Semiconducting polymers for light-emitting diodes and lasers
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 5

Stimulated emission from single crystals and vacuum-deposited thin films of a substituted oligo(\(p\)-phenylene vinylene)†

Abstract

Stimulated emission from both single crystals and vacuum-deposited polycrystalline thin films of a substituted 5-ring PPV oligomer has been demonstrated. In the case of the polycrystalline vacuum-deposited films, Amplified Spontaneous Emission (ASE) occurs within the individual crystalline domains and was only observed if the domain size was increased by annealing or recrystallization from the melt. The amplification length is restricted by the size of the crystalline domains due to high optical losses (scattering) from the crystallite boundaries. The threshold for mirrorless lasing for an individual crystalline domain is comparable to that for conjugated polymer films if the domain size is sufficiently large, as demonstrated in the recrystallized Ooct-OPV5 films.

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5.1 Introduction

The generation of laser light under pulsed optical excitation, using conjugated polymers as active medium, has been demonstrated in solution [1,2], dilute blends [3] and more recently in neat thin films [4-8]. Our efforts concerning lasing from alternating PPV copolymers are described in chapter 3 (solution) and chapter 4 (thin films) of this thesis. The reported stimulated emission from photopumped neat polymer films is an important observation, which shows that singlet intrachain excitons, which are thought to be responsible for light emission (see [9] for a recent review), can be generated with high yields in the condensed phase. It is well-established that electroluminescence from polymer diodes originates from the same excited states as created by photoexcitations (PL and EL spectra are in the majority cases identical) and this makes one envisage the possible development of an electrically pumped polymer laser. The two proposed photophysical processes responsible for the observed net gain in photopumped neat polymer films without external feedback system are ordinary Amplified Spontaneous Emission (ASE) [7,10] and Superfluorescence (SF) [6] with its more subtle temporal characteristics. Also the combination of the two processes (co-existing in competition with each other) was suggested to explain the emission narrowing [11]. The structural complexity of polymers due to chemical and structural imperfections (conformational defects/mislinkages/saturated sites/molecular weight distributions/presence of end-groups) and the poorly defined microstructure in polymer films makes it difficult to identify the precise mechanism for the observed narrowing and to reconcile all reported studies. Detailed knowledge about the precise molecular structure of conjugated polymers and the structural organization of these polymers in thin films is of great importance for a better understanding of the underlying photophysics and structure/properties relationships.

An important question to be answered is whether or not it is possible to obtain electrically induced net gain. Based on the lasing threshold under optical excitation, it is estimated [4] that current densities in excess of $10^3$ A cm$^{-2}$ are needed to establish net gain in such devices, which is substantially higher than currently achieved in polymer LEDs. The low current densities in polymer LEDs, especially for electron transport, are the result of the low charge carrier mobilities, high trap densities and poor charge injection in conjugated polymers. However, electroluminescence (EL) of a 3 nm thick PPV film by tunnelling injection from a scanning tunnelling microscope (STM) tip with current densities of the order of $10^4$ A cm$^{-2}$ has been reported recently [12]. Despite the extreme circumstances, an ultrathin film (3 nm) in combination with a nanometer-sized cathode (end of the STM tip, area roughly 1 nm$^2$), it indicates that light emission at high current densities is possible in polymer films.

Conjugated oligomers can be considered as an interesting alternative. They can serve as models for their parent polymers or chain segments thereof [13-17], due to
the precise control of conjugation length and chemical structure in combination with the ability of crystallization into well-ordered molecular crystals. This allows structural information to be obtained from X-ray diffraction data, which is useful as a guide for interpreting polymer diffraction data [18,19]. In the case of PPV oligomers, the optical properties (wavelength of absorbance, luminescence and photocconductivity maxima) as a function of the number of repeat units \((n-1\), where \(n\) is the number of phenyl rings in the backbone) are converging to that of the corresponding fully conjugated PPV polymer at the five ring level \((n = 5)\) [14-16]. Additionally, it is well-known that ordered conjugated organic materials exhibit low trap densities and high charge carrier mobilities, for both electrons and holes. As an example, in single crystals of anthracene [20] the hole and electron mobilities are approximately 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and the crystal photoluminescence (PL) quantum yield at room temperature is almost unity. Both electroluminescence [20] and optically induced lasing [21] have been demonstrated in anthracene single crystals. From application point of view, organic single crystals are rather inconvenient, because perfect crystals are difficult to grow, hard to handle and have relatively large dimensions (typical thickness around 1 - 100 \(\mu m\)). The possibility to process oligomers into high-purity polycrystalline thin films by vacuum deposition allows the desired geometry for LED applications [22,23] to be realized. However, it is evident that the optical quality of polycrystalline films is rather poor due to scattering from grain boundaries, which is particularly disadvantageous for laser applications. Additionally, grain boundaries also have a negative impact on the electrical properties of such films. Hence, under any circumstances sufficiently large, crystalline domains are required.

In this chapter we describe the emission properties of both solution-grown single crystals and vacuum-deposited thin films of an all-trans 5-ring \(n\)-dioctyloxy-substituted oligo(p-phenylene vinylene)s under intense laser excitation. The morphology of the thin films was varied by annealing just below the first melting point and by recrystallization from the isotropic melt. In this way the crystalline domain size could be varied from a few microns up to several millimetres in the latter case. In both single crystals and thin films, mirrorless lasing has been observed. Stimulated emission in the polycrystalline thin films was only observed after the domain size was increased by thermal treatment.

5.2 Experimental

Optical microscopy pictures were taken on an Zeiss Photomicroscope. UV-vis spectra were obtained on a SLM Aminco 3000 Array spectrophotometer. Luminescence spectra were recorded on a Perkin Elmer LS50-B spectrofluorometer. Absolute luminescence quantum yields of the vacuum-deposited films and solution-grown single crystals were determined in a calibrated integrating sphere and luminescence
decay measurements were performed using the time-correlated single-photon counting technique as described in chapter 2. The lasing experiments were performed in an integrating sphere, with the third harmonic of a Nd:YAG laser (Quantum-Ray GRC 130-50, λ = 355 nm, pulse width 15 ns, repetition rate 1 Hz) as photoexcitation source. Neutral density filters were used to attenuate the excitation energy. The vacuum-deposited films and single crystals were excited under normal incidence. The emitted light emerging from the sample was detected by an Optical Multichannel Analyzer (Chromex 250 SI polychromator with Chromcam I CCD detector). All optical measurements were performed under vacuum (glass cell, static vacuum better than 10^-4 mbar) unless otherwise stated.

5.3 Results and discussion

The synthesis and characterization of the all-trans 5-ring oligo(p-phenylene vinylene) (abbreviated as Ooct-OPV5) as well as the single-crystal structure [24] and the X-ray diffraction data of the thin-film morphologies are given in the Ph.D. thesis of R.E. Gill [25]. All solid-state optical properties of Ooct-OPV5 are described in more detail in chapter 2 of this thesis. For the sake of clarity a short description of the single-crystal structure and the thin-film morphologies is given in this section. The molecular structure of the oligomer is depicted in figure 5.1. The oligomer has a nematic liquid crystalline phase between 183 °C (crystal-mesophase transition, 77 J/mmol) and 204 °C (mesophase-isotropic transition, 0.98 J/mmol).

The oligomer is soluble in common organic solvents like chloroform and tetrahydrofuran and yellow needle-shaped single crystals were obtained when the oligomer crystallized from a THF/methanol solution. The unit cell of the Ooct-OPV5 solution-grown single crystals is monoclinic, space group \( I2/l \), and contains eight discrete molecules separated by normal van der Waals distances. Thin films were prepared by slow evaporation from a molybdenum boat just above the melting point (290 °C) and at a pressure of 10^-6 mbar, with the glass substrate positioned about 10 cm above the boat. Optical microscopy (crossed polarizers) and Atomic Force
Microscopy showed that the as-deposited oligomer films were pinhole-free and exhibited a granular structure, indicating some extent of crystallinity. Optical micrographs (crossed polarizers) of all different thin-film morphologies are shown in figure 2.14 C on page 41. Annealing the film at a temperature of 120 °C resulted in a morphological change, which was irreversible. This morphological change occurred below the first melting point of the oligomer and manifested itself in an increase of the crystal domain size from approximately 4 µm to 20 µm. X-ray diffraction studies on the as-deposited and annealed films confirmed the enhanced molecular order and the increase in crystal domain size upon annealing. The crystalline domains were found to be oriented with the ab-axis standing up on the substrate. The crystalline structures of the single crystal, the as-deposited and the annealed film differ slightly from each other. The existence of different crystalline forms is attributed to the compressibility of the aliphatic layer (side chains) between the conjugated backbone, resulting in a deformability of the unit cell [25].

Heating the film to the isotropic melt (210 °C) and subsequent slow cooling resulted in a different morphology. Large domains were formed with dimensions up to several millimeters. In figure 5.2 an optical micrograph (crossed polarizers) of a recrystallized

Figure 5.2 Optical micrograph (crossed polarizers) of a thin film of Ooct-OPV5, obtained after slow cooling from the isotropic melt. Scale bar: 250 µm.
Ooct-OPV5 film is shown. The highly birefringent domains consisted of small bundles running parallel to the substrate. An in-plane dichroic ratio of approximately $D = A_y/A_\perp = 30$ was determined from polarized absorption spectra recorded within one domain. Additionally, a dichroic ratio in luminescence emission of $I_y/I_\perp = 20 \pm 10$ was measured, both ratios indicate a high degree of orientation of the conjugated backbones. The exact microstructure of this morphology has not yet been revealed.

**Single crystals**

We have recorded emission spectra as a function of excitation energy from single crystals and thin films of Ooct-OPV5 photoexcited with ns pulses from a frequency-tripled Nd:YAG laser ($\lambda = 355$ nm). Our efforts were mainly focused on thin films, because of the possibility to make light emitting diodes out of them eventually in a later stage. The solution-grown single crystals were tried in first instance to check whether or not it was possible to generate stimulated emission in crystalline Ooct-OPV5, because of their large dimensions (millimeter-sized) and reasonable optical quality.

![Emission spectra of a solution-grown single crystal of Ooct-OPV5. Excitation energy: 0.2 mJ (dotted line, scaled for clarity) and 0.5 mJ (solid line). Excitation spotsize = 0.5 mm.](image)
The emission spectra of a 30 µm thick solution-grown single crystal at low and high excitation energy are shown in figure 5.3. The solution-grown single crystals showed spectral behaviour similar to that of SiPPV and Ooct-PPV as described in the preceding chapter. Above an excitation threshold, which depended on the illumination spot size, ASE with a spectral bandwidth of 6 nm (FWHM) was observed, centred at 540 nm, in close proximity of the fluorescence maximum. The broad luminescence tails were almost fully suppressed at high excitation energy \( (I_{\text{ASE, 540 nm}}/I_{\text{luminescence, 560 nm}}) > 100 \) at \( E_{\text{ex}} = 0.5 \) mJ). The intense emission was mainly emerging from the edge faces of the crystal. The observed behaviour is typical for organic single crystals with high PL quantum yield and was already reported a long time ago for anthracene [19].

It should be stated that the threshold and intensity dependence for optical pumping is highly dependent on the quality of the crystals, the perfection of the facets, and the crystal thickness, which resulted in reasonably large crystal-to-crystal variations. The solution-grown Ooct-OPV5 single crystals on the average were far from perfect, due to thickness variations, defects and damage (small cracks) resulting from handling. Especially the larger crystals had a larger quantity of growth defects. Attempts to cleave the Ooct-OPV5 single crystals in a controlled way, to obtain thinner crystals with improved optical quality failed, due to the relative softness of the crystals resulting from the presence of long aliphatic side chains.

Figure 5.4 Emission spectra of an annealed thin (300 nm) film of Ooct-OPV5. Excitation energy: (a) 0.9, (b) 1.6, (c) 2.1, (d) 3.1 and (e) 3.9 mJ, excitation beam diameter = 1.8 mm.
reproducibility of the measured characteristics was good, and we could measure up to excitation energies of 4 mJ without visual damage of the illuminated spot. Lasing was not observed in annealed films of 100 nm thickness, which indicated that waveguiding inside the domains is crucial.

The energy threshold for linewidth collapse is approximately 1.6 mJ with a round excitation spot size of \( \approx 1.8 \) mm, which corresponds to a threshold pump fluence of 63 mJ/cm\(^2\) and a pump intensity of \( 7 \times 10^{24} \) photons/cm\(^2\).s\(^{-1}\). This threshold value is three orders of magnitude higher than that reported for PPV’s [4,6-8,11]. This can be attributed to the polycrystalline structure of the thin films. We believe that laser generation in the annealed films occurs only within the individual single crystal domains, which on the average have dimensions of approximately 20 \( \mu \)m. Scattering at grain boundaries likely results in high optical losses, which prevents sufficient net gain to be realized over multiple domains. Hence, the amplification length is restricted by the size of the individual crystalline domains. The domain size in as-deposited films, approximately 4 \( \mu \)m, is too small to achieve significant gain at all. Based on this argument one should expect that the threshold fluence for linewidth collapse in the case of the annealed Ooct-OPV5 films remains constant if the excitation spot size is decreased (up to a diameter comparable to the crystalline domain size \( \approx 20 \) \( \mu \)m). This was checked experimentally by putting an adjustable iris before the focusing lens to vary the excitation spot size, while maintaining approximately the same excitation fluence. A reduction of the excitation spot size from 1.8 mm (pump energy 3 mJ) to 1 mm did not alter the shape of the emission spectrum significantly and the same magnitude of amplification was observed. This confirmed that the interaction length was significantly smaller than the diameter of the excited area. This behaviour differed significantly from that observed for neat copolymer films (chapter 4). In that case a reduction of the spot size resulted in a large decrease of the magnitude of amplification, indicating that the interaction length was equal to the diameter of the excited area.

Additionally, a smaller area of the films was excited by focussing the pump beam to a spot size with a diameter of approximately 30 \( \mu \)m. With such a beam size only a few single crystal domains are excited, at the most. Sample alignment was found to be crucial with such a small spot size. Mirrorless laser generation was not observed at each spot excited on the sample and the magnitude of spectral narrowing varied highly from spot to spot, indicating that the excitation beam should be well aligned above a crystalline domain. The best results obtained from these experiments at low and high excitation energy (6 and 180 \( \mu \)J, respectively) are shown in figure 5.6. Note that both spectra are recorded at excitation energies above the threshold for spectral narrowing. Furthermore, restricting the excitation area to only a few domains appears to result in a more pronounced suppression of the broad luminescence tail. The threshold fluence estimated from these experiments is roughly 100-200 mJ/cm\(^2\), which is a few times higher than obtained with an excitation spot size of 1.8 mm. The
excitation threshold observed in the experiments using a spot diameter of 1.8 mm is an average value over roughly 8000 crystal domains. Also the shape of the time-averaged emission spectra is determined by this. It is obvious that with a spot diameter of roughly the size of a crystalline domain, the chance to locate the most optimum domain is extremely small, which explains the discrepancy between the threshold values.

![Emission spectra recorded from an annealed Ooct-OPV5 film using a smaller excitation spot size (diameter ≈30 µm). Excitation energy: 6 µJ (dotted line) and 180 µJ (solid line).](image)

**Figure 5.6** *Emission spectra recorded from an annealed Ooct-OPV5 film using a smaller excitation spot size (diameter ≈30 µm). Excitation energy: 6 µJ (dotted line) and 180 µJ (solid line).*

It is evident from all these experiments that it is possible to generate ASE in thin films of the model oligomer Ooct-OPV5, but that the amplification length is restricted by the size of the crystalline domains. Increasing the domain size will likely result in excitation thresholds for ASE comparable to that reported for conjugated polymer films [4,6-8,11], which are typically in the range of 10 µJ.cm⁻² to a few hundred µJ.cm⁻², using ns pulses. This was checked experimentally with Ooct-OPV5 films recrystallized from the isotropic melt. Recrystallization of the films resulted in the formation of large domains with dimensions up to several millimeters (see figure 5.2). The normalized emission spectra for different excitation energies for a recrystallized film are shown in figure 5.7. The excitation spot diameter was 1 mm in these experiments and the beam was focused within one domain. The domains were excited
with the pump light polarized parallel to the molecular axis. The O.D. at 355 nm for
the recrystallized films was approximately twice as high of that for the annealed film.
The lowest measured energy threshold for linewidth collapse was approximately 4 µJ
(corresponding to a threshold fluence of ≈ 500 µJ.cm⁻²), which is substantially lower
than that measured for the annealed films and cannot be explained only on the basis of
the difference in optical density between the two morphologies.

![Normalized emission spectra of a recrystallized thin (300 nm) film of Ooct-
OPV5. Excitation energy: (a) 1, (b) 10, (c) 50 and (d) 70 µJ, excitation beam diameter
≈ 1 mm.](image)

The energy threshold was dependent on the excitation spot size at constant pump
intensity, which indicated that amplification occurred over the whole illuminated area.
It should be stated that despite the large domains, the optical quality within the
domains is less than that of the films annealed at 120 °C. This gives rise to additional
scattering losses which decreases the magnitude of the amplification.

### 5.4 Conclusions and outlook

In conclusion, stimulated emission from both single crystals and vacuum-deposited
polycrystalline thin films of a substituted 5-ring PPV oligomer has been
demonstrated. In the case of the polycrystalline vacuum-deposited films, ASE occurs within the individual crystalline domains and was only observed if the domain size was increased by annealing or recrystallization from the melt. The amplification length is restricted by the size of the crystalline domains due to high optical losses (scattering) from the grain boundaries. The threshold for mirrorless lasing for an individual crystalline domain is comparable to that for conjugated polymer films if the domain size is sufficiently large, as demonstrated for the Ooct-OPV5 films recrystallized from the isotropic melt ($\approx 500 \mu \text{J.cm}^{-2}$). Current research efforts are directed towards the preparation of Ooct-OPV5 thin films consisting of large domains with a higher degree of perfection.

5.5 References