''Plastic'' lasers: Comparison of gain narrowing with a soluble semiconducting polymer in waveguides and microcavities

María A. Díaz-García, Fumitomo Hide, Benjamin J. Schwartz,[a)]
Michael D. McGehee, Mats R. Andersson,[b)] and Alan J. Heeger[c)]
Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106-5090

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Gain narrowing and lasing from a soluble, highly photoluminescent conjugated polymer, poly(2-butyl, 5-(2′-ethyl-hexyl)-1,4-phenylene vinylene) (BuEH-PPV), are compared using two resonant structures: planar waveguides and microcavities. The gain narrowing and lasing thresholds are comparable, 0.05–0.1 μJ (10 ns pulse focused to $\sim$1.5 mm). Gain narrowing is not observed in films on indium tin oxide (ITO) unless a cladding layer is placed between the BuEH-PPV and ITO. Single-mode microcavity lasers are obtained when a cavity resonance occurs at the wavelength where the gain of the polymer is maximum. © *1997 American Institute of Physics.* [S0003-6951(97)00224-6]

The demonstration of gain narrowing by π-conjugated poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) with the aid of multiple scattering from titanium dioxide nanoparticles (to extend the path length in the gain medium) initiated interest in semiconducting polymers as solid-state laser materials.[1] Photopumped gain narrowing has now been reported for neat undiluted films of over a dozen soluble conjugated polymers in planar waveguide structures,[2,3] and lasing has been observed from poly(1,4-phenylene vinylene) (PPV) in microcavities.[4] New polymers have been developed that also show promise as solid-state laser materials.[5–8] It is not yet clear, however, that similar results can be achieved by electrical injection of charge carriers; diode lasers require carrier injecting electrodes, such as indium tin oxide (ITO) and metals, in the vicinity of the conjugated polymer. Since the photoluminescence (PL) is quenched within a few hundred angstroms of metal surfaces,[9–11] the presence of electrodes might complicate the development of polymer laser diodes.

In this letter, we compare the emission from conjugated polymer lasers constructed from microcavities (thin film polymer layer between a highly reflective distributed Bragg reflector (DBR), and a silver mirror) to the gain-narrowed PL produced in planar waveguides (thin polymer film spin-cast onto glass), and we explore the use of hole-transporting cladding layers to achieve gain narrowing in the presence of ITO. Although ITO suppresses the waveguiding, insertion of a layer of poly(*N*-vinylcarbazole) (PVK) between the PL polymer and the ITO restores the waveguiding and the gain narrowing. We find that the quality of the polymer microcavity laser is strongly dependent on matching the microcavity mode to the gain maximum of the PL polymer, but is insensitive to whether the PL polymer or PVK is in contact with the silver layer. Because the threshold for gain-narrowed emission is the same in waveguides and microcavities, there are advantages for each approach.

We focus on poly(2-butyl, 5-(2′-ethyl-hexyl)-1,4-phenylene vinylene) (BuEH-PPV),[12] a soluble alkyl-substituted PPV with PL (η_{PL}) of 75% in solution and 62% in neat films. Solid films of BuEH-PPV with gain maximum near 550 nm exhibit a relatively long stimulated emission (SE) decay time ($\approx$60 ps),[13,14] and show gain narrowing with thresholds below 10 μJ/cm^2 in planar waveguides.[2,3] When spin cast from solution, BuEH-PPV films can be used to obtain yellow/green EL in polymer light emitting diodes (LEDs), $\eta_{EL}\approx 2\%$ ph/el, and light emitting electrochemical cells (LECs), $\eta_{EL}\approx 3\%$ ph/el.[12] In LEDs, a thin PVK hole transport layer between ITO and BuEH-PPV significantly enhances device performance.

The DBR mirrors (type BBDI), obtained from CVI Laser Inc., have nominally greater than 99% reflectivity at normal incidence from 488 to 694 nm. The DBR consists of 1/4-wavelength dielectric layers (>60) with alternating high ($\approx$2.2) and low ($\approx$1.4) index. The high reflectivity over such a broad wavelength range results from the many layers with different layer thicknesses (chirped DBR) such that longer wavelengths are reflected deeper inside the stack. As a result, the microcavity supports several modes.

Waveguides and microcavities consisted of simple layered structures: glass/BuEH-PPV/air or glass/ITO/PVK/BuEH-PPV/air for the waveguides and DBR/PVK/BuEH-PPV/Ag or DBR/BuEH-PPV/PVK/Ag for the microcavities. Polymer films were prepared in nitrogen atmosphere by spin casting from solution onto DBR mirrors for microcavities and onto bare or ITO-coated glass for waveguides (thickness of ITO around 140 nm). Film thicknesses were measured with a Dektak profilometer. BuEH-PPV was dissolved at concentrations from 1% to 1.5% w/v in p xylene and spin cast to thicknesses of $\sim$200 nm for waveguides and $\sim$470 nm for microcavities. PVK films with thicknesses from $\sim$90 to $\sim$900 nm were spin cast from cyclohexanone with concentrations varying from 1.5% to 10% w/v. The transmittance of the silver layer ($\sim$60 nm, deposited by thermal evaporation at 2×10^{-6} Torr) at 435 nm was 11%. Samples were processed and stored in inert environment until immediately before use; the optical experiments were carried out under ambient conditions.

[a)]Permanent address: Department of Chemistry and Biochemistry, P.O. Box 951569, UCLA, Los Angeles, CA 90095-1569.
[b)]Permanent address: Departments of Organic Chemistry and Polymer Technology, Chalmers University of Technology, S-412 96, Göteborg, Sweden.
[c)]Electronic mail: ajh@physics.ucsb.edu

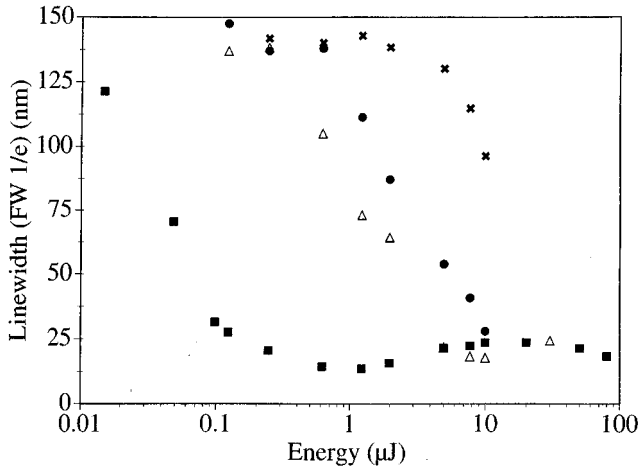

FIG. 1. Linewidth as a function of pump energy per pulse for BuEH-PPV-based waveguides: BuEH-PPV on glass (squares), BuEH-PPV on ITO (crosses), ~90 nm PVK and BuEH-PPV on ITO (circles), and ~340 nm PVK and BuEH-PPV on ITO (triangles).

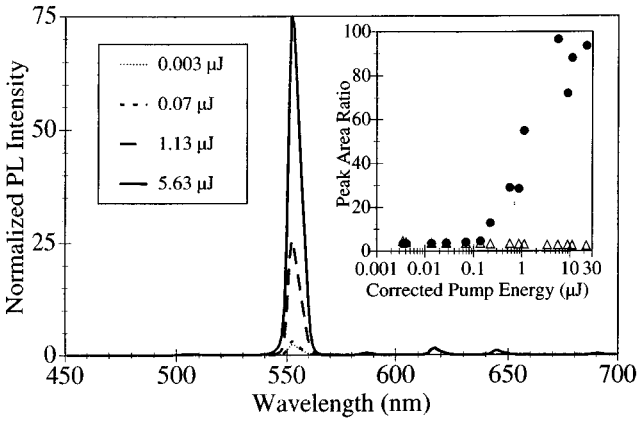

FIG. 2. Emission spectra from a microcavity: DBR/BuEH-PPV/PVK/Ag at various pump energies. The PVK layer is ~340 nm thick. Inset: Ratio of integrated intensities (mode ratio) of the ~552 nm peak to the ~645 nm peak (squares) and of the ~690 nm peak to the ~645 nm peak (triangles).

The instrumentation for gain narrowing experiments is described in detail elsewhere.[1] The ~10 ns pulsed, 435 nm pump light was focused at the sample to ~1.5 mm. The energy per pulse was controlled with calibrated neutral density filters. For microcavities, the pump light was incident from the silver side at an angle of about 30° from the normal, and emission was collected from the same side at the sample normal. Waveguides were pumped and the emitted light was collected from the film side (although gain-narrowed emission could be detected in all directions).[2,3]

When the PL polymer has a higher index of refraction than the surrounding media (substrate and air), an asymmetric waveguide is formed, confining the emitted light which travels along the plane of the polymer film.[15] Gain narrowing occurs when the path length exceeds the gain length in the pumped material. The gain-narrowed light is guided to the edge of the film or scatters off imperfections in the waveguide (enabling detection in all directions). The basic experiment used to characterize the optical waveguides measures the PL linewidth as a function of the excitation energy per pulse.

Results from BuEH-PPV films on glass, with and without ITO as well as with PVK cladding layers of two different thicknesses, are presented in Fig. 1. The PL spectrum shows gain narrowing with a well-defined threshold; the waveguide with BuEH-PPV on glass has the lowest threshold, ≈ 0.05 μJ/pulse. In contrast, when ITO is in contact with the BuEH-PPV layer, the gain narrowing threshold is increased by about three orders of magnitude. When a PVK layer is introduced between the ITO and BuEH-PPV gain narrowing is restored; the threshold decreases from 2 μJ/pulse to <1 μJ/pulse as the PVK thickness is increased.

The ITO electrode suppresses gain narrowing by preventing the formation of a planar waveguide.[2,3,15] Because of the high index of refraction of ITO ($1.8 \leqslant n_{\mathrm{ITO}} \leqslant 2.1$),[16] a guided mode cannot be supported in a BuEH-PPV film on ITO at the gain wavelength (≈ 550 nm) ($n_{\mathrm{BuEH\text{-}PPV}} = 1.69$ at 632 nm[2,3] and 1.78 at 550 nm). Waveguiding can be restored by inserting a PVK cladding layer ($n_{\mathrm{PVK}} = 1.68$ at 568 nm) of appropriate thickness, a promising result for LEDs which often show higher EL efficiency when PVK is used as a hole transport layer. The light can be then guided in the BuEH-PPV layer, although it penetrates into the PVK layer, leading to an increase in the threshold with respect to BuEH-PPV on glass, as observed. By using a cladding layer with a refractive index even lower than that of PVK, one would achieve a better confinement of the light into the active polymer and therefore, waveguiding could be restored with a thinner cladding layer. The conducting ITO also reduces η_{PL} of the polymer film;[9–11] however, polymers with η_{PL} substantially lower than that of BuEH-PPV, such as MEH-PPV ($\eta_{\mathrm{PL}} \approx 15\%$),[9] exhibit gain narrowing in waveguides.[2,3] Thus, for BuEH-PPV with $\eta_{\mathrm{PL}} \approx 62\%$, PL quenching by the ITO electrode would not, by itself, be expected to eliminate gain narrowing.

Since microcavities have relatively high Q and efficiently coupled emitted photons to only a few cavity modes,[17] the emission peaks are quite narrow ($\leqslant 7$ nm) even below threshold. Above threshold, the emission peak nearest the gain maximum (550 nm for BuEH-PPV) grows in intensity more rapidly than the other emission peaks as the pump energy increases. Thus, following Tessler *et al.*,[4] we define the mode ratio as the ratio of the integrated power of the lasing mode to that of one of the other spontaneous emission modes.

The emission modes from a BuEH-PPV microcavity (~340 nm of PVK between the BuEH-PPV and Ag mirror) are shown in Fig. 2. All pump energies were corrected for the transmission of the silver. There is a strong emission peak around 552 nm, close to the gain maximum of BuEH-PPV, and observable emission from four other microcavity modes. An abrupt increase in the mode ratio (see inset) is observed near 0.1 μJ/pulse, the lasing threshold. Note that the mode ratio approaches 100 at pump energies that are above threshold but still fairly low (~60 μJ/pulse). Thus, like waveguides, microcavities can produce single-mode emission with a narrow peak when pumped above threshold.

We find that the mode ratio is sensitive to the positions of the cavity modes. If the PVK thickness is adjusted such that resonance occurs at the maximum gain wavelength of

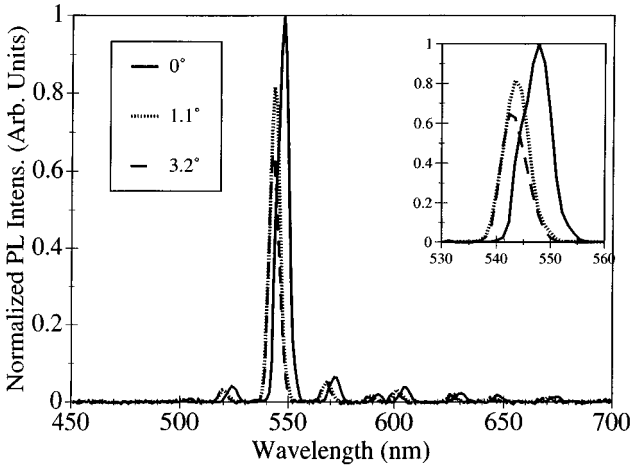

FIG. 3. External observation angle dependence of emission spectra of a microcavity DBR/BuEH-PPV/PVK/Ag at pumping energies above the lasing threshold. PL spectra are normalized to those obtained below threshold. The PVK layer is ~900 nm thick. Inset: Expanded view of the lasing peak near 550 nm.

BuEH-PPV, the normalized mode ratio is greatly enhanced, leading to effectively single-mode emission above threshold (cf. Fig. 2). Single-mode operation is only realized, however, when the lasing peak is located within ~5 nm of the gain maximum. BuEH-PPV microcavities with lasing peak at wavelengths less than ~547 nm or greater than ~554 nm showed mode ratios of only about five, even well above threshold. Hence, to obtain single-mode microcavity lasers, the cavity must be optimized to better than about 5 nm. This result is in contrast to the emission from planar waveguides, where single mode emission is routine.

By interchanging the order of the polymer layers, one can determine whether there is significant PL quenching of the active polymer by the Ag mirror. Regardless of the presence of PVK or the proximity of the BuEH-PPV to the Ag mirror, the lasing threshold was around 0.1 μJ/pulse. There was no indication that thresholds were lower for structures with a PVK buffer layer between the BuEH-PPV and Ag. Thus, although the metal electrode limits the Q of the microcavity, PL quenching by proximity to the metal is not of major importance.

The angular dependence of the emission from a microcavity with a ~900 nm PVK layer between BuEH-PPV and Ag is shown in Fig. 3. This structure showed essentially single-mode emission above threshold similar to the data in Fig. 2. To measure the angular dependence, the emitted light was collected through a 1 mm pinhole placed ~10 cm from the sample, providing angular resolution of ~0.5°. At pump energies below the lasing threshold, the integrated emission intensity decreased by nearly an order of magnitude as the collection angle deviated from 0° to 5° from the normal, a result which indicates fairly high Q. The emission spectra shown in Fig. 3 were collected at three different angles at a pump energy (~10 μJ/pulse) well above the lasing threshold (see Fig. 2 inset). The spectra are scaled such that the intensities of the main peak at below-threshold pumping levels are normalized to the same value so that the directionality that is inherent in microcavity structure has been divided out. Figure 3 shows that above threshold, the normalized intensity of the main peak is reduced by ~35% relative to its below-threshold value as the collection angle is increased from 0° to 3.2°. Thus, in addition to the relatively high degree of directionality expected for microcavities, the directionality is enhanced above the lasing threshold. These observations confirm that the light emitted from optically pumped semiconducting polymer microcavities is laser light.[4]

In summary, the lasing thresholds of the microcavities (~0.1 μJ/pulse) are comparable to the gain narrowing thresholds in planar waveguides[2,3] (0.05 μ J/pulse). Thus, the optical path length within the gain medium is approximately the same in the two structures. Microcavities provide the resonant feedback necessary for ''true'' lasing. The emitted laser light is directional and spectrally narrow. However, these advantages come at a significant expense in device fabrication. Waveguides are easily prepared by spin casting a polymer film from solution. The luminescence from the polymer is amplified when the distance traveled by the guided light exceeds the gain length. Waveguides offer clear advantages for applications which require bright, isotropic, spectrally narrow emission. Microcavities work best for applications where a well-defined beam of emitted light is desired. In both structures, the excited semiconducting polymer leads to amplification with a very short gain length.

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