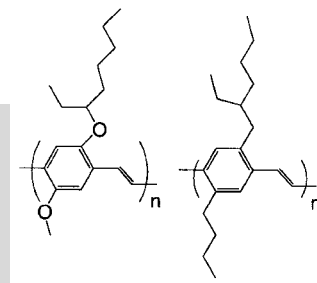


# Semiconducting (Conjugated) Polymers as Materials for Solid-State Lasers\*\*

By Michael D. McGehee and Alan J. Heeger\*

Light-emissive polymers are outstanding laser materials because they are intrinsically "4-level" systems, they have luminescence efficiencies higher than 60 % even in undiluted films, they emit at colors that span the visible spectrum, and they can be processed into optical quality films by spin casting. The important materials issues are reviewed and the prospects for making polymer diode lasers are discussed.



## 1. Introduction

Since the discovery of the metallic properties of doped polyacetylene in 1977,<sup>[1]</sup> remarkable progress has been made in synthesizing conjugated polymers, in understanding their properties, and in developing them for use in electronic and optical devices.<sup>[2]</sup> Currently, polymer light-emitting diodes (LEDs),<sup>[3,4]</sup> photodetectors,<sup>[5]</sup> photovoltaic cells,<sup>[6]</sup> sensors,<sup>[7]</sup> and field-effect transistors<sup>[8–10]</sup> are all being pushed towards commercialization by academic and industrial research teams. These devices are important not only because they perform well, but because they can be patterned by inexpensive techniques such as spin casting, photolithography,<sup>[11,12]</sup> ink jet printing,<sup>[13,14]</sup> screen printing,<sup>[15]</sup> and micromolding<sup>[16]</sup> onto almost any type of substrate, including flexible ones.<sup>[17]</sup>

Notably absent from the list of electronic and optical devices that can be made from conjugated polymers is one of the most important devices for modern technology—the diode laser. When a new class of materials is under development for possible use in diode lasers, it is usually beneficial to start by excitation through photopumping so that stimulated

emission (and gain) can be studied without the complications that are associated with current injection, charge transport, and electrode incorporation.

In 1992 Moses demonstrated lasing from conjugated polymers for the first time when he photopumped a cuvette that contained a solution of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV, Fig. 1).<sup>[18]</sup> After this demonstration, many researchers set out to observe stimulated emission or lasing from polymers in the solid state. Most of the early studies were based on pump-probe spectroscopy, which measures the stimulated emission and excited-state absorption spectra. Rothberg et al. reported that MEH-PPV only exhibited stimulated emission if it was in solution or diluted in a solid matrix such as polystyrene.<sup>[19]</sup> This observation implied that interactions between neighboring polymer chains were important and could prevent neat (undiluted) films from amplifying light. Early in 1996 Hide et al. observed

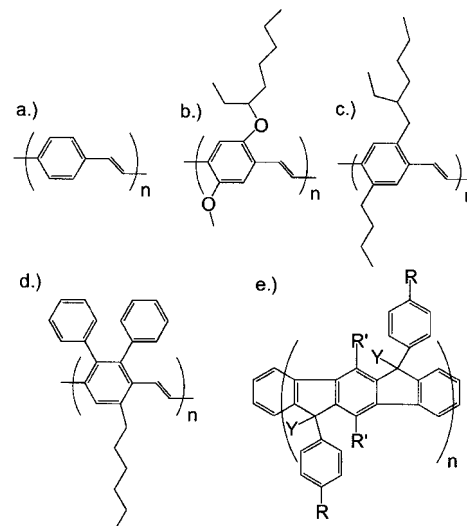


Fig. 1. The chemical structures of several luminescent polymers that have been used as gain materials in lasers. a) PPV. b) MEH-PPV. c) BuEH-PPV. d) DP6-PPV. e) PPP-type ladder polymer ( $Y = \text{CH}_3$ ,  $R = \text{C}_{10}\text{H}_{21}$ ,  $R' = \text{C}_6\text{H}_{13}$ ).

[\*] Prof. A. J. Heeger  
Institute for Polymers and Organic Solids  
Departments of Physics and Materials  
University of California at Santa Barbara  
Santa Barbara, CA 93106-5090 (USA)  
E-mail: ajh@physics.ucsb.edu

Prof. M. D. McGehee  
Department of Materials Science and Engineering  
Stanford University  
Stanford, CA 94305-2205 (USA)

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lasing from polymers in the solid state for the first time when they blended titania nanoparticles into a MEH-PPV/polystyrene film.<sup>[20]</sup> In these lasers, the random array of titania particles scattered the light emitted by the MEH-PPV in such a way that the feedback loops needed for lasing were provided.

Later in 1996, four research groups independently observed stimulated emission from photopumped neat films of conjugated polymers. These observations showed for the first time that neat films, which were capable of conducting current, could in fact amplify light and that it was not unreasonable to attempt to make polymer diode lasers. Graupner et al. observed stimulated emission from films of a poly(*para*-phenylene)-type ladder polymer (Fig. 1) using pump-probe techniques.<sup>[21]</sup> Tessler et al.<sup>[22]</sup> obtained lasing by sandwiching poly(*p*-phenylene vinylene) (PPV, Fig. 1) between a dielectric mirror and a silver mirror to form a microcavity. Hide et al.<sup>[23]</sup> and Frolov et al.<sup>[24,25]</sup> observed line narrowing from films of PPV derivatives that were not part of a resonant structure. The mechanism of line narrowing was a subject of intense debate, but most researchers now agree that the spectrally narrow light is amplified spontaneous emission (ASE).<sup>[26–29]</sup> ASE occurs even when the gain coefficient is small because the spontaneously emitted photons are waveguided and thus travel a large distance through the gain medium, where they are amplified by stimulated emission.

Over the last four years many groups have investigated the photophysical properties of conjugated polymers to understand why some polymers exhibit stimulated emission while others do not. In Section 2 we review this research, which

shows that controlling chain morphology and avoiding defect formation is important. In Section 3 we describe a series of ASE experiments and show that they provide simple methods for measuring the gain and loss of polymer waveguides. Section 4 shows that the threshold for ASE and lasing can be lowered by one order of magnitude by blending two polymers in such a way that energy is transferred from a host polymer to a guest polymer to move the emission wavelength to a spectral region where absorptive losses are smaller. In Section 5 we describe the different resonant structures that have been used to make polymer lasers. In Section 6 we outline the issues that must be addressed to make polymer diode lasers. Finally in Section 7 we draw some conclusions and provide an outlook for the future of research on polymer lasers.

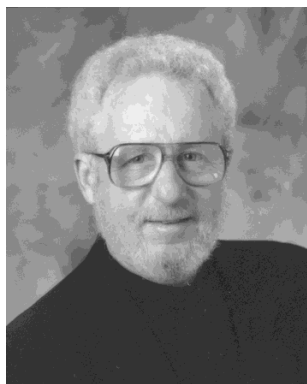
For this review we have attempted to cover most of the research on the use of conjugated polymers as laser materials, but have undoubtedly emphasized our own research. We apologize for any results we may have left out. Our review does not cover the excellent work that has been done on making lasers with small organic molecules. For this we refer the reader to the papers of Dodabalapur<sup>[30]</sup> and Forrest.<sup>[31,32]</sup> We also recommend the reviews on polymer lasers by Tessler<sup>[33]</sup> and Frolov.<sup>[34]</sup>

## 2. The Photophysical Properties of Conjugated Polymers

There are several properties that a material must have in order for it to be useful as the gain medium in a laser. First of



*Michael McGehee was born in 1972 and raised in Richmond, Virginia. After receiving his undergraduate degree in physics from Princeton University in 1994 he moved on to the University of California at Santa Barbara, where he received a Ph.D. in 1999 for his research accomplishments in Alan Heeger's group on the use of semiconducting conjugated polymers as materials for lasers and energy transfer from polymers to rare-earth complexes. After completing his graduate studies, he stayed in Santa Barbara briefly to study self-assembled block-copolymer/metal-oxide nanostructures in the research groups of Alan Heeger, Galen Stucky, and Bradley Chmelka. In the spring of 2000 he went to Stanford University to become an assistant professor in the Materials Science and Engineering Department.*



*Since his codiscovery of conducting polymers, Professor Alan Heeger and his colleagues at the University of California, Santa Barbara, have done pioneering research on semiconducting and metallic polymers. He was recently awarded the Nobel Prize in Chemistry for his many accomplishments in this area. His current interests lie in the development of the fundamental physics and the interdisciplinary materials science that determine the electronic and optical properties of this novel class of materials with the goal of developing semiconducting and metallic polymers for use in technology. UNIAX Corporation, co-founded by Professor Heeger in 1990, is focused on bringing plastic electronics into commercial products.*

all, it is desirable for the material to have the electronic structure of a four-level system so that the stimulated emission spectrum does not overlap with the ground state absorption spectrum.<sup>[35]</sup> Fortunately, most conjugated polymers naturally form a four-level system because structural and vibronic relaxation in the excited state shifts the energy levels.<sup>[36]</sup> Moreover, since there is disorder in polymer films, the conjugation length is not the same throughout the film and there are variations in the bandgap energy. Consequently, energy can be absorbed in one region and then transferred to another region where the bandgap is smaller.<sup>[37]</sup> Figure 2 shows a schematic of the energy levels of a conjugated polymer and typical absorption and emission spectra. Since the absorption spectrum is both broad and intense ( $\alpha_{\max} > 10^5 \text{ cm}^{-1}$ ), thin films (150 nm) can absorb more than 90 % of the photons from a pump source. At the same time, however, emitted photons can travel large distances (100  $\mu\text{m}$ ) without being reabsorbed. In contrast, the absorption of most inorganic semiconductors

at the peak emission wavelength is usually quite significant and transparency is only obtained at relatively high pump intensities.

A good laser material should have high luminescence efficiency and a high chromophore density. Fortunately, most conjugated polymers also excel in this regard. If the polymer side chains are designed in such a way that aggregates do not form between neighboring chains,<sup>[38,39]</sup> photoluminescence efficiencies higher than 60 % can be obtained even in undiluted films.<sup>[40]</sup> This property should not be taken for granted, because the efficiency of many laser chromophores, such as dyes and rare earth ions, drops significantly at high concentrations.

As light travels in a gain medium, its intensity grows exponentially according to  $I = I_0 \exp[(g - \alpha)l]$ , where  $I_0$  is the initial intensity,  $g$  is the gain coefficient,  $\alpha$  is the loss coefficient, and  $l$  is the length of the gain medium. The gain coefficient is given by  $g = \sigma n$ , where  $\sigma$  is the cross section for stimulated emission and  $n$  is the density of electrons in the excited state. For a laser material to have a large gain coefficient, it must have a large cross section for stimulated emission. Many conjugated polymers have an extremely large cross section ( $\sigma \approx 10^{-15} \text{ cm}^2$ )<sup>[25,41,42]</sup> because the  $\pi$ - $\pi^*$  transition is allowed and the quasi-one-dimensional electronic wavefunctions have a high density of states at the band edge.

One more important photophysical criterion for laser materials is that the excited-state absorption spectrum should not overlap with the stimulated emission spectrum. The two transitions that tend to be problematic for many laser materials are absorption from the radiative state into higher lying energy levels (Fig. 2a) and triplet absorption. Triplet absorption has been found to be particularly problematic for many laser dyes because of the long lifetime of the triplet state. (The triplet problem in dye lasers is avoided by flowing the dye solution or by using a triplet quencher). Fortunately, for most polymers the triplet absorption spectrum lies lower in energy than the emission spectrum.<sup>[43-46]</sup> On the other hand, for many polymers, excited-state absorption into higher lying energy levels can be a serious problem. In fact, excited-state absorption is the problem that prevented the observation of lasing from polymers before 1996.

The primary technique for measuring excited-state absorption is time-resolved pump-probe spectroscopy. An ultrafast pulse of intense laser light is used to pump the sample and then weaker pulses of light at varying time delays and with varying wavelengths are used to probe the sample. At wavelengths where stimulated emission is dominant, the probe beam is amplified; at wavelengths where excited-state absorption is dominant, the probe beam is attenuated. When Rothberg et al. did their first studies on MEH-PPV, they found that the stimulated emission spectrum looked similar to the photoluminescence spectrum if the MEH-PPV chains were isolated in solution or in a polystyrene matrix; the excited-state absorption spectrum was in the near infrared (IR) and did not overlap with the stimulated emission spectrum.<sup>[19]</sup> However, when they studied neat films of MEH-PPV, they found that the excited-state absorption spectrum broadened

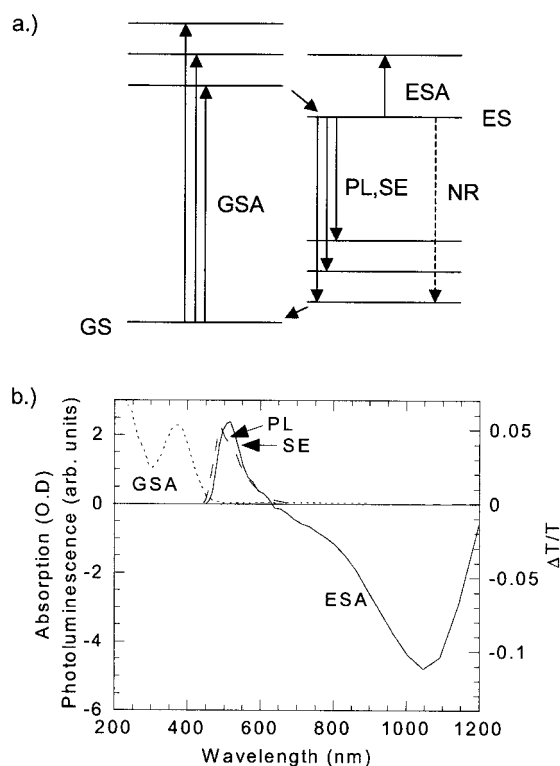


Fig. 2. a) A schematic diagram of the “four-level” energy system and important transitions for a polymer such as DP6-PPV that does not form aggregates or contain a substantial number of defects. When the ground state (GS) is photo-pumped, ground-state absorption (GSA) occurs and a manifold of excited-state vibrational levels are generated. Within 100 fs, excited electrons cascade into the lowest energy vibrational state and induce a structural relaxation, which shifts the energy of the excited state (ES). From there, several processes can occur. At low photon densities, photoluminescence (PL) and non-radiative (NR) recombination are the dominant processes and the excited-state lifetime is slightly less than 1 ns. If the photon density is high, stimulated emission (SE) can become the dominant process and the excited-state lifetime can be shortened. Excited-state absorption (ESA) does not compete with SE in DP6-PPV because it occurs at longer wavelengths. Once an electron falls from the excited state, structural relaxation occurs rapidly. Consequently, the population inversion needed for lasing to occur can be obtained at low excitation densities. b) The ground state absorption (dotted line), PL (dashed line), and excited-state spectrum (solid line) of DP6-PPV. The methods used for obtaining these data are described in [55].

and shifted to cover the photoluminescent region of the spectrum. Consequently, there was no region of the spectrum that had net gain. Their conclusion was that some of the excited states spread out over multiple chains to create weakly emissive aggregate states that absorb light in the photoluminescent region of the spectrum.<sup>[47]</sup>

Since the first reports from Rothberg et al., there have been many more studies of MEH-PPV and other luminescent polymers, and a wide variety of seemingly contradictory results have been reported. For example, there are now several reports that MEH-PPV can exhibit stimulated emission, even in neat films.<sup>[23,48–50]</sup> The first clues that led to an explanation of the discrepancies in the literature were the observation by Hide et al.<sup>[23]</sup> that MEH-PPV films cast from tetrahydrofuran (THF) solutions gave off ASE at much lower pump intensities than films cast from chlorobenzene or *p*-xylene solutions and the observation by Denton, Harrison et al.<sup>[51,52]</sup> that photo-oxidation could cause excited-state absorption to replace stimulated emission. Nguyen et al. have carefully studied the photophysical properties of MEH-PPV films cast from different solvents. They found that solvents such as THF, which interacts preferentially with the polymer side chains, cause the polymer chains to form tight coils, while solvents such as chlorobenzene (CB), which interacts preferentially with the aromatic rings, cause the polymer chains to lie open and flat.<sup>[39,53]</sup> Furthermore, they found that aggregate formation was much more common in the films that had open and flat chains because of the enhanced  $\pi$ -stacking that occurs between neighboring chains. The dramatic impact that chain morphology can have on photophysical properties can be seen in Figure 3, which shows the photoluminescence spectrum of films cast from 0.25 % (weight/volume) and 1.0 % solutions of MEH-PPV in THF and CB. The films spin cast from the more concentrated solutions have a significantly red-shifted spectrum. The shift is attributed to aggregate fluorescence and to a change in the vibronic structure of the emission spectrum. Nguyen et al. have also shown that the time dynamics of the excited states, the shape of the excited-state spectrum, the sensitivity to degradation, and the threshold for exciton-exci-

ton annihilation (E-EA) all depend on the chain packing morphology. They reviewed much of the literature on the photophysical properties of PPV derivatives and concluded that the differing results probably arose because data had been collected from films made under different conditions. An important lesson to be learned from these studies is that the properties of conjugated polymer films are quite sensitive to chain packing morphology, which can vary dramatically depending on preparation conditions. It is unfortunate that the morphology of polymer films is difficult to quantify and that most reports on the photophysical properties of conjugated polymers do not address this issue.

Aggregate formation can be avoided by introducing side groups onto the conjugated main chain that twist the chain to prevent  $\pi$ -stacking and/or shield neighboring chains from one other. Examples of such polymers are poly(2-butyl-5-(2'-ethylhexyl)-1,4-phenylene vinylene) (BuEH-PPV)<sup>[40]</sup> and poly(2,3-diphenyl-5-hexyl-*p*-phenylene vinylene) (DP6-PPV).<sup>[54]</sup> These polymers have luminescence efficiencies higher than 60 %. Their chemical structures are shown in Figure 1. Figure 2 shows the absorption, photoluminescence and excited-state spectrum of DP6-PPV. Note that the stimulated emission spectrum has almost exactly the same shape as the photoluminescence spectrum. This indicates that excited-state absorption does not compete with stimulated emission and hence does not reduce the gain. Moreover, the photoluminescence lifetime and the lifetimes of the states responsible for stimulated emission and excited-state absorption are all the same. This indicates that only one type of excited state is formed in DP6-PPV, which implies that migration of excitations to defect sites or to aggregates is not important.

We conclude that polymers like DP6-PPV are well-suited to laser applications: they can be accurately described as having the electronic structure of a four-level system, they are highly fluorescent, they have a large stimulated emission cross section, and they are not hindered by excited-state absorption.

There have been some concerns that E-EA,<sup>[55]</sup> a process by which neighboring excited states destroy each other, could interfere with lasing in polymers. Fortunately, E-EA only becomes significant at excitation densities of  $10^{-18} \text{ cm}^{-3}$  or higher.<sup>[39,56]</sup> Since the stimulated emission cross section for most luminescent polymers is approximately  $10^{-15} \text{ cm}^2$ , the gain coefficient is  $100 \text{ cm}^{-1}$  at an excitation density of only  $10^{17} \text{ cm}^{-3}$ . For the best laser polymers, the losses from ground-state and excited-state absorption are small, so lasing occurs at excitation densities of approximately  $10^{17} \text{ cm}^{-3}$ ,<sup>[42]</sup> where E-EA is negligible. Moreover, with host-guest blending (see Sec. 4) the ASE threshold can be further reduced to approximately  $10^{16} \text{ cm}^{-3}$ . Consequently, we conclude that E-EA does not hinder the performance of polymers as laser materials. It is worth noting that some of the discrepancies in the literature over the threshold for E-EA may have arisen because some researchers incorrectly attributed a decreased excited-state lifetime to E-EA when ASE was actually occurring instead.<sup>[39,57]</sup>

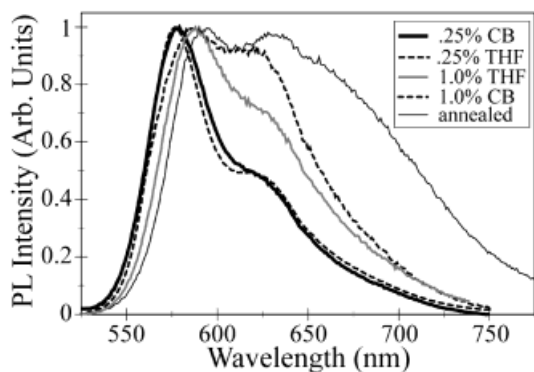


Fig. 3. PL of MEH-PPV films spin cast from a 0.25 % w/v solution in CB (thick solid curve), a 0.25 % w/v solution in THF (dotted curve), a 1.0 % solution in THF (gray solid curve), a 1.0 % CB solution (dashed curve), and a film that was annealed at 215 °C (thin solid curve). This figure was provided by Benjamin Schwartz.

### 3. Amplified Spontaneous Emission

Although pump-probe spectroscopy provides detailed information on the nature of the excited states in a material, it is certainly not the easiest method for characterizing a polymer as a laser material. A much easier technique is to photopump a thin-film waveguide, which can be made by casting a film on a low-refractive-index substrate. When the pump intensity is high enough for the polymer to have net gain, the spontaneously emitted photons are exponentially amplified by stimulated emission as they travel through the waveguide. Since the gain is maximal near the peak of the spontaneous emission spectrum, the spectrum exhibits “gain narrowing”. Consequently, an intense, spectrally narrow beam is emitted from the ends of the waveguide. An experimental advantage of this technique is that the “probing” photons are internally created. For this reason there is no need to generate an external probe beam or to couple the probe into the waveguide. Structures that give off ASE are sometimes referred to as “mirrorless lasers”, because they have most of the properties of a laser.<sup>[35]</sup> As we will show in Section 5, it is straightforward, but non-trivial, to convert a mirrorless laser into an actual laser by incorporating resonant feedback. For this reason, most polymer characterization for laser development is done with mirrorless laser structures knowing that the polymers can be incorporated into a resonant structure once they have been optimized.

Our research group and several others have done studies of ASE from polymer films.<sup>[23,26–29,36,57–59]</sup> As an example, here we summarize our data obtained with 150–300 nm thick films of BuEH–PPV on silica.<sup>[26]</sup> In some cases, a film of polymethylglutarimide ( $n = 1.54$ ) was deposited on top of the BuEH–PPV to form a protective cladding. The refractive index (at  $\lambda = 550$  nm) of the polymer was measured by variable angle spectroscopic ellipsometry (VASE); for the electric field in the plane of the film, the index was 1.76, while for the electric field perpendicular to the film, the index was 1.51.<sup>[60]</sup> The anisotropy in the refractive index is a consequence of the polymer chains lying preferentially in the plane of the substrate.<sup>[61,62]</sup> Waveguide modeling of the structures shows that because of this anisotropy, for 150–300 nm thick films, there is only one transverse electric (TE) mode, and there are no transverse magnetic (TM) modes. The samples were photopumped at 435 nm, which is close to the absorption maximum of BuEH–PPV,<sup>[40]</sup> using 10 ns pulses from the output of a hydrogen Raman shifter that was pumped by a frequency doubled Nd:YAG laser (532 nm, 10 Hz repetition rate). Since the photoluminescence (PL) lifetime of BuEH–PPV is approximately 0.9 ns,<sup>[63]</sup> which is small compared to the pulse time, the measurement conditions were quasi-steady state. Consequently, the excitation density is a function of the pump intensity, not the pump energy. For this reason we show our data as a function of pump intensity. In some cases, other groups made measurements with pump pulses that are much shorter than the PL lifetime. Under those conditions, the excitation density is a function of pump energy. When data from

these two different types of experiments are compared, the excitation density should be calculated since it is not meaningful to compare pump intensities or energies if one experiment was run at steady state and the other was not. In our experiments an adjustable slit and a cylindrical lens were used to shape the YAG beam into a stripe with a width of approximately 350  $\mu\text{m}$  and a length that could be varied. The stripe configuration was chosen because it is easier to analyze ASE from a one-dimensional gain region than from a two-dimensional disk. When ASE occurs in a long, narrow stripe, most of the light is emitted from the ends of the stripe.<sup>[35]</sup> For this reason, the pump stripe was positioned right up to the edge of the BuEH–PPV films and the edge emission was collected. In order to observe a clean emission beam, the original edge of the sample was snapped off to remove the edge bead formed by spin casting.

Figure 4a 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  $0.6 \text{ kW/cm}^2$ , the spectrum was broad with overlapping vibronic peaks; i.e., characteristic of spontaneous emission from conjugated poly-

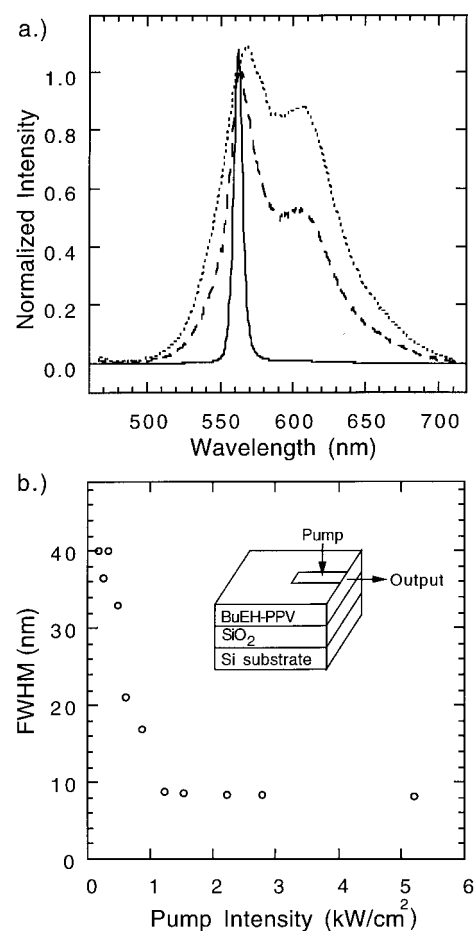


Fig. 4. a) Emission spectra collected from the edge of a 2 mm long excitation stripe at pump intensities of  $0.34 \text{ kW/cm}^2$  (dotted line),  $0.61 \text{ kW/cm}^2$  (dashed line), and at  $5.2 \text{ kW/cm}^2$  (solid line). The spectra were normalized at their peak wavelength. b) The dependence of the FWHM of the emission spectra on the pump intensity. The FWHM was taken for the main vibronic peak only. The inset shows the experimental configuration that was used.

mers. 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/cm<sup>2</sup>, ASE became evident, and the intensity at the peak of the spectrum grew much more than the intensity at other wavelengths. The full width at half maximum (FWHM) of the spectrum dropped to 8 nm (Fig. 4b). For BuEH-PPV, ASE occurs at the wavelength where the spontaneous emission spectrum is strongest. For some other polymers, the ASE wavelength is shifted to larger wavelengths (relative to the peak spontaneous emission wavelength) because absorption near the band edge reduces the net gain.<sup>[58]</sup> For other polymers, the ASE wavelength is closer to the band edge because excited-state absorption reduces the net gain at larger wavelengths.<sup>[49]</sup> In general, however, for the best lasing polymers, losses do not affect the gain spectrum too seriously and ASE occurs at the wavelength where spontaneous emission is strongest because the gain is highest there.

Figure 5 shows the dependence of the light intensity emitted from the edge, integrated over all wavelengths, on the

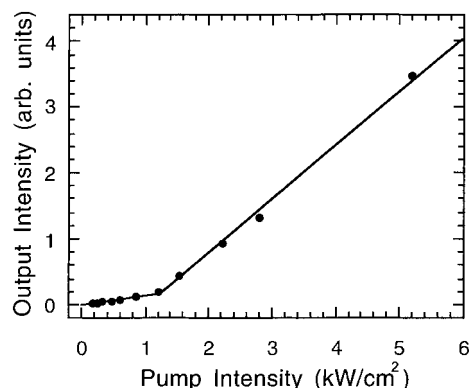


Fig. 5. The total emission intensity from the edge of a BuEH-PPV waveguide (integrated over all wavelengths) versus pump intensity. The pump stripe length was 2 mm.

pump intensity. The measured relative efficiency, as inferred from the change in slope at 1 kW/cm<sup>2</sup>, increased by a factor of six at the threshold for spectral narrowing. The increase arose because only edge emission was being detected; above the threshold for ASE, most of the excitations were stimulated to emit into the waveguide modes, so a larger fraction of the light went out the edge.<sup>[33]</sup> These data highlight one of the advantages of lasers and even mirrorless lasers—their light emission is directional.

The ASE from polymer waveguides is highly polarized parallel to the substrate. The polarization arises because, as noted above, the anisotropic waveguides support only TE modes. In Section 6 we discuss some ways in which this anisotropy might be exploited to reduce the losses in electrically driven structures.

Following the initial observations of spectral narrowing, it was proposed that the mechanism of narrowing was superfluorescence<sup>[24,25,64]</sup> or bi-excitonic emission<sup>[65]</sup> instead of ASE. An easy way to distinguish between these mechanisms

is to vary the length of the pump 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 expression:

$$I(\lambda) = \frac{A(\lambda)I_p}{g(\lambda)} (e^{g(\lambda)l} - 1) \quad (1)$$

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 (i.e., the gain minus the loss), and  $l$  is the length of the pumped stripe.<sup>[66–68]</sup> In contrast, if superfluorescence or bi-excitonic 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).

When the pump stripe length was varied on the BuEH-PPV waveguides, the spectra did indeed narrow as the length was increased, and the output grew exponentially in accordance with Equation 1.<sup>[26]</sup> These data provided strong evidence that spontaneous emission was being amplified by stimulated emission. Additional evidence for ASE was obtained in separate studies by measuring the time dynamics of the spectrally narrow emission.<sup>[57]</sup> As predicted by ASE models, the emission lifetime steadily decreases with increasing excitation density due to the increased stimulated emission rate.

Figure 6 shows the output intensity at the peak of the emission spectrum ( $\lambda = 562$  nm) as a function of pump stripe length at four different pump intensities. Each curve fits nicely to Equation 1 (at least in the low output intensity regime). By fitting the data to Equation 1, the net gain of the wave-

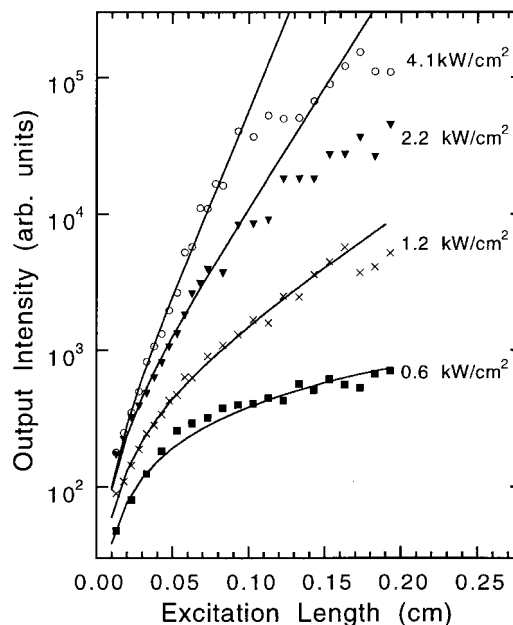


Fig. 6. The dependence of the emission intensity at  $\lambda = 562$  nm on the excitation length at the indicated pump intensities. The solid lines are fits to the data using Equation 1 with the parameters listed in Table 1. The net gain of the waveguide can be determined from the fits.

guides was measured as a function of pump intensity (Table 1).<sup>[67,68]</sup> At the higher pump intensities, the output intensity increased exponentially at excitation lengths of less than 1 mm, as expected, but then leveled off at longer excitation

Table 1. Parameters obtained from fits of Equation 1 to the data in Figure 6. For the curves where gain saturation was present, only points at short excitation lengths were used for the fit.

Pump intensity [kW/cm <sup>2</sup> ]	$A_I$ [arb. units]	$g_{\text{net}}$ [cm <sup>-1</sup> ]
0.6	3700	0.1
1.2	5500	18
2.2	7700	41
4.1	7100	62

lengths. This behavior can be attributed to gain saturation, which occurs when the light traveling in the waveguide becomes so intense that it depletes a substantial fraction of the excitations and thereby reduces the gain coefficient.<sup>[66]</sup> When gain saturation occurs, spectral narrowing stops. Consequently, the smallest spectral width that can be obtained with ASE is determined by gain saturation.<sup>[66]</sup>

As noted above, light cannot be amplified in BuEH-PPV unless it is pumped at, or above, an intensity of 0.6 kW/cm<sup>2</sup>, which corresponds to an excitation density of approximately 10<sup>17</sup> cm<sup>-3</sup>. At lower excitation levels, there is stimulated emission, but the gain is less than the loss, so the net gain is negative. To lower the threshold, it was necessary to reduce the loss. Before doing this, however, it was helpful to measure the loss. To do this, experiments similar to the net gain measurements described above were performed, but the length of the pump stripe was held constant and the pump stripe was moved away from the edge of the sample (see the inset to Fig. 7). Since the emission from the end of the pumped region,  $I_0$ , was constant, the emission from the edge of the sample decreased (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

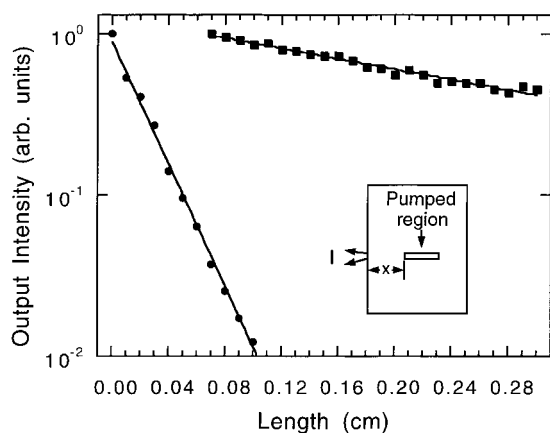


Fig. 7. The intensity of ASE at its peak wavelength emitted from the edge of a waveguide versus the distance between the pump stripe and the edge of the sample. The inset shows a schematic diagram of how this measurement was performed. The polymers were BuEH-PPV (circles) and a 4 wt.-% blend of BEH-PPV in HB265 (squares). From the exponential curve fits, it can be inferred that the loss coefficient of BuEH-PPV and the blend is 44 cm<sup>-1</sup> and 3 cm<sup>-1</sup>, respectively.

and  $\alpha$  is the loss coefficient. Figure 7 shows the intensity of the emission at the peak of the ASE spectrum for BuEH-PPV as a function of  $x$ . By curve fitting these data to an exponential, the loss coefficient was determined to be approximately 44 cm<sup>-1</sup>. Similar values were measured for films of several other PPV derivatives. This technique for measuring waveguide loss, developed twenty years ago for CdS,<sup>[67]</sup> is extremely convenient because it does not involve coupling external light sources to the waveguide<sup>[69]</sup> and it gives the loss coefficient at the ASE wavelength.

Waveguide loss can arise from either self-absorption or scattering. Ideally there would not be any self-absorption at the ASE wavelength in conjugated polymer waveguides since the emission is shifted in wavelength from the main  $\pi$ - $\pi^*$  absorption. In practice, however, there is a sub-gap absorption tail that arises from defect states. Several groups have employed photothermal deflection spectroscopy, a very sensitive technique for measuring low absorption coefficients, to determine the sub-bandgap absorption spectrum of conjugated polymers. They have found that the absorption tail extends more than 1 eV from the band edge and that the absorption coefficient at the peak emission wavelength is typically around 50 cm<sup>-1</sup>.<sup>[70,71]</sup> Since this value is similar to the loss coefficients we measured, we concluded that most of the waveguide loss in our samples arises from self-absorption rather than scattering. It should be noted, however, that other groups have seen signatures of scattering in their films.<sup>[29]</sup> A challenge that remains is to reduce the sub-bandgap absorption by reducing the defect density.

#### 4. Lowering the Lasing Threshold with Energy Transfer

The fact that most luminescent polymers have a slight amount of residual absorption at the peak emission wavelength implies that they do not have the absorption/emission properties of a perfect four-level energy system. The self-absorption problem can be alleviated by shifting the emission to longer wavelengths where the residual absorption is smaller. This can be done by blending a small amount of a guest molecule or polymer into the host.<sup>[72,73]</sup> In such blends, energy transfer by dipole-dipole coupling (Förster transfer) occurs if the emission spectrum of the host overlaps with the absorption spectrum of the guest and if the dipoles are sufficiently close to each other.

Gupta et al. have blended several red-emitting PPV derivatives into green-emitting PPV derivatives and determined the conditions under which Förster transfer occurs.<sup>[74]</sup> They found that it was not necessary for the absorption spectrum of the guest to completely overlap with the emission spectrum of the host, but that higher degrees of spectral overlap did lead to energy transfer at lower guest concentrations. Figure 8 shows the absorption and emission spectra of a soluble PPV derivative obtained from Covion (HB265), pure poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylene vinylene) (BEH-PPV), and a

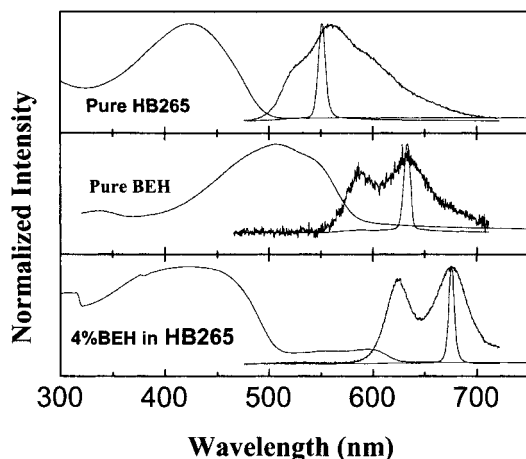


Fig. 8. Ground-state absorption (left curves), spontaneous emission (broad curves on right), and ASE spectra (narrow curves on right) for pure HB265, pure BEH-PPV, and 4 wt.-% BEH-PPV in HB265.

blend of 4 wt.-% BEH-PPV in HB265. It is apparent that most, but not all, of the absorption occurs in the HB265, and that almost all of the emission comes from the BEH-PPV. The threshold for ASE was only  $100 \text{ W/cm}^2$  when waveguides made with the blends were photopumped using the same techniques described above for characterizing the BuEH-PPV waveguides. The ASE spectrum is shown in Figure 8. Shifting the emission wavelength farther from the absorption edge reduced the loss coefficient to  $3 \text{ cm}^{-1}$  (Fig. 7). Although most of the reduction in the ASE threshold is probably attributable to this reduction in absorption, it should be noted that using a guest as the emitter also tends to reduce aggregate formation and energy migration to defect sites. For this reason, ASE can be observed at low pump intensities even if the host polymer is not an efficient emitter! This feature could be useful in electrically driven devices since the polymers that tend to transport current well usually have strong interchain interactions, which can be detrimental to lasing performance as we have discussed in Section 2.

The Förster energy transfer process has been time-resolved by Dogariu et al. with pump-probe spectroscopy. They monitored the stimulated emission and photoinduced absorption of the blends as a function of time following pulsed excitation and found that the spectral signatures of the host were replaced by those of the guest in a manner that agreed quantitatively with theoretical predictions based on Förster's model.<sup>[75]</sup> Complete energy transfer occurred within 10–20 ps, which is much less than the photoluminescence decay time. The high rate of the energy transfer process explains why almost all of the emission comes from the guest.

McGehee et al. have recently observed energy transfer from conjugated polymers to europium complexes.<sup>[76]</sup> Blends with 5 wt.-% of a Eu complex in a blue-emitting polymer have a PL efficiency of 27 %, an emission bandwidth of only 3.5 nm, and a remarkably long PL lifetime of 570  $\mu\text{s}$ . Unfortunately, films made from the blends did not give off ASE even when pumped at an intensity of  $10^5 \text{ W/cm}^2$ . This is not too surprising given the long PL lifetime, which is a result of

the radiative transition in europium being a forbidden process that only occurs because of slight symmetry breaking. Since the PL lifetime is six orders of magnitude longer than that of most luminescent polymers, the cross section for stimulated emission is probably on the order of  $10^{-21} \text{ cm}^2$ .<sup>[77]</sup> To observe lasing from the Eu complexes, it will probably be necessary to use a long optical path length or a high  $Q$  resonant cavity so that the threshold gain will be low.<sup>[78]</sup> Comparison of the ease of seeing ASE from polymer films to the difficulty of achieving ASE from Eu complexes, which were once considered to be very attractive laser chromophores,<sup>[79]</sup> highlights how good the photophysical properties of conjugated polymers are for laser applications.

Recently it has been demonstrated that phosphorescent dyes and sensitizers can be used to accept energy from triplet excitations and generate light.<sup>[80–83]</sup> Since triplets are formed much more readily in electrically driven devices than in optically driven ones, these molecules could play an important role in the development of diode lasers. To the best of our knowledge, however, there have not yet been any reports of stimulated emission in systems where energy was transferred from a semiconducting host to a phosphorescent dye or sensitizer. Phosphorescent dyes are likely to have a stimulated cross section somewhere between that of conjugated polymers and Eu complexes.

## 5. Laser Resonant Structures

The waveguide structures described in Sections 3 and 4 have many of the properties of a laser; the ASE is concentrated in a beam, polarized, efficient, and nearly monochromatic.<sup>[33]</sup> They are not lasers, however, because they do not have resonant modes. Despite the fact that most of the photons are generated by stimulated emission, the output beam is not coherent because the spontaneously emitted photons are not coherent with each other. In order to achieve coherent emission, it is necessary to incorporate the gain medium into a resonator.<sup>[35]</sup> The most common approach to making a resonator is to place mirrors at the ends of the gain region. Then there are modes in the cavity formed between the two mirrors. Lasing occurs when the amplification of photons traveling in one of the modes is sufficient to overcome the losses in the gain medium and through the mirrors.<sup>[35,84]</sup> Since all of the photons in a particular mode are coherent with each other, the emission from a laser can be coherent.

Tessler et al. made the first laser based on undiluted conjugated polymers.<sup>[22]</sup> Their approach was to sandwich a film of PPV between a commercially available dielectric mirror and a thermally evaporated silver mirror to create a microcavity (Fig. 9). Since even the spontaneous emission from microcavities is spectrally narrow due to quantum electrodynamic effects,<sup>[85]</sup> it was not trivial to determine whether or not lasing occurred in their devices. Fortunately, their microcavities had several spontaneous emission modes. They observed that these modes grew linearly in intensity as they increased the



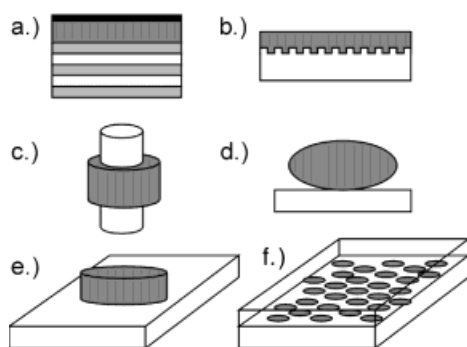


Fig. 9. Schematic of several resonant structures used to make polymer lasers. a) Vertical microcavity. b) Distributed feedback. c) Micro-ring. d) Micro-drop. e) Micro-cylinder. f) 2D photonic crystal.

pump energy until they reached a threshold. Above threshold, they found that the mode closest to the peak of the gain spectrum grew at an even faster rate, but that the other modes stopped growing. This behavior is a signature of lasing; above the lasing threshold non-lasing modes stop growing because all of the additional excitations are quickly stimulated to emit into the lasing mode, which becomes the dominant mode.<sup>[84]</sup> Although subsequent reports<sup>[31,86]</sup> have questioned whether or not the structures studied by Tessler et al. were really lasers, we see no reason to doubt that they observed lasing. Recently, Tessler has written a nice review that gives criteria for identifying lasing.<sup>[33]</sup> Since the initial report of microcavity lasing, several groups have lowered the lasing threshold by using better polymers<sup>[87]</sup> and by replacing the silver mirror with a dielectric mirror.<sup>[42,86,88]</sup>

Microcavity lasers have several attractive advantages: they are easy to make; their architecture is similar to that of polymer LED's; and they emit perpendicularly from the substrate plane, which is useful for many applications. Unfortunately, the distance traveled by light during each pass through the gain region is small (<200 nm). Consequently, the lasing threshold is high unless the mirrors are extremely reflective (>99.9%). Lower thresholds can be achieved by using laser resonator structures where light is waveguided through large distances in the gain medium.

When inorganic crystalline semiconductors are used to make waveguide lasers, mirrors are sometimes made simply by cleaving the crystal. The resulting facets at the ends of the waveguide reflect light because of the refractive index mismatch between the crystal and air. Unfortunately, polymer lasers cannot be made so simply. Since the semiconductor film is a polymer, breaking the film does not result in a high-quality facet. Furthermore, even if good facets were formed by techniques such as reactive ion etching, laser ablation, or freeze fracture, the reflectivity at the polymer-air interfaces would be less than 10% because the refractive index of luminescent polymers is relatively low (1.6–2.0).

An alternative way to reflect light in a polymer waveguide is to incorporate a periodic modulation of the refractive index so that light can be reflected by Bragg scattering (Fig. 9). Lasers of this type, known as distributed feedback (DFB) lasers,

were first developed with films containing organic dyes<sup>[89]</sup> and have since been used extensively with inorganic laser materials.<sup>[84]</sup> They are somewhat different from most other types of lasers in that the mirror is actually incorporated into the gain region. The DFB structure can be thought of as a one-dimensional “photonic crystal” that has a photonic bandgap centered at the Bragg wavelength,  $\lambda_{\text{Bragg}} = 2n_{\text{eff}}\Lambda$  ( $n_{\text{eff}}$  is the effective refractive index of the waveguide and  $\Lambda$  is the period of the grating). Light with energy in the photonic bandgap cannot propagate in the direction perpendicular to the refractive index grating. Hence, lasing does not occur at  $\lambda_{\text{Bragg}}$ , but at wavelengths corresponding to the edges of the photonic bandgap. At these wavelengths light can propagate, but it is still reflected by the grating.

McGehee et al. made low-threshold ( $1.5 \text{ kW/cm}^2$ ) DFB lasers by spin casting films of BuEH-PPV onto gratings in silica.<sup>[90]</sup> The observed signatures of DFB lasing were: a kink in the output versus input curve, highly polarized emission from the ends of the waveguide, and two closely spaced lasing modes with linewidths equal to 0.2 nm. As expected for a DFB laser, the lasing wavelengths depended on the grating period (Fig. 10). By varying the grating period, the lasing wavelength was tuned from 540 to 583 nm. As explained

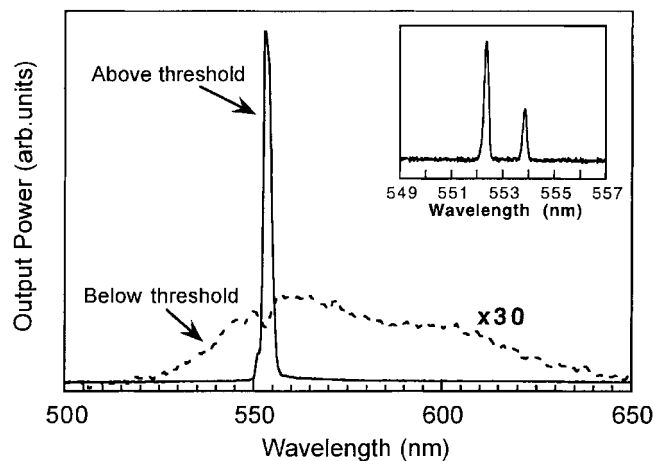


Fig. 10. Spectra of a DFB laser taken below (dashed line) and above (solid line) the lasing threshold. The below-threshold spectrum was multiplied by a factor of 30. Inset: A high-resolution spectrum taken above the lasing threshold showing two narrow laser emission lines (FWHM = 0.2 nm).

above, the double-mode spectral pattern is characteristic of a DFB laser with a refractive-index-induced “stop band”. By replacing the BuEH-PPV with the energy transfer blends described in the previous section, Gupta et al. recently lowered the lasing threshold by another order of magnitude to the remarkably low value of  $0.1 \text{ kW/cm}^2$ .<sup>[91]</sup>

Kallinger et al. made flexible surface-emitting DFB lasers by depositing films of ladder type poly(*p*-phenylene) (LPPP) onto plastic second-order gratings.<sup>[92]</sup> In their structures, second-order reflections provided the feedback needed for lasing while first-order reflections coupled the light out in a direction perpendicular to the substrate. They observed single-mode emission, which indicates that gain modulation contrib-

uted more to the distributed feedback than index modulation. They explained that gain modulation arose in their films because the thicker regions of the film absorbed more light and thus had higher gain.

Another approach to making low-threshold lasers is to use a micro-ring resonator.<sup>[29,93]</sup> In micro-ring resonators, light is totally internally reflected around the perimeter of the ring in so-called “whispering gallery” modes. Resonances occur at wavelengths where the circumference is equal to an integral multiple of the wavelength. The easiest ways to make whispering gallery mode lasers are to dipcoat a polymer film onto a glass fiber<sup>[29,94,95]</sup> or to melt small pieces of polymer on Teflon in such a way that they bead up into nearly spherical microdroplets.<sup>[96]</sup> Micro-disk lasers can also be made by photolithography and etching.<sup>[97]</sup> Lasers of this type typically show narrow-linewidth lasing modes with spacing that varies inversely with the ring diameter. Single-mode lasing has been observed from rings with a diameter of 5 μm.<sup>[98]</sup> Although micro-ring lasers have very low thresholds, they are less convenient for most applications because they do not give off a beam of light.

Most polymer laser researchers have studied undiluted films since these semiconducting films can potentially be pumped electrically. There have, however, been several reports on lasing from polymers diluted either in a solvent<sup>[18,41,99,100]</sup> or another polymer.<sup>[101,102]</sup> These lasers differ from the ones described above in that their chromophore density is lower, the size of the gain region is larger, the output is well collimated, and the lasing wavelength can be tuned by an external diffraction grating. Proof of coherence has been obtained by passing the output beam through a Michelson interferometer.<sup>[102]</sup> In the quest to make a diode laser, many researchers may have overlooked the potentially important possibility of using diluted conjugated polymers to make high-power tunable photopumped lasers.

Polymer lasers have also been made by incorporating polymers into photonic crystals, which are materials that have a periodic perturbation in their refractive index with a periodicity comparable to the wavelength of light. The microcavity and DFB lasers described above can be thought of as one-dimensional photonic crystals. Two-dimensional photonic crystal lasers have been made by depositing films over two-dimensional arrays of holes.<sup>[30,103–105]</sup> Three-dimensional lasers have been made by infiltrating polymers into porous synthetic silica opals.<sup>[106]</sup> Dodabalapur et al. pointed out that organic chromophores could be quite useful for developing photonic crystal technology since they can be easily incorporated into many different structures.<sup>[107]</sup>

## 6. Towards Diode Lasers

Can electrically pumped polymer lasers be made? That is the question that many have been asking. Now that good photopumped polymer lasers have been made, the information needed to address this question is available.

The best photopumped lasers, which are made with energy transfer polymer blends, have pump intensity thresholds of 100 W/cm<sup>2</sup>.<sup>[91]</sup> In a carrier-balanced diode structure, where most of the electrons and holes recombine, the current density needed to achieve the same excitation density that is needed for lasing in the photopumped structures is approximately

$$J_{\text{th}} = \frac{q}{h\nu} I_{\text{th}} \quad (2)$$

where  $q$  is the electron charge,  $h\nu$  is the energy of the photons used in the photopumping experiments, and  $I_{\text{th}}$  is the photopumping lasing threshold pump intensity. Inserting numbers into Equation 2 yields a threshold current density of approximately 100 A/cm<sup>2</sup>. This calculation is only intended to provide a rough estimate. It does not, for example, take into account that some of the excitations in a diode are non-emissive triplets. Polymer LEDs have been driven at current densities as high as 1000 A/cm<sup>2</sup> in a pulsed mode.<sup>[108,109]</sup> Yet, despite the fact that the estimated threshold current density can be exceeded by an order of magnitude, no one has made a polymer diode laser at the time this review is being written. The principal reason for this is that the losses in diode structures are higher than in simple photopumped waveguides because of two additional loss mechanisms:

- Charge-induced absorption
- Metal electrode absorption

The charge-induced absorption problem is reminiscent of the excited-state absorption problem discussed in Section 2. The only difference is that the absorption arises from charge carriers rather than neutral excitons that are formed by photoexcitation. Tessler et al. have measured the charge-induced absorption spectrum for PPV and found that it extends from the ground state absorption band edge well into the IR.<sup>[110]</sup> They modeled the carrier and exciton dynamics in polymer diodes and found that under steady-state conditions, there are many more charge carriers than emissive excitons. For this reason, charge-induced absorption is stronger than stimulated emission. They concluded that it is probably not possible to make a continuous wave diode laser with PPV. The crucial question that their study introduces is whether or not other polymers will behave similarly. As we have seen, the photoinduced absorption spectrum overlaps the stimulated emission spectrum of some, but not all, conjugated polymers. For some polymers, the degree of overlap even depends on how the films are prepared. Consequently, we certainly do not think that efforts to make diode lasers should be abandoned because of the charge-induced absorption problem. Studies should be performed on polymers other than PPV to see if it is possible to make films that exhibit net gain with electrical pumping. There have already been some encouraging preliminary reports that charge-induced absorption is not substantial for some polymers.<sup>[111]</sup>

Even if it turns out that the charge induced absorption spectrum of all semiconducting polymers overlaps with the stimulated emission spectrum, there are several potential solutions to the problem. The first is to significantly improve the

mobility of the polymers so that charge carriers meet each other faster to form emissive excitons; this would enhance the ratio of stimulated emission to charge-induced absorption. The mobility could be improved by increasing the structural order of the polymer chains. In addition to improving the transport properties and reducing charge-induced absorption, improving the degree of order would probably also reduce the sub-bandgap ground state absorption. Another potential solution is to use energy transfer to shift the emission wavelength to a spectral region where there is no charge-induced absorption. This could be difficult or impossible, however, because charge-induced absorption tends to extend all the way across the sub-bandgap spectral region; energy transfer could actually make the problem worse. A third approach is to pump the diode with fast current pulses and transfer the energy to a long-lived chromophore, such as a rare earth complex<sup>[76]</sup> or a phosphorescent dye.<sup>[83]</sup> In this case, lasing might occur just after the current is turned off since there would no longer be any charge-induced absorption. A fourth approach would be to orient the charge-carrying polymer chains in a direction perpendicular to the polarization of the lasing mode. In this case it is possible that the charged chains would not be able to absorb the light. The possibility of using films with oriented chains is further discussed later in this review.

The other major obstacle to making a diode laser is to incorporate metal electrodes without introducing excessive waveguide loss. If metal electrodes were placed directly on the polymer waveguide layer, the loss from light being absorbed in the metal would be on the order of  $1000 \text{ cm}^{-1}$ ,<sup>[33]</sup> which is clearly too high. The waveguide loss problem can be avoided completely by using a vertical microcavity, but then additional problems are presented: the threshold gain is higher and the electrodes must be inserted inside the cavity. Since polymers cannot realistically be expected to handle current densities of more than  $1000 \text{ A/cm}^2$  (some would set this number much lower), the low-threshold DFB design is the most promising. Hence, the waveguide loss problem must be solved.

The most obvious way to reduce the waveguide loss from the metal electrodes, is to use the double heterostructure design that is used to make inorganic diode lasers.<sup>[84]</sup> In these lasers, the emissive layer is separated from the two electrodes by cladding layers (Fig. 11). The cladding material is chosen to have a lower refractive index and a higher bandgap than the emissive layer. Since the bandgap of the cladding is higher, the light that penetrates into the cladding is not absorbed strongly. With inorganic heterostructures, it is possible to have metal electrodes and still keep the waveguide loss coefficient under  $10 \text{ cm}^{-1}$ .<sup>[84]</sup>

In principle it should also be possible to make a polymer heterostructure waveguide with metal electrodes that will have a loss coefficient of less than  $10 \text{ cm}^{-1}$ . In practice, however, there are some non-trivial difficulties. Figure 12 shows the waveguide mode pattern for a structure in which the emissive layer has a refractive index of 1.75 and the claddings have a refractive index of 1.54. The mode penetrates approximately  $0.5 \mu\text{m}$  into the cladding. Tessler has modeled cladded struc-

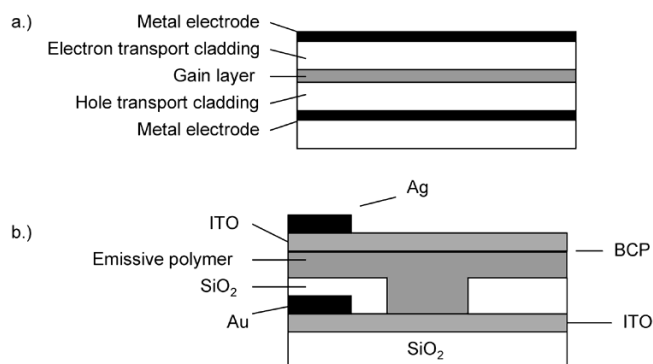


Fig. 11. a) Schematic of a proposed double heterostructure laser diode. b) Schematic of a proposed laser diode structure with thin (20 nm) ITO electrodes. The laser light would be emitted from the stripe (in the direction perpendicular to the page).

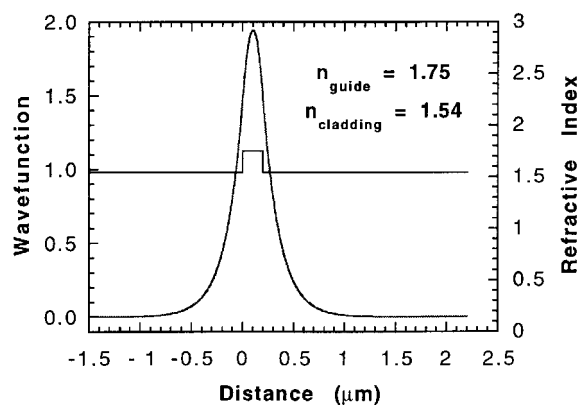


Fig. 12. The waveguide mode shape for a planar waveguide with a guide refractive index of 1.75 and a cladding refractive index of 1.54.

tures that have metal on the outside and concluded that the cladding would need to be approximately  $0.5 \mu\text{m}$  thick for the metal-induced loss to be less than  $10 \text{ cm}^{-1}$ .<sup>[33]</sup> Hence, the total thickness of the polymer layers in the diode would need to be on the order of  $1\text{--}1.5 \mu\text{m}$ . This presents a serious problem. Since the mobility of known luminescent conjugated polymers is low ( $10^{-5}\text{--}10^{-2} \text{ cm}^2/\text{Vs}$ ),<sup>[109]</sup> the voltage needed to drive  $100 \text{ A/cm}^2$  of current through  $1 \mu\text{m}$  of polymer would be in excess of several 100 V. Such voltages would almost certainly induce sparking and catastrophic breakdown. Clearly, something other than undoped polymers must be used as the cladding material.

There have not been many reports on the development of claddings for diode lasers, probably because no one has been successful at finding a good cladding material. The approach we have taken in our labs is to test potential cladding materials by photopumping candidate structures to look for ASE. Although our results have not been encouraging, we will report them here.

One candidate class of cladding materials is the transparent conducting oxides (e.g., indium tin oxide (ITO) and  $\text{GaInO}_3$ ). Unfortunately, ITO has a higher refractive index (1.8–2.0) than most conjugated polymers; hence, it cannot be used as a cladding.<sup>[112]</sup> We did observe ASE from BuEH-PPV films on

ITO, but the threshold was three orders of magnitude higher than when glass was used as the cladding.<sup>[87]</sup> GaInO<sub>3</sub> has a refractive index of 1.65, but has an absorption coefficient of greater than 200 cm<sup>-1</sup>.<sup>[113]</sup> If transparent conducting oxides are improved, they might become feasible cladding materials, but for now they are not adequate. An intriguing possibility is to introduce porosity into transparent conducting oxides to reduce their refractive index and absorptivity.<sup>[114,115]</sup>

Metallic polymers such as doped polyaniline,<sup>[17]</sup> polypyrrole,<sup>[116]</sup> or poly(3,4-ethylenedioxythiophene) (PEDOT) are fairly transparent and have sufficient conductivity to be used as electrodes in LEDs with low turn-on voltage; hence, they would seem to be good candidates to be cladding materials in diode lasers. Unfortunately, their absorption coefficient is actually rather high ( $\approx 10^4$  cm<sup>-1</sup>). Hence, these polymers are not suitable for claddings. We attempted to obtain ASE from BuEH-PPV films cast on polyaniline and PEDOT, but were unsuccessful.

It is important to understand why it is difficult to make conjugated polymer films that have high conductivity and low absorption (in the visible spectral region) at the same time. When the conductivity of a conjugated polymer is enhanced by doping, polarons and bipolarons form because the polymer chains relax around the added charges.<sup>[117]</sup> Unfortunately, these defects have broad absorption bands in the sub-gap spectral region.<sup>[118]</sup> At this time it is not known if it will be possible to find a polymer that has a transparency window in some useful wavelength range even when doped. The situation is different, but not necessarily better, when conjugated polymers are doped so strongly that they become metals. In this case polaron and bipolaron formation is no longer relevant (since the Fermi velocity is much greater than the sound velocity).<sup>[119]</sup> The frequency-dependent conductivity,  $\sigma(\omega)$ , is Drude-like:

$$\sigma(\omega) = \sigma_0 / (1 + \omega^2 \tau^2) \quad (3)$$

where  $\omega$  is the frequency,  $\tau$  is the carrier scattering time, and  $\sigma_0 = 1/4(\omega_p^2)\tau$ . The “metallic” polymers studied to date, such as PANI, PEDOT, and polypyrrole, are near the boundary of the disorder-induced metal-insulator transition with  $k_F l \approx 1$  and  $\omega_p \tau \approx 1$ , where  $k_F$  is the Fermi wavenumber,  $l$  is the mean free path, and  $\omega_p$  is the plasma frequency.<sup>[120]</sup> As a result, they exhibit localization modified Drude behavior. Thus, transparency in the visible is limited by the residual Drude-like absorption tail. The achievement of higher quality metallic polymers would serve two purposes. The higher DC conductivity would enable such polymers to perform better as electrodes, and the larger  $\tau$  would reduce the high frequency conductivity (and thus reduce the residual losses). To achieve the required improvements, it will be necessary to improve the structural order through chain extension and chain alignment. As we explain in the next paragraph, increasing the structural order could have additional benefits as well.

A novel way to take advantage of some of the special properties of polymers to reduce the cladding absorption in a diode

structure would be to use claddings made from oriented polymer chains. Conjugated polymers are intrinsically anisotropic; they absorb light that is polarized parallel to the chain axis.<sup>[121,122]</sup> Therefore, since the lasing modes in a polymer waveguide are polarized (parallel to the plane),<sup>[26,90]</sup> the claddings would not absorb the waveguided light if they were made of chains that were oriented perpendicular to the polarization direction. Highly doped chains (or even carbon nanotubes<sup>[123]</sup>) could be used because absorption would be prevented by the orientation between the photon polarization and the chain or nanotube axis. The problem with this approach lies in the fabrication. Currently there are no techniques for making films with polymer chains or carbon nanotubes aligned to the degree that would be needed. However, as conjugated liquid crystals,<sup>[124,125]</sup> organic-inorganic nanostructures,<sup>[126]</sup> and techniques for self-assembling carbon nanotubes are improved, this approach could become feasible.

Recently, Kozlov et al. have proposed a new design for diode lasers that avoids the cladding problem.<sup>[32]</sup> With their design (Fig. 11), 20 nm thick layers of ITO are used as electrodes. One of the electrodes is coated with a 5 nm thick film of bathocuproine (BCP) so that it can inject electrons. Since the electrodes are so thin, a waveguide mode can be supported in the luminescent layer even though the refractive index of ITO is higher than that of the luminescent layer. This can happen because the mode penetrates through the ITO and into the substrate and air; the substrate must be a non-absorbing, low-refractive-index material, such as glass or silica. Since the ITO films are too thin to carry current over large distances without an excessive voltage drop, metals such as gold and silver are placed along the edge of the waveguide stripe, just outside of the region occupied by the optical mode. Kozlov et al. have fabricated structures with this design using small organic molecules as the gain material. They measured a loss coefficient of only 27 cm<sup>-1</sup>, which is low enough to permit lasing at attainable current densities. They did not obtain lasing, however, because of charge-induced absorption.

## 7. Conclusions

When films of conjugated polymers are prepared in such a way that defects and interchain interactions are minimized, gain can be obtained by photopumping to excitation densities as low as 10<sup>17</sup> cm<sup>-3</sup>. The key photophysical properties that make these polymers so good as laser materials are the shift between the absorption and emission spectrum that leads to low self-absorption, the high PL efficiency combined with high chromophore density, the high stimulated emission cross section and the absence of excited-state absorption in the luminescent spectral region. Gain can be obtained at even lower excitation densities (10<sup>16</sup> cm<sup>-3</sup>) when energy is transferred from a host polymer to a guest polymer in order to move the emission wavelength farther from the absorption edge. This excitation density can be obtained with a steady-state pump intensity of only 100 W/cm<sup>2</sup>.

So far, however, efforts to make polymer diode lasers have been unsuccessful because of charge-induced absorption and electrode-induced absorption. Recently, however, there has been progress in designing structures that minimize electrode-induced absorption, so the primary remaining challenge is to eliminate charge-induced absorption. Given that the morphology of polymer chains has been shown to have a dramatic effect on photoinduced absorption, it will be very important to carefully measure the charge-induced absorption spectrum of a variety of polymers under conditions in which the chain morphology is systematically varied. Materials issues that need to be addressed in the quest to make a diode laser include improving the carrier mobility of the polymers, using energy transfer in polymer blends (or copolymers), using current pulses with long-lived chromophores, and orienting the polymer chains to enable crossing the lasing mode polarization with the orientation of the polymer chains.

An alternative approach is to fabricate a two-component diode laser; i.e., an optically pumped polymer laser that is optically coupled to an electrically driven compact InGaN light source, the latter being capable of emitting at the necessary intensity levels to pump the polymer laser above threshold.<sup>[127]</sup> This hybrid InGaN/polymer laser concept takes advantage of the special features of both components; i.e., the low threshold of optically pumped polymer lasers (100 W/cm<sup>2</sup>) and the efficiency and high current carrying capacity of blue-emitting InGaN diodes and lasers. Since the blue emission of InGaN is nearly ideal for pumping the  $\pi$ - $\pi^*$  transition of luminescent polymers, the proposed InGaN/polymer hybrid laser technology provides a route to electrically pumped hybrid lasers with a full range of colors.<sup>[127]</sup>

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**Note Added in Proof:** After this article was submitted, a team of researchers at Lucent Technologies used high-quality crystals of tetracene to make the first organic diode laser. Diodes made with tetracene have a higher mobility than those made with conjugated polymers and do not have as much charge-induced absorption. This breakthrough is described in the literature.<sup>[128]</sup>

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