

Polymer gel light-emitting devices

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Polymers can be processed into several forms such as solid films, solutions, and gels. Traditional conjugated polymer electroluminescent devices are thin film, solid-state devices consisting of a thin polymer film sandwiched between two electrodes. Recently, a light-emitting device based on polymer solutions has been demonstrated. In this letter, we report the generation of luminescence from a polymer gel in a compact cell configuration. This unique polymer gel light-emitting device (GLED) consists of a thin layer of a polymer gel sandwiched between two electrode/glass substrates. The emission spectrum is consistent with the photoluminescence spectrum obtained from the polymer gel. The device shows an operating mechanism similar to the electrogenerated chemiluminescence. © 1999 American Institute of Physics. [S0003-6951(99)01044-X]

Traditional polymer light-emitting diodes are solid-state devices consisting of a thin polymer film, typically 100 nm thick, sandwiched between an anode and a cathode.¹ On application of a suitable bias, electrons and holes are injected from the cathode and the anode, respectively, into the polymer. Some of the injected carriers subsequently undergo radiative recombination within the polymer thin film, giving rise to an electroluminescence emission. In order to achieve a good device performance, disordered organic or polymeric materials are usually used. The maximum disorder in the organic and polymeric materials can be found in the solution phase; hence it would be of great interest to investigate polymer light-emitting devices using polymer solutions as the active medium. Recently, we demonstrated this concept of the polymer solution light-emitting device (SLED).² In the SLEDs, polymer solutions were sandwiched between transparent indium tin-oxide (ITO)/glass substrates, with the thickness of the solution layer ranging from 1 to 2 μm . On the application of a suitable bias, the onset of a strong luminescence was observed at slightly above the band-gap energy. Preliminary investigations have identified the operating mechanism of the SLED to be an electrogenerated chemiluminescence.^{2,3} The SLED involves the movement of electrically charged polymer chains under the influence of an applied electrical field. When biased, some of the polymer chains are oxidized near the anode side and some of them are reduced near the cathode side. Under the influence of the applied electric field, the oxidized molecules (or chains) migrate toward the cathode while the reduced molecules migrate toward the anode. Radiative recombination occurs when the positive charged, oxidized molecules encounter the negative charged, reduced molecules.

A polymer gel is an intermediate phase between a polymer solution and a solid-state thin film. Therefore, the discovery of polymer SLED brought about the interesting possibility of using a polymer gel as the active medium for the polymer light-emitting device. Since the polymer chains in a gel light-emitting device (GLED) no longer possess the long-range movement as found in a dilute polymer solution,

it was anticipated that the physical mechanism, such as charge injection and transport, would be somewhat closer to that of the solid-state polymer thin film light-emitting diode.

In this letter, we demonstrate the generation of luminescence from devices using a polymer gel as the active medium. The fabrication process of the GLED is fairly simple, typically consisting of three steps. In the first step, a small amount of polymer gel is deposited on top of a precleaned ITO/glass substrate. The precleaned ITO/glass substrates were baked at 100 °C for several hours to remove surface moisture before use. Next, another precleaned ITO/glass substrate was placed on top of the first ITO/glass substrate, thereby sandwiching the polymer gel. In the third step, these two substrates were pushed against each other by the application of an external force resulting in the simultaneous ejection of the excess polymer gel from the sides of the GLED. Upon drying, this extra polymer gel forms a natural seal around the edge, thereby preventing the solvent vaporization from the sandwich structure. The controlled thickness of the polymer gel layer was controlled to around 0.5 μm . The detailed device structure is shown in Fig. 1. The polymer gel preparation and device fabrication were carried out in a nitrogen environment. Due to its simplicity, the device fabrication process can be completed within a few minutes. We have examined polymer solutions, 8% by weight concentration of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (or MEH-PPV) prepared in dichlorobenzene (DCB). The GLEDs were then characterized by optical and electrical measurements. The current-voltage (I - V) and

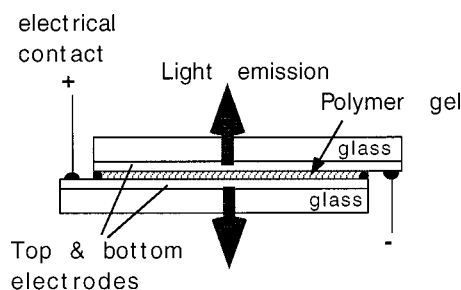


FIG. 1. Typical device structure of a polymer GLED. ITO was used as both the anode and the cathode.

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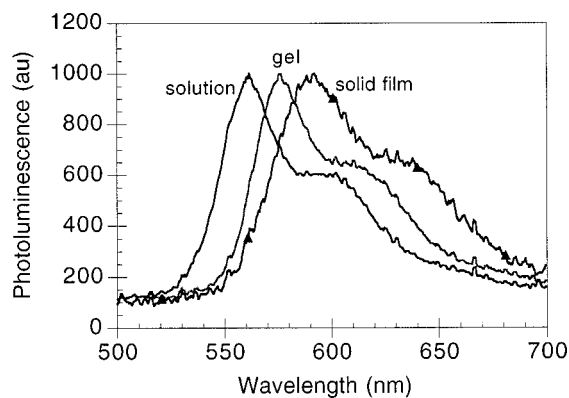


FIG. 2. PL spectra of different phases of MEH-PPV, solid film, gel and solution, are shown. The EL spectra are consistent with their corresponding PL spectra.

brightness–voltage (L – V) characteristics were measured using an HP 4145A semiconductor parameter analyzer along with a calibrated silicon photodiode functioning as an optical sensor. The PL and EL spectra were measured using an Ocean Optics spectrometer. The absorption spectra were measured using an HP 8453 diode array spectrometer.

The photoluminescence (PL) spectra of MEH-PPV in the solution, gel, and solid-state forms are shown in Fig. 2. The device emission spectra (EL) or (ECL) for the LED, GLED, and SLED were found to be identical to their PL spectra. The emission peaks were found to redshift from 560 nm for the MEH-PPV solution, to 575 nm for the MEH-PPV gel, and to 592 nm for the MEH-PPV solid films. The redshift of emission peaks from solution to solid film indicates the electronic interactions (or the overlap of the π -electronic orbitals) between the polymer chains increases as the polymer chain separation decreases.

The devices made of pure MEH-PPV gel show poor performance and require a high voltage to turn on. This problem was significantly alleviated when a surfactant, dibenzo-18-crown-6 was blended into the polymer in the ratio 30:1 of the polymer to the surfactant. The role of the surfactant in the GLED and SLED is still not clearly understood. However, one possible explanation is that the surfactant molecules significantly enhance the contact between the polymer and electrode. Another possibility is the enhancement of the polymer morphology (network formation) between the polar solvent and the nonpolar MEH-PPV polymer.⁴ Judging by the chemical structure of DCB and MEH-PPV, it is likely that DCB has a much higher polarity than MEH-PPV. A phase separation between the polar solvent and MEH-PPV is likely to occur when MEH-PPV solution reaches a high concentration or in the solid film. Cao *et al.*⁴ demonstrated that excellent polymer networks could be formed by adding a surfactant into such polymer blending systems. Subsequently, the performance of the resulting polymer light-emitting electrochemical cells was significantly enhanced. All the results reported in this letter are based on the MEH-PPV/surfactant blends as the active medium. We have also examined different solvents, such as cyclohexanone (CHO). We found that DCB and CHO yield a similar device performance after blending with the surfactant.

The I – V and L – V curves for the GLED using the MEH-PPV-surfactant blend are shown in Fig. 3. The voltage

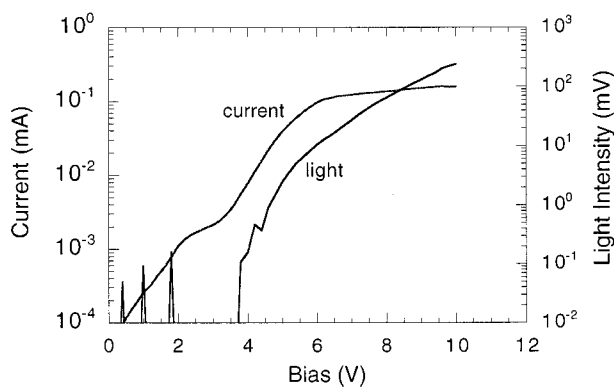


FIG. 3. The semilog plot of the I – L – V curves of a GLED. Current saturates at voltages higher than 6 V.

scan rate is about 0.5 V/s. The I – V curves show several distinct features dissimilar to the solid-state device and the SLED. There are three different regions of charge injection: region (I) for biases less than 2.2 V, region (II) for biases between 2.2 and 4 V, and region (III) for biases above 4 V. In region I of the I – V curve, the dark current increases rapidly and reaches a level of about 10–20 $\mu\text{A}/\text{cm}^2$. Significant charge injection begins at around 3 V and ends at 5.5 V (region II). Within this region, the current increases exponentially. Light emission can be observed around 3.5 V. However, this exponential increase of injection current saturates for biases above 5.5 V. The injection current remains nearly constant even though the bias voltage increases from 6 to 10 V. The dynamic resistance which is defined as the $\Delta V/\Delta I$ is estimated to be 20000 Ω in this region. Due to the slow vaporization of the organic solvent, it is also suspected that the device emission spectrum may change during the device stress test. The ECL spectrum of our MEH-PPV GLED did not show any significant change during the course of our stress test. The device lifetime is about 1 h and the device failure mechanism is still unclear.

In the gel phase, the polymer chains form a network, and the solvent molecules are present within this network. Hence, polymer chains in the gel phase no longer possess the ability for long-range movement as in the dilute polymer solution. Still, we believe the device operating mechanism is due to the electrogenerated chemiluminescence. When biased, the solvent molecules are reduced near the cathode and the MEH-PPV polymer chains are oxidized near the anode. Under the influence of the applied electric field, the reduced solvent molecules migrate through the bulk of the gel and subsequently recombine with the oxidized MEH-PPV molecules near the anode. (The movement of MEH-PPV polymer chains is essentially negligible.) However, due to the gel phase, both the charged MEH-PPV chains and the solvent molecules suffer low carrier mobilities, and it is expected that at high current injections, there will be a charge accumulation near the interface. The observed saturation of injection current at voltages above 5.5 V is perhaps indicative of this accumulation of reduced solvent molecules near the cathode and oxidized MEH-PPV polymer chains near the anode. These accumulated charges prevent any significant charge injection into the bulk of the polymer gel, hence the saturation in injection current.

The problem of charge accumulation can be resolved by

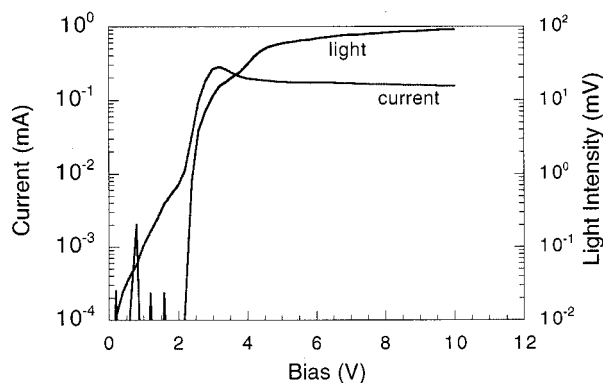


FIG. 4. The semilog plot of the I - L - V curves of a GLED with the addition of a very small amount of salt. Charge injection was significantly enhanced at low voltages. However, current saturates at voltages higher than 6 V.

adding an electrolyte (salt) so that these counter ions are able to neutralize the accumulated oxidized and reduced molecules near the interfaces. We examined this simple assumption by adding a small amount of lithium triflate into our GLED in the ratio of 600:1 (MEH-PPV:lithium triflate). The charge injection significantly improved. This current enhancement of the GLED on the addition of a salt is a clear indication that the accumulation of charges at the interface has been compensated by the counter ions. When the salt is added to the GLED, the device is believed to behave similarly to the polymer light-emitting electrochemical cell (LEC),⁵ in which the devices turn on at the band-gap voltage (~ 2 V). However, when a limited amount of counter ions are present, they are consumed completely, thereby once again leading to charge accumulation. The dynamic resistance, which is about 20 000 Ω , of the bulk polymer gel once again limits the injection current. Figure 4 shows the semilog plot of the I - V curve of the GLED with the addition lithium triflate.

For comparison, the linear I - V plots of the polymer GLED without (Fig. 3) and with the addition of the salt (Fig. 4) are shown in Fig. 5. These two devices have a consistent current saturation behavior at high voltages, and, as indicated earlier, this is due to the accumulation of the charged carriers near the metal/organic interface. A negative resistance region has also been identified in the GLED w/salt between 3 and 4.5 V.

In summary, we have demonstrated a new type of polymer light-emitting device, the polymer GLED, using the polymer gel as the active medium. At low biases, the device mechanism is similar to the electrogenerated chemiluminescence. However, under high biasing conditions, the GLED

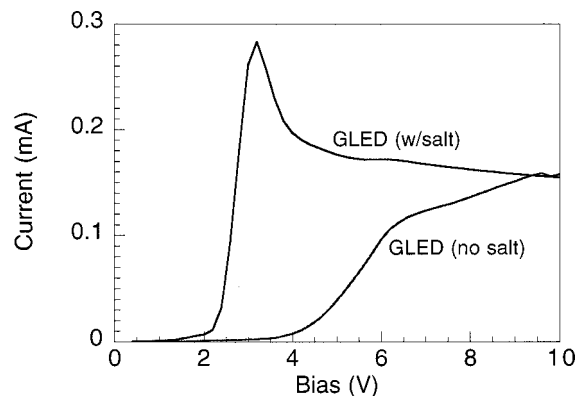


FIG. 5. The linear I - V plots of GLED without and with salt (w/salt). Despite the difference in the low voltage bias conditions, these two devices show remarkably similar current behavior at higher voltages.

device performance is limited by the accumulation of charge carriers near the metal/organic interface, due to the low drift mobility of the oxidized and reduced molecules. The accumulation of the charge carriers near the interface prevents the further increase in injection current. Adding a very small amount of lithium triflate into the system alleviates this problem. The counter ions neutralize the charged species near the interfaces, and charge (or current) injection subsequently increases. In the future, it will be interesting to observe the system crossing from polymer GLED to the polymer solid state LED by further increasing the polymer concentration.

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