Device performance and polymer morphology in polymer light emitting diodes: The control of thin film morphology and device quantum efficiency

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We present the results of a systematic study on how the processing conditions of spin casting affect the morphology of polymer thin films, and how the morphology affects polymer light-emitting diode (LED) performance. The absorption peaks of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene) (MEH-PPV) thin films, which reflects the conjugation of π electrons, are strongly correlated to the spin-casting conditions. At high spin speed, better conjugation is observed. In addition, the photoluminescence emission peak of MEH-PPV films at ~630 nm has a strong correlation to polymer aggregation. By proper selection of organic solvents, polymer solution concentrations, and spin speeds, we are able to control the aggregation of the polymer chains. Subsequently, we are able to control the emission color and the quantum efficiency of the MEH-PPV LEDs by simply adjusting the spin-casting conditions. Although spin casting is the most commonly used technique for the preparation of polymer thin films, our finding suggests that the thin-film preparation, and thus the formation of polymer morphology, is a much more complicated process than previously assumed. © 2000 American Institute of Physics. [S0021-8979(00)02109-5]

I. INTRODUCTION

Since the first successful fabrication of a polymer light emitting diode (PLED) using poly(p-phenylenevinylene) as the active material,¹ there has been a widespread research interest in conjugated polymers. The lightweight, flexibility, ease of processing, and unique electrical and photonic semiconducting properties are among the most attractive characteristics of this class of materials. Since some of these materials can be obtained in solution form, spin casting has become the most commonly used technique for obtaining uniform thin films of these materials. It is often noticed that the luminescence spectra, both photoluminescence (PL) and electroluminescence (EL), of polymer films are somewhat different when the film thickness varies. This observation is often associated with the microcavity effect,^{2,3} which is an optical effect, while the differences in the film morphology and polymer chain aggregation, primarily controlled by the spin-casting conditions (the concentration of the polymer solution, the solvent, and spin speed, etc.) are usually ignored. Baltchford *et al.*⁴ have observed that the PL spectrum of a poly(*p*-pyridyl vinylene) powder is different from that of the spin-cast film. In addition, films that are cast with different solvents also showed different PL spectra.⁴ This observation suggests that the morphology or the aggregation of polymer chains has a remarkable effect on its emission spectrum. However, the effects of the spin-casting conditions on the film morphology, and thus the physical properties of the film, have not been systematically studied. Since spin casting has come one of the most commonly used techniques for preparing polymer thin films, it will be particularly important to have a complete understanding of the nature of polymer chain aggregation, the relationship between the morphology and the processing conditions, and their influence on the electronic and photonic properties of polymer thin films. Furthermore, the device performance of polymer LEDs will be optimized by better device fabrication process.

The photoluminescence properties of conjugated polymers and the role of aggregation in these properties have been heavily investigated in recent years.^{4–8} It is generally believed that both the electroluminescence and the photoluminescence of the polymer films originate from the same excited state.^{1,9} It is also believed that the aggregation of polymer chains enhances the excimer formation, which reduces the PL quantum efficiency.¹⁰ In this article, we produce evidence to suggest that proper aggregation may increase the quantum efficiency of polymer LEDs. We have also found evidence to suggest that the emission peak of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene) (MEH-PPV) films at $\lambda_{max}{\approx}630\,\text{nm},$ which has been previously associated with the vibronic structure, has a strong correlation to different aggregation states of the polymer chains. The detailed experimental approach and results are discussed below.

II. EXPERIMENT

The polymer LEDs discussed in this article consist of a polymer active layer sandwiched between a cathode and an anode. For this study, calcium was used as the cathode, and 3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT)/ITO was used as the anode unless otherwise indicated. MEH-PPV was chosen as the active material in our

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FIG. 1. The normalized absorption spectra for MEH-PPV films spin cast on glass plates using 0.3 and 1 wt % MEH-PPV solutions. The spin speed used was 8000 rpm.

study.¹¹ The molecular weight (M_w) is ~1000000 as determined by gel permeation chromatography which was calibrated using polystyrene standards. The ITO substrates underwent a routine cleaning procedure, which included sonication in detergent followed by repeated rinsing in deionized water, acetone and isopropanol, and finally treated with ultraviolet (UV) ozone. PEDOT was first spin cast onto an ITO/glass substrate at a spin speed of 4000 rpm, which corresponds to a thickness of 85 nm, and baked at 120 °C for 2 h before spin casting the MEH-PPV film. The cathode of the polymer LED was formed by the thermal evaporation of Ca and Al from tungsten boats at a pressure of around 1 $\times 10^{-6}$ Torr. The thickness of the calcium layer and the aluminum protective layer was approximately 200 and 1000 Å, respectively. The diode area was 12 mm². MEH-PPV solutions were prepared and spin cast in an inert nitrogen gas environment. The EL and PL emission spectra were obtained from an S2000 fiber optic spectrometer by Ocean Optic Inc. The Commission International de L'Eclairage (CIE) coordinators were measured using a Spectra-scan PR 650. The UV-Vis absorption spectra were recorded on a HP 8453 spectrophotometer. For easy comparison, the absorption spectra as well as the EL spectra were normalized. The film thickness data were measured using an Alphastep profilometer. The viscosity was measured at ambient temperature using a DV-II+ viscometer produced by Brookfield Inc. Contact angles were determined on a contact angle meter from March Instrument, Model Cam-F1 at room temperature.

III. RESULTS AND DISCUSSIONS

A. UV-visible absorption spectrum

The morphological dependent phenomena were first observed by comparing the UV–Vis absorption spectra of the polymer thin films prepared from different concentrations of polymer solutions as well as different spin speeds. The λ_{max} of a polymer film obtained from a more dilute solution and/or spun from a higher spin speed is significantly red-shifted. Figure 1 shows the absorption spectra of two films spun at the same speed (8000 rpm), but at two different concentrations: a thinner film (180 Å) using a 0.3 wt % MEH-PPV solution, and a thicker film (900 Å) using a 1



FIG. 2. The normalized absorption spectra for MEH-PPV films spin cast on glass plates using different spin speeds (2000 and 8000 rpm). The MEH-PPV solution used was 0.7 wt % in cyclohexanone.

wt % MEH-PPV solution in cyclohexanone (CHO). For easy comparison, the spectrum of the thinner film is normalized. It can be easily seen from Fig. 1 that the absorption of the polymer film spun with the more dilute solution is significantly redshifted (λ_{max} =510 nm) as compared to that spun with the more concentrated solution (λ_{max} =496 nm).

Similar spectral shifts were also demonstrated by using constant polymer concentration (0.5–0.8 wt%) but different spin speeds. For example, a 0.7 wt% solution spun at 2000 rpm resulted in a film with an absorption peak at λ_{max} =499 nm (700 Å), whereas the same solution spun at 8000 rpm resulted in a film with λ_{max} =509 nm (300 Å) (Fig. 2). At higher (≥ 1 wt%) or lower (<0.4 wt%) concentrations, however, the UV–Vis spectra were not observed to shift with spin speed. These effects are reproducible in other solvents such as tetrahydrofuran (THF), chloroform, *p*-xylene, etc.

It is commonly observed that polymers tend to form aggregates in polymer solutions of sufficiently high concentration.¹² The origin of aggregation is the interchain attraction forces. Since these interactions are short-range forces, the polymer chains are isolated in dilute solution, thus these intermolecular forces can be neglected. It is expected that the probability for the coiled polymer chains to penetrate into each other is small. As the concentration increases and the distance between the polymer chains become smaller, these interchain forces become more significant. As a result, polymer coils start to entangle with each other to form "loose aggregates." It is predicted that further increases in the concentration will eventually result in heavy interpenetration of the polymer chains, or the formation of "strong aggregates." From this point of view, one would expect that these interactions are maximized in the solid state when the polymer chains are densely packed. In fact, the formation of aggregates in thin films is well documented for various polymers.¹³

From the above discussion, one would expect that the morphology of a spin-cast film depends on the relative strength of the cohesive force of the solution and the cen-



FIG. 3. The reduced viscosity of MEH-PPV solution (cyclohexanone as solvent) vs the concentration of the polymer solution. The curved region represents the concentrations for loose aggregation (CLA).

trifugal force asserted by the spinning. When the centrifugal force is comparable to the cohesive force of the solution, one would expect to see a spin speed dependence of the film morphology. In this regard, the viscosity of the polymer solution can, to a certain extent, reflect these intermolecular forces. That is, higher solution viscosity suggests higher intermolecular forces, and vice versa. A plot (Fig. 3) of the reduced viscosity (η/η^*) of the polymer solution, where η is the viscosity of the MEH-PPV solution and η^* (1.85 cP) is that of the pure solvent (CHO) at ambient temperature, versus the polymer concentration (wt%) clearly reveals these three concentration regions. It can be seen from this plot that at lower concentrations (<0.4%), the plot is nearly linear. The slope of the curve is 2.18, corresponding to an intrinsic viscosity of 1.87. At higher concentrations (>0.9%), the plot is also linear, except that the slope is much larger (11.2). In the central region (0.4% - 0.9%), however, the plot is significantly curved. We found that this region corresponds to the concentrations for loose aggregation (CLA) of the polymer chains, which was proposed earlier. It is in this region that the morphology, or the aggregation state of the polymer films, is dependent on spin speed. It should be pointed out that the CLA is dependent on the molecular weight as well as the solvent used. For example, the CLA for our MEH-PPV sample ($M_w \approx 1\,000\,000$) in THF is approximately 0.3%-0.7% (wt %), which is slightly different from that in cyclohexanone.

Therefore, the fact that no spin speed dependence was observable for films prepared with concentrations >1 wt% can be explained by the formation of such strong aggregates, that spinning the solution at 8000 rpm is insufficient to break the aggregates apart. In addition, high concentrations also result in heavy entanglement of the polymer chains, which decrease the conjugation of the polymer backbone and result in a small λ_{max} (496 nm). As the concentration decreases, the adhesive forces of the polymer solutions will decrease, and thus the aggregates become "looser." It is therefore expected that such loose aggregates can be more easily separated by the centrifugal force. In addition, the centrifugal



FIG. 4. The normalized EL emission spectra for MEH-PPV films spin cast at different spin speeds. The arrow indicates the decrease of spin speed, 8000, 4000, 2500, and 1500 rpm.

force and the radial flowing of solvent will also tend to stretch the polymer chains to the more extended conformation. If the centrifugal force is large in comparison to the cohesive force of the solutions, it is expect that high spin speeds will lead to a spectral redshift in the absorption spectrum of the resulting polymer films as shown in Fig. 2.

In dilute solutions (<0.4 wt %), the λ_{max} of the resulting films is usually close to 510 nm and is nearly independent of the spin speed (within 1000–8000 rpm), suggesting that the polymer chains can be more easily stretched to the more extended form. In addition, polymer films spun at these lower concentrations are usually so thin that they dry almost instantly during the spin-coating process, and therefore this more extended (and thus more conjugated) conformation is "locked" upon vaporization of the solvent. Therefore, it is not surprising that films spun at these concentrations always have the highest $\lambda_{max}(510 \text{ nm})$.

B. Electroluminescence and photoluminescence spectra

1. MEH-PPV processed using aromatic solvents

The electroluminescence and photoluminescence spectra of spin-cast films are also morphology dependent. It is found that within the range of the CLA, the EL and PL spectra of spin-cast MEH-PPV films are strongly dependent on spin speed. Such an example is shown in Fig. 4. It is consistently observed that when the polymer solution is cast at high speeds (e.g., 4000-8000 rpm, 0.7 wt%), the resulting devices have a strong yellow EL emission peak (λ_{max} \approx 575 nm) and a weak red shoulder (\sim 630 nm, Fig. 4). The spectrum of this yellow emission is similar to the PL spectrum of a dilute MEH-PPV solution, which has been assigned to the unaggregated single chain exciton emission.⁷ As discussed earlier, it is expected that films resulting from high spin speeds should mostly consist of the more extended and less coiled polymer chains. Therefore, it will be reasonable to suggest that this yellow EL emission (\sim 575 nm) observed in films is also due to the single chain exciton from the more extended polymer chains. As the spin speed decreases, the spectrum redshifts, and the intensity of the red emission peak (630 nm) increases (refer to Fig. 4). This effect is also observable in aromatic solvents such as chlorobenzene (CB), 1,2-dichlorobezene (DCB), toluene, and p-xylene, and is independent of the applied electric field. Similar effect can also be demonstrated in the photoluminescence spectra of the corresponding thin films. However, these changes of the emission spectra are limited to the polymer solution with concentration within the CLA. At concentrations above the CLA, the red emission (630 nm) always dominates. In contrast, the yellow emission (575 nm) dominates at concentrations below the CLA.

Levitsky and co-workers¹⁴ have also observed similar spectral changes when they compared a poly(p-ethynylene) thin film prepared by Langmuir-Blodgett technique with that prepared using the spin-casting technique. They suggested that the observed spectral changes were the result of interactions (π - π stacking) between the polymer backbones in the thicker film. Although the 630 nm peak in the emission spectrum of the MEH-PPV film has been traditionally considered as the intrinsic vibronic structure of the spectrum, the similarity between the two systems led us to consider the possibility that this emission was resulted from another species, i.e., an excimer- or exciplex-like interchain species. As discussed earlier, the film morphology varies with spin speed when the polymer concentration is within the CLA. As the spin speed decreases, more and more loose aggregates survive the centrifugal force. On the other hand, lower spin speeds also result in thicker films, in which the rate for solvent evaporization from inside the film is slower. This allows the polymer chains to have more time to relax into a more thermodynamically favorable conformation rather than being locked in an unfavorable conformation caused by the solvent molecules and the centrifugal force. Since the polymer coils will tend to penetrate and entangle each other more heavily as the concentration increases, it is expected that slow evaporation of the solvent (and thus a slow increase of the polymer concentration within the film) should favor the entanglement of the polymer chains and the formation of stronger aggregates, which should favor the formation of the interchain species. Therefore, the assignment of the red emission peak to the interchain species reasonably explains the above experimental observations. However, more experiments are required to further confirm this statement.

It is generally observed for many polymers that the aggregation of the polymer chains leads to a spectral redshift in their absorption spectra.¹³ Quantum mechanics calculations also suggest that a $\pi - \pi$ stacking of the polymer backbones can redshift the absorption spectrum.¹⁵ If this explanation also applies to MEH-PPV films, a spectral redshift in the absorption spectrum is expected as the aggregation of a MEH-PPV film increases. However, this prediction is inconsistent with our experimental observations, in which the absorption spectrum of a film resulted from a lower spin speed, implying denser aggregates, is blueshifted. One possibility that could account for this contradiction is to suggest that the $\pi - \pi$ stacking of the polymer backbones in MEH-PPV is hindered in the ground state, probably due to the bulky 2-ethyl-hexyloxy side chains. Such interactions become more pronounced only in the excited state.

The PL decay dynamics of MEH-PPV in film as well as in solution have been well documented.^{8,16} More recently,

Rothberg and co-workers^{8,17} have reported that the PL decay dynamics of the MEH-PPV film at room temperature is nonexponential, which consists of a fast component (τ \approx 300 ps) and a slower component. They suggested that this was probably due to the inhomogeneity of emission rates and to the dynamics of excited-state diffusion to the quenching defects. An alternative interpretation for this dynamic behavior, based on our results, is that the slower component could be due to the interchain species (we assign this interchain species as Ex-I in this article). Samuel et al.¹⁶ have shown that the kinetics of the MEH-PPV films at 600 nm is dominated by an exponential decay with a time constant of 580 ps, which is significantly different from that reported by Rothberg and co-workers.^{8,17} Although we cannot rule out the possibility that this discrepancy is due to the intrinsic difference between the polymer samples used by the two groups, the fact that they have markedly different PL spectra cannot be ignored. The PL spectrum reported by Samuel et al.¹⁶ closely resembles the EL spectrum of our orange-red devices, while that reported by Rothberg and co-workers is similar to that of a yellow device. It is therefore very likely that the spectrum of Samuelet al. was dominated by the Ex-I species, while that reported by Rothberg and co-workers contained more emission from the single chain exciton. Thus, it is not surprising that the Ex-I dominated spectrum decays significantly slower than the typical single chain exciton decay (300 ps) observed in dilute solutions and films.18-20

We have attributed the above spectral changes to the differences in film morphology. However, it is well known that the EL emission from a LED could be modulated by the microcavity effect and this has been used for color tuning in polymer and organic light-emitting diodes.^{2,3,21,22} These devices usually need electrodes with good reflectivity (e.g., gold electrodes) in order to achieve a pronounced microcavity effect. Wittmann et al.2 indicated that the microcavity effect is less significant in devices using ITO electrodes. More recently, So and Choi²³ have demonstrated the microcavity effect in ordinary OLEDs with only one reflective electrode. In all of these cases, the microcavity devices are characterized by thickness dependent emission spectra. In order to check for this possibility, devices of the same film thickness but spun at different spin speeds are studied. Shown in Fig. 5 are the EL spectra of a regular "single layer" device (curve-a) and that of a "multilayer" device (curve-b) with the same film thickness. These devices were prepared using the same polymer solution (0.7%, CHO) but the polymer films were coated differently. In the single-layer device, the polymer film was formed by a single spin-casting procedure at a lower spin speed (1000 rpm, film thickness 1000 Å). For the multilayer device, the film was obtained by nine consecutive spin castings using the same polymer solution, but at higher spin speed (7000 rpm, film thickness 1000Å). Based on the above discussion, it is expected that the multilayer device should have stronger yellow emission since it is spun at higher speed, which is indeed observed experimentally (Fig. 5).

When comparing the EL spectrum of the above multilayer device to that of a regular single layer device spun



FIG. 5. The normalized EL emission spectra for a "single layer" (curve *a*) and a "multilayer" (curve *b*) device. Curve a: the polymer film was formed by a single spin casting from a 0.7% MEH-PPV solution at 1000 rpm. Curve *b*: The film was formed in nine consecutive spin casting at 7000 rpm using the same solution. The thickness of both films is approximately 1000 Å.

at the same spin speed, the former has a stronger red emission than the latter (refer to Figs. 4 and 5), suggesting that more interchain species are presented in the multilayer device. This is not surprising since during every secondary spin coating, some of the polymer molecules near the surface will be redissolved by the added solution, which produces locally higher concentrations (near the interface) and thus more aggregated species. Therefore, repeated casting of the MEH-PPV solution intensifies the red emission.

2. MEH-PPV processed using nonaromatic solvents

In nonaromatic solvents such as THF and $CHCl_3$, the spin speed dependence of the emission spectrum is more complicated. At the lower end of the CLA, the observed spin speed effect is similar to that observed for aromatic solvents and cyclohexanone (high spin speed results in stronger yellow emission and low speed results in stronger red emission). Such an example using a 0.4% polymer solution in



FIG. 7. The spin speed dependent EL spectra (normalized) of MEH-PPV films observed at the higher end of CLA (0.7 wt %) in THF. The film thicknesses are 1400 Å (2500 rpm), 1200 Å (4000 rpm), 1000 Å (6000 rpm), and 800 Å (8000 rpm).

THF (CLA $\approx 0.3\% - 0.7\%$, in THF) is shown in Fig. 6. A notable result is that this effect is reversed at the higher end of the CLA. For example, spin coating a 0.7 wt % MEH-PPV solution (THF) at high spin speeds (e.g., 6000-8000 rpm) resulted in the orange-red devices while at lower speeds (e.g., ≤ 2500 rpm) resulted in yellow dominated devices (Fig. 7). The absorption λ_{max} of the film is almost unaffected by the spin speed at this concentration (0.7 wt%, THF). A similar effect is also observed when the polymer was spun with CHCl₃. This "reversed effect" clearly indicates that both the molecular conformation in the solution and the morphology of the film are substantially different from those obtained using aromatic solvents and cyclohexanone. Schwartz and co-workers⁷ have already observed by light scattering experiments that the MEH-PPV aggregates in THF and chlorobenzene (CB) have different sizes. Heeger and co-workers²⁴ also indicated that the polymer films spun with THF and *p*-xylene have different morphology. All these sug-



FIG. 6. The spin speed dependent EL spectra (normalized) of MEH-PPV films observed at the lower end of CLA (0.4 wt %) in THF.

gest that the solvation effect plays an important role in the morphology of the spin-cast films, which will be discussed in more detail below.

C. The solvation effect

1. The aggregation of polymer chains

The driving force for the mixing of two species (1 and 2) is the loss of free energy ($\Delta G_M < 0$), which is determined by

$$\Delta G_M = \Delta H_M - T \Delta S_M < 0, \tag{1}$$

where *T* is the absolute temperature of the system, ΔH_M the change in enthalpy, and ΔS_M the change in entropy due to mixing. Generally, ΔS_M is always positive, while ΔH_M can be either positive or negative. When dissolved in an ordinary organic solvent, the polymer chains should achieve the conformations that can minimize the free energy (largest negative ΔG_M). In other words, the thermodynamically stable conformation should have the minimum ΔH_M and the maximum ΔS_M . Generally, the major contribution in ΔH_M is the internal energy change ΔE_M due to the physical mixing of the two components, which is determined by

$$\Delta E_M = (\epsilon_{1-1} + \epsilon_{2-2})/2 - \epsilon_{1-2}, \qquad (2)$$

where ϵ_{1-1} , ϵ_{2-2} , and ϵ_{1-2} are the interaction energies between the 1-1, 2-2, and 1-2 pairs, respectively. Usually, ΔE_M and ΔH_M are small when the two components are similar in structure, and large when the two components are dissimilar. For example, the heats of mixing for the aromatic/aromatic or alkane /alkane systems are usually either equals to zero or a very small (several tens J/mol) positive number.25,26 For aromatic/alkane systems, however, the ΔH_M is significantly larger (hundreds J/mol).²⁷ Since the chemical structure of the MEH-PPV molecule consists of an aromatic polymer backbone and many ethyl-hexyloxy side chains, it is expected that aromatic solvents can solvate the polymer backbone better than the alkyl side chains. As a result, the aggregation of the alkyl side chains may lower the ΔH_M . It is therefore expected that strands of MEH-PPV aggregate lengthwise in the form of a spiral cylinder; the aromatic backbones of the long molecules form the shell of the cylinder due to greater solvation. The alkyl side chains of the molecules point radially inwards inside the cylinder (Fig. 8).

Results from molecular dynamic calculations suggest that a twisted conformation shown in Fig. 9 is the most stable conformation. Such a conformation may also benefit from gaining more configurational entropy since the side chains have higher freedom of rotation in comparison with those shown in Fig. 8. However, the twisting of the polymer backbone will interfere with the conjugation along the chain and thus lead to an extra internal energy increase (ΔE_{coni} >0). Therefore, the final conformation of the polymer chains should reflect a good balancing of all these factors in order to reach the minimum free energy. In this regard, this twisted conformation will not be the best choice unless $2\epsilon_{1-2}$ is much larger than the sum of ϵ_{1-1} and ϵ_{2-2} [Eq. (2)] so that ΔE_M (or ΔH_M) is sufficiently negative to compensate ΔE_{coni} . Although the exact ΔE_M or ΔH_M values for MEH-PPV dissolved in many ordinary organic solvents are



FIG. 8. The aggregation of MEH-PPV molecules in an aromatic solvent results in the aromatic polymer backbone facing the solvent and the side chains pointing inwards towards each other.

not known at this time, a qualitative estimation can be made based on the heats of mixing for similar, smaller molecular systems. For example, mixing many aromatic compounds with THF or CHCl₃ have relatively large negative heats of mixing (hundreds to nearly one thousand J/mol),²⁷ suggesting especially strong solvent-solute interactions (large ϵ_{1-2}). In contrast, the heats of mixing between two aromatic compounds are usually either zero or only slightly positive. Therefore, the twisted conformation shown in Fig. 9 is more



FIG. 9. Nonaromatic solvents result in the twisted conformation/aggregation of the MEH-PPV molecules.

likely to be attained in THF and CHCl₃ rather than in the aromatic solvents. Therefore, a more planar (more conjugated) conformation will be expected in aromatic solvents. As a result, the polymer chains are expected to coil more tightly in nonaromatic solvents and more extended in aromatic solvents.⁷ It is observed that the absorption λ_{max} in THF is significantly blueshifted^{7,28} relative to the λ_{max} in aromatic solvents. This is consistent with the above hypothesis.

It should be pointed out that the twisted conformation shown in Fig. 9 is a quasistable state, which should only exist in the presence of a proper solvent. Once the solvent is removed, the polymer chains should spontaneously recover the more conjugated conformations, although such recovery is perhaps limited by the restricted motion of the polymer molecules in the solid state. This prediction is supported by experimental observation: Although the absorption λ_{max} of the polymer solution in THF is significantly smaller than the λ_{max} in aromatic solvents,^{7,28} the films spun with aromatic and nonaromatic solvents have essentially the same λ_{max} value.

On a closer look at Fig. 9, one expects that with the bulky side chains pointing irregularly to all directions, the π - π stacking of the polymer backbones will be hindered. Therefore, the excimer emission should be less. When sufficiently viscous solutions (e.g., 0.7–0.8 wt %, THF or CHCl₃) and low spin speeds (e.g., ≤ 2500 rpm) are used, this conformation is "memorized" by the polymer film. It is therefore not surprising that these films give yellow dominated emission (Fig. 7). The fact that high spin speed enhances the interchain emission ($\lambda_{max} \approx 630$ nm, Fig. 7) suggests that the centrifugal force has resulted in a large conformational change. However, there is no noticeable spectral change observable in the absorption spectra, and neither in the contact angles (vide infra). This indicates that the centrifugal force is not sufficient to completely break apart the heavily entangled polymer chains. Instead, the polymer coils are stretched open, to some extent, which allows the insertion of additional polymer chains thereby resulting in the formation of the interchain species.

In contrast, the aggregation style shown in Fig. 8, presumably attained in aromatic solvents, will allow a better $\pi-\pi$ overlapping and thus favors the formation of the interchain species. At high spin speeds, this aggregation style is destroyed by the centrifugal force, which results in less interchain species. On the other hand, with the conducting polymer backbones arranged outside, this conformation (or aggregation state) is also expected to be more "conductive" than the twisted conformation shown in Fig. 9. This prediction is indeed observed experimentally. It is found that films spun from aromatic solvents exhibit a higher current than those spun from THF at the same applied voltage and film thickness.²⁹

It should be pointed out that the solvation effect is more significant at sufficiently high concentrations and becomes less pronounced in more dilute solutions. This is because $T\Delta S_M$ is usually much larger than ΔH_M in highly dilute solutions. As the concentration increases, the interchain interactions and/or the interchain penetrations become more

TABLE I. Contact angles (θ) and surface tension of MEH-PPV films. Polymer films were spun from ~0.7% MEH-PPV solutions at ~2000 rpm. There is no noticeable spin speed dependence of the contact angles at this concentration.

Solvent	$\theta(\rm H_2O)$	$\theta(Ch_2I_2)$	γ^d (dynes/cm)	γ^{p} (dynes/cm)
Toluene	96°	37°	41	2.0
Chlorobenzene	96°	40°	39	2.3
1,2-Dichlorobenzene	97°	34°	45	1.2
<i>p</i> -xylene	95°	35°	42	2.3
Cyclohexanone	94°	38°	39	3.1
Chloroform	86°	41°	33	7.2
Tetrahydrofuran	87°	42°	33	6.8

significant, which decreases ΔS_M and thus the contribution from ΔH_M becomes more significant [refer to Eq. (1)]. It is not surprising that at highly dilute solutions ($C < 1 \times 10^{-6}$ M) the absorption λ_{max} is essentially independent of the solvent properties. In addition, the solvent dependence of other physical properties, such as the contact angle and surface energy of the film, also tend to be insignificant at more dilute concentrations (*vide infra*).

2. The surface energy of polymer films

The fact that the solvent can markedly change the optical properties of the polymer films leads to the question of whether this effect is also reflected on the surface of the film. The contact angles (θ) between an ordinary liquid (H₂O or CH₂I₂) and the MEH-PPV films spun from different solvents are measured (Table I). It can be seen from Table I that the contact angles $(86^{\circ}-87^{\circ})$ between H₂O and the polymer films spun from THF and CHCl₃ are significantly smaller than those (average $\sim 95^{\circ}$) spun from aromatic solvents, indicating that these films have different surface energies. On the other hand, MEH-PPV film spun from cyclohexanone solution has a contact angle of 94° with water, which is close to that of the aromatic solvents. This is consistent with its aromatic-like behavior observed in the spin-speed dependent EL spectrum experiments (vide supra). Although not technically an aromatic solvent, it is obvious that the six-member ring structure of this molecule leads to an aromatic-like behavior. The fact that films spun with THF and CHCl₃ have smaller contact angles with water indicates that these films are less hydrophobic (or, more hydrophilic). Since water is a highly polar and an H-bonding solvent, the increase of hydrophilicity indicates that the surface of the film is more polar. In general, the polarity of a surface can be quantitatively characterized by the polar component (γ^p) of its surface tension, which can be computed from the θ values with water and CH₂I₂ using the method of Wu.³⁰ The results for the dispersion (γ^d) and the polar (γ^p) components of the surface tension are also tabulated in Table I. It can be seen from the data that the films spun with THF and CHCl₃ have much larger polar terms ($\gamma^{p} \approx 7$ dynes/cm) than those spun with aromatic solvents and cyclohexanone (γ^p) =1-3 dynes/cm), indicating that nonaromatic solvents result in more polar surfaces. The contact angles with CH₂I₂, however, are distributed irregularly. This is because the dif-



FIG. 10. Two possible orientations of the aromatic ring on the surface: (i) the more polar (parallel) conformation exposes both oxygen atoms on the surface; (ii) the less polar (perpendicular) conformation only exposes one of the two oxygen atoms on the surface.

ferences between the θ values are too small, in this case, and thus hidden by the relatively large experimental error.

Since the MEH-PPV solutions were made from the same batch of polymer, the difference in surface tension values observed in Table I should be due to the different aggregation state (or packing style) of the polymer chains, resulting from the different solvation effects. The polar components of a MEH-PPV molecule predominately come from its C-O bonds. Therefore, the polarity of the surface will depend on how many C-O bonds (of the methoxy and the 2-ethylhexyloxy groups), or likewise the number of oxygen atoms available on the surface to interact with H₂O molecules. It was demonstrated that the spin-coated films have polymer chains that lie primarily in the plane of the surface.³¹ Therefore, the dihedral angle between the aromatic ring and the plane of the surface should determine the amount of oxygen atoms (or C-O bonds) available (to H bond or interact via dipole with the water molecules) on the surface (Fig. 10). When the benzene ring is parallel to the surface, both the methoxy and the 2-ethyl-hexyloxy groups are exposed on the surface. When it is perpendicular to the surface, however, only one of the oxygen atoms is exposed. Therefore, it is expected that films with more aromatic rings parallel to the plane of the surface should be more hydrophilic or more polar, and films with more aromatic rings perpendicular to the surface are more hydrophobic. In conclusion, films spun with THF or CHCl₃ may have more aromatic rings lying parallel to the plane of the surface than those spun from aromatic solvents. In contrast, the aggregation of the 2-ethylhexyloxy side chains with the aromatic backbone exposed outside the aggregate means that C-O bonds of the side chain groups are hidden inside the aggregate (Fig. 8). This may explain the observation that the surfaces of films spun with aromatic solvents are less polar than those spun with nonaromatic solvents, such as THF and CHCl₃. We are conducting further research to confirm this confirmation.

As discussed earlier, the solvation effect is expected to become less significant at lower concentrations. If this is indeed the case, the above solvent dependence of the contact angle should decrease when more dilute solutions are used, which is indeed observed. For example, the contact angle between water and a MEH-PPV film spun with a 0.4% solution in THF has the same value (95°) as that spun from *p*-xylene under the same concentration (0.4%) and the same spin speed (4800 rpm).

TABLE II. Spin speed dependent quantum efficiency and emission color.

	Speed	Thickness	QE	С	IE	λ_{max}
Solvent	(rpm)	(Å)	(%)	X	Y	(nm)
DCB	2500	860	3.0	0.62	0.38	632
	4000	720	2.4	0.59	0.40	588
	6000	630	2.1	0.57	0.43	584
	8000	590	2.0	0.56	0.43	580
THF	2500	1150	2.1	0.59	0.41	580
	4000	970	2.2	0.61	0.39	630
	6000	850	2.8	0.61	0.39	632
	8000	780	3.8	0.62	0.38	632

D. LED quantum efficiency

There have been a lot of discussions in recent years regarding the role of aggregation and excimer formation in conjugated polymers. It is generally believed that aggregation quenches the excited state.^{8,10} The mechanism for this aggregation quenching has been attributed to interchain interactions.^{17,18} These issues have also been addressed theoretically by Conwell and co-workers.^{32,33} In the meantime, tremendous efforts have been made to modify the polymer structure at the molecular level,^{34–39} with the intention of suppressing such interchain interactions and thus achieving better quantum efficiencies. From our results, however, the observed EL quantum efficiency (QE) of a device has a strong correlation with the emission spectrum and therefore the polymer morphology. Heeger and co-workers⁴⁰ suggested that the QE of MEH-PPV devices is strongly correlated to the film thickness. However, in our laboratories it is consistently observed that the orange-red devices always give higher QE (by 30-80% higher, Table II) than the yellow devices. This observation is reproducible in all the solvents that have been studied, and it is independent of the thickness (within the range of 500-1500 Å) of the MEH-PPV films. This strongly suggests that the formation of the Ex-I species actually enhances the quantum efficiency, which is contrary to the general belief that the formation of interchain species quenches the PL quantum yield of the MEH-PPV polymer film.^{17,32–35}

Excimer formation has traditionally been associated with aggregation,^{7,8} while the possibility for the unaggregated chains to form excimers has rarely been discussed. In dilute solutions, excimer formation in the unaggregated polymer chains is relatively improbable since the small diffusion rates of these macromolecules cannot compete with the decay of the excited state. In films, however, the polymer chains are closely packed. It is likely that the unentangled species are close enough in the film to form excimers. Rothberg and co-workers⁸ have recently identified an excimer species $(\lambda_{max} \approx 700 \text{ nm}, \text{ referred to as Ex-II in this article})$ in the PL spectrum of MEH-PPV films. This emission is also observed in the EL spectra of MEH-PPV films (Figs. 4-7) and in solutions.⁷ It is consistently observed that the Ex-II emission is always accompanied by the appearance of a reasonably strong yellow emission ($\lambda_{max} \approx 575$ nm, refer to Fig. 2). This observation implies that there is a connection between the Ex-II species and the yellow emissive species. The fact that the Ex-II emission has a longer lifetime (820 ps, Ref. 16) and

a longer emission wavelength ($\lambda_{max} \approx 700 \text{ nm}$) than the Ex-I species suggests that it is probably resulted from a better aligned $\pi - \pi$ overlap. In contrast, the Ex-I is more likely due to a partial or angled $\pi - \pi$ overlap within the aggregates. Rothberg and co-workers^{8,17} have shown, by time resolved fluorescence experiments, that the exciton fluorescence is quenched by the rapid formation of the much less emissive Ex-II species. If this is also the case in the EL emission, the correlation between the QE and the color of the device can be rationalized by the relative rates for the formation of the Ex-I and Ex-II species (Scheme I). When $k_1 \ll k_2$, the device is yellow and the QE is low. When $k_1 > k_2$, the 630 nm emission peak grows and QE is higher. Therefore, the highest QE can be achieved if the conformations of the polymer chains are optimized for the formation of Ex-I rather than the Ex-II species $(k_1 \ge k_2)$. This can be achieved by the proper selection of the spin-coating conditions, as already been discussed.



E. Conclusions

In summary, we have demonstrated that the optical and electrical properties of a spin-cast MEH-PPV film can be adjusted by controlling the aggregation of the polymer chains. By using the proper solvent, one can selectively control the aggregation state: Either the exposure of the aromatic backbone or the alkyl side chains. The aggregation of the polymer chains in the thin film can be further modified by adjusting the spin speed. In this regard, the concentration of the polymer solution is critical. Generally, the higher end of CLA (concentration for loose aggregation) results in the best device performance. The CLA for an individual polymer can be quantitatively determined from the curved region of a plot of the solution viscosity versus the concentration. Since the emission peak of MEH-PPV films at $\lambda_{max} \approx 630$ nm have different absorption and emission spectra, different quantum efficiency, and different fluorescence decay lifetime from those of the single chain exciton. We suggest that this red emissive species is probably due to an interchain excimer species. This species has a higher quantum efficiency than that of the single chain exciton. Therefore, the improvement of the quantum efficiency of a polymer LED device depends on the control of the polymer aggregation so as to maximize the rate for the formation of the Ex-I species and to minimize that of the less emissive Ex-II species.

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