Amplified spontaneous emission from photopumped films of a conjugated polymer

Michael D. McGehee, Rahul Gupta, Siegfried Veenstra,* E. Kirk Miller, María A. Díaz-García, and Alan J. Heeger
Institute for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, California 93106-5090
(Received 20 January 1998; revised manuscript received 9 March 1998)

By measuring the gain and loss in thin-film planar waveguides using a standard technique developed for inorganic laser materials, we show that the narrow-line emission from photopumped waveguides of the conjugated polymer poly[2-butyl-5-(2’-ethyl-hexyl)-1,4-phenylenevinylene] results from amplification of spontaneous emission (ASE). The narrowed linewidth of the ASE spectrum is determined by gain saturation. The ASE emitted from the edge of the waveguide is polarized because the waveguide is birefringent and only allows TE modes to propagate and be amplified. We compare our results and conclusions to other reports that claim that spectral narrowing in conjugated polymers is a result of superfluorescence or excitonic interactions. The techniques presented in the paper offer a simple and useful way for evaluating conjugated polymers as materials for solid state lasers. [S0163-1829(98)00635-3]

I. INTRODUCTION

Conjugated polymers offer promise as high-gain materials for solid-state lasers.1–12 They undergo population inversion at very low photopump intensities (< 1000 W/cm²), they can be easily integrated onto any type of substrate, they emit at wavelengths that span the visible spectrum, and they can be pumped electrically in a diode configuration.13,14 Several groups have photopumped thin films of conjugated polymers and observed that as the pump intensity is increased the full width at half maximum (FWHM) of the emission spectrum narrows to less than 10 nm. The mechanism of spectral narrowing has been a subject of debate. Reports that narrowing occurs only if the refractive index of the polymer film is higher than that of the substrate and if the film is thick enough to support waveguiding1 suggest that spectral narrowing results from amplification of spontaneous emission (ASE), a process by which spontaneously emitted light is amplified by stimulated emission as it travels down the waveguide.1,2,4,8,10 ASE narrows the emission spectrum because the amplification is maximum at the wavelength where the net gain is highest.15,16 Other reports have attributed spectral narrowing to superfluorescence,5,6 a phenomenon in which emitters interact with each other over relatively large distances through their overlapping radiation fields and form a coherent state that undergoes cooperative spontaneous emission.17 It has also been suggested that both ASE and superfluorescence occur with the superfluorescent emission being amplified by stimulated emission as it travels down a waveguide.18 Finally, there have been proposals that the spectral narrowing might result from interacting excitons (biexcitons9 or condensed excitons), which form a state that has a narrow emission spectrum. It is clearly important to distinguish between these mechanisms since it is only possible to make lasers from conjugated polymers if stimulated emission plays the dominant role.

The approach we have taken to identify the mechanism of spectral narrowing is to photopump the sample with a stripe of variable length and to measure the intensity of the light out the end of the stripe. If ASE occurs, the spectra should be broad at short stripe lengths and should narrow as the excitation length increases. The output intensity from one end of the stripe should be given by the following expression:

\[
I(\lambda) = \frac{A(\lambda)I_p}{g(\lambda)} (e^{g(\lambda)l} - 1),
\]

where \(A\) is a constant related to the cross section for spontaneous emission, \(I_p\) is the pump intensity, \(g\) is the net gain coefficient, and \(l\) is the length of the pumped stripe.15,20,21 In contrast, if superfluorescence or biexcitonic emission is the mechanism of spectral narrowing, the emission spectrum should not depend on the size of the excited region and the output should only increase linearly with the length of the excited region (or sublinearly if waveguide losses are substantial).

In this paper, we present the results of measuring the emission spectra from the ends of waveguides made from films of the conjugated polymer poly[2-butyl-5-(2’-ethyl-hexyl)-1,4-phenylenevinylene] (BuEH-PPV). The data show that the emission spectra change exactly as predicted by ASE theory when the pump intensity and pump stripe length are varied.

II. EXPERIMENTAL METHODS

Planar waveguides were made by spin casting 150–300-nm-thick films of BuEH-PPV (Ref. 22) from 12.5 mg/ml xylene solutions onto silicon wafers that were coated with a 1-μm-thick layer of SiO₂. We measured the refractive index of the BuEH-PPV using variable angle spectroscopic ellipsometry; at 550 nm, the index is 1.76 for the electric field in the plane of the film and 1.51 for the electric field perpendicular to the film. This anisotropy is a consequence of the polymer chains lying preferentially in the plane of the substrate.23,24 Waveguide modeling of these structures shows that for 150–300 nm-thick films, there is only one TE mode and that there are no TM modes.

Since the shape of a waveguide mode depends on the film thickness, it is desirable to have a film with uniform thickness. The spin-cast BuEH-PPV films were uniform and of high quality everywhere except near the edge of the substrate. To remove the nonuniform edge bead region, we cleaved the silicon substrates and performed the measure-
ments at the cleaved edge. Even though BuEH-PPV films are not brittle, they snap to form relatively nice edges if the silicon wafer is cleaved with the BuEH-PPV film in tension.

The samples were photopumped at 435 nm, which is close to the absorption maximum of BuEH-PPV, using 10-ns pulses from the output of a hydrogen Raman shifter pumped by a frequency doubled Nd:YAG (yttrium aluminum garnet) laser (532 nm, 10 Hz repetition rate). The energy of the pulses was controlled using a set of calibrated neutral density filters. The beam had a relatively uniform top-hat spatial profile with a diameter of 10 mm. An adjustable slit and a cylindrical lens were used to shape the beam into a stripe with a width of approximately 350 μm and a length that could be varied. In order to ensure that the intensity of the stripe was uniform along its length, we used the adjustable slit to select only the central portion of the beam and used stripe lengths of 2 mm or less. We confirmed that the intensity was uniform along the length of the stripe by imaging the stripe with a charge-coupled device (CCD) camera and zoom lens.

When ASE occurs in a long, narrow stripe, most of the light is emitted from the ends of the stripe. For this reason, we placed the pump stripe right up to the edge of the BuEH-PPV films and collected the edge emission with a 5-cm-diameter, 10-cm focal length lens. The emission spectra were detected using a grating spectrometer equipped with a thermoelectrically cooled CCD detector. Zenz et al. observed that the spectral position of the narrowed spectrum varied by approximately 2 nm when they took single pump shot spectra. To look for this effect, we also took single shot spectra, but did not see variations in the spectral position. To improve the signal-to-noise ratio, we integrated 10–50 shots for all of the data that are presented in this paper.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the emission spectra that were collected at various pump intensities with a constant pump stripe length of 2 mm. When the pump intensity was less than 0.6 kW/cm², there was a broad spectrum with overlapping vibronic peaks, which is characteristic of spontaneous emission from conjugated polymers. At these low intensities the shape of the spectrum did not depend on the pump intensity. As the pump intensity was increased above 0.6 kW/cm², the intensity at the peak of the spectrum grew much more than the intensity at other wavelengths, resulting in a spectrum with a FWHM of only 8 nm at pump intensities of 1.5 kW/cm² or higher [Fig. 1(b)].

The photoluminescence lifetime of BuEH-PPV is 900 ps, which is much shorter than the length of the pump pulses (10 ns) that were used. Consequently, the excited state dynamics are a quasisteady state, and the excitation density is determined by the pump intensity. The pump intensities reported in this paper are average values because the temporal profile of the pump pulses was not a square wave. When results obtained on different polymers are compared, it is important to take into account that in some cases only a fraction of the pump light is absorbed. A 150-nm-thick film of BuEH-PPV absorbs approximately 90% of the pump light at the wavelength of 435 nm.

Although the spectra presented in Fig. 1 are not sufficient to conclusively identify the mechanism of spectral narrowing, we note that the narrowed spectrum is located at the peak of the fluorescence spectrum, as one would expect for ASE. Most reports of spectral narrowing have shown that the narrowed spectrum was located at either the 0-0 or 0-1 vibrational peak of the fluorescence spectrum. In some cases the 0-1 peak became the dominant peak at high excitation densities even though the 0-0 peak was taller at low excitation densities. ASE occurs at the vibronic peaks because this is where the gain is highest; the 0-1 peak sometimes has a higher net gain than the 0-0 peak because it is farther from the absorption edge and therefore has less self-absorption loss. For some polymers the maximum gain wavelength might not coincide with the vibronic peaks in the fluorescence spectrum because of highly dispersive self-absorptive loss or photoinduced absorption.

Figure 2 shows the dependence of the light intensity emitted from the edge, integrated over all wavelengths, on the pump intensity. It can be determined from the change in slope at 1 kW/cm² that the measured relative efficiency increased by a factor of 6 when spectral narrowing occurred. This contrasts the results of Gelinck et al. who observed a
reduction in efficiency when spectral narrowing occurred. An important difference between our experiments and those of Gelinck et al. is that we measured the light emitted from the edge of the film while they measured the light emitted at 45° from the surface. When ASE occurs in a long, narrow excitation region, most of the light is emitted out of the two ends of the region because light is highly amplified if it travels across the full length of the gain region. In accordance with ASE theory, we observed a strong beam emitted from the edge of the waveguide when spectral narrowing occurred. The main reason we measured an increase in efficiency when ASE took place is that we were detecting the edge emission, which is enhanced by ASE. We suspect that Gelinck et al. saw a decrease in efficiency above the threshold for spectral narrowing because most of the excitations were stimulated to emit into waveguide modes, which traveled away from the direction of their light detection. A second reason for the increase in the efficiency measured from the end of the waveguide is that the quantum efficiency increases as a result of stimulated emission being faster than most nonradiative processes. This factor cannot be very large, however, because the quantum efficiency of BuEH-PPV is already 62%, even at low-excitation densities.

Although the dependence of the light emission on pump intensity presented above is fully consistent with ASE, it does not conclusively prove that the mechanism of line narrowing is a result of ASE, nor does it rule out the possibility that another mechanism could be present. Figure 3 shows the dependence of the FWHM of the emission spectra on the length of the pump stripe at two different pump intensities. As predicted by ASE theory, the spectra are broad when the pump stripe length is short, but become narrower as the pump stripe length is increased. At a pump intensity of 0.6 kW/cm², the emission spectrum narrows very gradually with excitation length because the gain is very low. At higher pump intensities, spectral narrowing occurs more rapidly as the excitation length is increased because the gain is higher. Once the FWHM reaches approximately 8 nm, gain narrowing is halted by gain saturation, as we will discuss below. These results rule out the possibility that the spectral narrowing is a result of superfluorescence or spontaneous emission from a biexcitonic state since the emission spectra would have been narrow at short excitation lengths if either of these phenomenon were the mechanisms of spectral narrowing.

Figure 4 shows the output intensity at the peak of the emission spectrum (λ = 562 nm) as a function of pump stripe length at four different pump intensities. By fitting the data to Eq. (1), (see Table I) we were able to measure the net gain of the waveguides as a function of pump intensity. At a pump intensity of 0.6 kW/cm², the net gain was less than 1 cm⁻¹ and very little amplification took place over the stripe length of 2 mm. Since g₁l<1 even when l=2 mm, most of the light was emitted by spontaneous emission and the spectrum was not fully narrowed (Fig. 3). At a pump intensity of 1.2 kW/cm², the net gain was 18 cm⁻¹ and the output intensity increased by almost two orders of magnitude as the excitation length was increased. The excellent agreement of the data with Eq. (1) is strong evidence for amplification of spontaneous emission by stimulated emission.

At higher pump intensities the net gain was higher and the output intensity increased exponentially at excitation lengths of less than 1 mm, as expected, but then saturated at longer
excitation lengths. To see if the saturation was a result of sample degradation, we repeated the measurements at the same sample spot and were able to obtain the same curves. We can, therefore, rule out the possibility that the amplification saturated at the higher pump intensities because of sample degradation. Another possibility is that gain saturation occurred because the light traveling in the waveguide was so strongly amplified that it depleted a substantial fraction of the excitations. When gain saturation occurs, the gain coefficient is reduced and light is not amplified further as the length of the stripe is increased.\textsuperscript{15} We have not attempted to precisely calculate the pump intensity at which gain saturation should occur in conjugated polymers because we do not know to what extent the polymers are inhomogeneously broadened and hence do not know how many of the excited states are able to emit at the peak wavelength of the ASE spectrum. We note, however, that $g \approx 4$ where gain saturation onsets. It is not surprising that gain saturation occurs when $g \approx 4$, since spontaneous emission that is amplified by the factor $\exp(4)$ is most likely intense enough to significantly depopulate the excitation density. Comparing Figs. 3 and 4, one sees that when gain saturation occurs, gain narrowing ceases and the FWHM of the emission spectrum is constant at 8 nm. Thus, the FWHM of the ASE spectra well above the threshold for gain narrowing is determined by gain saturation, not the lifetime of the emissive state as has been claimed in reports\textsuperscript{6} that attributed spectral narrowing to spontaneous emission that is amplified by the factor $\exp(4)$.

We have measured the polarization of the light emitted from the edge of the samples. Below the threshold for ASE the intensity of light polarized parallel to the substrate was approximately three times the intensity polarized perpendicular to the substrate. Above the threshold for ASE, the emission was fully polarized parallel to the substrate plane, regardless of the polarization of the pump beam. The polarization arises because the polymer chains lie preferentially in the plane of the substrate. In the ASE regime, the edge emission is highly polarized because the birefringent waveguide does not support TM modes and hence only allows TE light to be substantially amplified. At low pump intensities (below the onset of ASE), the birefringent waveguide does not have as much of an effect on the polarization of the edge emission because the waveguided light is attenuated due to waveguide loss (see below). Consequently, only light that is emitted near the edge is detected.

To more fully characterize conjugated polymers as laser materials, we measured the loss of the waveguides by performing experiments where we kept the length of the pump stripe constant and moved the pump stripe away from the edge of the sample (see inset to Fig. 5). Assuming that the emission from the end of the pump stripe $I_0$ is constant, the emission from the edge of the sample should decrease (as a result of waveguide losses) as $I = I_0 \exp(-\alpha x)$, where $x$ is the length of the unpumped region between the end of the pump stripe and the edge of the sample and $\alpha$ is the loss coefficient. Figure 5 shows the intensity of the emission at $\lambda = 562$ nm as a function of $x$. By curve fitting these data to an exponential, we measured the loss coefficient to be approximately 44 cm$^{-1}$.

One of the keys to reducing the pump intensities needed for net gain is to reduce the loss, which arises from scattering and self-absorption. Although our films appear to be quite homogeneous, it is possible that there are inhomogeneities at the submicrometer length scale that could cause scattering. Work is in progress to improve film quality by filtering and heating the solutions just before spin casting. Following the work of Berggren \textit{et al.}\textsuperscript{26} and Kozlov \textit{et al.}\textsuperscript{27} we have blended small amounts of a red-emitting polymer in a green-emitting host. In these blends self-absorption is reduced because energy transfer from the host to the emitter moves the emission wavelength farther from the absorption edge. The blends have losses of less than 3 cm$^{-1}$ and exhibit net gain at substantially lower pump intensities.\textsuperscript{28}

As a final test and important application of our hypothesis that thin films of conjugated polymers function as gain materials through amplification by stimulated emission, we have fabricated optically pumped distributed feedback (DFB) lasers.\textsuperscript{29} The thin-film samples described above are not lasers because they do not have a resonant structure and hence do not have discrete lasing modes. In the DFB structures, we have incorporated resonant feedback by etching a grating into the silicon dioxide before spin casting the polymer films. The grating provides a periodic perturbation in the refractive index of the waveguide, which results in reflections at wavelengths near $\lambda_{\text{Bragg}} = 2n_{\text{eff}}\Lambda$, where $n_{\text{eff}}$ is the effective refractive index of the waveguide and $\Lambda$ is the period of the index perturbation.\textsuperscript{30,31} By varying the grating

<table>
<thead>
<tr>
<th>Pump intensity (kW/cm$^2$)</th>
<th>$A_{I_p}$ (arb. units)</th>
<th>$g_{\text{net}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>3700</td>
<td>0.1</td>
</tr>
<tr>
<td>1.2</td>
<td>5500</td>
<td>18</td>
</tr>
<tr>
<td>2.2</td>
<td>7700</td>
<td>41</td>
</tr>
<tr>
<td>4.1</td>
<td>7100</td>
<td>62</td>
</tr>
</tbody>
</table>
period, we were able to systematically vary the lasing wavelength from 540 to 583 nm. The fact that we are able to make a laser and tune the emission wavelength is further evidence that thin films of conjugated polymers exhibit amplification by stimulated emission when photopumped. If the spectral narrowing were a result of superfluorescence or biexcitonic emission, the emission wavelength would not depend on the grating period.

IV. CONCLUSIONS

We have presented unequivocal evidence that thin films of the conjugated polymer BuEH-PPV exhibit light amplification by stimulated emission. We suspect that reports that attributed spectral narrowing to superfluorescence or biexcitonic emission incorrectly identified the mechanism of spectral narrowing, which was probably also ASE. However, since those reports dealt with different polymers and experimental configurations, we cannot be certain that other mechanisms were not present. In some cases, ASE might have been prevented by using samples that did not allow waveguiding or by using very small excitation spot sizes. In some cases, very high-excitation densities were required for spectral narrowing, phenomena other than ASE cannot be ruled out. We caution, however, that if one does not measure the edge emission from a polymer waveguide and explore a wide range of pump intensities and pump stripe lengths, it is possible to obtain results that are characteristic of changes in the spatial pattern of emission or of gain saturation. These results might be misinterpreted even if ASE has occurred.

The techniques used in this paper, discovered almost 30 years ago for characterizing the inorganic semiconductor CdS, offer a very simple method for measuring the gain and loss of conjugated polymer waveguides. Characterizing conjugated polymers in this way will be helpful in evaluating conjugated polymers as materials for solid-state lasers and in developing polymer diode lasers.

ACKNOWLEDGMENTS

We would like to thank Dan Cohen for several helpful discussions. This work was funded as a seed project by the NSF-MRSEC at UCSB (Contract No. DMR96-32716) with additional support from the Office of Naval Research (Kenneth Wynn, Program Director). M.A.D.-G. was partially supported by the Government of Spain. S.V. was partially supported by the Royal Dutch Chemical Society, the Royal Institute for Engineers, and the University of Groningen, and wishes to thank Professor G. Hadziioannou for his support.

*Present address: Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.


