Variations in how the polymer is processed can alter the packing of the polymer chains and thus change the electronic properties of the resulting conjugated polymer film. This means that film morphology, and hence, the performance of conjugated polymer-based devices, can be controlled by a number of factors, which include: changing either the solvent or the concentration of the solution from which the polymer film is cast [5–7]; varying the spin speed [8,9]; growing the films layer-by-layer using Langmuir–Blodgett techniques [10,11]; annealing the films after they have been cast [6,7,12,13], etc. This dramatic variability of device performance with casting conditions is the result of electronic interactions between the polymer chains in the film. Strong interactions between conjugated polymer

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chains promote good carrier transport through the film but also reduce luminescence quantum efficiency, leading to a fundamental trade-off in optimizing film morphology for device performance [5–7]. To form emissive excitons by electrical injection, high carrier densities and mobilities are required, necessitating a large degree of interaction between the polymer chains in the device. Once the carriers recombine and the exciton is formed, however, minimal interchain contact is required to achieve the highest luminescence efficiency.

Why are the properties of conjugated polymer films so sensitive to their preparative history? The answer lies in the fact that conjugated polymers behave very differently in different solution environments, and that these differences can survive the casting process and persist into the film [5–7,14,15]. The physical conformation of a conjugated polymer chain, for example, can change as the solvent or the temperature of the polymer solution is varied. Altering the chain conformation, in combination with the polymer concentration, in turn affects how easily the conjugated polymer chains can aggregate together in a manner that affects the polymer's electronic structure [16,17]. Conjugated polymer chains dissolved in "good" [1] solvents tend to have an open conformation, allowing easy access for chromophores to come into interchain contact. Conjugated polymer chains in "poor" solvents, on the other hand, tend to form tight coils, making it difficult for chromophores to become physically adjacent even through the chains tend to clump together [5]. Depending on the volatility of the solvent and the choice of spin speed, memory of both the chain conformation and the degree of electronic interactions between the chains in solution can be preserved through the spin-coating process and remain in the film [6,8,9].

In addition to LED performance, the ways in which different degrees of interchain interaction affect the behavior of conjugated polymer films can be investigated through a wide variety of experiments. For example, scanning force [6] and near-field microscopies [18] as well as contact angle measurements [8,9] demonstrate that conjugated polymer films cast from different solvents have different surface topographies, while X-ray diffraction shows that casting films from different solvents changes the way the polymer chains are packed together [19,20]. Moreover, films comprised of tightly coiled chains have a higher propensity for photo-oxidative damage than films in which the chains have a more open configuration; the spaces between tightly coiled chains make such films more permeable to ambient gases [6,18]. In addition, the photoluminescence (PL) of conjugated polymer films undergoes a spectral red-shift and a decrease in quantum yield with increasing interchain interactions, a direct result of the formation of weakly luminescent interchain species such as aggregates [5,6,21–26] or excimers [16,17,27–29]. Finally, the high-intensity photophysics of conjugated polymer films are also morphology dependent. Several groups have shown that spectral line narrowing and lasing in conjugated polymer films depends sensitively on how the films are prepared, presumably the result of subtle changes in the overlap of the gain and loss characteristics with differences in film morphology [30–34]. Moreover, the bimolecular recombination coefficient for exciton–exciton annihilation can be an order of magnitude higher in films with a high degree of interchain contact relative to films where the chains are relatively isolated, simply because excitons have an easier time finding each other when the chains are in contact [6].

Given all this variability in the behavior of interchain interactions, it is clearly important to control all the details of the polymer processing in order to optimize conjugated polymer films for desired applications. This makes it imperative that the solutions from which the films are cast can be prepared in a straightforward and reproducible manner. Yet, conjugated polymers, especially those with high molecular weights, are notoriously *insoluble* in most of the common solvents used for casting films. Even in a "good" solvent, full dissolution of most conjugated polymers takes place only after stirring a solution for hours or even days. In many cases, the solvent must be heated while stirring in order to get the polymer to dissolve. The high-concentration polymer solutions typically used for spin-casting films also show a great propensity to gel, especially if the solutions have been stored for any length of time. All these facts lead to an obvious but important question: are the morphology and electronic properties of conjugated polymer films affected by the way in which the polymer is dissolved into solution?

In this paper, we explore this question in detail by studying both conjugated polymer solutions and the films cast from them as the way the polymer is dissolved is systematically varied. We find that even after stirring a solution of a relatively low-molecular weight polymer at room temperature for up to 2 days, the polymer is not completely dissolved: instead, the polymer becomes a suspension of small aggregated clusters in solution. Photophysics experiments show evidence for film-like behavior from the aggregates in the incompletely dissolved solutions, and the films cast from these solutions have a highly variegated topography. Heating the polymer solutions while stirring, however, does fully solubilize the polymer; the isolated chains in solution lead to spin-cast films with a smooth surface. Once the polymer is fully dissolved, however, we find that additional heating of the solution can have somewhat of the opposite effect: films cast from fully dissolved solutions that were heated have a higher degree of interchain contact than films cast from fully dissolved solutions stirred at room temperature, leading to differences in both exciton–exciton annihilation and device behavior. All of the results indicate that it is easy to take the dissolution of conjugated polymers for granted: small differences in the way a polymer is dissolved into solution lead to easily measurable changes in the photophysics or the

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[1] By "good" solvent, we mean a solvent in which, with sufficient stirring and heating, the polymer can dissolve to concentrations of several percent w/v without gelation.

device performance of conjugated polymer films. We believe that much of the conflicting data presented in the literature results from the fact that different groups follow different procedures when dissolving their polymers into solution, so that the films studied by these different groups have different electronic properties.

2. Experimental

The conjugated polymer chosen for this study is poly(2,5-bis[*N*-methyl-*N*-hexylamino]phenylene vinylene) (BAMH-PPV), whose chemical structure is shown in the inset of Fig. 1. The polymer used in this study, provided by Lindsay and Stenger-Smith, was synthesized according to standard literature procedures [35] and used as received. The polymer powder was stored in the dark under an inert atmosphere until ready for use. The average molecular weight of the polymer used in this study was determined by gel permeation chromatography (GPC) to be ∼55,000 g/mol. The distribution was asymmetric with a tail towards low molecular weights, with the 10 and 90% points of the distribution occurring at molecular weights of approximately 7000 and 132,000, respectively. All sample storage, handling, and processing were carried out in the inert environment of a nitrogen glove box. Optical experiments were carried out by placing the polymer samples into an optical cryostat within the glove box, sealing the cryostat, and then removing the sealed cryostat from the glove box. For films, the samples were then placed under vacuum; for solutions, the samples were studied under nitrogen. In this way, all the polymer samples were studied without ever having been exposed to ambient conditions.

Solution samples of BAMH-PPV were prepared by first dissolving the appropriate amount of polymer into *o*-xylene to prepare a 1.0% w/v solution. Since the purpose of this study is to investigate how the differences in polymer solubility affect the electronic properties and morphology of conjugated polymer films, we prepared our polymer solutions in two fundamentally different ways. Other than the differences in treatment of the solutions enumerated, all subsequent processing of the solutions (spin-coating, film drying, etc.) was done in an identical fashion. We designed the first set of experiments to test the effectiveness of heating the solution during the initial dissolving of the polymer powder. In these experiments, we prepared two identical BAMH-PPV solutions, both of which were stirred for 2 days. The only difference in how these solutions were handled is that one of them was heated to 50°C for 6 h when stirring, while the other was stirred only at room temperature. The second set of experiments was designed to explore the role of heating the solution once the polymer was fully dissolved. For these experiments, a BAMH-PPV solution was prepared by stirring for ∼2 weeks at room temperature, which as will be argued below produces a fully dissolved polymer solution. This fully dissolved solution was then divided into two portions, one of which was stirred and heated to 50°C for an additional 2 days, while the other was stirred only at room temperature during this time.

Film samples were prepared by spin-coating one of the four BAMH-PPV solutions described above onto glass substrates (or for LEDs, ITO-coated glass substrates) at a spin speed of 1500 rpm. The spin-coated films were then heated at 50°C for 2–3 h to ensure removal of the solvent. All the films used in this study were prepared identically; the only differences are in how long the solutions were stirred and whether or not the solutions were heated before casting the films. The spin-cast films had an optical density ≈ 1.0 at the absorption maximum of 475 nm. To minimize the effects of self-absorption from the optically dense samples, PL was collected from the front face of the film samples using a Fluorolog-3 (Instrument S.A. & Co.); PL quantum yields were determined using Rhodamine 101 in ethanol as a standard with unit quantum yield [36]. For the femtosecond pump-probe experiments, the laser pulses passed through the transparent substrate. All the pump-probe scans presented below were completely reproducible, and we saw no signs of irreversible sample damage at laser fluences below 50 μJ/cm^2, even when the samples were in air. For LEDs, a ∼100 nm thick, ∼1 mm^2 10:1 Mg:Ag electrode capped with ∼100 nm of Ag was evaporated on top of the spin-cast polymer film; details of the LED fabrication and characterization are described elsewhere [6,7].

Topographic images of the BAMH-PPV film samples were obtained using a scanning force microscope (Park Scientific) with 5 μm scanners. The microscopy experiments were done in the air at room temperature in constant force mode with an applied loading of ∼1 nN using a scanning frequency between 0.5 and 1 Hz. The scanning conditions were similar to our previous work on poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-pheylene vinylene) (MEH-PPV) films [6]. Light-scattering measurements were performed on a Microtrac Ultrafine Particle Analyzer (Leeds & Northrup), with conditions similar to those used in our previous work on MEH-PPV solutions [5]. Differential scanning calorimetry scans at 10°C/min were taken with a Perkin-Elmer Pyris-1 Instrument using In and Zn as standards under nitrogen flow. The glass transition temperature (T_g) of the BAMH-PPV used in our experiments was determined by DSC to be 134 ± 5°C. Thermogravimetric analysis showed that the polymer undergoes a 5% weight loss at 200°C.

The laser system used for the femtosecond pump-probe experiments is a regeneratively amplified Ti:sapphire laser (Spectra Physics) that produces 1 mJ, ∼120 fs pulses at 790 nm at a 1 kHz repetition rate. The amplified pulses pump a dual-pass optical parametric amplifier (OPA) that generates tunable signal and idler beams in the infrared. Both the signal and idler beams pass through additional nonlinear crystals to produce tunable visible pulses via sum frequency mixing with the residual 790 nm fundamental light. The probe light in the experiment is split into signal and reference beams, which are detected on a shot-by-shot basis with matched Si photodiodes. The system is sensitive enough to measure absorption changes of $\sim$1 mOD averaging as few as 600 laser shots per point; the full details of our pump-probe spectrometer have been described elsewhere [6]. The pump beam intensity was controlled using calibrated neutral density filters.

3. Results and discussion

The absorption (solid curve) and PL (dashed curve) spectra of dilute BAMH-PPV that has been fully dissolved in *o*-xylene are shown in Fig. 1. The absorption spectrum of BAMH-PPV is quite similar to its better-studied cousin, MEH-PPV [5,14,15,19,20,28,29]; both substituted polymers have their absorption maximum shifted about 40 nm to the red of unsubstituted PPV. This indicates that the amino side groups are similar to alkoxy side groups in their electron-donating ability and in the degree of steric interactions they provide to break up of the planarity of the PPV backbone [35]. The PL spectra of BAMH-PPV (dashed curve) and MEH-PPV are also similar, except for the lack of distinct vibronic structure in the emission of BAMH-PPV. The PL quantum yield for BAMH-PPV in solution, determined to be 79 ± 2%, is quite a bit higher than that of MEH-PPV and is in fact the highest quantum yield we know of for a PPV-based polymer. Our choice of BAMH-PPV for studies of the relationship between polymer morphology and electronic properties is predicated not only on its large PL quantum yield but also on the fact that the amino side groups can be easily protonated by lowering the solution pH. This makes it possible to use pH as a "knob" to turn the neutral polymer into a polyelectrolyte without significantly altering the electronic properties of the PPV backbone. By changing solvents or adding polyvalent salts, the charging of polymer chains into ionomers can dramatically alter their solution conformation and degree of aggregation [37], leading to an entirely new method for controlling the interactions between chains of semiconducting polymers that we will describe in future work [38]. For the purposes of the present study, we will use only the unprotonated, neutral form of the polymer as a prototype for exploring the relationship between polymer solubility and the electrical properties of spin-cast polymer films.

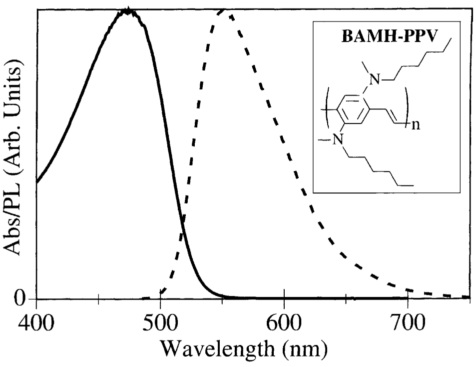

Fig. 1. Normalized UV–VIS absorption (solid curve) and 480 nm excited PL (dashed curve) of BAMH-PPV in a dilute, fully-dissolved solution of *o*-xylene. Inset: chemical structure of BAMH-PPV.

3.1. Heating to dissolve the polymer into solution

The basic question we ask in this study is how does the dissolution of a conjugated polymer affect the performance of devices made by casting films from a polymer solution? In this section, we focus on one relatively simple aspect of this question: when dissolving the polymer, does it matter if the solution is heated while stirring? To address this question, we will compare the properties of two BAMH-PPV solutions that were prepared identically, except that the polymer in one of the solutions was dissolved by heating to 50°C for 6 h while stirring ("heated" solution), while the polymer in the other solution was dissolved merely by stirring at room temperature ("unheated" solution). Given the relatively low molecular weight of the BAMH-PPV used in these experiments, our initial expectation was that after stirring for 2 days, heating would make little difference to the dissolution of the polymer in a "good"[1] solvent like *o*-xylene. Instead, we found that without heating, the polymer does not completely dissolve after 2 days of stirring, even though the solution was visibly similar to a fully dissolved solution. As we will argue below, incomplete dissolution leaves a large amount of interaction between the polymer chains; instead of behaving like isolated polymer chains in solution, the unheated samples behave more like a liquid suspension of small pieces of polymer film. We will also argue that the small pieces of coagulated polymer in the unheated solution survive the spin-casting process, leading to a rougher film morphology and thus poorer LED performance than comparable devices with films cast from the fully dissolved polymer in the heated solution.

Perhaps the most direct method to determine how well a polymer goes into solution is to measure the physical size of the dissolved polymer molecules. Dynamic light scattering can provide this information by measuring the diffusion constant(s) of the polymer chains in solution. Using the measured diffusion constants in the Stokes–Einstein relation and assuming a spherical polymer coil, light scattering allows the distribution of hydrodynamic radii (R_{H}) to be directly inferred [39]. Fig. 2 presents the size distributions that result from dynamic light scattering experiments on the heated (solid curve) and unheated (dashed curve) 1.0% w/v BAMH-PPV solutions. It is clear that the average size of the diffusing species is $\sim$23 nm in the unheated solution, but only $\sim$9 nm in the heated solution. The figure also shows that the size distribution is significantly narrower in the heated solution than in the unheated solution.

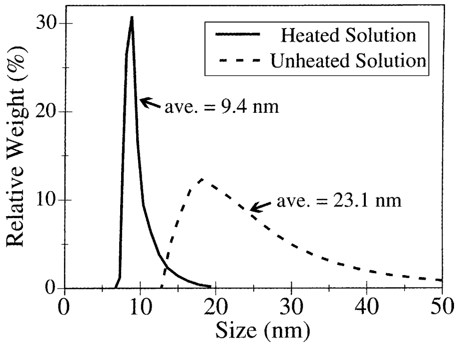

Fig. 2. Size distributions (hydrodynamic radii) from light scattering for BAMH-PPV solutions that have been stirred for 2 days at room temperature (unheated solution, dashed curve) or stirred for 2 days with heating at 50°C for 6 h (heated solution, solid curve).

How can we rationalize the differences in the size distributions of the two solutions? We expect the physical size of a polymer coil to scale as the polymer's molecular weight to a power slightly greater than 1 [40]. The hydrodynamic radius of MEH-PPV with an average molecular weight of 611 kg/mol was measured to be ~36 nm in xylene [41], and MEH-PPV with an average molecular weight of 535 kg/mol has an R_H of ~21 nm in chlorobenzene [5]. Given that we expect MEH-PPV and BAMH-PPV to coil in a similar fashion, a simple extrapolation says that the ~55 kg/mol BAMH-PPV chains in our experiments should have a size more like the ~9 nm R_H measured in the heated solutions rather than like the ~23 nm R_H seen in the unheated solutions. Thus, the logical assignment is that the narrow size distribution in the heated solution arises from scattering by individual polymer molecules, while the broad size distribution in the unheated solution results from scattering by aggregates of polymer molecules. By comparing to the scattering data in Fig. 2 to that on MEH-PPV [5,41], the ~23 nm average size seen in the unheated BAMH-PPV solution suggests an average aggregate molecular weight on the order of ~550 kg/mol, or roughly 10 BAMH-PPV polymer chains. The broad width of the distribution indicates that the solution is comprised of aggregates with a variety of sizes. Overall, the data of Fig. 2 lead us to conclude that heating the solution leads to complete dissolution of the polymer, while simply stirring at room temperature does not adequately dissolve the polymer and instead produces aggregated clumps of polymer chains suspended in solution. These results are quite similar to the work of Zheng et al. on polyaniline solutions [42].

Although the data in Fig. 2 indicate that the polymer remains aggregated in the unheated solution, it is not clear whether the chains are simply loosely tangled together or whether they are in contact so that there is a significant electronic interaction between neighboring chromophores. A quick comparison of the PL quantum yields, 79% in the heated solution but only 71% in the unheated solution, suggests that there are indeed interactions between the chromophores in the unheated solution that can partially quench the polymer's luminescence.[2] This difference in PL quantum yields correlates well with the lifetime of the emissive species measured in femtosecond pump-probe stimulated emission experiments, as shown in Fig. 3. In these experiments, the BAMH-PPV solutions are excited near their absorption maximum at 480 nm, and the gain due to stimulated emission near the PL maximum at 580 nm is monitored as a function of delay time between the pump and probe pulses. The circles in the upper and lower panels show the data at low excitation intensities for the heated and unheated solutions, respectively. The stimulated emission dynamics of both solutions fit well to single exponential decays as shown by the thin solid lines through the data points. The decay of the emission from the heated solution has a 1.18 ± 0.04 ns time constant, while that from the unheated solution has a 1.04 ± 0.04 ns time constant. Both these decay times are consistent with the measured PL quantum yields if the ra-

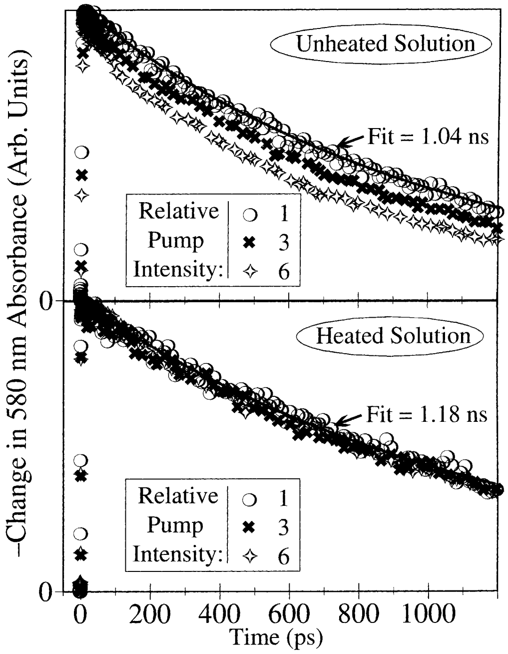

Fig. 3. Effects of heating during dissolution on the intensity-dependence of the excited-state decay of 1.0% w/v BAMH-PPV solutions. In both panels, the data show the magnitude of the stimulated emission at 580 nm following 480 nm excitation of the BAMH-PPV, normalized to the same maximum change in absorbance for ease of comparison. The circles show the data for the lowest excitation intensity, the crosses display the results with an excitation intensity three times that of the lowest, and the diamonds represent the data at an excitation intensity six times the lowest. The upper panel shows the data for solutions that were stirred at room temperature; the solid line is a single exponential fit to the low-intensity data with a time constant of 1.04 ns. The lower panel shows the data for solutions that were heated at 50°C for 6 h; the solid line is a single exponential fit to the low-intensity data with a time constant of 1.18 ns.

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[2] We expect that the overall quantum yield of the unheated solution is a superposition of the high quantum yield from the isolated chromophores present in the aggregates and the very low quantum yield from those aggregated chromophores with significant electronic interactions.

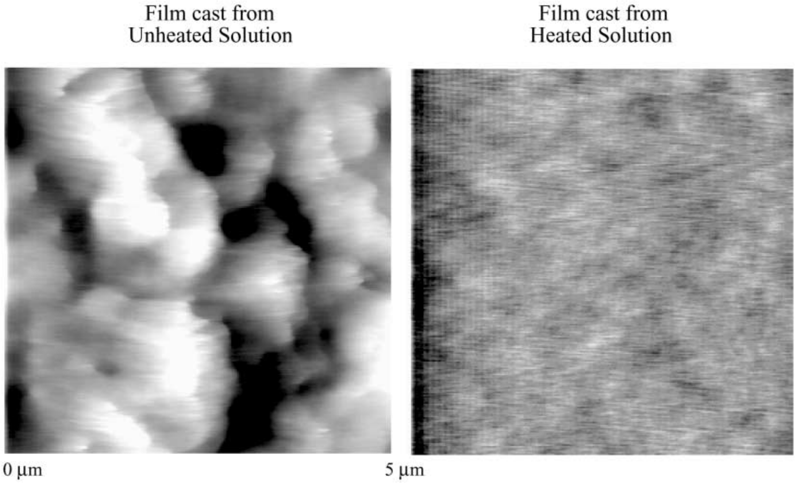

Fig. 4. The 5 μm × 5 μm scanning force micrographs of BAMH-PPV films cast from the solutions studied in Figs. 2 and 3. The right panel shows the topography of a film cast from a solution stirred for 2 days at 50°C; the black-to-white color scale represents height differences of 40 Å. The left panel depicts the topography of a film cast from a solution stirred for 2 days at room temperature; the black-to-white color scale represents height differences of 400 Å.

diative lifetime of BAMH-PPV is ~1.48 ns, well in accord with what is expected for phenylene vinylene polymers [43]. Thus, the PL quantum yields and lifetimes suggest that there is indeed an interaction between the aggregated polymer chains in unheated solutions.[2]

The crosses and diamonds in Fig. 3 also show another distinct difference in the emission behavior of the heated and unheated BAMH-PPV solution: the emission lifetime in the unheated solution depends on the excitation intensity, but the emission lifetime in the heated solution does not. It is well known that at high excitation intensities, excitons on neighboring chain segments can interact destructively, leading to an intensity-dependent decrease in the emission lifetime and quantum yield known as exciton–exciton annihilation [44–48]. Exciton–exciton annihilation is typically not observed for conjugated polymers in solution when the chains are isolated [46–48]; it is a phenomenon that appears to take place exclusively in films. Thus, the decrease in the emission lifetime with increasing excitation intensity in the unheated solution is a signature of film-like behavior: the aggregated polymer chains in the unheated solution behave photophysically as if they were in a film. The lack of intensity dependence for the emission lifetime of BAMH-PPV in the lower panel of Fig. 3 verifies that the polymer is completely dissolved and that the chains are isolated in the heated solution. Clearly, Figs. 2 and 3 show that the local environment of BAMH-PPV chains depends sensitively on whether or not the solution is heated during dissolution of the polymer.

How does changing the local environment of the polymer by heating (or not heating) the solution during dissolution affect the morphology of the films cast from these solutions? Fig. 4 presents scanning force micrographs of BAMH-PPV films cast from the two solutions whose properties were explored in Figs. 2 and 3. Both scans show an area 5 μm on a side. The color change from black to white in the left portion of the figure (film cast from the unheated solution) represents a height difference of 400 Å; the same color scale in the right portion of the figure (film cast from the heated solution) indicates a height change of only 40 Å. The two images make it clear that the surface topography of the BAMH-PPV films changes dramatically depending on whether or not the solution was heated. The surface of the film cast from the unheated solution is rough on many length scales: the film is clearly comprised of a network of polymer pieces that are stuck together. The typical height of these pieces is about half the color scale in the scan, or ~200 Å, in good agreement with the size of the aggregated clumps of polymer in solution measured by light scattering. The surface of the film cast from the unheated solution, in contrast, is quite smooth, especially considering that the color scale in the image is expanded by a factor of 10 relative to that for the unheated solution. Altogether, Fig. 4 suggests that films cast from the unheated solution form by the precipitation of suspended BAMH-PPV aggregates, while films cast from the heated solutions form by the spreading of individual polymer chains followed by loss of the solvent. We also note that the difference in film topographies seen in Fig. 4 fits well with our previous work, where we were able to correlate the presence of surface features on MEH-PPV films with the degree of aggregation in solution [6,18].

Perhaps the most important ramification of Fig. 4 is that a simple thing like whether or not the solution is heated while the polymer is dissolving affects the film morphology enough to significantly alter the electronic structure of these materials. The UV–VIS absorption and PL of the film cast from the unheated solution show a red tail indicative of aggregates [5,6] that is absent in the films cast from the heated solution (not shown). This change in electronic structure also affects the performance of light-emitting devices based on these materials. The aggregated clusters that make up the unheated films are in poor electrical contact with each other, leading to low injection currents and poor carrier mobilities relative to films cast from the heated solution. Moreover, the efficiency of devices based on unheated films is lower than those based on heated films. This could possibly be a direct result of the lower emission quantum yield of the aggregated chromophores, or it might be an indirect result of the poor carrier mobility which causes recombination to take place close to one of the electrodes, quenching the emission. Overall, it should not be surprising that use of incompletely dissolved polymer solutions leads to devices with inferior performance.

3.2. Heating the already-dissolved polymer in solution

The results of the previous section make it clear that it is critical to guarantee that a conjugated polymer is completely dissolved before using the solution to cast films for use in optoelectronic devices. We have already seen that heating the solution while stirring is sufficient to ensure complete dissolution of the polymer; the two questions we consider in this section are: can the polymer ever be completely dissolved without heating the solution, and does heating the solution make any difference once the polymer is already dissolved? Determining the answer to the first of these questions is straightforward: we continued to stir the unheated BAMH-PPV solution at room temperature until the light-scattering signature and the emission dynamics were the same as those for the heated solution. We found that after 2 weeks of continuous stirring at room temperature, there were no discernable differences between the heated and unheated solutions. The answer to the second question, however, turns out to be much subtler. What we will show below is that films cast from fully dissolved polymer solutions that had been heated, while stirring for 2 days prior to use ("dissolved-and-heated" solutions) have different optical and electrical properties than films cast directly from fully dissolved solutions prepared without heating.

At first, the fact that heating an already-dissolved BAMH-PPV solution can affect the resultant film seems surprising. There appear to be no changes in the UV–VIS absorption or PL spectra upon heating a fully dissolved solution, and heating a fully dissolved solution has little effect on the PL quantum yield. We know, however, that only subtle changes in the solution conformation of a conjugated polymer are needed to alter the degree of interaction between chains. Based on the evidence presented below, we believe that heating a fully dissolved BAMH-PPV solution causes the chains to become slightly more extended, increasing the probability for interchromophore interactions. This heating-induced entanglement of the interacting chains likely lies in a local thermodynamic minimum in conformation space: the results presented are reproducible, even when the heated-and-dissolved solutions have been sitting at room temperature for weeks, indicating the existence of a barrier to breaking up the heating-induced interchain contact. The situation is analogous to our previous work on MEH-PPV: what we find is that films cast from the fully dissolved BAMH-PPV solutions behave like MEH-PPV films cast from tetrahydrofuran (THF), while films made with the dissolved-and-heated BAMH-PPV solutions act more like MEH-PPV films cast from chlorobenzene [5–7].

Fig. 5 presents the results of intensity-dependent femtosecond pump-probe stimulated emission experiments on BAMH-PPV films cast from fully dissolved solutions (upper panel), and from dissolved-and-heated solutions (lower panel). As discussed in the previous section, exciton–exciton annihilation causes the emission lifetime to decrease with increasing excitation intensity. Since excitons are much more likely to encounter each other in films that have a higher degree of contact between chromophores, films with a higher degree of interchain interactions will have a larger decrease in emission lifetime for a given increase in excitation intensity. At the lowest excitation intensities, the circles in Fig. 5 show that the emission dynamics of the films cast from the fully dissolved and dissolved-and-heated solutions are identical within the signal-to-noise, suggesting that the chromophores in both films are in roughly similar environments. At the higher excitation intensities shown by the crosses and diamonds in Fig. 5, however, the emission lifetime of the film cast from the fully dissolved solution is only just beginning to decrease, while the emission of the films cast from the dissolved-and-heated solution has already been significantly quenched. This difference signifies that the degree of interactions between chains is different in the two films.

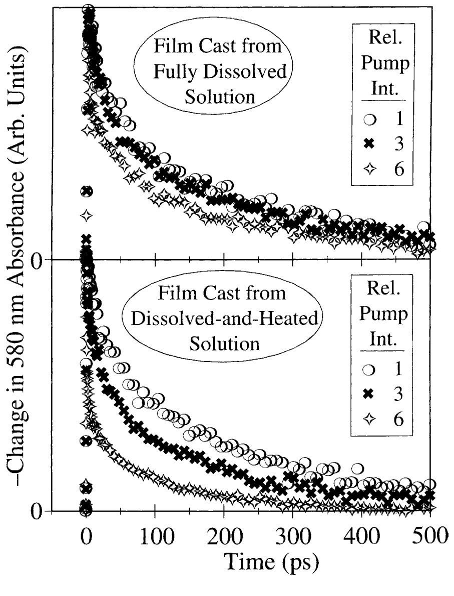

Fig. 5. Effects of heating fully-dissolved solutions on the intensity-dependence of the excited-state decay of BAMH-PPV films. The symbols have the same meaning as in Fig. 3. The upper panel shows the data for a film cast from a fully dissolved (stirred at room temperature for 2 weeks) solution. The lower panel shows the data for a film cast from a fully dissolved solution that was heated to 50°C for 2 days prior to spin-coating.

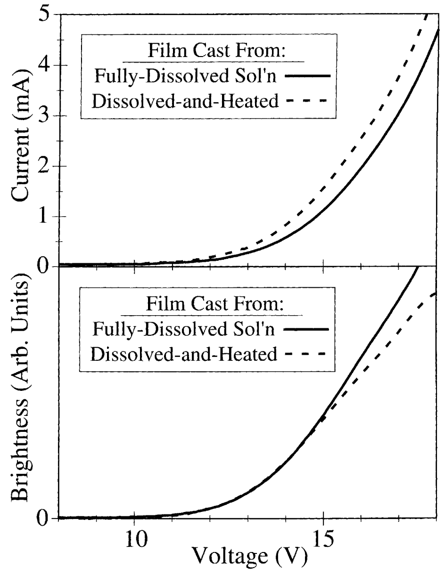

Fig. 6. The dependence of the current (upper panel) and brightness (lower panel) on applied bias for ITO/BAMH-PPV/Mg:Ag sandwich-structure LEDs when the BAMH-PPV active layer is cast from: a fully-dissolved solution (solid curves) or a fully-dissolved solution that had been heated to 50°C for 2 days prior to use (dashed curves). The data in this figure come from the same films studied in Fig. 5.

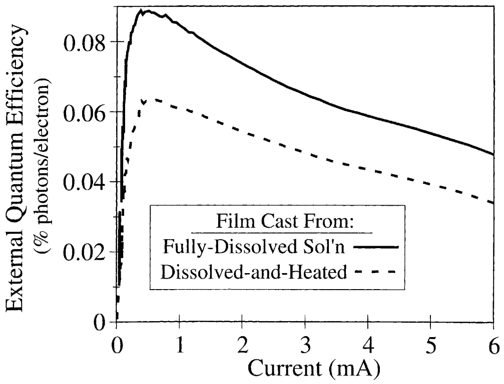

Fig. 7. Absolute external quantum efficiency (in % photons/electron) for the BAMH-PPV devices whose current and brightness characteristics were presented in Fig. 6, with the device based on the film cast from the fully-dissolved solution shown as the solid curve, and the device based on the film cast from the dissolved-and-heated solution depicted as the dashed curve.

Thus, even though only minor differences in surface morphology are seen with scanning force microscopy, Fig. 5 provides strong evidence that heating an already-dissolved BAMH-PPV solution enhances the electronic interaction between polymer chains.

While Fig. 5 makes it clear that heating the fully dissolved solution before casting can change the degree of exciton–exciton annihilation in a BAMH-PPV film, a more important question is whether or not heating the solution affects the behavior of light-emitting devices. In Fig. 6, the upper panel displays current–voltage (*I*–*V*) curves and the lower panel shows brightness–voltage (*L*–*V*) curves for ITO/BAMH-PPV/Mg:Ag sandwich-structure LEDs. The solid curves show the data for devices based on films cast from a fully dissolved solution, while the dashed curves correspond to devices with films made from a dissolved-and-heated solution. The upper panel of Fig. 6 demonstrates that the devices fabricated from the dissolved-and-heated solutions have a slightly higher working current than their counterparts based on the fully dissolved solutions. This is a direct result of the higher degree of interchain interactions in the dissolved-and-heated films: charge carriers are more mobile when there is better contact between the polymer chains, allowing for higher current injection at a given voltage [6,7].

While the increased interchain interactions afforded by making LEDs from dissolved-and-heated solutions lead directly to improvements in working current, they do so at a price. The bottom panel of Fig. 6 shows that despite the lower current, the devices based on the film cast from the fully-dissolved solution actually have a higher brightness than the devices based on the dissolved-and-heated solution. This result is quantified better in Fig. 7, which shows the absolute external quantum efficiency (percent of photons per electron) of the two devices whose *I*–*V* and *L*–*V* curves are shown in Fig. 6. It is clear that at all currents, the efficiency of the devices based on films cast from fully dissolved solutions is ~25% higher than the efficiency of the devices based on films cast from the dissolved-and-heated solutions. The efficiency differences in these otherwise-identical devices are a direct reflection of differences in the degree of interchain interactions in the two films [6,7]. Even though fewer injected carriers can find their way into the interior of the film cast from the fully dissolved solution, those that do tend to recombine into excitons on isolated chain segments, producing luminescence with high efficiency. Many more carriers flow through the devices based on films cast from the dissolved-and-heated solution, but a significant fraction of those that recombine do so in regions with a high degree of interchain contact, leading to poorer overall luminescence efficiency. Overall, Figs. 5–7 make it clear that simple differences in solution processing, such as heating the solution after the polymer is fully dissolved, can be used to trade off device performance characteristics such as carrier transport and luminescence quantum efficiency.

4. Conclusions

In summary, we have shown that both the electronic properties and the morphology of conjugated polymer films depend on the details of how the polymer is dissolved into solution. When the polymer is not completely dissolved, the solution behaves like a suspension of small fragments of polymer film, as evidenced by large particle sizes in light scattering and the presence of exciton–exciton annihilation in solution. Films cast from the incompletely dissolved solutions are simply agglomerations of the suspended polymer fragments, leading to a rough surface morphology and poor performance in light-emitting devices. The polymer can be completely dissolved either by heating the solutions while stirring for a relatively short amount of time (2 days for our BAMH-PPV samples), or by stirring for a much longer time at room temperature (2 weeks for BAMH-PPV). Although heating the solutions helps the polymer to dissolve, heating also produces solutions that have more interactions between polymer chains than solutions prepared simply by stirring at room temperature for long times. The enhanced interchain interactions created by heating the dissolved solutions lead to polymer films with a higher degree of exciton–exciton annihilation, and produce polymer LEDs with higher injection currents but lower luminescence quantum efficiencies.

All of the above results have important implications for the construction of optoelectronic devices based on conjugated polymer films. For example, to maximize the efficiency of a polymer-based light-emitting device, the best solution preparation route is to stir the polymer at room temperature until it is fully dissolved (after all, heating the solutions leads to lower device efficiency). How long does a polymer need to be stirred to ensure full dissolution? The answer to this question is not necessarily obvious. In this paper, we used relatively low molecular weight BAMH-PPV in a good solvent, *o*-xylene, and yet it took nearly 2 weeks of continuous stirring at room temperature to achieve complete solubility. For higher molecular weight polymers or solutions made with slightly poorer solvents, dissolution might take even longer or may never be complete by simply stirring at room temperature. For heated solutions, the length of time the solution is re-equilibrated at room temperature before use should also alter the amount of interchain interactions and affect the performance of the resulting devices. Polymer solutions that are left to sit at room temperature without stirring may again start to coagulate, so that devices prepared at different times from the same solution may behave quite differently. Clearly, dissolution of a conjugated polymer is something that cannot be taken casually; for each polymer/solvent combination, we believe it is important to do a series of studies to ensure that the casting solution is fully dissolved or has the desired degree of interchain interactions.

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