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Semiconducting polymers for light-emitting diodes and lasers

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Chapter 1

Introduction

Abstract

In this chapter a brief historical overview is presented concerning the progress made in the field of luminescent conjugated polymers in the past decade. The current understanding concerning the device operation of polymeric Light-Emitting Diodes is described, as well as the problems encountered. Furthermore, the synthetic approach towards the development of well-defined highly luminescent copolymers is explained. Finally, the aim and outline of this thesis are presented.

1.1 Conjugated polymers a new class of semiconducting materials

Conjugated polymers attract much interest nowadays for use as active component in electronic, optical and optoelectronic applications, like light-emitting diodes [1,2], light-emitting electrochemical cells [3,4], photodiodes [5,6], photovoltaic cells [7,8], field-effect transistors [9,10], optocouplers [11] and optically pumped lasers in solution [12,13] and solid state [14 -16]. They combine the properties of classical macromolecules, such as low weight, good mechanical behaviour (strength and flexibility) and processability with semiconductor properties, arising from their particular electronic structure. Conjugated polymers have a backbone consisting of alternating single and double bonds (see figure 1.1). The overlap of π bonding and π^* antibonding molecular orbitals forms a continuous system of electron density along the backbone. The extent of this overlap (conjugation length) together with the bond alternation determines the HOMO-LUMO bandgap. Conjugated polymers have bandgaps in the range of 1 to 4 eV, allowing stable optical excitations and mobile charge carriers.
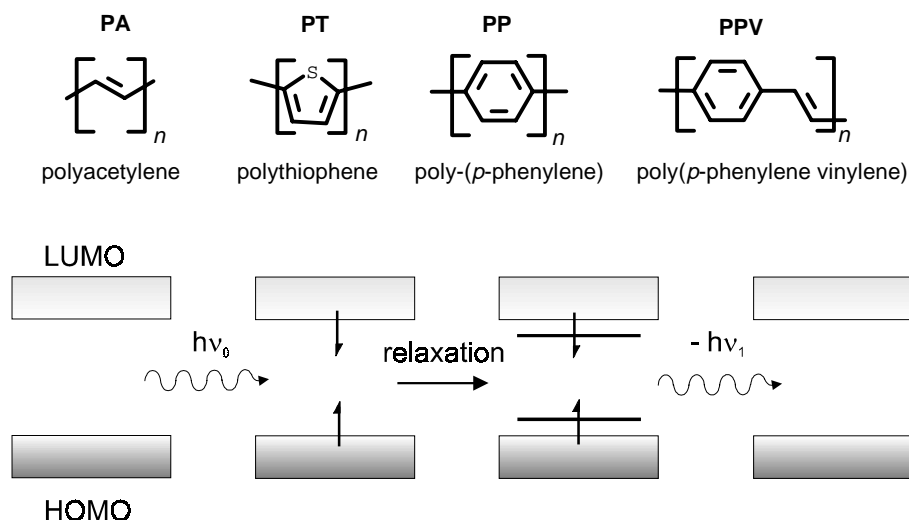
Figure 1.1 *Some examples of conjugated polymers. Below: schematic representation of radiative decay on a polymer chain after photoexcitation.*

Excitations can be created by charge injection, light and chemical doping. Excitation (see figure 1.1) results in a local deformation of the molecule around the site of electronic excitation [17,18]. The change of chain geometry (from aromatic to quinoid) has the effect of pulling levels away from the band edges into the gap. The degree of (de)localization is likely to depend on the nature of the conjugated system. Aromatic

rings tend to localize the excitation because the alternative electronic configuration, the quinoid one, is higher in energy. These materials are often strongly fluorescent and emit in the range from near infrared to the ultraviolet. Especially PPV and soluble derivatives thereof, are of great interest, due to the combination of emission in the visible wavelength region and high luminescence quantum yields.

The wavelength of emission depends on the extent of conjugation/delocalization, and can be controlled by modification of the chemical structure. This can be done by the attachment of functional groups, which alter the electronic structure of the conjugated backbone or by making copolymers with non-π-conjugated sequences, which interrupt the π-orbital overlap. So, light emission is possible over the entire visible range of the visible spectrum, by "chemical" tuning of the HOMO-LUMO energy gap of the polymer. The tuneable emissive properties are particularly attractive for lighting and display applications, especially in combination with (relatively) low material cost and the possibility of large-area device fabrication by means of simple casting techniques.

1.2   Brief historical overview

Light-Emitting Diodes

The first report concerning electroluminescence of an organic semiconductor by Pope *et al.* [19] goes back to 1963. They observed luminescence from single crystals of anthracene (a few tens of microns thick) using silver paste electrodes and bias voltages of a few hundred volts. An extensive and excellent survey of the photophysics, charge injection/transport and electroluminescence in organic crystals can be found in the book "Electronic processes in organic crystals" by Pope and Swenberg [20]. The difficulties with respect to crystal growth and the large voltages required for light emission limited the practical application of organic crystals as LED. Tang *et al.* [21,22] revived the interest in organic EL by using evaporated thin films of ≈100 nm as emissive layer, which reduced the operating voltages significantly (≈10 V). The first publication describing electroluminescence from a polymer (polyvinylcarbazole) by Partridge [23], in 1983, remained largely unnoticed. It lasted untill 1990 before a large academic and industrial interest in the field of light-emitting conjugated polymers was established, initiated by a publication from Friend and co-workers [1] describing EL from PPV films. A lot of research in the field has been directed towards the development of new efficient polymeric emitters (for a recent review see [24,25]). A whole range of polymeric LEDs, emitting over the whole visible wavelength region from blue to red, has been reported [26,27]. Furthermore, the LED performance was greatly improved, by means of additional charge-transport layers [28,29]. Double-layer LEDs with high peak brightness and internal electroluminescence efficiencies up to 4% [30] have been reported. Despite the rapid progress in the field of polymeric light-emitters, no commercial displays

based on polymer LEDs have been manufactured yet. The long-term device stability and device efficiencies of polymer LEDs are rapidly increasing, but improvements are still desired, especially for polymers emitting in the blue wavelength region. The main problem for commercialization of organic LEDs is the device lifetime. Especially oxygen has a dendrimental effect on device operation [37]. Oxygen can attack the vinylene bond and result in aldehyde-like chain terminations. These moieties are more electronegative and can act as quenching sites (charge transfer quenching of excitons). Evidence has been reported that even in an inert environment (nitrogen-filled glovebox, $[O_2]< 1$ ppm) this type of photooxidation reactions can occur due to oxygen diffusion from the ITO contacts [31]. Schlatmann *et al.* [32] already demonstrated that tin, indium and oxygen can diffuse out of the ITO contact into the polymer layer. It has been shown that the LED performance and stability can be significantly enhanced by coating the ITO contact with conducting polyaniline (PAni) [33]. PAni is transparent, has a higher work function than ITO, planarizes the ITO surface (avoiding shorts) and can act as a barrier to avoid diffusion of elements into the polymer layer. Another problem is the interface and contact stability. Low work function metals oxidize in the presence of either water or O_2. For instance it has been shown that an ITO/PAni/MEH-PPV/Ca device operated in water vapour loses 90% of its efficiency (but only one-third of its current) in 37 seconds! [34]. At that point the electrode is far from being oxidized, and still has its shiny colour, indicating a highly porous morphology. Also water-induced delamination of Mg cathodes in Alq$_3$ devices, resulting in blackspot formation has been reported. The temperature stability is an important parameter for display applications; displays must withstand extremes in temperature and thermal cycling. It has been shown that for example an ITO/PAni/MEH-PPV/Ca device shows a reduction of lifetime of a factor 20 upon changing the operating temperatures from 30$^{\mathrm{o}}$C to 60$^{\mathrm{o}}$C [34].

Lasing in polymer solutions and thin films

Excited states formed in conjugated polymers by charge injection or photoexcitation have photophysical characteristics similar to those of small organic chromophores such as laser dyes. It was realized that the high photoluminescence (PL) quantum yield and appreciable Stokes shift of conjugated polymers made them promising candidates as laser media in diluted solutions and solid state, the ultimate target being the elaboration of electrically pumped polymer lasers operating in the visible wavelength regime. Soon after the introduction of polymer LEDs, efficient laser action of the semiconducting polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) in the liquid state [12], operating in the yellow/red wavelength region, was reported. This was followed by blue laser emission from solutions of an alternating PPV copolymer [13]. More recently, laser emission from

dilute blends and blends containing titanium dioxide nanocrystals [35,36] has been demonstrated.

However, the prospects for solid-state lasing of neat polymer films seemed less hopeful. In solution and in dilute blends, the individual polymer chains are spatially well separated by the host medium, minimizing interchain interactions, that result in luminescence quenching. Despite the fast sub-nanosecond decay, the substantially decreased PL quantum efficiency (in comparison with solutions) and the photo-induced absorption, stimulated emission was observed in optically pumped neat polymer films in several ultrafast spectroscopy studies [37,38], indicating the possible development of solid-state polymer lasers. This was positively confirmed recently by Tessler *et al.* [14], who reported lasing from spincast PPV films under pulsed optical excitation in a microcavity construction. Furthermore, gain narrowing in optically pumped neat films of various PPV's without the use of an external feedback system by several groups [15,16,39,40] was reported, including ours.

The observation of lasing in optically pumped neat polymer films with and without external feedback system gives hope for the possible development of an electrically pumped laser diode. The major limiting factor at this moment is the drive-current necessary for electrically pumped lasing to be realized. One can make a rough estimation of the current threshold, based on the excitation density at which spectral narrowing occurs in optically pumped polymer films. It was estimated that current densities in excess of 10^3 A.cm^{-2} [15] are needed to establish electrically induced lasing. The highest reported current density achieved in a polymer LED until now is ≈ 25 A.cm^{-2} [41] and illustrates the barriers which have to be overcome concerning the development of a polymer laser diode. 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 by Bradley

Charge injection. Indium-tin-oxide (ITO) is the most commonly used hole-injection contact, it has a high work function (ϕ_{ITO} = 4.5-5.3 eV) close to the HOMO-level of conjugated polymers and is transparent, which allows the escape of the generated light out of the device. As electron-injecting contact, low work function metals such as Ca (ϕ_{Ca}=2.9 eV), Mg (ϕ_{Mg}=3.7 eV) or Al (ϕ_{Al}=4.3 eV) are used. The exact charge-injection mechanism is still controversial. It is generally believed that injection of holes at the ITO anode into the polymer is controlled by a superposition of field-emission tunneling and thermionic emission, the important parameter being the magnitude of the injection barrier [43,44]. Parker [43] showed that the I-V characteristics at high fields in a polymer LED can be described reasonably well with a Fowler-Nordheim tunnelling injection model of tunneling through a triangular potential barrier. A recent analysis by Davids *et al.* [45] suggests that tunneling dominates only for barriers higher than several tenths of an electronvolt, with a strong contribution of charge flowback, due to the low mobility of conjugated polymers. For smaller barriers, space-charge-limited thermionic injection is dominant. The influence and importance of an interfacial layer, formed between the polymer and electrode metal, on the injection barrier is still under investigation. It is known that Al forms covalent bonds with PPV [46] and Ca undergoes charge transfer, forming cationic Ca and bipolarons (doubly charged anions) in PPV [47]. A recent study with the inert transition metal ZrC (ϕ_{ZrC}=3.6 eV) as cathode metal, revealed that the efficiency in Au/MEH-PPV/ZrC devices is well below that obtained with Al as cathode material [48]. This gives a strong indication that the work function of the injecting contact probably cannot alone account for the charge injection barrier.
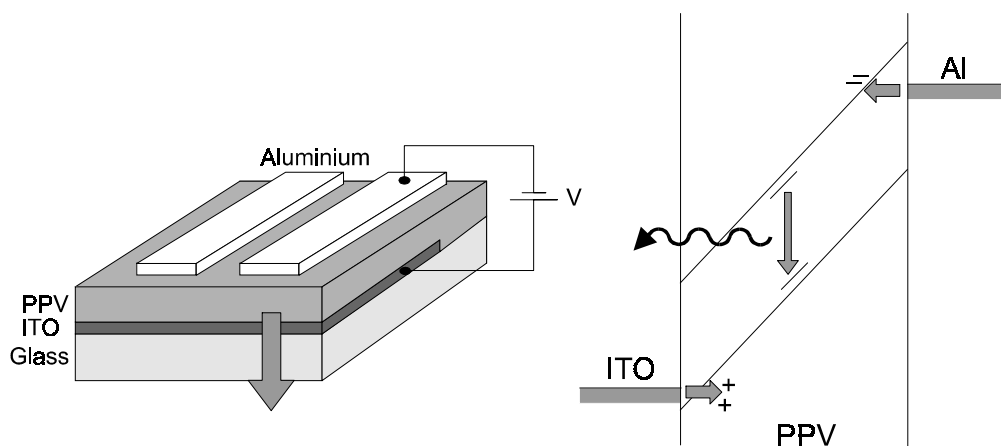

Figure 1.2 *Left: schematic representation of a polymer LED. Right: simple energy level diagram of a polymer LED operating in forward bias.*

The injection barrier for electrons is often significantly higher, which limits the injection rate for electrons severely. So, the emissive performance of a single-layer device is usually governed by field-driven electron injection. This has as a consequence that in single-layer devices the injection of opposite charges is unbalanced resulting in large loss (hole) currents and low efficiencies. Low work function metals like Ca [49] improve the injection rates but have the disadvantage of being highly reactive (oxidation).

Charge transport. The charge mobility is an important parameter, which has a significant impact on the device performance (brightness and EL efficiency). Charges move by electron transfer reactions or hopping between polymer chains [50]. Interchain transport is expected to be slower than intrachain transport, because electrical transport through a polymer chain is far more efficient than through space [51]. Conformational disorder and chemical defects can reduce intrachain transport significantly, however. The electron and hole mobilities in conjugated polymers are in general low, in the range of 10^{-4}-10^{-8} cm^{2}V^{-1}s^{-1} [52]. This puts a constraint on the maximum amount of charges which can be injected into the bulk (so limiting the brightness of the device). In addition, there is good evidence that holes are considerably more mobile than electrons in conjugated polymers due to deep trapping of electrons [53], which makes them preferentially hole transporters. The lower electron mobility results in unbalanced transport and recombination close to the interface of the electron-injecting metal electrode, which has the effect of quenching the emission.

Balanced injection and transport. So, for efficient LED operation balanced injection and transport are required. It has been shown that this requirement can be fulfilled in a polymer LED by using additional transport layers [28,30]. A concept which has proven its success in LEDs based on evaporated thin films of small organic emitters [21]. For example the introduction of an appropriate electron transport layer (ETL) can lower the electron-injection barrier, and create an energy offset for holes at the emissive layer/transport layer interface. This energy offset effectively blocks the hole current at the interface and results in a positive space-charge interfacial zone in the emissive layer. The space-charge zone will increase the field over the ETL layer resulting in enhanced electron-injection from the cathode. In addition, recombination will take place in a region (near the hetero-junction) away from the metal cathode. This concept poses some challenges for polymers, because the upper layer of the device must be cast without redissolving the lower one.

Recombination and decay. It is obvious that the EL efficiency of a polymer LED is for a large part determined by the efficiency of radiative decay of the excitations formed upon recombination. Charge recombination produces excitons, but generates both singlets and triplets. According to spin statistics, only approximately one quarter of the initially formed excitons will be singlets [28,54]. In PPV a variety of evidence, including the vibronic structure on the emission spectrum, strongly

suggests that the luminescence is from an intrachain singlet exciton [55,56]. This is also reflected in the EL spectrum of PPV, which is identical to its PL spectrum. The importance of this is that the estimated upper limit of the EL-efficiency is set to 25 % of the PL efficiency for which the dominant photoexcitation is an intrachain singlet exciton. In fact the situation is far more complicated as described above, because interchain interactions have a large influence on the decay pathways in the condensed state. Time-resolved photoluminescence studies give valuable information about the nature of the excited states, their lifetime, energy migration and decay pathways [57,58] and therefore helps to understand the photophysics of luminescent polymers. Yan *et al.* [37] reported a photoluminescence study of PPV films, and claimed that intrachain singlet excitons are not the primary photoexcitations generated. They proposed that the majority excitations are interchain excitations (modelled as interchain polaron pairs [59]) which decay non-radiatively, and speculated that they may be formed upon charge recombination to a lesser extent. However, Friend *et al.* [25] claimed that PPV films with 80% PL-efficiency can be prepared, which implies the generation of singlet excitons with unit quantum yield upon photoexcitation. This illustrates the importance of the way of preparation of PPV (amount of chemical and conformational defects as a result of the synthesis), film morphology, intermolecular organization ("packing"), the influence of impurities and oxidation products, etc. The importance of chain packing was also elegantly demonstrated in cyano-substituted PPV derivatives. In this type of polymers the backbones are closely packed, due to strong coulombic interactions. A photoluminescence study by Samuels *et al.* [60] of thin films of cyano-substituted PPV, has shown that in this case interchain excitations are the dominant species, which can give rise to highly efficient luminescence. They based their conclusion on the large Stokes shift, the broad structureless spectrum and the long luminescence lifetime of ≈6 ns found upon photoexcitation. The exact origin of this emission, whether it originates from dimers/aggregates or excimers is not clear at present. The above-mentioned PL studies illustrate that the design of highly luminescent polymers for light-emission applications is not only a question of choosing a suitable chromophore, but also of controlling their interactions in the condensed state.

1.4 Well-defined alternating semiconducting copolymers and oligomers

Alternating PPV copolymers

In conjugated homopolymers the actual conjugation length is an average value determined by random conformational or chemical defects in the polymer backbone and is difficult to control. Our approach to controlling the conjugation length and make the link between the luminescence properties of oligomers and those of

polymers, is through multiblock copolymers containing well-defined conjugated sequences (Fig. 1.3). Luminescent chromophores (A: typically π-conjugated oligomers) are either separated by higher band gap blocks (B), or directly linked to each other in a non-coplanar way. In both molecular structures the conjugation of the polymer main chain is regularly interrupted, giving well-defined tunable optical properties [61,62]. This approach is particularly suitable for blue-light emission, since this demands a short conjugation length. This molecular design can also enhance the luminescence efficiency through confinement of the excitons to the conjugated blocks, hindering their migration to quenching sites [63].
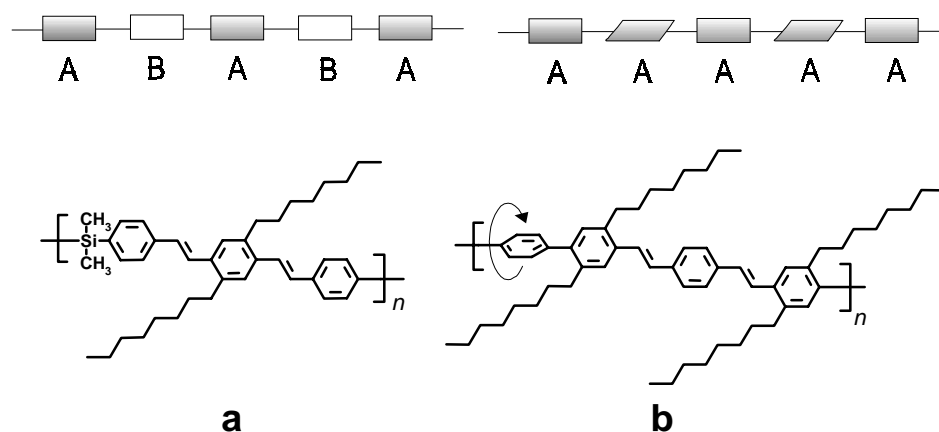

Figure 1.3 *Schematic representation of alternating copolymers; A is the conjugated chromophore, B is the interruption unit. For both approaches an example is given.*

Two examples of blue-light-emitting alternating PPV copolymers made following this approach are shown in figure 1.3a and b. In structure (a), abbreviated as SiPPV, PPV oligomers (distyrylbenzene) are linked through dimethylsilylene units. The dimethylsilylene units provide flexibility to the polymer backbone. The choice of this interrupting block is based on previous studies carried out in our group on poly[(silanylene)thiophene]s [64]. In this study it has been shown that the presence of only one silicon atom in the backbone effectively interrupts the conjugation. Structure (b), abbreviated as TOP-PPV, can be regarded as a copolymer of PPV and PP. Actually the PPV blocks are linked through an aromatic phenyl ring within a fully rigid-rod chain. The desired control of the conjugation length is achieved through steric interactions between the side chains and the rings within the terphenylene parts of the copolymer. As can be seen from figure 1.3b (arrow) the middle ring in the

terphenylene unit is twisted out of coplanarity, effectively interrupting the π-orbital overlap along the backbone. Also in this copolymer the active chromophore is a distyrylbenzene unit. The wavelength of emission of the copolymers can be tuned by increasing the size of the oligomeric blocks or by the introduction of substituents, which alter the electronic structure of the chromophore. For instance, by introducing electron-accepting cyano-substituents on the vinylene linkage or by changing the side-chains from alkyl to alkoxy (an electron-donating moiety), the emission can be considerably shifted to the red part of the spectrum.

PPV oligomers

From the preceding section (1.3) it became clear that the efficiency of radiative decay of photoexcited species (photoluminescence) is strongly dependent on the actual chemical structure of the polymer and on its state of aggregation (solid or solution). Since the processes of intramolecular exciton diffusion, intermolecular exciton stabilization, hopping, and exciton trapping at conformational defects, chemical defects or impurities are considered important factors in the competition between radiative and nonradiative decay, the conformation of the polymer molecule and the intermolecular organization ("packing") are of utmost relevance. These factors however, are hardly controllable if at all, especially in amorphous polymers. The study of small model compounds, which can be obtained in ultra pure form and with controllable molecular structure and organization (single crystals or polycrystalline films), can help in understanding the influence of those factors. With this in mind, a series of soluble 3 and 5-ring oligo(*p*-phenylene vinylene)s representing the PPV blocks of the copolymers have been synthesized and their single-crystal structure has been determined [65,66]. Furthermore, PPV oligomers gained considerable interest, not only as model compounds [67,68], but also for application as active layer in LEDs [69,70]. They are highly fluorescent, and they can be processed by vacuum-deposition from the vapour phase into high-purity thin films. The morphology of the thin films can be controlled by means of adjustment of the substrate temperature during deposition [70], or by annealing after deposition [71]. The optical properties of PPV oligomers (wavelength of absorbance, luminescence and photoconductivity 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 ($n = 5$) [68,72].

Alternating copolymer versus model oligomer

The effective interruption of π-orbital overlap in our copolymers is illustrated in

figure 1.4, where the UV-vis absorption and fluorescence spectra of TOP-PPV and its corresponding PPV model oligomer (tetraoctyl-substituted distyrylbenzene, abbreviated as Oct-OPV3) are shown. The shape and the width of the emission spectrum of the copolymer are very similar to that of the model oligomer, confirming that the distyrylbenzene units are the active chromophores. In addition, the quantum yield and luminescence lifetimes of the copolymer and model oligomer are comparable. The small red-shift of the copolymer spectra is probably due to a slight electronic contribution of the non-coplanar phenyl rings. The high luminescence quantum yield of these well-defined alternating PPV copolymers indicates their potential as emissive component in light emission applications like LEDs or lasers.
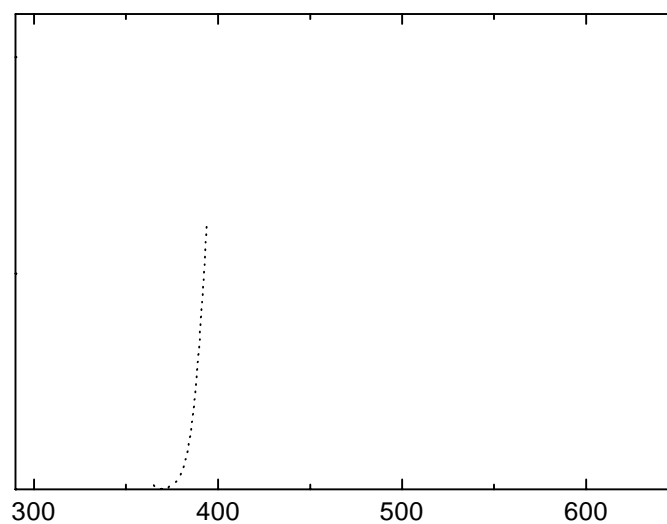
evaluated [73]. The influence of different substitution patterns on the optical properties as well as the differences between the optical properties in dilute solution and thin films are discussed. The spectroscopic properties of the copolymers in dilute solution are compared with those of distyrylbenzene model oligomers representing the chromophores in the backbone. The optical properties of solution-grown oligo(*p*-phenylene vinylene) single crystals are discussed in terms of molecular conformation and packing based on the X-ray diffraction data of the single crystals. Furthermore, the optical properties of oligomer thin films prepared by vacuum-deposition from the vapour phase are described. The influence of the thin-film morphology of the oligomers on the optical properties was investigated by means of annealing.

Chapter 3 deals with the application of alternating PPV copolymers as laser dyes in solution. Laser action of an efficient blue-light-emitting copolymer poly[(2, 5, 2'', 5''-tetraoctyl)-*p*-terphenyl-4,4''-ylene vinylene-*p*-phenylene vinylene] is demonstrated [13]. Three different solvents (*n*-hexane, *p*-xylene and tetrahydrofuran) were used to investigate the influence of the molecular environment on the lasing properties. The commercially available laser dyes, Coumarin 47 and 120, were used as a reference to compare the lasing efficiency and wavelength tunability of the copolymer with that of conventional laser dyes.

Chapter 4 describes the emission properties of spincast neat films of the blue-light-emitting silylene-*alt*-oligo(phenylene vinylene) copolymer (SiPPV) under pulsed laser excitation [16,74]. Spectral narrowing was observed above a well-defined excitation energy threshold. The influence of film thickness and the size of the excitation area on the threshold of spectral narrowing are discussed, as well as the angular dependence of the emission. Furthermore, laser action in films of a red-light-emitting homopolymer, poly(2,5-di-*n*-octyloxy-*p*-phenylene vinylene) (Ooct-PPV) in a microcavity configuration is demonstrated.

Chapter 5 describes the emission properties of both solution-grown single crystals and vacuum-deposited thin films of an octyloxy-substituted oligo(*p*-phenylene vinylene) under intense laser excitation. The morphology of the thin films was varied by annealing and by recrystallization from the isotropic melt. In this way, the crystalline domain size could be varied from a few microns up to several millimeters in the latter case. In both single crystals and thin films mirrorless lasing was observed. Stimulated emission in the polycrystalline thin films was only observed after the crystal domain size was increased by a thermal treatment [73,75].

In *chapter 6* the electrical and optical characteristics of light-emitting diodes based on alternating PPV copolymers [61,76] and 5-ring oligo(*p*-phenylene vinylene)s are evaluated. The influence of thin-film morphology on LED performance is discussed for an octyloxy-substituted 5-ring OPV. Device optimization by means of additional charge-transport layers and blending has been applied to enhance the electroluminescence efficiency. A novel polymer with oxadiazole-based side-chains has been used as an electron-transport/hole-blocking layer.

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