Circularly Polarized Electroluminescence from a Polymer Light-Emitting Diode

Emiel Peeters,[†] Marwijn P. T. Christiaans,[†]
René A. J. Janssen,[†] Herman F. M. Schoo,[‡]
Harry P. J. M. Dekkers,[§] and E. W. Meijer*,[†]

Laboratory of Organic Chemistry
Eindhoven University of Technology, P.O. Box 513
5600 MB Eindhoven, The Netherlands
Philips Research Laboratories, Prof. Holstlaan 4
5656 AA Eindhoven, The Netherlands
Leiden Institute of Chemistry, Gorlaeus Laboratory
Leiden University, P.O. Box 9502
2300 RA Leiden, The Netherlands

Circularly polarized luminescence (CPL), i.e., luminescent light having different intensities for left (*L*) and right (*R*) circularly polarized components, may occur when the emissive state is optically active as a consequence of the intrinsic dissymmetry of the molecule. CPL effects have been observed in photoluminescence,[1] chemiluminescence,[2,3] and bioluminescence.[4] For some time it has been known that optical activity can be induced in the backbone of a π-conjugated polymer by introducing enantiomerically pure chiral pendant groups or chiral dopants.[5] The rotation of plane polarized light (optical rotatory dispersion, ORD) and circular dichroism (CD) in these chiral conjugated materials is strong when the polymer chains are in an aggregated phase, such as in a solid film or a microcrystallite which is formed during the onset of precipitation in a poor solvent or in a good solvent upon cooling. The origin of the strong optical activity in the π−π* transition in these materials is associated with the regiospecific substitution pattern of enantiomerically pure side groups on the chain, which results in the formation of small chiral aggregates. Presently only one example has been reported of circular polarization in the photoluminescence of a π-conjugated polymer.[6] For this polythiophene derivative, carrying two optically active (*S*)-2-methylbutoxy side groups per thiophene ring, the circular polarization in absorption, g_{abs}, defined as $2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R)$, is on the order of 2×10^{-2}, while the circular polarization in emission, g_{lum}, defined as $2(I_L - I_R)/(I_L + I_R)$, is 5×10^{-3}. With the recent advances in molecular and polymer light-emitting diodes (LEDs),[7,8] circular polarization of electroluminescent light and, hence, the construction of intrinsically dissymmetric light sources come within the realm of technology. Here, we present the first example of circularly polarized electroluminescence (CPEL) of a polymer LED which is constructed using a chiral π-conjugated poly(*p*-phenylenevinylene) (PPV) derivative as an active layer. The circular polarization of the electroluminescence is a direct consequence of the intrinsic molecular chirality of the conjugated polymer
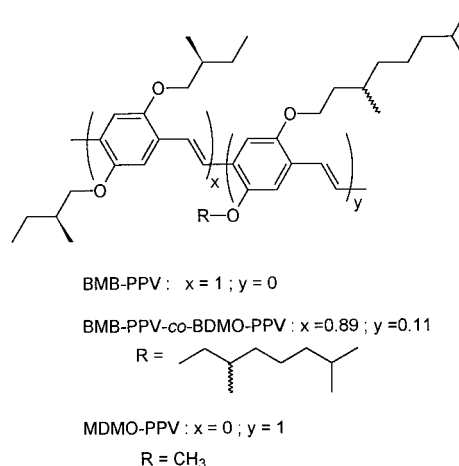

BMB-PPV : x = 1 ; y = 0

BMB-PPV-*co*-BDMO-PPV : x = 0.89 ; y = 0.11

R =

MDMO-PPV : x = 0 ; y = 1

R = CH₃

Figure 1. Structure of polymers used in this investigation.

and requires no macroscopic orientation of chromophores as for linear polarized electroluminescence.[9]

For the construction of a CPEL-LED the use of a PPV derivative is preferred because of the favorable luminescence efficiency that can be attained in solid films of these polymers. First, enantiomerically pure poly{[2,5-bis[(*S*)-2-methylbutoxy]-phenylene]vinylene} (BMB-PPV) has been prepared.[10] This polymer exhibits circular polarization in absorption and photoexcited emission ($g_{abs} = -1.2 \times 10^{-2}$ and $g_{lum} = -7 \times 10^{-3}$) in 1,2-dichlorobenzene solution at room temperature, where the material is partly aggregated. Hence, it is possible to prepare chiral aggregates of PPVs that emit circularly polarized luminescence. The highly stereoregular and regioregular substitution pattern of the BMB-PPV side chains favors aggregation and results in a low solubility (max. 0.05 mg/mL in chloroform), which precludes spin casting homogeneous thin films and, hence, the preparation of polymer LED devices. Therefore, we prepared poly{[2,5-bis[(*S*)-2-methylbutoxy]-1,4-phenylene]vinylene}-*co*-{[2,5-bis[(3*R*,3*S*)-(3,7-dimethyloctyl)oxy]-1,4-phenylene]vinylene} (BMB-PPV-*co*-BDMO-PPV) (Figure 1).[11] In this copolymer the enantiomerically pure (*S*)-2-methylbutoxy pendant groups account for the optical activity in the π−π* transition ($g_{abs} = -7.4 \times 10^{-3}$ at λ = 581 nm and $g_{lum} = -1.0 \times 10^{-2}$ at λ = 600 nm for aggregates in an anisole solution at 20 °C), while the longer racemic (±)-(3*R*,3*S*)-(3,7-dimethyloctyl)oxy pendant groups enhance the solubility by 2 orders of magnitude (∼10 mg/mL in chloroform) as compared to BMB-PPV. The monomer ratio of 8:1 in the polymer was found to be the best compromise of various important parameters, viz. fluorescence efficiency, optical activity, processability, and film formation.

The linear electronic absorption and CD spectra of a thin film of BMB-PPV-*co*-BDMO-PPV reveal a maximum absorption at $\lambda_{max} = 504$ nm with an associated strong bisignate CD effect in the region of the π−π* transition ($g_{abs} = -5.1 \times 10^{-3}$ at λ = 572 nm) (Figure 2a,b). Photoexcitation of the copolymer film at 528 nm produces a broad fluorescence emission, with peaks at 599 and 642 nm (Figure 2c). The electroluminescence (EL) of a polymer LED[12] with BMB-PPV-*co*-BDMO-PPV as

[†] Eindhoven University.
[‡] Philips Research Laboratories.
[§] Leiden University.
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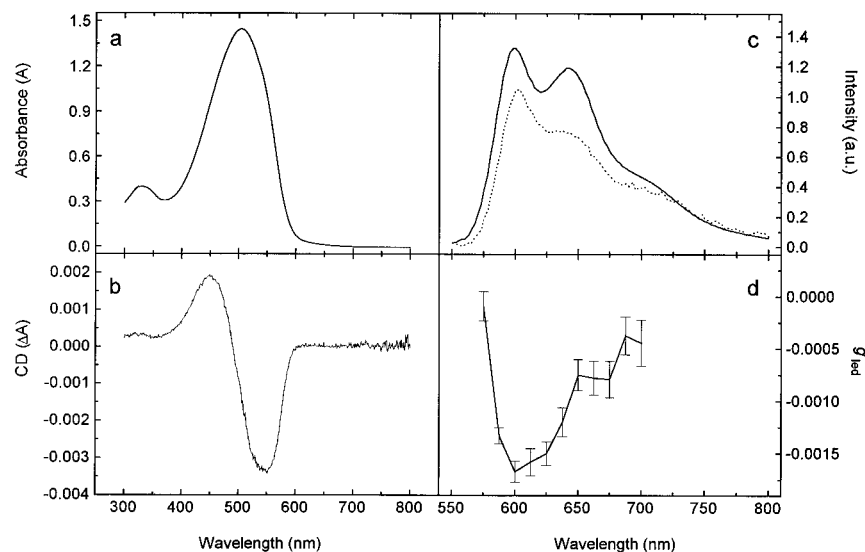(4) Wynberg, H.; Meijer, E. W.; Hummelen, J. C.; Dekkers, H. P. J. M.; Schippers, P. H.; Carlson, A. D. *Nature* **1980**, *286*, 641.
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(11) BMB-PPV-*co*-BDMO-PPV was synthesized by copolymerization of 1,4-bis(chloromethyl)-2,5-bis[(*S*)-2-methylbutoxy]benzene and 1,4-bis-(chloromethyl)-2,5-bis[(−)-(2,7-dimethyloctyl)oxy]benzene in a ratio of 8:1 with K*t*BuO in dry refluxing 1,4-dioxane for 1.5 h. The polymerization was stopped by addition of acetic acid, and BMB-PPV-*co*-BDMO-PPV was isolated by filtration of the reaction mixture, washing, precipitation, trituration, and drying. The polymer was characterized using FT-IR, ¹H-NMR, and elemental analysis.

Figure 2. Absorption (a), circular dichroism (b), photoluminescence (c, solid line), electroluminescence (c, dashed line), and circularly polarized electroluminescence (d) spectra of thin films of BMB-PPV-*co*-BDMO-PPV. Error bars indicate the standard error of the experimental result.
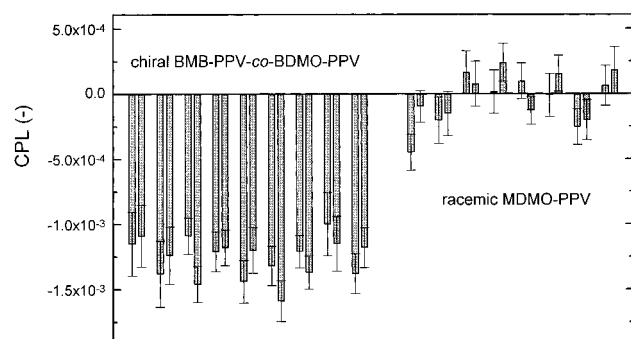
Figure 3. Results of the measurements of the CPEL effect for nine independent polymer LEDs having an enantiomerically pure polymer layer (BMB-PPV-*co*-BDMO-PPV) and eight LEDs with a racemic layer (MDMO-PPV). Error bars indicate the standard error of the experimental result.

an active layer is similar to the photoluminescence (PL) spectrum of the thin film (Figure 2c), indicating that the emission occurs from the same state. The circular polarization of the electroluminescence of these LED devices was measured at a wavelength of 625 nm (bandwidth 20 nm), beyond the onset of the linear absorption, to prevent reabsorption of the emitted light.[13] The results of these measurements are shown in Figure 3 for various independent LED devices and clearly demonstrate that the electroluminescence of optically active BMB-PPV-*co*-BDMO-PPV is circularly polarized. The average degree of circular polarization of nine LED devices is $g_{led} = -1.26 \times 10^{-3}$ ($\pm 3.5 \times 10^{-5}$). The magnitude of the CPEL effect varies in the emission band and has a maximum of $g_{led} = -1.7 \times 10^{-3}$ ($\pm 1.0 \times 10^{-4}$) at $\lambda = 600$ nm (Figure 2d). In a control experiment we subjected eight LEDs prepared from racemic

poly{[2-methoxy-5-[(3*R*,3*S*)-(3,7-dimethyloctyl)oxy]-1,4-phenylene]vinylene} (MDMO-PPV) to the same measurement and found no evidence of circular polarization in the electroluminescence: $g_{led} = -1.7 \times 10^{-5}$ ($\pm 4.6 \times 10^{-5}$) (Figure 3). This demonstrates that the CPEL effect is an intrinsic property of the dissymmetric active layer and is not due to the device architecture.

The magnitude of the circularly polarized electroluminescence of BMB-PPV-*co*-BDMO-PPV at $\lambda = 625$ nm is a factor of 6 smaller than the magnitude of g_{lum} in the photoluminescence of the aggregated polymer in solution ($g_{lum} = -7.5 \times 10^{-3}$ at $\lambda = 625$ nm). This difference is partly related to the device architecture. Reflection via the metal back electrode inverts the circular polarization of the light and is detrimental to the net degree of circular polarization of the LED. Reflection experiments with a 632.8 nm He−Ne laser (outside the absorption band) on various LED devices show that 50−65% of the incoming light is reflected on the metal surface. Hence, the intrinsic g_{lum} of the electroluminescence is expected to be larger by a factor of 3−5 than the measured value for g_{led}. In addition, we have observed that the g_{abs} value of an aggregated solution is usually higher by a factor of 1.5−2 than the g_{abs} value for thin films of the same material. The latter is explained by the higher degree of interchain order that can be obtained when aggregates are formed in solution via slow cooling than the order obtained via spin casting a thin film. This is further corroborated by the fact that g_{abs} for a thin film increases by annealing the film at elevated temperatures. The reflection losses and the differences between solutions and films rationalize the difference between g_{lum} in solution and g_{led}.

The observation of the CPEL effect demonstrates that inherent dissymmetry on a molecular level results in a net macroscopic chirality of a polymer semiconductor device. Although the CPEL effect has a molecular origin, the optical activity of the $\pi-\pi^*$ transition is, in our view, associated with the aggregation of chains and likely to be enhanced when full control over interchain interactions in solid films can be attained.

(12) Polymer light-emitting diodes (LED's) were prepared on glass substrates covered with patterned indium−tin oxide (ITO) as hole injecting electrodes. A 130 nm thick polymer layer of BMB-PPV-*co*-BDMO-PPV was spun cast on the ITO substrate from a chloroform/*o*-dichlorobenzene (7:1 v/v) solution (3.75 mg/mL). The low work function metal PHWB601 (Philips Electronics, Eindhoven, The Netherlands) was deposited as electron injecting contact on top of the polymer film by vacuum evaporation at pressures below 2×10^{-6} mbar to form active device areas of 4, 9, 25, and 81 mm². The onset voltage of the LED devices was 6−7 V.

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