Abstract. We study optical gain and laser emission from semiconducting conjugated polymers after strong optical excitation with femtosecond laser pulses. Stimulated emission from few-hundred-nanometer thin films results in a sharp increase in emission intensity and emission line narrowing. Very large optical gain due to the stimulated emission is measured directly by pump-probe spectroscopy. Using the large light amplification in these conjugated polymers, we demonstrated planar and ring lasers of very small sizes that are suitable for applications in integrated optics. Vertical cavity surface emitting lasers, distributed feedback through surface relief grating, and whispering-gallery mode emission from ring resonators are demonstrated. © 1998 Society of Photo-Optical Instrumentation Engineers. [S0091-3286(98)01204-5]

1 Introduction

Conjugated polymer semiconductors have attracted attention lately for device applications in areas that are traditionally domains of inorganic semiconductors, such as electronic devices (e.g., diodes, field-effect transistors) and photonic devices, including holographic storage, light modulators, and light-emitting diodes (LEDs). The structural flexibility, easy processing, and low cost of polymers make polymer devices competitive. One of the most useful properties for optical applications is that the absorption and emission of conjugated polymers can be tuned over the whole visible spectrum by changing their chemical structure. Recently, photoluminescence (PL) line narrowing and stimulated emission (SE) have been reported in a variety of conjugated polymers.1-6 The prospect of compact electrically pumped polymer lasers using their semiconductor properties is exciting. First reports on the emission properties of optically pumped polymer films in microcavity structures showed increased directionality and threshold behavior in the mode structure, indicating feedback effects of the cavity.1,5 Very recently, using an improved resonator configuration, we have been able to obtain unambiguous features of laser emission such as directionality close to the diffraction limit and a high degree of polarization.7

In this paper, we focus on the optical properties of thin solid-state films of semiconducting polymers and related microstructures under high excitation conditions. Femtosecond spectroscopy is used to study the optical response and its dynamics after excitation with short optical pulses. We show that very large optical gain and stimulated emission can be achieved in extremely thin polymer films. The large light amplification per unit length allows laser action to occur with small interaction lengths between the conjugated polymer and the electromagnetic light field. Small planar and ring laser configurations can provide the optical feedback that makes these solid-state organic lasers particularly interesting for integrated optics applications. Under optical excitation we demonstrate threshold behavior of the laser modes in various microcavity configurations and discuss characteristic features of the laser output.
2 Experimental
Films of 100- to 500-nm thickness of the semiconducting conjugated polymer BEH:PPV [poly(2,5-bis(2'-(polymerized colliding pulse mode-locked CPM) laser system providing tunable pulses of 100-fs duration. The central wavelength of the excitation pulses, 555 nm, was in resonance with the τ−τ* absorption band of BEH:PPV. Additionally, a spectrally broad (>100 nm) probe pulse was generated by the same laser system that was used to measure the dynamics of absorption changes and light amplification in a pump-probe setup. Taking careful account of linear and quadratic chirp in the broad probe continuum, we analyzed the dynamics of light amplification with a time resolution of the order of the pulse length. For the waveguide ring resonator we present results under quasistationary excitation conditions using 7-ns pulses from a frequency-doubled Nd:YLF laser at 524 nm. The optical signals were detected by an optical multichannel analyzer with a spectral resolution better than 0.3 nm. All experiments are carried out at room temperature.

3 Photoluminescence and Stimulated Emission
The energy-level structure of the conjugated polymer that dominates absorption and emission properties is schematically shown in Fig. 1. Characteristic of organic materials, each electronic level is associated with a set of vibrational energy levels that are spaced very closely compared to the electronic energy level spacing. Absorption of radiation takes place from the bottom of the S₀ level to one of the S₁ levels. From there, the excitation nonradiatively decays very quickly down to the bottom of S₁ or to energy levels that are not coupled radiatively to S₀. Radiative emission is accompanied by the transition from the bottom of S₁ to one of the vibronic levels in S₀. This energy transition scheme leads to the well-known mirror-image-like relation between absorption and emission spectra that is typical for organic molecules and also for semiconducting conjugated polymers such as BEH:PPV. The very fast decay from higher vibrational levels to the bottom of S₁ and S₀ leads to an energy-level scheme that is similar to a four-level system (right-hand side in Fig. 1), known to be well suited for laser applications.

Figure 2 shows the normalized PL spectra of BEH:PPV for three different pump intensities. The arrow marks the excitation wavelength and its position in the absorption manifold that is inhomogeneously broadened due to chain segments with different effective conjugation lengths. The PL at low excitation (curve i in Fig. 2) is due

Fig. 1 Schematic drawing of the energy-level diagram of an organic material (left) and the corresponding approximate four-level picture (right).

Fig. 2 Normalized PL spectra of a 100-nm BEH:PPV film after excitation with 100-fs pulses (λexc=555 nm) and excitation fluences of (i) 30, (ii) 50, and (iii) 120 μJ/cm². For comparison the absorption spectrum is also given.
to the recombination of singlet excitons and exhibits a dominant vibrational structure with an energy spacing of about 150 meV that corresponds to the frequency of phenylene backbone vibrations. A closer look indicates additional vibronic substructures. It has been shown that excitons not only undergo very fast vibrational relaxation, but also migrate efficiently to chain segments of longer conjugation length.\(^9\)\(^\text{-}^{12}\) Relaxation and migration within a few hundred femtoseconds result in a red shift of the PL relative to the absorption and emission lines, which are substantially narrower than those in absorption. Therefore, the low-excitation PL spectrum is dominated by excitons at the longest conjugation segments. In this regime, we find a quantum efficiency of only 5% measured with an integrating sphere, i.e., 95% of the excited excitons decay via the nonradiative recombination channels that are indicated in Fig. 1. This is in agreement with time-resolved PL measurements, where we observed a nonradiative decay time of about 50 ps, while the time constant for radiative recombination is about 1.2 ns.\(^9\)

On increasing the excitation intensity, the initially broad PL spectrum collapses into a single line, centered at 630 nm, of about 9-nm width (curve iii in Fig. 2). This transition occurs at about 50 \(\mu\text{J/cm}^2\), corresponding to an average exciton density of \(5 \times 10^{18} \text{ cm}^{-3}\). Simultaneously, the emission intensity at 630 nm increases dramatically, as does the quantum efficiency. The reason is that above 50 \(\mu\text{J/cm}^2\) the exciton recombination is dominated by SE. In contrast to the constant rate for spontaneous emission, the probability for SE is proportional to the light intensity at the given wavelength. If the number of spontaneously emitted photons is large enough, this radiation can stimulate the recombination with a probability higher than that for the nonradiative decay. In turn, the number of photons is further increased and SE becomes even more probable, leading to a complete bypass of all nonradiative recombination channels. At about 100 \(\mu\text{J/cm}^2\) the dominance of SE leads to a quantum efficiency of almost 100% while the emission intensity decays faster than 10 ps.\(^10\)

### 4 Optical Gain

The measured PL line narrowing and fast SE indicate large optical gain in the thin polymer films. The strong anisotropy in conjugated polymers due to the molecule arrangement results in large dipole moments and, correspondingly, absorption coefficients on the order of \(10^3\) to \(10^6 \text{ cm}^{-1}\). According to Einstein’s theory, gain coefficients can be expected that are comparable to the absorption coefficients provided that we can create a large inversion between the initial and the final state of the stimulation process.

In Fig. 3 we present the measured changes of the optical response of a 190-nm-thick BEH:PPV film in the spectral region around the band-gap energy of the semiconducting polymer for the case of optimized temporal overlap (\(\Delta t = 0\)) between the exciting pump pulse (555 nm) and the probe pulse. The spectra are shown for three different excitation intensities above the SE threshold. At shorter wavelengths, where the material is absorbing (left-hand side of Fig. 3), the relative absorption bleaching (\(\Delta \alpha / \alpha_{\text{lin}}\)) is plotted, while at longer wavelength (right-hand side of Fig. 3) the net optical gain (\(\Delta \alpha / \alpha_{\text{lin}}\)) is shown, where \(d\) is the sample thickness, \(\alpha_{\text{lin}}\) the linear absorption coefficient, and \(\Delta \alpha\) the change in absorption in the presence of the pump beam. To obtain \(\alpha_{\text{lin}}\) and \(\Delta \alpha\) we measured the spectra of the incident probe pulse (\(I_0\)), of the transmitted probe pulse without pump (\(I_1 = I_0 \exp (\alpha_{\text{lin}} d)\)), and of the transmitted probe pulse with pump beam (\(I_2 = I_0 \exp (\alpha_{\text{lin}} + \Delta \alpha) d\)). Below and above the onset of the linear absorption we observe a negative \(\Delta \alpha\), i.e., in the presence of pump pulses, the absorption is reduced (bleached) at shorter wavelengths but still exists as long as \(\Delta \alpha / \alpha_{\text{lin}} < 1\). At longer wavelengths where \(\Delta \alpha / \alpha_{\text{lin}} > 1\) (\(\Delta \alpha / \alpha_{\text{lin}} > 0\)) the probe light is amplified during the interaction with the polymer film due to stimulated emission.

Absorption bleaching is observed at the spectral position of the pump laser (555 nm) and in a broad spectral region that covers more than 180 meV around this wavelength. Three different transitions can be distinguished in the energetic region below the excitation wavelength. These transitions can be assigned to different vibronic levels in the \(S_1\) band. Since absorption bleaching reflects the exciton population in these levels, the spectra provide evidence for very fast relaxation (<150 fs) to the bottom of the \(S_1\) band and successive filling of higher vibronic levels at higher excitation intensities. However, the relative bleaching, i.e., the occupation, is always the largest for the level with the lowest energy.

The gain spectra on the right-hand side show very large optical amplification in a broad spectral region (>150 meV) starting just below the band-gap energy. A net gain of 0.19 translates into a large gain coefficient of \(10^4 \text{ cm}^{-1}\). This is by far the largest value reported for a semiconducting polymer. It can be clearly seen in the gain spectra that light amplification is due to SE of at least four distinguishable optical transitions, each with a full width at half maximum of about 8 nm. Since their energy separation displays mirror symmetry with respect to the transitions observed in absorption bleaching, they can be assigned to
transitions from the bottom of the $S_1$ band to the vibronic levels in the $S_0$ band. Note that a superposition of the same transitions yields the low-density PL spectrum of Fig. 2, as we have shown recently. Increasing the excitation results in larger amplification. Furthermore, higher vibrational levels of $S_1$ become more and more occupied, leading to a stronger increase of the corresponding gain at shorter wavelength.

Figure 4 shows the gain coefficients ($\Delta t = 0$) as a function of the excited exciton density taken at the four transitions wavelengths and from two films of different thicknesses. The data show that the measured gain values are intrinsic material parameters that do not depend on film thickness or sample geometry. Up to exciton densities of $3 \times 10^{19}$ cm$^{-3}$ the gain increases linearly with density at all four transitions. We find a common cross section (gain per exciton per cubic centimeter) for SE of $2 \times 10^{16}$ cm$^{-2}$, which indicates the possibility of considerable amplification even at densities below the threshold where SE dominates the emission from the thin films. Above an exciton density of $3 \times 10^{19}$ cm$^{-3}$ the gain at longer wavelength starts to saturate because of the finite density of states available at the bottom of $S_1$. At 595 nm the gain can further increase due to the contributions from transitions starting at higher vibrational levels of $S_1$, which become more and more occupied.

Decay curves of absorption bleaching at 575 nm and optical gain at 621 nm are shown in Figs. 5(a) and 5(b) for two different intensities, respectively. The main figures show the decay on a semilogarithmic scale at early times. In the insets we plot the temporal development for longer times and on a linear scale. At the excitation fluences of 100 and 150 $\mu$J/cm$^2$ no significant gain saturation has yet occurred. Absorption bleaching [Fig. 5(a)] and optical gain [Fig. 5(b)] display the same dynamics. This behavior indicates that the same optically excited species are responsible for absorption bleaching and amplification by SE. Both signals reflect the dynamics of the excited exciton density. The decay of bleaching and gain is clearly nonexponential. Initially the absorption changes decay very fast, on a 100-fs scale. After a few hundred femtoseconds the decay slows down and the signals decrease with a characteristic time constant of about 2 ps. This can be explained in terms of a reduction of the excited-exciton density by SE. Since the probability for SE depends on the exciton density itself, the density is expected to decay nonexponentially and to slow down markedly for longer times (smaller densities). Additionally, we find a component of the absorption changes that persists for several hundred picoseconds without any significant decay. The magnitude of this plateau is found to be proportional to the initially excited density. Our results indicate that the long-lived component is due to localized excitons preferentially formed by initially excited excitons with large momenta that are able to move to localization sites. For laser applications we can exploit the fact that about 10% of the initial optical gain is still present after more than 500 ps.

5 Laser Action

The large optical gain makes semiconducting conjugated polymers promising candidates as new laser materials. For laser applications, however, the polymer as the active material has to be combined with a structure that provides optical feedback. Although electrically pumped laser diodes are the devices of choice for applications, optical pumping is a suitable method to study the properties of different laser structures. By studying the cavity emission it is sometimes difficult to decide whether or not the cavity emission should be called laser emission. Cavity modes can be seen in the low-density PL spectrum of any material embedded in a resonator. Laser action requires that the optical gain due to SE at least balance the total loss of the cavity structures. This condition leads to a thresholdlike increase of the cavity emission intensity when laser emission occurs. However, the interpretation of cavity-emission data using polymers as active material is additionally complicated in that a thresholdlike increase in emission intensity can also be seen from polymer films without any feedback (see Sec. 1) due to the onset of SE. The best argument for laser oscillation is to provide evidence for temporal and/or spatial coherence of the emission.
Fig. 6 (a) Emission spectra of a single BEH:PPV layer (thick lines) and a planar polymer cavity of 9-μm optical thickness (thin lines). The excitation intensities are 40 μJ/cm² (dashed lines), 63 μJ/cm² (dotted lines), and 100 μJ/cm² (solid lines), respectively. In the inset the structure is shown schematically. (b) Spectrally integrated single-layer emission intensity and lasing cavity mode intensity as a function of pump laser fluence.

The most straightforward way to provide feedback is to design a cavity that uses two plane mirrors. Emission properties from such planar cavities under optical pumping have been reported recently. Figure 6(a) directly compares emission spectra from a thin BEH:PPV film outside and inside a cavity formed by highly reflective dielectric mirrors \( M_1 \) and \( M_2 \). The mirrors are also designed to allow optical pumping through the mirror \( M_1 \), which is characterized by 80% transmission at the excitation wavelength of 555 nm. In all cases shown in Fig. 6 the excitation is so strong that SE dominates the recombination. Simply removing \( M_2 \) allows an immediate study of the cavity effect.

Obviously, the emission properties are dramatically changed in the presence of the cavity. Whereas the single-layer emission shows the characteristic narrow 8-nm emission band centered at 620 nm, two longitudinal cavity modes at 605 and 626 nm dominate the cavity emission. For the single layer the spectral shape of the emission is almost the same for all three excitation intensities. In contrast, the intensity ratio between the cavity modes changes dramatically. A clear indication for laser emission from the 626-nm mode is given in Fig. 6(b), where we compare the intensity of the spectrally integrated thin-film emission with the intensity of the lasing mode at 626 nm. SE sets in at 25 μJ/cm² (for both structures), whereas a clear lasing threshold occurs at 50 μJ/cm². Above the threshold the laser emission increases linearly with the excitation, and the measured intensity clearly exceeds that from the film. Since the emission efficiency cannot be larger than 100%, the larger cavity output indicates high directionality of the laser emission, i.e., for the laser the entire emission falls into our detection cone of 10-deg half apex angle, whereas only about 10% of the almost isotropic single-film emission is detected.

Figure 7(a) shows that the whole laser emission is indeed concentrated in a cone of smaller than 3-deg half apex angle (63-μJ/cm² excitation). This degree of directionality provides striking evidence for spatial coherence of the laser emission. Since the Huygens wavelets from different points all add up coherently, the beam divergence is nearly diffraction-limited. The presence of higher-order transverse modes is indicated by the intensity reduction on the high-energy side of the laser emission for the smallest aperture. Additional evidence for coherent laser emission is given by the high degree of polarization (better than 50 : 1) parallel to the polarization of the exciting laser [see Fig. 7(b), 55-μJ/cm² excitation]. In contrast, neither the SE of the film nor the cavity emission at 605 nm has a noticeable degree of polarization.

An example of a distributed feedback resonator is shown in Fig. 8. Here the surface emission from a 200-nm BEH:PPV film deposited on top of a surface relief grating is observed. The exciting laser is focused to a stripe of 3-mm length and 50-μm width to get sufficient feedback by the grating. The optical feedback results in an emission line of only 3.5-nm width, which is considerably narrower than the 8-nm-wide SE band observed by exciting a part of the same film without a grating. The inset of Fig. 8 shows that we also observe a thresholdlike increase in emission intensity at about 40 μJ/cm². However, it should be noted that this structure has not been optimized so far, and large scattering losses as well as a dependence on the spot position due to a nonuniform grating have also been observed.

Ring lasers are an alternative to cavity configurations with plane mirrors and gratings. Figure 9 shows the emission of a microring cavity formed by a thin polymer encircling an optical fiber of 56-μm diameter. It has been shown recently that this kind of structure forms a high-quality cavity for whispering-gallery modes (WGMs). These modes propagate around the edge of the coated fiber with a strong optical confinement in the gain material. Whereas in the previous study a laser dye dissolved in a polymer host provides the optical gain, we show in Fig. 9 that the gain in a conjugated polymer can also be sufficient to achieve laser...
oscillations of the WGMs. For excitation below 25 \( \mu \text{J/cm}^2 \) the emission is similar to the low-density PL without a particular mode structure. Supported by the optical gain in the BEH:PPV, the WGMs clearly dominate the emission above 30 \( \mu \text{J/cm}^2 \), as can be seen in Fig. 9. They are only observed in a spectral region between 618 and 638 nm, where the gain is largest. The mode separation of 1.5 nm agrees well with the separation of the eigenvalues of the WGMs for a 56-\( \mu \text{m} \)-diam microring. The inset of Fig. 9 shows the emission intensity as a function of excitation.

The threshold for lasing of the WGMs is found to be 30 \( \mu \text{J/cm}^2 \), and gain saturation sets in above 100 \( \mu \text{J/cm}^2 \).

Figure 9 shows the emission spectra from a polymer microring encircling an optical fiber of 56-\( \mu \text{m} \) diameter at three different excitation intensities. Lasing of whispering-gallery modes is found for excitation above 30 \( \mu \text{J/cm}^2 \). The inset: Integrated emission intensity of the laser structure as a function of excitation.

In Fig. 9 we show the output spectra of the waveguide ring resonator after excitation of the polymer from the top with 7-ns pulses at 524 nm from a Nd:YLF laser. Increasing the excitation, we find a clear threshold in emission intensity, as can be seen in the inset of Fig. 10, where the spectrally integrated and normalized waveguide output is plotted as a function of excitation. Above the lasing threshold of 2.2 MW/cm\(^2\) the integrated emission intensity increases linearly with excitation until saturation is observed above 4 MW/cm\(^2\). The waveguide output spectra in Fig. 10 shows that we indeed observe the ring cavity modes imprinted by the waveguide structure. In agreement with the ring diameter of 35 \( \mu \text{m} \) we find a mode separation of 1.7 nm. The envelope of the output corresponds in good approximation to the spectral profile of the optical gain in Fig. 3. The emission starts between 620 and 632 nm, where the highest gain is observed. For higher excitation the emission spectrum becomes broader with a larger extension to higher photon energies. For excitation below 2.2 MW/cm\(^2\) the emission intensity is several orders of magnitude smaller.

Fig. 8 Comparison of the emission spectra from a 200-nm BEH:PPV film: Spontaneous emission at low excitation (dashed line), stimulated emission without feedback (solid line), and laser emission with feedback provided by a surface relief grating (dotted line, \( \Lambda = 500 \text{ nm} \)). Inset: Integrated emission intensity of the laser structure as a function of excitation.

Fig. 9 Emission spectra from a polymer microring encircling an optical fiber of 56-\( \mu \text{m} \) diameter at three different excitation intensities. Lasing of whispering-gallery modes is found for excitation above 30 \( \mu \text{J/cm}^2 \). Inset: Integrated emission intensity as a function of excitation.

Fig. 10 Emission spectra of a waveguide ring resonator structure covered with a 200-nm BEH:PPV film for different excitation levels of the polymer layer. The spectra are observed at the output of a channel waveguide that is slightly coupled to the ring resonator. Inset: Spectrally integrated output of the straight waveguide as a function of optical excitation of the polymer film. The emission has been normalized to the excitation fluence.
In the spectrum, cavity modes with the same spacing of 1.7 nm can be seen. However, the envelope now reflects the low-density PL of the polymer (curve i in Fig. 2).

Since in the case of nanosecond excitation the exciting pulse is much longer than the exciton lifetime, we are operating here in a quasi-steady-state regime. To get a comparison with the femtosecond experiments, the respective excitation in watts per square centimeter has to be multiplied by the exciton lifetime $\tau_{exc}$. Using $\tau_{exc}=60$ ps, the threshold corresponds approximately to $130 \mu W cm^{-2}$ excitation fluence in the femtosecond regime, which is slightly larger than for the other cavities. However, this kind of structure is of particular interest, since it can be easily integrated and the emitted light can be coupled from the waveguide into an optical fiber.

6 Conclusions

In conclusion, we have demonstrated that stimulated emission and very large optical gain can be achieved in semiconducting conjugated polymers. The gain covers a spectral range of about 50 nm in a region where the polymer is transparent and can be as high as $10^4$ cm$^{-1}$. Utilizing the large light amplification in the polymer, we obtain laser action for various integrated planar and microring cavities.

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References

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