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Photonic Materials for Electroluminescent, Laser and Photovoltaic Devices

A. Hilberer, M. Moroni, R. E. Gill, H.-J. Brouwer, V. V. Krasnikov, T.-A. Pham, G. G. Malliaras, S. Veenstra, M. P. L. Werts, P. F. van Hutten, G. Hadziioannou*

Department of Polymer Chemistry, University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract

This article presents an overview of the work that has been done recently in our laboratory concerning the development and application of new conjugated materials with tunable properties. We have designed polymers containing oligo(phenylenevinylene)-type conjugated segments of well defined size and structure isolated either in their main-chain or in the side-chains. Model oligomers corresponding to the conjugated parts of the polymers have also been studied. We show how these materials perform in light-emission applications (light-emitting diodes, lasers) or photovoltaic cells.

Introduction

In conjugated polymers and oligomers the overlap of the π -orbitals forms a continuous system of electron density along the molecule. The extent of this overlap (the "conjugation length") determines the HOMO-LUMO gap which is found to be in general within the visible spectrum region. The photonic properties can thus be tuned by the precise control of the "conjugation length". Such conjugated polymer and oligomer materials are very attractive since they combine tunable photonic properties with easy processing, excellent mechanical properties and most important, low cost of fabrication. In this paper we present the design of new conjugated polymer and oligomer materials and we discuss some of their basic properties regarding the electroluminescent, laser and photovoltaic devices.

Conjugated Polymers and Oligomers for Light Emission*Basic principles*

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 control 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). 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 [1-3]. This approach is particularly suitable for blue-light emission since this demands short conjugation lengths. This molecular design can also enhance the luminescence efficiency through

* To whom correspondence should be sent (e-mail hadzi@chem.rug.nl)

confinement of the excitons in the conjugated blocks, hindering their migration to quenching sites.

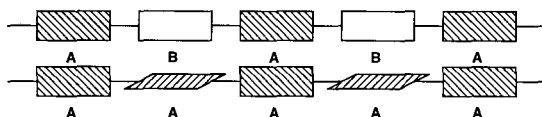


Fig. 1. Schematic representation of conjugated multiblock copolymers; A is a conjugated chromophore, B is an interruption unit.

Polymer materials

One family of conjugated copolymers, based on polyphenylenevinylene (PPV) blocks, designed to offer tunable optical properties is shown in figure 2. In structure I the PPV segments are linked through a silylene unit which interrupts the π -conjugation. In type II the PPV blocks, linked by an aromatic ring, are assembled in a fully unsaturated rigid-rod chain. The desired control of the conjugation length is achieved through steric interactions induced by the side-chains within the terphenyl part of the copolymer [4]. The structure III comprises simultaneously the two previously mentioned conjugation-interrupting units, with a simple stilbene-like chromophore. Different side-chains on the polymer backbones, which provide the adequate solubility, have been considered, such as alkyl C_nH_{2n+1} or alkoxy $O-C_nH_{2n+1}$ with lengths of C_4 and C_8 . Variation of the substituents provides also a way to fine tune the optical properties of the materials.

All the copolymers have been obtained by using the Heck coupling [5]. This reaction is a palladium-catalyzed vinylation of organic halides. It is a very convenient method which leads to the formation of carbon-carbon double bonds in pure *trans* configuration. The use of bifunctional monomers allows the synthesis of polymers, and the potential of this approach has been demonstrated previously.

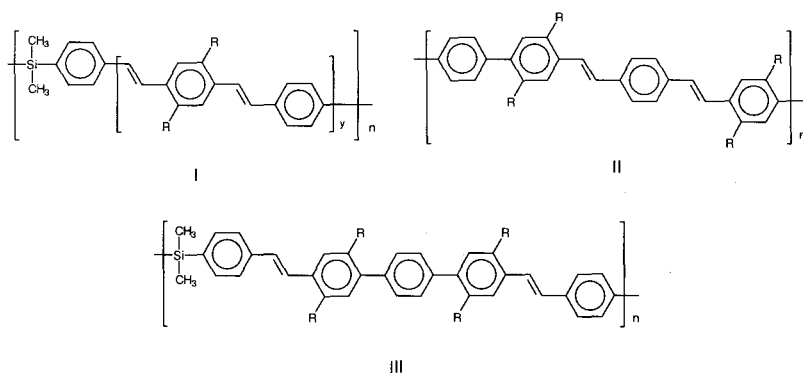


Fig. 2. PPV-based conjugated block copolymers; $y=1$ or 2 ; R =alkyl or alkoxy.

From polymers to model oligomers

The efficiency of radiative decay of photoexcited species (photoluminescence) is strongly dependent on the actual chemical structure of the polymer and on its state (solid or solution), which determine the symmetries and energies of the excited states. 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 crystalline films), helps in understanding the influence of those factors. With this in mind, model compounds representing the PPV blocks of the copolymers (Fig. 3) have been synthesized and their single crystal structure was determined [5-7].

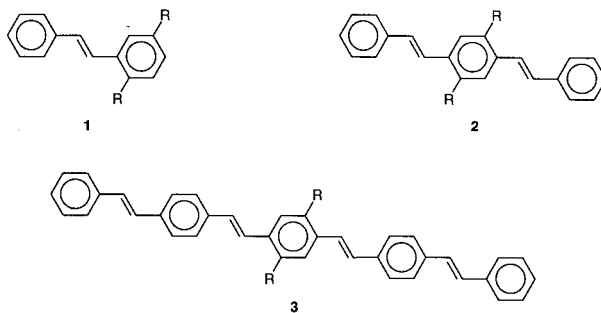


Fig. 3. Model PPV oligomers; R=alkyl or alkoxy.

Optical properties

In both the copolymers and the model oligomers an increase in the length of the PPV chromophore results in a red shift in absorption and emission [5-7]. For the series of materials described here, the fluorescence maxima cover the blue to green wavelength region. The change of the type of side-chain from alkyl to alkoxy is accompanied by a 25 to 50 nm red shift in the absorption and emission maxima. This result is mainly due to the increase of the electron density in the chromophore when the electron-donating alkoxy side-chains are attached [5]. If one compares polymers and models, there is a striking similarity of the optical properties. These results confirm that the active chromophores in the copolymers are the PPV blocks. The solution fluorescence quantum yields are very high (0.4-0.9) for polymers and oligomers, indicating a great potential in light-emission applications like LED's or lasers.

Light Emitting Diodes from Conjugated Polymers

In a simple electroluminescent device, a conjugated polymer film is sandwiched between two metal electrodes with a high and a low workfunction, that inject holes and electrons respectively. A simple band picture with a minor barrier between the electrode and polymer at the hole-injection interface and a much larger one at the electron-injection interface (e.g., approx. 1.5 eV for PPV/aluminum), is usually employed to describe the operation of the device [8].

Luminescence requires two opposite charges to form a singlet exciton instead of a more probable, long-lived triplet. Because of this, electroluminescence efficiencies are predicted to be substantially lower than photoluminescence efficiencies. In general, the spectrum of the light emitted has been found to be very similar to the photoluminescence spectrum of the same polymer under identical conditions. Electroluminescence spectra from devices utilizing PPV copolymers are shown in figure 4. Color tuning of the luminescence over the entire visible spectrum is demonstrated [9].

In light-emitting devices, the charge injection and transport characteristics can be tailored by introducing one or more charge-transport layers between active polymer and electrode(s) or by dispersing the active polymer in a matrix polymer with favorable charge transport properties, such as the photoconductor poly(*N*-vinylcarbazole). Applying these concepts and using a PPV-based copolymer, we have made blue-light emitting devices showing an external quantum efficiency of 0.8 % [10].

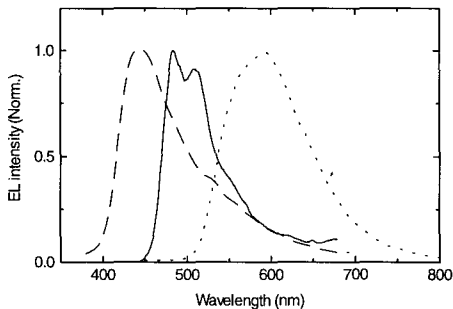


Fig. 4. Electroluminescence spectra of the PPV copolymers (Structure II in figure 2) with different types of side-chains: R=alkyl (left); R=alkoxy (middle); R=alkoxy, and additionally one cyano group on each vinylene bond (right) [9].

Lasing from Conjugated Polymers, Oligomers and Single Crystals.

The high photoluminescence quantum yield of conjugated polymers makes them promising candidates for active laser media in the liquid or solid state. Furthermore, due to their good processability and mechanical properties, polymeric dyes have a potential advantage as active gain media in dye-doped polymeric optical devices. The lasing efficiency of a PPV copolymer (TOP-PPV, figure 2 II, R=octyl) in hexane solution,

pumped with the third-harmonic radiation of a Nd:YAG laser, was found to exceed that of Coumarin 120 and Coumarin 47 dyes [11].

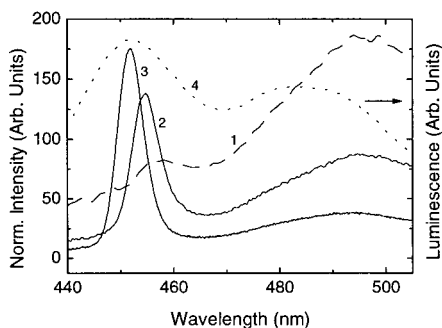


Fig. 5. Fluorescence (4) and emission spectra normalized on excitation energy. (1) is below the lasing threshold, ($E_{\text{ex}}=0.0075\text{mJ}$), (2) is at $E_{\text{ex}}=0.25\text{mJ}$ and (3) is at $E_{\text{ex}}=1\text{mJ}$ [14].

Recently, lasing from neat conjugated polymer films has been observed [12-14]. In figure 5, the typical spectral evolution of the light emitted from a PPV polymer (figure 2 I, R=octyl, y=1) film is shown. An increase in the pump energy results in spectral narrowing and the appearance of a sharp peak, surrounded by a broad luminescence tail. Above an energy threshold of approximately 0.1 mJ, narrow blue emission with a full width at a half maximum of 6 nm was emerging from the edge of the film.

We have also measured light emission spectra from single crystals and thin films of a five-ring PPV oligomer, Ooct-OPV5 (figure 3, 3, R=octyl) under intense optical excitation with third harmonic radiation of a Nd:YAG laser ($\lambda = 355 \text{ nm}$). Two emission spectra at low and high excitation energy of a solution grown single crystal, (thickness 30 μm) are shown in figure 6.

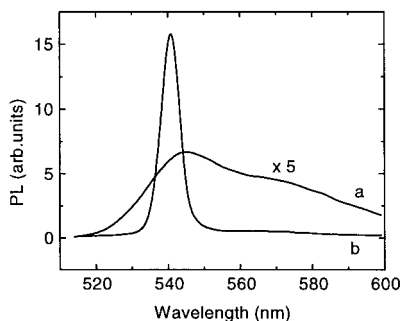


Fig. 6. Emission spectra of a solution grown single crystal of Ooct-OPV5. Excitation energy: (a) 0.2 and (b) 0.5 mJ

At low excitation energy only the normal broad fluorescence spectrum is observed, above a well defined excitation threshold a sharp emission peak appeared surrounded by a broad luminescence tail. The higher the excitation energy the more dominant the spectrally narrowing emission became, while the broad luminescence background being suppressed. The observed appearance of a spectrally narrow peak above a well defined energy threshold and the suppression of the broad luminescence tails, indicating the spectral energy redistribution within the emitted light, is a clear signature of light induced net gain due to stimulated emission. The observed behaviour is typical for molecular crystals with high luminescence quantum yield and has been known for a long time [15].

For possible practical applications single crystals grown from solution or melt are not appropriate, however evaporated or spincoated thin films offer the desired geometry for device application. For this study thin films with a thickness of 300 nm were prepared by vacuum evaporation on to glass substrates. The as deposited films showed no spectral narrowing at any pump energy up to the damage threshold. Stimulated emission was only observed in annealed films. In figure 7 the emission spectra of an annealed thin film are shown as function of excitation energy. The annealed thin films show the same typical spectral behaviour as the solution grown single crystals. Above threshold, stimulated emission with a narrow spectral bandwidth (FWHM = 5 nm, $\lambda_{\text{max}} = 548$ nm) was emerging from the film, while the broad fluorescence was suppressed. This becomes even more evident in figure 8, where the integrated intensity and linewidth as function of excitation energy is shown. The linear dependence of the integrated intensity indicates that there is energy redistribution within the emitted light. The lasing threshold for these thin films, approximately 1.6 mJ, which is three orders of magnitude higher than that of thin films from conjugated polymers. This can be attributed to the polycrystalline structure of the evaporated and annealed thin films of oligomers. We believe that laser generation occurs within the individual single crystal domains, which have dimensions of approximately 20 μm . Under our experimental conditions the average excitation energy received by the individual crystalline domains is approximately 8000 times less than the total excitation energy. Therefore the laser generation threshold for an individual crystal domain is estimated to be ~ 0.2 μJ per pulse, which is comparable to that of conjugated polymer films. The observation of lasing with a low energy threshold in thin polymer and oligomer films gives hope for the possible development of solid state, electrically pumped organic laser diodes.

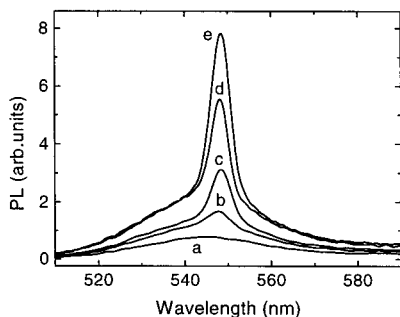


Fig. 7. Emission spectra of an evaporated thin (300 nm) film of Ooct-OPV5. Excitation energy: (a) 0.9, (b) 1.6, (c) 2.1, (d) 3.1 and (e) 3.9 mJ.

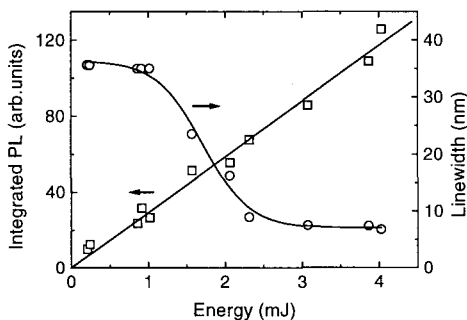


Fig. 8. Integrated PL (□) and linewidth (○) as function of excitation energy for an evaporated thin (300 nm) film of Oct-OPV5.

Organic Blends and Copolymers for Photovoltaic Devices

The photovoltaic effect involves the production of electrons and holes when light impinges on a semiconductor device, and their subsequent collection at the corresponding electrodes. Single layer and heterojunction-type organic photovoltaic devices have been extensively studied in the past, but their commercial application is hindered due to their low efficiencies.

Basic principles for photovoltaic devices engineering

Recently, a novel type of device, based on interpenetrating blends of donors and acceptors sandwiched between two asymmetric contacts (two metals with different work function) has been proposed [16-17]. When a donor is optically excited, the electron in the lowest unoccupied molecular orbital (LUMO) will lower its energy by transfer to the LUMO of the acceptor. In this way, very efficient dissociation of excitons into free carriers is achieved. Under the influence of the built-in electric field, caused by the asymmetric contacts, selective separation of the opposite charges takes place, with the holes being transported in the donor phase and the electrons in the acceptor. In this way, the blend can be considered as a network of donor-acceptor heterojunctions that allows efficient exciton dissociation and balanced bipolar transport throughout its whole volume.

Blends of oligothiophenes and C₆₀

One example of blend-based photovoltaic devices consists of α -sexithiophene (6T, which functions as the donor) and C₆₀ (which functions as the acceptor). The blends are prepared by vacuum coevaporation and exhibit a micro-phase separated morphology [18]. A strong quenching of the photoluminescence from 6T was observed, indicating that the size of the 6T domains is likely to be comparable to the exciton diffusion range in 6T. In the dark, the cell is behaving like a normal diode. During illumination a large photocurrent flows under reverse bias, that corresponds to an absolute quantum efficiency (electrons collected per absorbed photon) as high as 50% at only -1.4 V. Such high efficiencies make blend-based photovoltaic devices interesting for applications as photodetectors.

Homopolymer blends versus diblock copolymers

Another approach is the use of homopolymer blends or block copolymers. Such systems can undergo macro-/micro-phase separation with controlled morphology and structure. The type of structure is of utmost importance for the optimization of electro-optic devices such as LED's or photovoltaic cells. For instance, in the case of LED's it is desired to have a multilayer structure, whereas for photovoltaics, an interconnected bicontinuous structure is wanted.

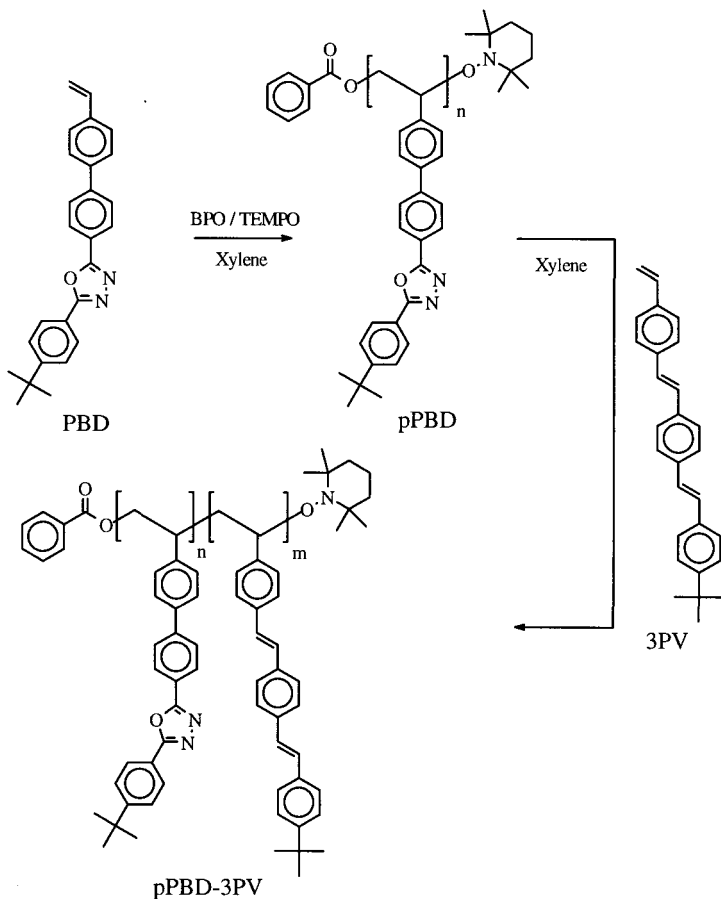


Fig. 9. Synthesis of a PBD-3PV diblock copolymer via TEMPO-mediated free radical polymerization

We have successfully applied the TEMPO-mediated “living” free-radical polymerization technique (Fig. 9) to the synthesis of a diblock copolymer bearing PPV-type conjugated side-chains (3PV) which can act as donor, on the one block, and

oxadiazole-based side-chains (PBD) which are good electron acceptors, on the other block [19-20]. The diblock copolymer has a molecular weight of $M_w = 56\ 000$ (polydispersity 1.53), the weight composition being 2/3 of PBD and 1/3 of 3PV.

Figure 10 gives the current versus voltage curves of devices made with the pPBD-3PV copolymer, the homopolymer p3PV and a blend (2:1) of the homopolymers, sandwiched between ITO and aluminum. The conductivity of the blend is slightly increased compared to that of the homopolymer p3PV, while the diblock shows significantly higher conductivity. Figure 11 shows the light emission of the same devices. The blend shows an enhanced emission whereas for the diblock copolymer the luminescence is almost completely quenched.

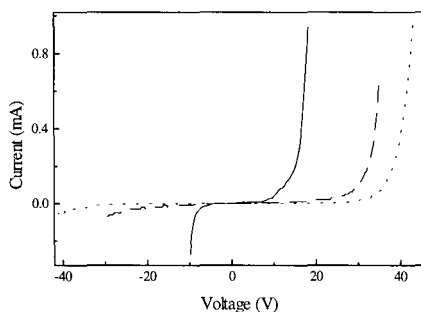


Fig. 10. Current-voltage (I-V) characteristics of devices (ITO-polymer-Al) made with the diblock copolymer pPBD-3PV (continuous line), the p3PV homopolymer (dotted line) and a 2:1 blend of the homopolymers pPBD and p3PV (dashed line).

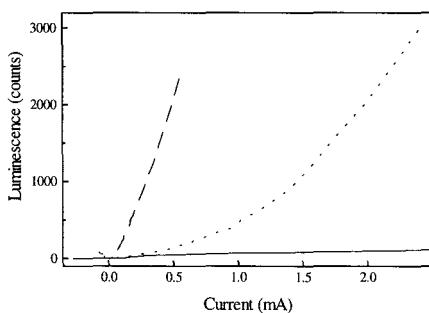


Fig. 11. Luminescence-voltage (L-V) characteristics of devices (ITO-polymer-Al) made with the diblock copolymer pPBD-3PV (continuous line), the p3PV homopolymer (dotted line) and a 2:1 blend of the homopolymers pPBD and p3PV (dashed line).

By illuminating the same devices with UV light, a current is detected at the electrodes. With excitation at 350 nm (40 mW/cm^2), without applied bias, the internal efficiency is 0.007 % for a blend, and 120 times more (0.87 %) for the diblock copolymer.

These results indicate that in the case of the block copolymer we have bicontinuous interconnected PBD and 3PV microphases, at the interphase of which an efficient exciton dissociation can occur with a consequent efficient charge transport of the corresponding charges through the microphases. The homopolymer blend of pPBD and p3PV seems to favor the light emission through its macrophase separation.

These preliminary results show how the molecular structure can affect, via its influence on the morphology, the light emission and photovoltaic properties.

Acknowledgments

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