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Polymer Electroluminescence Using ac or Reverse dc Biasing

Z. Yang, B. Hu, and F. E. Karasz*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: Poly(2,5-diheptoxy-*p*-phenylenevinylene-*alt*-2,5-dimethoxy-*p*-phenylenevinylene) (DHDMPPV) exhibits electroluminescence (EL) at room temperature when either a conventional dc forward bias, or a reverse bias, or an ac voltage is applied to the test device, which has a simple ITO (indium tin oxide)/polymer/Al configuration. DHDMPPV is a soluble derivative of poly(*p*-phenylenevinylene) (PPV) synthesized using a Wittig condensation polymerization. Its EL spectrum lies in the orange region with a maximum intensity at 582 nm and a shoulder at 620 nm. The EL spectra either under a dc forward or reverse bias or on the imposition of an ac voltage are qualitatively identical. The threshold biases are ~5 V for dc forward bias, ~6 V for dc reverse bias, and ~5 V (10 V peak-to-peak) for ac operation, for a polymer emitter film thickness of ca. 80 nm. The EL emissions are bright and relatively stable at room temperature and can be easily seen under normal light conditions. Two other EL-active copolymers were also tested in similar configurations; no significant dc reverse bias EL was observed. However, blends of DHDMPPV with another EL-active copolymer previously described show the same behavior as DHDMPPV itself; for example, a 1:1 weight ratio blend with a green-light-emitting multiblock copolymer shows only an enhanced orange emission from the narrow-band-gap DHDMPPV.

Introduction

Research on electroluminescence (EL) polymers has become an active area since EL in poly(*p*-phenylenevinylene) (PPV) was described in 1990 by Burroughes et al.[1] Many EL-active polymers have been synthesized, and emission colors reported have covered the whole range of the visible spectrum[2–7] with increasing quantum efficiencies.[7] The usual analysis of the phenomenon postulates that these polymers emit light under an appropriate forward bias voltage when a relatively low work function cathode and a high work function anode, typically ITO (indium tin oxide) or polyaniline, are incorporated into a simple sandwich device. This configuration facilitates the double injection of charge carriers. Rectification in such polymer EL devices occurs because of the asymmetry of the injection capability of the respective electrodes. Minor EL activity under a reverse dc bias in a polymer LED has been reported,[8] and in poly(phenyleneacetylene) an unstable light emission was observed.[9] In contrast, in this work, we have found that poly(2,5-diheptoxy-*p*-phenylenevinylene-*alt*-2,5-dimethoxy-*p*-phenylenevinylene) (DHDMPPV) (see Figure 1), a soluble (chloroform and THF) derivative of poly(*p*-phenylenevinylene) (PPV), exhibits stable and intense electroluminescence when either a dc forward bias, or a reverse bias voltage, or an ac voltage is applied to a device with a simple ITO/copolymer/Al configuration. The reverse bias emission threshold voltage is always somewhat higher than that of the forward one. In the ac-activated EL process, two peaks in the EL intensity are seen in phase with the 60-Hz sinusoidal wave cycle of the ac input. One of the peaks is somewhat lower in intensity, has a higher EL threshold, and corresponds to the reverse bias portion of the ac input voltage. Similar devices using previously described EL-active copolymers[10] did not respond in the same manner and yielded only one peak per full cycle in the forward bias portion of the ac operation at low voltage; an increase in voltage led to device breakdown. The EL output of DHDMPPV is in the orange region of the visible spectrum with a maximum intensity at 582 nm and a shoulder at 620 nm. The EL spectra from forward or reverse bias as well as ac voltage operation are qualitatively identical. A blend of DHDMPPV with the EL copolymer CNMBC-St[10] (Figure 1) shows the same behavior as DHDMPPV; thus, a 1:1 weight ratio blend of these materials shows only an enhanced orange emission emanating from the narrow-band-gap DHDMPPV.

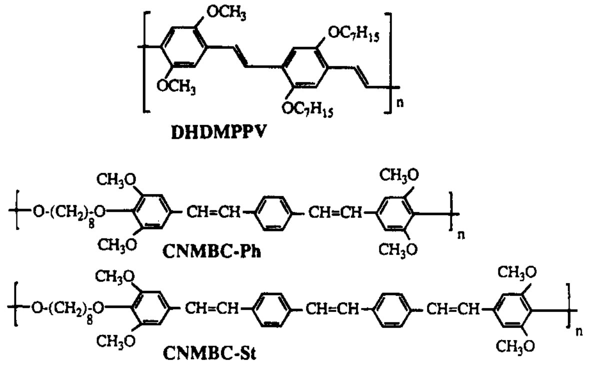

Figure 1. Molecular structures of copolymers.

Experimental Section

Synthesis of Copolymer. Poly(2,5-diheptoxy-*p*-phenylenevinylene-*alt*-2,5-dimethoxy-*p*-phenylenevinylene) (DHDMPPV). DHDMPPV was synthesized using the Wittig condensation polymerization of 2,5-dimethoxyterephthaldicarboxaldehyde and 2,5-diheptoxy-α,α′-bis(triphenylphosphonium chloride)xylylene in a procedure similar to that described for analogous polymers.[11] The copolymer was an orange powder before it was isomerized into a deep red material with an *all-trans* configuration using catalytic amounts of iodine in refluxing toluene. The yield was 85%. The copolymer is soluble in chloroform and tetrahydrofuran (THF) and yields a red–orange solution. Elem anal. Calcd: C, 78.0; H, 9.0; O, 13.0. Found: C, 77.2; H, 9.0; O by difference, 13.8. GPC measurement, with polystyrene calibration standard: $M_w = 1.2 \times 10^4$, dispersity = 2.0. FTIR: ν(CH) 3007 (Ph); ν_{as}(CH) and ν_s(CH) 2928 and 2855 (aliphatic CH); ν(C═O) 1714 (end group), 1501 and 1464 (Ph breathing); ν(C–O) 1206 and 1045 (Ph–O–C); γ(CH) 970 (*trans*-vinylene); 872 cm^{-1} (1,2,4,5-substituted Ph). ^{1}H NMR: δ 7.20 (4H, Ph), 6.80 (4H, vinylene),

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* To whom correspondence should be addressed.

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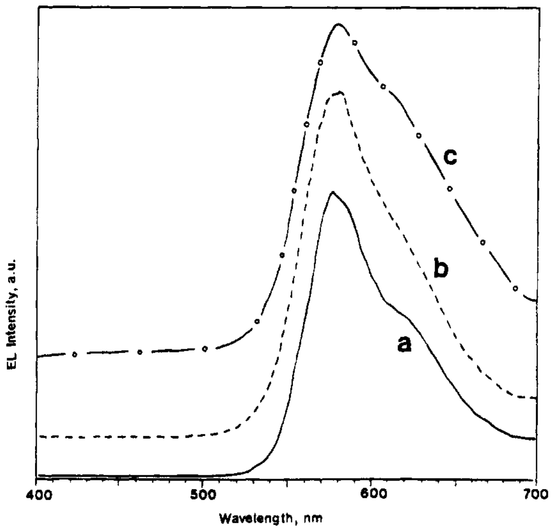

Figure 2. Electroluminescence spectrum of DHDMPPV under dc forward bias (a), dc reverse bias (b), and ac operation (c). Spectra are offset for clarity.

3.94 and 3.51 (10H, $-OCH_2-$ and $-OCH_3$), 1.80−1.28 (26H, aliphatic).

Characterization of the Polymer. The ^{1}H-NMR spectrum was obtained using a Bruker/IBM 200AC NMR spectrometer. GPC measurements (THF) were performed on a Waters Model 500 with a Waters 416 differential refractometer and a Waters Data Module 730. The FTIR spectrum was obtained on an IBM IR/3X Type 913X spectrometer equipped with Nicolet PC/IR operation software. Elemental analyses were carried out by the Microanalysis Laboratory, University of Massachusetts at Amherst. UV spectra were recorded on an IBM 9420 UV−vis spectrophotometer.

EL Device Fabrication and Measurements. The fabrication of EL devices used procedures previously described.[4] In brief, a 19 mg/mL solution of DHDMPPV in chloroform was used to spin coat a film onto an ITO glass substrate. A typical thickness of the polymer emitter film was 80 nm. Al was deposited on the polymer film to form the second electrode. EL and photoluminescent spectra were recorded using a system assembled in our laboratory and calibrated against a Perkin-Elmer MPF-66 fluorescence spectrophotometer previously standardized with PL measurements of compounds of known fluorescent properties.

Results and Discussion

The ITO/copolymer/Al device configuration yielded the EL spectra in Figure 2. Curve a shows the EL spectrum with conventional forward bias; curve b was obtained with reverse bias, showing a very similar spectrum. The dc reverse bias operation has a somewhat higher threshold bias compared to the forward bias operation. When the same device was subjected to an ac voltage (60 Hz; 15 V peak-to-peak), the copolymer yielded an EL spectrum (Figure 2c) again very similar to that obtained in the dc operation. The photoluminescence (PL) spectrum of a DHDMPPV film is qualitatively identical to its EL spectrum. The similarity of the PL and EL emissions from both dc forward and reverse biases and from ac operation indicates a common origin of the emissions and is attributed to a singlet−singlet radiative decay of excitons. Normally, polymer EL devices exhibit significant rectification because the electrodes used are designed to facilitate double-charge carrier injection by using a low and a high work function metal for cathode and anode, respectively. Such a configuration yields a device in which reverse bias injection is difficult before dielectric breakdown takes place. However, in the EL device using DHDMPPV as the emitter, rectification is very greatly reduced even though the electrodes used are those commonly employed in conventional polymer LED fabrication. Figure 3 shows a typical current−voltage curve; it can be seen that the forward and reverse bias *I*−*V* curves are almost symmetrical. For EL operation, we found that the forward bias process in a typical device has an emission threshold bias of ~5 V, while the reverse bias threshold is ~6 V. This difference is reasonably attributed to a larger barrier to charge carrier injection in the reverse bias mode as compared with forward bias operation. A corresponding difference in threshold voltage as well as in relative EL intensity, for a given electric field, was also encountered in the ac operation discussed below. A device using a polymer similar to DHDMPPV, namely, poly[2-methoxy-5-[(2′-ethylhexyl)oxy]-*p*-phenylenevinylene] (MEH-PPV), as emitter has recently been described as operating as a photodiode[12] under reverse bias, but no reverse bias EL was reported; a later report from the same group mentioned a minor light output under reverse bias conditions with n-Si and Au electrodes.[13]

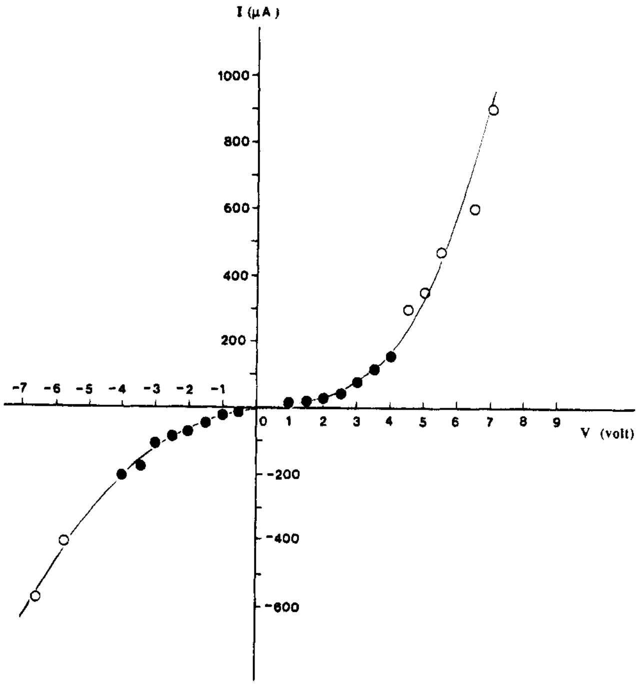

Figure 3. Current−voltage curve of an ITO/DHDMPPV/Al EL device under dc forward and reverse bias. Open circles denote voltages at which observable EL emission occurs.

Figure 4 shows the EL output intensity of the present device as a function of imposed ac voltage. Figure 4a shows EL at a low operating voltage (ca. 12 V); EL emission is detected only during the forward bias section of the sinusoidal ac cycle. As the voltage is increased (to ca. 18 V), EL emission from the reverse bias operation of the cycle also appears (Figure 4b). Both emissions from the forward and reverse bias operations then increase with increased applied voltage to 30 V (Figure 4c). That the reverse bias EL maximum is lower than the forward bias EL output agrees with the difference in thresholds described above. Again, we believe that the reverse bias operation gives rise to a larger barrier to injection of the two different carriers in the polymer emitter film. On the other hand, no dependence of EL intensity on ac frequency over 2 or 3 orders of magnitude was observed, which suggests there is no impact ionization electroluminescence in DHD-

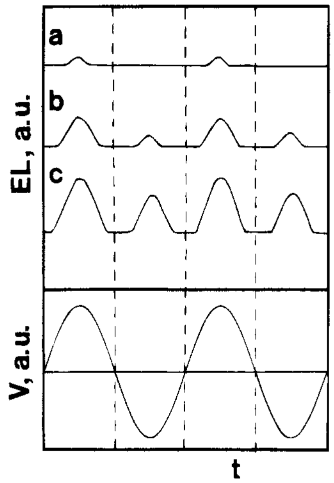

Figure 4. EL intensity in ac operation, ITO/DHDMPPV/Al device, at 12 (a), 18 (b), and 30 V (c). Peak-to-peak voltages.

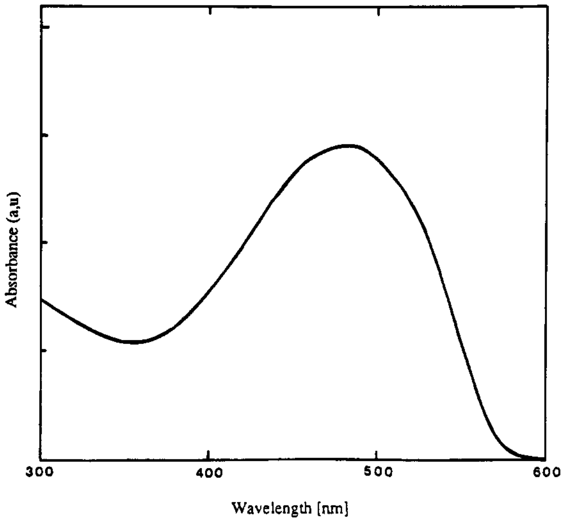

Figure 5. UV−vis absorption spectrum of DHDMPPV.

MPPV. Therefore, we believe that the ac-induced EL of DHDMPPV is also due to double-charge carrier injection.

To further understand the ac EL behavior of DHDMPPV, we examined previously fabricated devices using other known EL-active copolymers, CNMBC-Ph[4] and CNMBC-St[10] (Figure 1), which emit light in the blue and green regions of the spectrum with maximum intensities of EL emission at 465 and 513 nm, respectively. Neither of these copolymers showed any EL under dc reverse bias before breakdown was seen. With a low ac voltage, the two copolymers showed extremely weak EL emission qualitatively similar to the forward bias spectra shown in Figure 4a. A further increase of the ac voltage caused a breakdown before any significant EL effect could be observed.

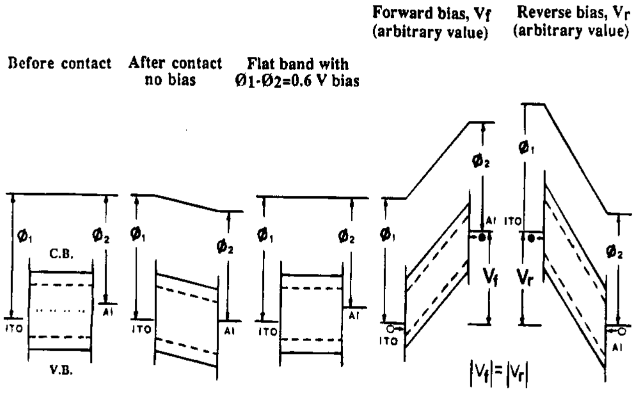

Figure 6. Schematic band diagram showing conduction and valence bands symmetrically located with reference to the average of the ITO and Al work functions for two systems with 2.0 and 3.0 eV band gaps, respectively. The two diagrams on the right illustrate the tilted bands with arbitrary but equal forward and reverse bias. Solid and empty circles correspond to electron and hole charge carriers, respectively. V.B. and C.B. denote valence and conduction bands, respectively, for the 3 eV band gap material bounded by the solid horizontal lines. The dashed lines represent the top and bottom of these bands for the 2 eV band gap material. The dotted line (left-hand diagram) represents the average electrode work function.

One can estimate from the absorption spectrum of the DHDMPPV film (Figure 5) that DHDMPPV has an energy gap of ca. 2.2 eV. We believe that the small band gap of the emitter polymer and a serendipitous approximately symmetric location of this band gap relative to the work functions of the electrodes together account for ac or reverse bias EL. This concept is illustrated in the energy band schematic shown in Figure 6. It is seen that forward and reverse biases minimally affect charge carrier injection in this simplified model provided that there is a symmetric location of the band gap relative to the electrode work functions. A straightforward calculation for this model shows, for an arbitrary but realistic 5-nm tunneling length, 13 V is required for forward biasing and 22 V for reverse biasing for a 2.0 eV band gap chromophore, similar to that of DHDMPPV, and with a 80-nm film and ITO and Al electrodes. On the other hand, for a higher, e.g., 3 eV gap, a 5-nm tunneling length requires some 21 V for forward and 30 V for reverse bias operation with the same device parameters. This asymmetry is accentuated by an offset chromophore band gap. Thus, a small band gap, symmetrically located, and a small electrode work function difference *together* represent optimal conditions for ac or reverse bias EL operation. From this model we would therefore anticipate that an asymmetric location of the valence and conduction bands relative to the work functions of the respective electrodes would be less favorable for this effect to be observed. It is also clear that the likelihood of this manifestation is decreased as the electrode work function difference is increased, even with a symmetrically located band gap. Consistent with this prediction, it was indeed found that DHDMPPV operated with ITO and Ca electrodes did not exhibit significant reverse bias EL. Further, a small band gap is a desirable but not sufficient condition, as can be seen from the fact that MeHPPV does not exhibit this effect with ITO/Ca electrodes even though this polymer is known to have a ~2.1 eV band gap. It is possible (though not demonstrated) that the correct choice of electrodes in certain cases could alone facilitate reverse EL. We also note that gap states (localized energy levels), either from impurity or defects present or from interfacial states, might be involved in the observed phenomenon. However, as we do not observe reverse bias operation in either the blue or green light emitters discussed above, it seems probable that the phenomenon is intrinsic to DHDMPPV in the arrangement described. We note that this contribution only deals with the simplest one-layer LED configuration. In more complicated multilayer configurations incorporating transport layers (presently under investigation), the necessary conditions for reverse EL could be met by suitable band offsets even for polymers which do not by themselves fulfill the necessary three conditions stipulated above.

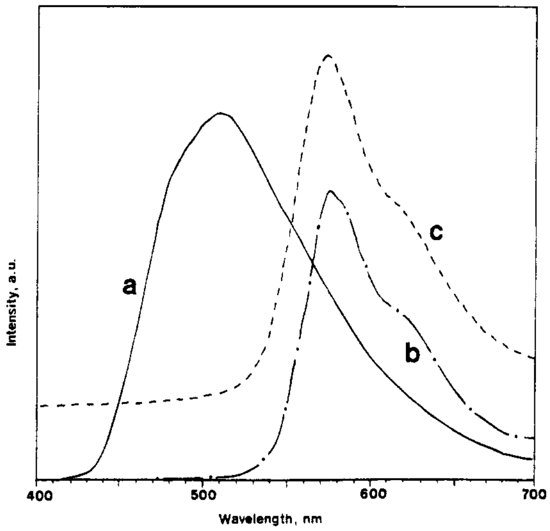

Figure 7. EL spectra of CNMBC-St (a), DHDMPPV (b), and of their 1:1 weight ratio blend (c). Offset for clarity; 6-V dc forward bias.

In further studies extending this investigation to polymer blend chromophores,[14] a 1:1 weight ratio blend of DHDMPPV with CNMBC-St was prepared from a chloroform solution. Both EL and PL outputs from this blend only show an emission from the DHDMPPV component (see Figure 7). The blend shows dc forward, dc reverse, and ac EL similar to those of the pure DHDMPPV, but the EL intensity of the blend is increased by a factor of 2 compared to that of pure DHDMPPV. EL enhancement by blending is discussed in a separate paper.[14]

Conclusion. A copolymer, DHDMPPV, was found to exhibit EL with dc forward and reverse biases and also with an imposed ac voltage in a simple EL device with a ITO/polymer/Al configuration. The intensity of the reverse bias induced EL was somewhat lower for a given electric field than that seen under forward bias. A model based on a simple band-gap calculation accounts for this observed phenomenon.

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