Polydispersity Effects on Conjugated Polymer Light-Emitting Diodes

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This paper reports the effects of polydispersity in conjugation length on polymer light-emitting diode (PLED) device performance. For this study a di-alkoxy substituted pentamer of *p*-phenylenevinylene (5PV) was blended with a small amount of a lower band gap poly-(*p*-phenylenevinylene) (PPV) or a small amount of a di-alkoxy substituted *p*-phenylenevinylene type nonamer (9PV). We also fractionated two different di-alkoxy substituted oxadiazole-PPVs and blended the high molecular weight, lower band gap fraction, into a matrix of the lower molecular weight, higher band gap, polymer. It was found that incorporation of a small amount of the low band gap material significantly degraded PLED device performance. To further test the significance of polydispersity we synthesized a low molecular weight narrow polydispersity PPV. Devices made with this PPV were about 2 orders of magnitude better in LED external quantum efficiency when compared to a high molecular weight, higher polydispersity PPV of identical structure. These findings are significant in that they point to the importance of controlling the polydispersity in conjugation length for obtaining efficient PLEDs. They also indicate the importance of controlling polydispersity when comparing one polymer structure to another.

Introduction

Solution-processible conjugated polymers and organic small molecules are on the verge of spawning an industry of cheap electronic and optoelectronic devices.[1–4] To continue this rapid advance in product development it is, however, important to understand the fundamental structure/property relationships that govern performance in this class of materials. This paper will address the significance of one specific structure/property relationship: namely, the importance of energetic disorder or in other words polydispersity in conjugation length. Energetic disorder is known to have dramatic effects on charge transport in organic semiconductors. A model assuming hopping transport through an inhomogeneous site distribution with energies chosen from a Gaussian distribution reproduces many features of the transport including the energy and temperature dependences of the mobility in molecularly doped polymers.[5] Small changes in the width of the Gaussian distribution of site energies are found to make enormous differences in the mobility because the transport is dominated by the lowest energy end of the distribution, where carriers may require many k_BT to hop to neighboring sites. Bassler and co-workers have generalized this theory to conjugated polymers and used it to explain time-of-flight photoconductivity measurements in ladder polyphenylenes.[6] On the basis of this understanding of charge mobility in disordered semiconductors, it is reasonable to expect that polydispersity often found in conjugated polymers will have profound effects on the charge carrier transport and thus have a significant effect on PLED efficiency.

The presence of a few segments with a much longer than average conjugation length in a matrix of segments with a shorter conjugation length may result in migration of carriers and/or excited states to the low energy, longer conjugated segments. Electrochemical studies have shown that as the conjugation length increases, the energy level of the LUMO decreases and that of the HOMO increases[7] resulting in a lower band gap. This means that once a carrier, either hole or electron, moves onto a longer conjugation segment, it would be uphill in energy for that carrier to transfer onto a segment of shorter conjugation length. In other words, a segment with a longer conjugation length surrounded by short conjugation segments could act as a trap for both holes and electrons. In a LED this would translate into the holes being trapped near the anode (indium tin oxide

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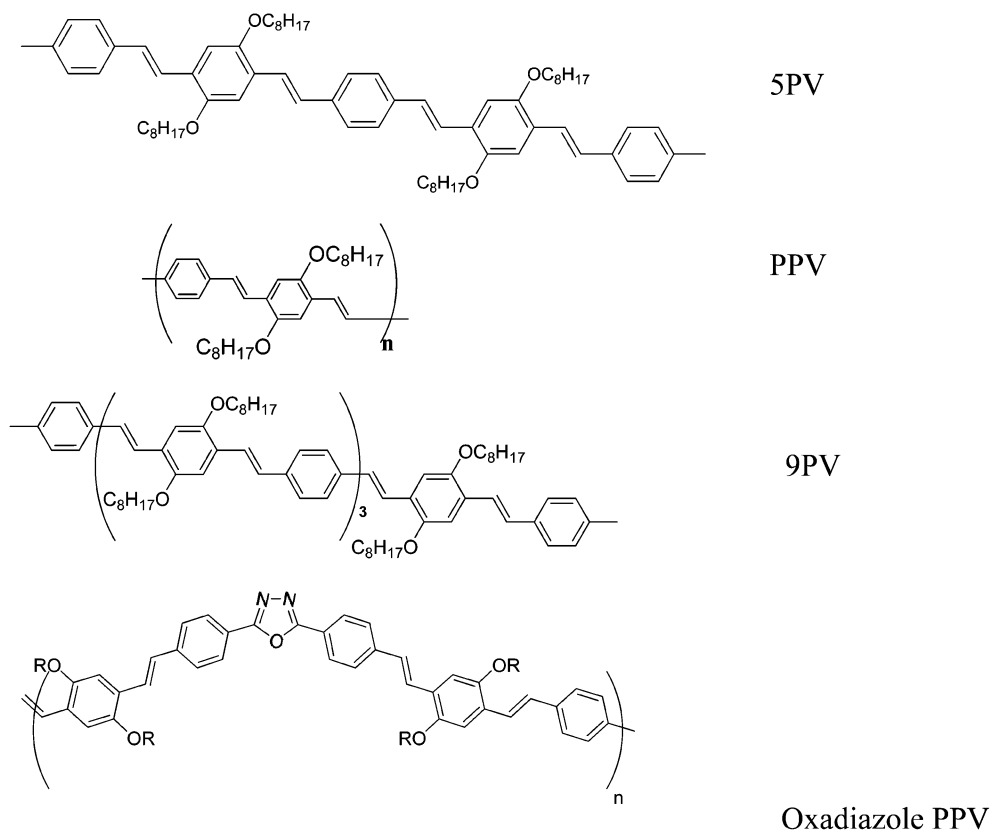(4) Shaw, J. M.; Seidler, P. F. *IBM J. Res. Dev.* **2001,** *45* (1), 3–9.
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Chart 1. Structure of Compounds Used in the Studies

5PV

PPV

9PV

Oxadiazole PPV

Oxa-L : R $= CH_2(CH_2)_6CH_3$

Oxa-B : R $= CH_2CH(C_2H_5)(CH_2)_3CH_3$

(ITO) electrode), and the electrons being trapped near the cathode (or metal electrode), which will be aluminum in our studies.

The question then becomes how does this migration to segments with longer conjugation lengths affect device performance. Will the low band gap segments act as dyes do, increasing device efficiency? Alternatively, it is possible that trapped carriers could quench exciton emission or that there could be preferential trapping of one type of carrier, hole or electron, over the other. These last two scenarios would decrease device efficiency. For example, if the electrons were trapped more than the holes, recombination could occur closer to the cathode, resulting in a decrease in luminescence due to both charge imbalance and quenching by the metal. We have attempted to probe the significance of this effect by blending either a very low concentration of a dialkoxy-substituted poly(*p*-phenylenevinylene) polymer (PPV) or a PPV di-alkoxy nonamer (9PV) with the corresponding pentamer (5PV) so as to create low energy sites in the higher band gap pentameric matrix. The blending of a very pure 5PV of known energy levels with lower band gap polymer or 9PV will be used to mimic the formation of localized trap states created by the polydispersity in conjugation lengths present in polymers. A systematic study of the spectral data and LED device performance of these blends should reveal the importance of this energetic disorder. In addition to studying this model system, we also report on the practical significance of polydispersity in conjugation length in a di-alkoxy oxadiazole containing-PPV (oxa-

PPV) via fractionation of the polymer. Specifically, we studied the performance and properties of the individual molecular weight fractions and blends of the fractions. Finally, we demonstrated that the efficiency of a device could be significantly increased by utilizing a low molecular weight narrow polydispersity polymer.

Experimental Section

Materials. The chemical structures of all the oligomers and polymers used in this study are shown in Chart 1. The 5PV and 9PV were prepared via minor modifications to the orthogonal approach developed by Yu.[8,9] The dialkoxy-PPV was synthesized via a Wittig−Horner reaction, but with a shortened reaction time to reduce the molecular weight. To prepare the very low molecular weight PPV, we added 1% of a monoaldehyde to the polymerization reaction to terminate chain growth. The dialkoxy-substituted oxadiazole PPV was synthesized according to previously published procedures.[10]

Measurements. Mass spectra were obtained with a Bruker BIFLEX III spectrophotometer (MALDI source). UV−vis spectra were recorded with a Beckman DU 640 spectrophotometer. Absorption and emission spectra were obtained from dilute solutions in THF and films spun cast from 1,1,2,2-tetrachloroethane (TCE) onto ITO substrates. The films were dried under a vacuum of 4×10^{-7} Torr overnight prior to the measurements. For optical measurements in solution all the concentrations were dilute and equivalent with an absorbance

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Table 1. Properties of Oligomers and the Polymer

material	M_n	M_w	polydispersity	band gap (eV)	PL efficiency ($\pm$15%)
5PV	1027	1027	1[a]	2.99 eV	63%
9PV	1949	1949	1[a]	2.42 eV	55%
PPV	4195	5830	1.3[b]	2.45 eV	81%

[a] Molecular weight of 5PV and 9PV were measured by MALDI-TOF. [b] Molecular weight of polymer was measured by using GPC with polystyrene standard.

maxima <0.1. Luminescence spectra were recorded on a SPEX Fluorolog-2 spectrofluorimeter using DM3000F software with a built-in reference quantum counter to correct for excitation intensity fluctuations. Quantum efficiencies of the same sample in different solvent mixtures were measured relative to Coumarin 480 in dilute ethanol solution according to Williams et al.[11] Molecular weights were measured with a GPC having mixed-beads columns (Polymer Laboratories) using polystyrene standards. The numbers are, therefore, "polystyrene-equivalent" molecular weights and are likely to be larger than the absolute molecular weights since the polymers studied have a rigid rod like character. The values are, however, good for comparative purposes, especially since we are using them only to compare molecular weight differences between fractions of the same polymer batch.

Device Fabrication and Testing. The films of the oligomers and polymers were spun from a solution of freshly distilled TCE. The concentration in all solutions was maintained at 20 mg/mL. The blend solutions were made from a stock solution of PPV of concentration 1 mg/mL added to a calculated amount of oligomer in TCE such that the overall concentration was maintained at 20 mg/mL. The solution was sonicated to ensure complete mixing. Films of the polymers were obtained by spin-coating onto a clean ITO substrate at 1000 rpm for 120 s, resulting in a film thickness of 1000 Å. Since the 5PV and 9PV tend to crystallize and have a lower solution viscosity than the polymer solutions, the rate of spinning was lowered to keep the film thickness constant at ca. 1000 Å. Single layer LEDs were fabricated with the emissive layer sandwiched between an ITO anode and an aluminum cathode. The evaporation of aluminum contacts was performed at $(4-6) \times 10^{-7}$ mbar vacuum and the rate of deposition was maintained between 7 and 10 Å/s. To measure device efficiency the PLED was placed about 3 mm from a silicon photodiode and current−voltage characteristics were measured using a HP 4155B Semiconductor Parameter Analyzer. Efficiency was calculated from the ratio of photocurrent to diode current, correcting only for the sensitivity of the silicon photodiode at the wavelength of the emission maximum. Some devices were fabricated and tested in an MBraun drybox equipped with an Edwards evaporator and a silicon photodiode and leads to the HP 4155. Oxygen and water sensors indicated that the atmosphere was below 0.1 ppm in oxygen and 0.1 ppm in water. Other devices were tested in air immediately after they were removed from an inert atmosphere. The efficiency of the devices did not vary between these testing protocols.

Results and Discussion

Blends with Model Compounds. The relevant properties of the 5PV, 9PV, and PPV are presented in Table 1. It is clear from the data that the band gap of both the 9PV and PPV are lower than that of the 5PV, which will serve as the high band gap matrix in our experiments. Both 9PV and PPV will be used as the low band gap dopant in two separate sets of experiments. There are a few reasons for using two model systems. First they provide a measure of the universality of any effect. Second, because of the difference in the synthetic
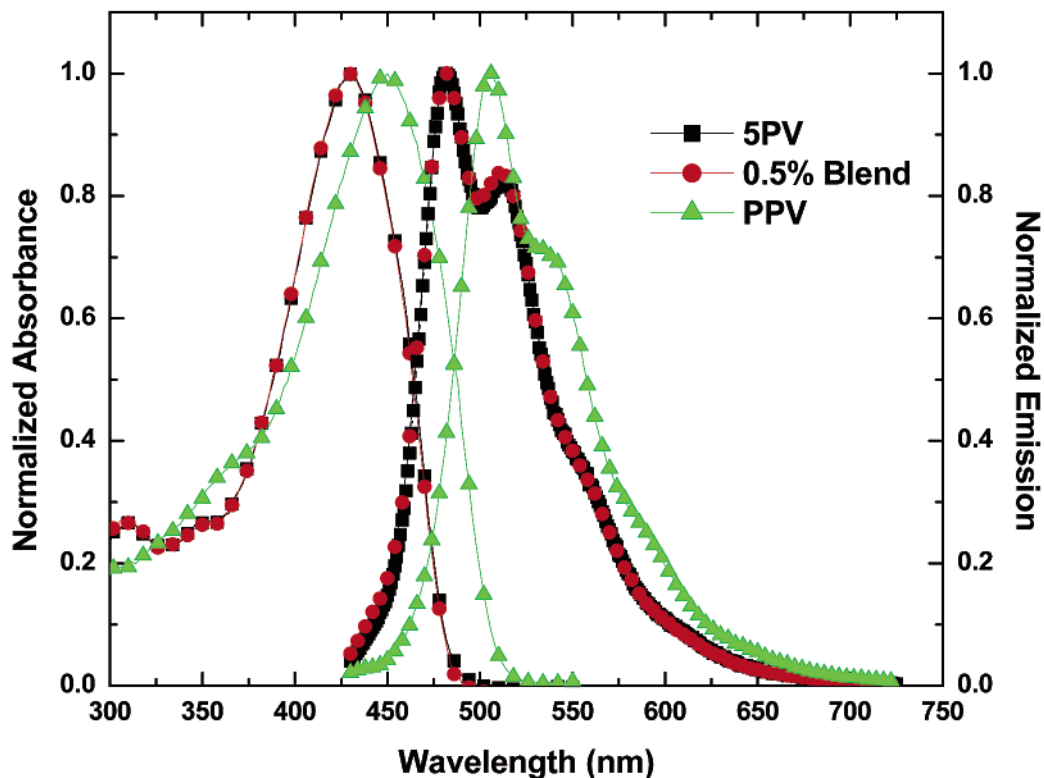
routes used to produce PPV and the 9PV, they have different end functionalities. Specifically, the PPV has aldehyde and phosphonate ends from the Wittig−Horner coupling, while the 9PV has methyl endgroups, as does the 5PV. By utilizing both molecules as dopants we can eliminate the possibility of the endgroup being responsible for any consistent effect. The effect on the morphology of the film produced from blending PPV or 9PV into 5PV will also be different. Given the fact that both 9PV and the 5PV have a strong propensity to crystallize, spinning was optimized to obtain homogeneous films of 100-nm thickness. The PPV is amorphous and as such does not have as strong a driving force to phase separate from the 5PV.

Considering the 5PV/PPV system, it is clear from Table 1 that the quantum yields of photoluminescence in dilute solution are high, although the yield for PPV is higher than for the 5PV. These high quantum yields support the results of chemical analysis that both materials are very pure. We can, therefore, assume that when the 5PV is doped with PPV the experimental results can be attributed to a difference in energetic disorder, i.e., conjugation length, and is not a consequence of the addition of chemical defects in the PPV. Note that the synthesis of the PPV was modified to produce a low molecular weight narrow polydispersity batch. This was done to make the band gap distribution in the blends as close to bimodal as possible. To determine the effect of adding a low band gap material to a high band gap matrix, photoluminescence studies of the system were conducted. In Figure 1 the absorption spectrum and emission spectrum of dilute solutions of a blend consisting of 99.5% 5PV and 0.5% PPV is plotted along with the spectra of the pure components. Since the chains are isolated from each other, both the absorption and emission spectra of the blend look like the spectrum of the majority component, the 5PV.
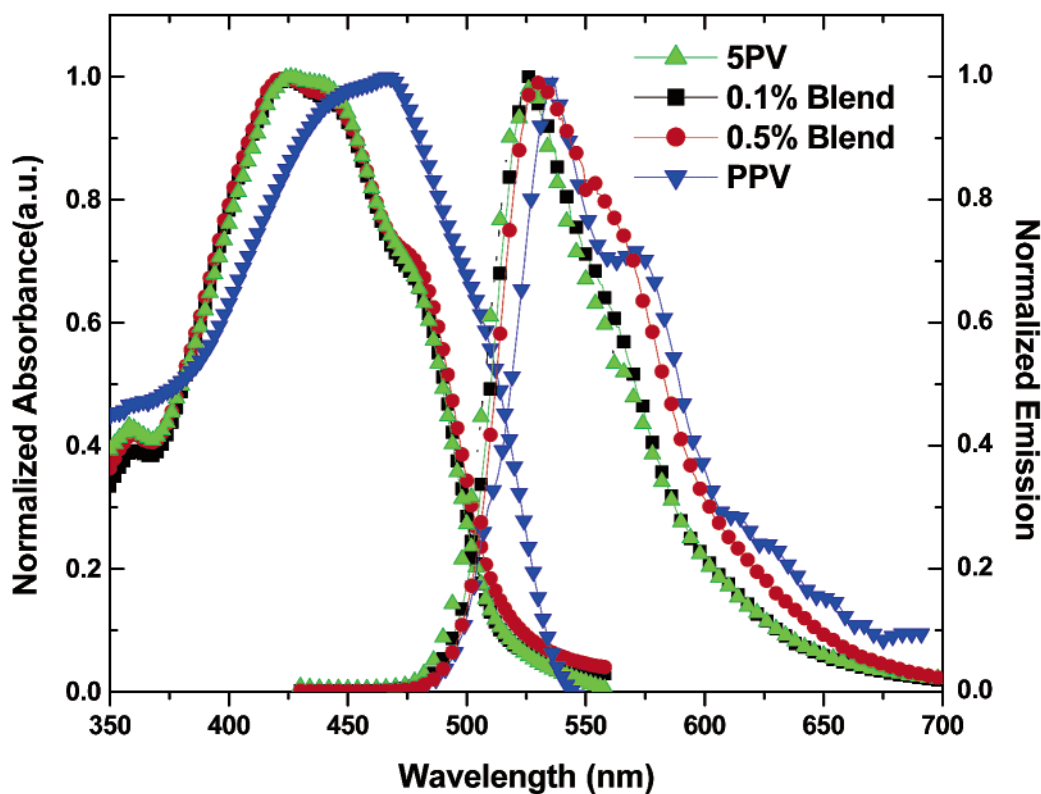
After obtaining the solution spectra, films of 2 blends, 99.5% 5PV:0.5% PPV and 99.9% 5PV:0.1% PPV, were formed by spin coating from TCE. The absorption and normalized emission spectra of these films are plotted in Figure 2 along with the spectra for films of the pure components. The absorption spectra of the blends are superimposable on that of the 5PV, consistent with the fact that the 5PV is at least 99.5% of the film. The emission spectra, however, provide evidence for transfer to the long PPV chains, since they progressively red shift toward PPV as the percentage of PPV in the blend increases. In another experiment we have established that beyond 2.0% PPV the emission spectrum of the blend is virtually identical to that of PPV. The noticeable shift, even at 0.1% PPV, indicates that the controlled introduction of the low band gap moiety provides easy pathways for the excited states to lower their energy and decay radiatively or nonradiatively on the PPV chain. The results provide evidence that polydispersity in conjugation length, i.e., energetic disorder, is important.

Having shown that PL is affected by the presence of a small percent of low band gap material, we fabricated light-emitting diodes (LEDs) to study the effect of blending a relatively high molecular weight, low band gap polymer into a 5PV. Electrochemical measurements on PPVs of varying conjugation lengths have revealed

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Figure 1. Absorption and emission spectra in solution (THF) of 5PV, PPV, and a 0.5% blend of PPV in 5PV. The excitation wavelength is 410 nm.

Figure 2. Absorption and emission spectra of films of 5PV, and PPV and 0.1% and 0.5% blends of PPV in 5PV. The excitation wavelength is 420 nm. All films were spun from 1,1,2,2 tetrachloroethane.

that the HOMO moves up and the LUMO moves down in energy as the conjugation length increases.[7] The PPV should, therefore, trap both carriers, electrons and holes, but at the opposite electrodes. The question is then how these trapped carriers would affect device performance.

A comparison of the external efficiencies of the two blends, 5PV and PPV, are listed in Table 2. The external efficiency of the low M_n, narrow polydispersity PPV is highest at 0.01%. This value is much higher than for normal, larger M_n, PPV[1]. The 5PV-based device gave

Table 2. Device Performance of 5PV, PPV, and Blend

material	PLED efficiency[a]
PPV	0.011%
5PV	0.006%
99.9% 5PV:0.1% PPV	0.004%
99.5% 5PV:0.5% PPV	0.002%

[a] 99.5% confidence level by statistical analysis.

Table 3. Device Performance of 5PV, 9PV, and Blend

material	PLED efficiency
5PV	0.006%
9PV	0.004%
0.1%9PV:99.9% 5PV	0.001%

an average efficiency of 0.006%. The 0.1% blend device gave an average external efficiency of 0.004%, lower than the efficiencies of either individual component. For the 0.5% blend, device performance efficiency further degraded to a value of 0.002%. Despite the proximity of the efficiencies, the differences are real. Each value is the statistical mean of the efficiency from many replicate devices. Data analysis proved that to a 99.5% confidence level the differences are significant. There is a drop in the device performance as the amount of PPV blended into the system is increased. The 0.1% blend performs better than the 0.5% blend because of fewer energetic disorder sites associated with a lower amount of dopant.

Since the efficiencies of our blend devices are low and the differences between them small, it is deemed important to look at how universal are the trends observed in Table 2. We know that efficiency can be influenced by other variables such as end groups, morphology or deleterious chemical impurities present in the PPV polymer chains that we are adding to the 5PV matrix. For these reasons we also synthesized 9PV and blended it into the 5PV. While the synthesis of the 9PV is tedious, the chemical purity of this compound is easier to control than that of PPV. LEDs were fabricated using the procedure mentioned in the experimental part. The data for LEDs fabricated from these materials are reported in Table 3. Both the 5PV and the 9PV have lower efficiencies than PPV, with the 9PV having a slightly lower value than the 5PV. These low efficiencies are in part attributable to the tendency for these molecules to crystallize. Once again, however, the blend has a device performance lower than devices from either individual component. While these efficiencies are low, the trends are the same as observed in the PPV:5PV system, providing more credence to the idea that polydispersity in conjugation length is an important variable in a model system with a relatively bimodal distribution of conjugation lengths.

Blends in Oxadiazole-PPV Polymers. In a real polymer sample there is a continuous distribution of conjugation lengths, resulting from a distribution of defects and molecular weights. To further complicate matters, it is impossible to directly measure the conjugation lengths. We can only monitor increases or decreases in the average conjugation lengths by observing shifts in the absorption maxima and band edge. To determine if polydispersity in conjugation length matters in a real system, we, therefore, chose to rely on fractionation. Although polymer fractionation works on differences in molecular weight instead of conjugation

length, it is reasonable to assume that longer polymer chains are statistically more likely to have longer conjugated segments. In addition, by fractionating the same batch of polymer, we are more likely to ensure that the different fractions have the same chemical purity. For these studies we used two different di-alkoxy substituted oxadiazole poly(*p*-phenylenevinylene)s (oxa-PPV). The oxa-PPV polymer was dissolved in excess of chloroform, a good solvent, then methanol, a nonsolvent, was added slowly while vigorously stirring the solution until a constant turbidity was obtained. Stirring was then stopped and the solution was allowed to sit for 2 h to allow the highest molecular weight fraction to precipitate. The precipitate was collected and the process was repeated two to three more times, with all the manipulations performed under nitrogen. After the fractions were dried under vacuum at 50 °C overnight, they were characterized using GPC, UV−vis spectroscopy, and PL measurements. PLEDs were fabricated by the standard procedure. For the first batch of polymer fractionated we report the characterization for all the fractions. In the subsequent batches, in the interest of brevity, we report on only those fractions used in blending experiments. Universally, the absorption and PL maxima red shifted while the device efficiency decreased as the molecular weight and polydispersity of the fraction increased.

The relevant data for a branched di-alkoxy oxadiazole PPV (OXA-B) are given in Table 4. There are several key points to note about the data in Table 4. First, we have succeeded in separating the polymer into fractions with very different molecular weights. Second, the peak maxima for absorption and emission, from dilute solutions and films of the fractions, blue-shift with decreasing molecular weight. The large 24 and 27 nm blue shift in the absorption maxima of the dilute solution and film spectra, respectively, that occurs between the lowest molecular weight fraction and the highest molecular weight fraction is consistent with the low molecular weight fraction having a shorter conjugation length. Third, the PLED device efficiency is considerably higher (2.5 times higher) for the low molecular weight fraction than for the high molecular weight fraction. This trend of higher PLED efficiency with lower M_n is the same as that observed with the di-alkoxy-PPV used in our oligomer studies. There the low molecular weight, narrow polydispersity, PPV used was about five times more efficient than the higher molecular weight samples. The trend is, therefore, not specific to the oxadiazole containing PPVs and is not a function of the synthetic route since the oxa-PPV was made with a Heck coupling reaction whereas the PPV was made via a Wittig− Horner reaction. This highlights the importance of keeping the molecular weights and polydispersities constant when trying to compare the performance of one polymer to another. Differences in the PLED efficiency may be due to a difference in the polydispersities of the samples not the change in chemical structure that one is trying to study.

As with the oligomer system, we chose to test the effect of energetic disorder on the performance of a PLED by blending a small amount of high molecular weight, low band gap, polymer into the lowest molecular weight, highest band gap, fraction. PLEDs were fabri-

Table 4. Properties of Oxa-B (branched) Oxadiazole PPV

			solution (λ_{max}) nm		film (λ_{max}) nm		
fraction	M_n	M_w	absorption	emission	absorption	emission	PLED efficiency
all	7700	19000	444	506	441	570	0.006%
F1	16000	29500	454	506	443	564	0.004%
F2	10000	21200	446	507	442	568	0.008%
F3	3500	6000	430	504	416	552	0.01%

Table 5. Device Performance of Batch I of Oxa-B (branched) Oxadiazole PPV in Blends

polymer	M_n	PLED efficiency
all: high molecular weight	7700	0.006%
F3: low molecular weight	3500	0.010%
98% F3:2% all		0.003%

cated by the mentioned procedure. The concentrations of the two fractions were adjusted to produce a film that was 98% of the low molecular weight fraction, F3, and 2% of the higher molecular weight unfractionated polymer. The device efficiencies are reported in Table 5. Tabulated efficiencies are an average over several devices. Note that the efficiency of the blend is lower than that of devices from either individual component. In fact, the blend has an efficiency which is only one-third that of a device made from only the low molecular weight matrix and half that of a device made with only the high molecular weight fraction.
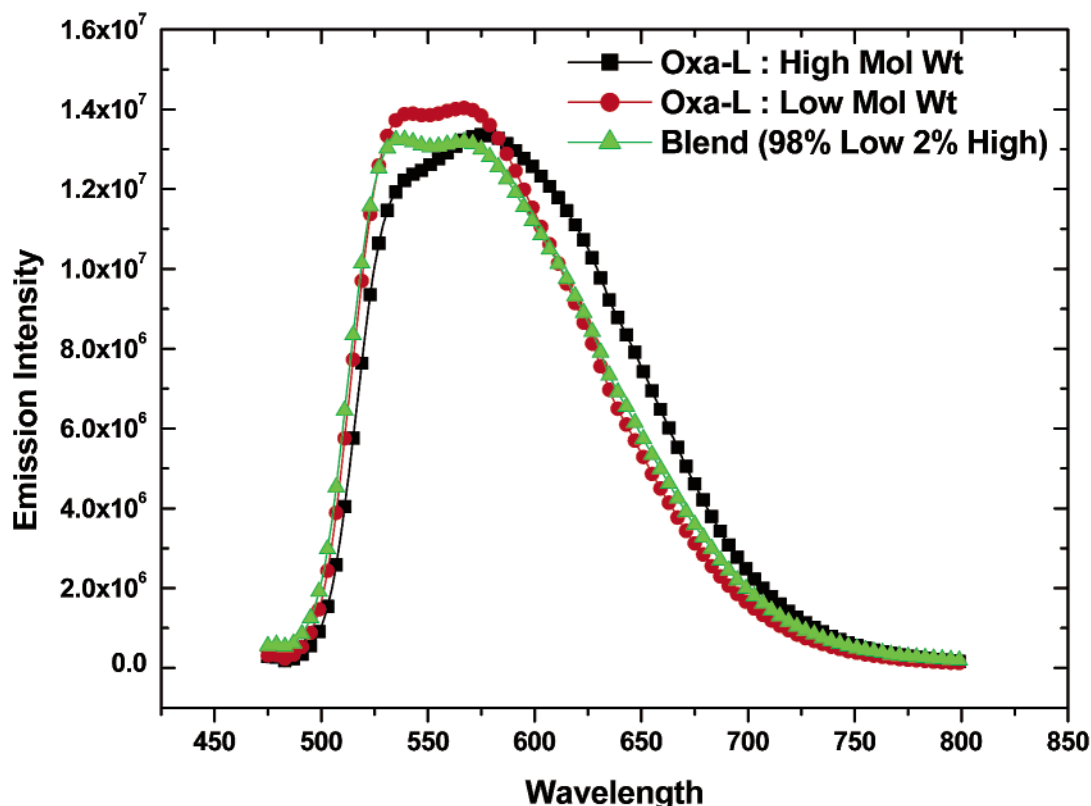
To ensure the reproducibility of these results, we have repeated these experiments with other batches of polymer. Data from a second higher molecular weight batch are reported in Table 6. With this batch the blue-shift in the absorption maxima, between the lowest molecular weight fraction and the highest molecular weight fraction, is only 10 nm and the PL quantum efficiencies of the two fractions are close. The smaller blue-shift can be attributed to the fact that the M_n of the lowest molecular weight fraction is close to the saturation point (12 000 for this system) beyond which no increase in the maximum in absorption is observed with increasing molecular weight. When LEDs are prepared from blends we again see that, although the differences are smaller, the blend performs worse than either individual component. Note that the efficiency of the matrix is cut in half by the addition of 2% of the low band gap fraction.

From studies we have conducted on oxadiazole-PPVs, we learned that device efficiency could be increased by using a linear octyl alkoxy side chain as opposed to a branched side chain. We, therefore, have also fractionated two different batches of Oxa-L (linear side chain oxadiazole-PPV) and prepared devices with blends of the various fractions. That data is reported in Table 7. Again the lowest molecular weight fraction has the highest device efficiency, twice that of the high molecular weight fraction. The blends have an efficiency one-third to one-half that of the matrix. It is important to note that the decrease in device efficiency seen in these blends is not accompanied by a decrease in the fluorescence emission from the film. In Figure 3 we plot the emission intensity from the three films whose efficiencies are reported as batch 1 in Table 7. The films were prepared under conditions that yielded a thickness of 1000 Å. The height of the curves in Figure 3 has not been normalized. For the same thickness, these fractions and the blend have the same PL intensity.

Identical experiments done on the films of the 5PV/PPV blends also showed that PL intensity is not affected by blending, supporting the idea that the problem arises from carrier injection, carrier transport or carrier imbalance.

We realize that morphology has a large impact on device performance and that blending could potentially change the morphology resulting in changes in device performance. We do not, however, believe this explains our results. We are blending in very small amounts of the low band gap polymer, 0.1% in the 5PV/PPV case and 2% in the oxadiazole-PPV case. It seems unlikely that these small concentrations would cause the morphological differences needed to degrade the performance of the PLEDs. A decrease in device efficiency due to morphology is usually correlated with an increase in chain aggregation. It is difficult to imagine why the addition of 0.1% PPV to 5PV would cause the 5PV to aggregate more. For the polymer fractions, we argue that since all of the fractions are relatively low in molecular weight and are similar in structure and amorphous, there should not be a morphological difference between the individual fractions and the blends. In fact, AFM and STM studies support these arguments since we have not observed any difference in morphology between the blends and the matrix. As noted earlier, end groups could impact device efficiency, but we do not believe that this explains our results since the systems studied had varying end groups. The only variable common to all the systems is the difference in conjugation lengths between components of the blends.

Low Polydispersity PPV. As a final test of the importance of polydispersity in conjugation length, we decided to synthesize a sample with as low a polydispersity in conjugation length as possible. Since it is synthetically more difficult to make a high molecular weight sample have a low polydispersity in conjugation length, we prepared a very low molecular weight dialkoxy-PPV. It should be recalled that though we measure molecular weight, the polydispersity in conjugation length is what we care about. Since the polymerization reactions result in a small fraction of defects that break the conjugation length, higher molecular weight fractions are more likely to have both short conjugated segments and long conjugated segments, i.e., a higher polydispersity in conjugation length. To limit chain growth and, thereby, narrow the polydispersity in conjugation length, we included 1% of a monoaldehyde in the Wittig−Horner polymerization reaction. The reaction time and temperature were also decreased. NMR confirmed that other than the number of end groups, this polymer (L-PPV) was chemically the same as the other batches. Device efficiencies for three different molecular weight PPVs are listed in Table 8. The efficiency of high molecular weight PPV (H-PPV) PLEDs is close to values reported in the literature.[12−14] As the molecular weight and polydispersity decrease,

Figure 3. Emission spectra of a film of Oxa-L from high molecular weight fraction, low molecular weight fraction and a blend of 98% low molecular weight and 2% high molecular weight.

Table 6. Device Performance of Batch II of Oxa-B (Branched) Oxadiazole PPV

			solution (λ_{max}) nm			
polymer	M_n	M_w	absorption	emission	solution quantum yield ($\pm$15%)	PLED efficiency
high molecular weight	33400	78800	455	509	50%	0.010%
low molecular weight	6800	11800	445	506	57%	0.015%
98% L:2% H						0.008%

Table 7. Device Performance of Oxa-L (Linear Sidebranch) Oxadiazole PPV

			solution (λ_{max}) nm			
polymer	M_n	M_w	absorption	emission	solution quantum yield ($\pm$15%)	PLED efficiency
batch 1: air						
high molecular weight	18 800	41400	450	503	67%	0.010%
low molecular weight	6 000	10200	428	502	74%	0.021%
98% L:2% H						0.009%
batch 2: N$_2$						
high molecular weight	11 300	24,850	450	510	50%	0.013%
low molecular weight	4 200	6,400	442	510	53%	0.025%
98% L:2% H						0.007%

Table 8. Effect of Molecular Weight on Device Performance on Three Batches of PPV

polymer	M_n	M_w	PLED efficiency ($\pm$0.001)
L-PPV	3300	4100	0.080%
PPV	4195	5830	0.011%
H-PPV	19000	125000	0.001%

the device efficiency increases. The value for the lowest molecular weight polymer is 80 times better than that

of the highest molecular weight PPV. This difference is much larger than usually reported between polymers with different chemical structures. In practical terms, it means that the light from this low molecular weight based PLED was easily visible in room light. When H-PPV is used to fabricate the device, the room must be dark to observe the light from the device.

Further studies are being conducted to fully understand why these low molecular weight, narrow polydispersity PPVs lead to much better performances in LEDs. It is possible that the higher concentration of end groups matters or that they have fewer chemical defects that quench luminescence, but in light of the blending experiments we conducted on model oligomers and fractionated polymers, we feel that the polydispersity in conjugation length is an important contributing

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factor. It is not just the molecular weight that is increasing but, as discussed earlier, the polydispersity in conjugation length should increase with the molecular weight. Our blending experiments show that it is not an absolute or low molecular weight that matters, but a narrow polydispersity. Note that the device efficiency decreased significantly when a small amount of a low band gap material was added to a higher band gap matrix. This trend held whether the matrix was a 5PV, a polymer with a M_w of 6 000 or a polymer with a M_w of 11 800.

Conclusions

The results from the fractionated polymers combined with those from the PPV/5PV and the PPV/9PV systems lead us to conclude that polydispersity in conjugation length is an important variable in determining PLED performance. In each case, when a small amount of material with a longer conjugated sequence is added to a matrix with a shorter conjugated sequence, PLED efficiency dramatically dropped below that of either individual component. Additionally, we note these trends cannot be attributed to a decrease in PL efficiency. Collectively the data suggest that the long chains are acting as traps and that one of the carriers is affected more than the other. Further studies on carrier mobility in these blends are planned to probe the exact causes of the decrease in PLED efficiency created by a polydispersity in conjugation length.

Our results are significant in two regards. First, polydispersity in conjugation length should be minimized in order to maximize device performance. Second, polydispersity in conjugation length must be kept constant when trying to determine if one polymer performs better than another in a light-emitting diode. The differences in PLED efficiency between molecular weight fractions from the same batch of polymer, or between batches with different molecular weights were large. In fact, we obtained almost 2 orders of magnitude improvement in device performance by controlling the polydispersity of PPV. This difference is larger than many differences reported in the literature to prove that a polymer with one chemical structure was better than a polymer with another chemical structure.

Note Added after ASAP Posting

This article was released ASAP on 8/29/2002 with minor errors in a table. The correct version was posted on 8/30/2002.

CM010936M