Circular Dichroism and Circular Polarization of Photoluminescence of Highly Ordered Poly{3,4-di[(S)-2-methylbutoxy]thiophene}

6 AUTHORS, INCLUDING:

Stefan Meskers
Technische Universiteit Eindhoven

197 PUBLICATIONS **6,683** CITATIONS

SEE PROFILE

Circular Dichroism and Circular Polarization of Photoluminescence of Highly Ordered Poly{3,4-di[(S)-2-methylbutoxy]thiophene}

B. M. W. Langeveld-Voss,[†] R. A. J. Janssen,[†]
M. P. T. Christiaans,[†] S. C. J. Meskers,[‡]
H. 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
Leiden Institute of Chemistry, Gorlaeus Laboratories
Leiden University, P.O. Box 9502
2300 RA Leiden, The Netherlands*

The interesting electrical and optical properties of semiconducting polymers critically depend on the conformation of the π-conjugated chain in both ground and excited state and on the interchain orientation.[1] By introducing chirality, the structural characteristics can be assessed with chiroptical techniques, like circular dichroism (CD) and circular polarization of luminescence (CPL). Both techniques are well accepted for probing the conformation of ground and excited state, respectively.[2] Enantiomerically pure side chains or chiral dopants can afford chiral semiconducting polymers that exhibit optical rotatory dispersion and circular dichroism in the π–π* band.[3] Large optical rotations and strong, bisignate, CD bands have been observed, provided that well-defined and regioregular polymers are used in an associated phase in a poor solvent or in the solid phase.[3] Here we report on the (chir)optical properties of optically active poly{3,4-di[(S)-2-methylbutoxy]thiophene} (PDMBT) and demonstrate that in aggregated phases a splitting of the excited state into two exciton levels occurs. This splitting which cannot be detected in linear absorption or emission is important for understanding photoluminescence and electroluminescence behavior of conjugated polymers.[4]

Optically active PDMBT is prepared from 3,4-di[(S)-2-methylbutoxy]thiophene. The monomer is prepared from 3,4-

dimethoxythiophene,[5] which is treated with 2.2 equiv of (S)-(−)-2-methylbutanol under slightly acidic conditions in toluene at 80 °C to give 3,4-di[(S)-2-methylbutoxy]thiophene in 79% yield after distillation.[6] Polymerization is accomplished using anhydrous ferric chloride. The polymer is purified and isolated by Soxhlet extractions (M_w = 15.4 kg/mol, D = 3.49). ^{1}H- and ^{13}C-NMR spectroscopies reveal the desired 2,5-polymerization without any observable irregularities. This reaction sequence represents a convenient general synthetic route to poly-(3,4-dialkoxythiophene)s, since the transetherification is applicable for most of all primary alcohols, making 3,4-dimethoxythiophene an interesting synthon.

Linear absorption and circular dichroism spectroscopy of PDMBT in dichloromethane at 20 °C show that conformationally disordered polymer chains are present with no optical activity in the π–π* transition at λ_{max} = 438 nm. Cooling to −30 °C affords a highly ordered form of PDMBT as evidenced from the significant red-shift of the onset of the absorption and the appearance of a series of well-resolved vibronic transitions at λ_{max} = 508, 544, and 592 nm (Figure 1). The thermochromic behavior is accompanied by the appearance of a strong, bisignate, and vibronically coupled Cotton effect in the CD spectrum.[7] The CD spectrum follows the first derivative of the linear absorption spectrum (Figure 1). In *n*-decanol, PDMBT is already highly ordered at room temperature and the degree of circular polarization in absorption, defined as $g_{abs} = (\epsilon_L - \epsilon_R)/\epsilon$, is an unsurpassed high for a π–π* transition. Typically we find $g_{abs} = 2 \times 10^{-2}$ for PDMBT in *n*-decanol at 20 °C, although the actual value critically depends on sample preparation, and values as high as 8×10^{-2} have been recorded. This ordered phase of substituted polythiophenes is usually associated with the formation of small aggregates or microcrystallites with interchain interactions.[8–10]

The formation of an ordered phase of PDMBT also results in significant changes in photoluminescence (Figure 2). The emission of the free chains (*n*-decanol, 110 °C, excitation at λ_{ex} = 450 nm) is strong, with λ_{max} = 558 nm. The excitation spectrum (emission recorded at λ_{em} = 580 nm) closely follows the absorption spectrum of free PDMBT chains. The emission of the aggregated phase, recorded at 20 °C, is weaker by 1 order of magnitude, but exhibits a well-resolved vibronically structured emission at λ_{max} = 606, 660, and ∼730 nm when using excitation light with λ_{ex} > 530 nm. When the sample is excited at λ_{ex} = 450 nm, some remaining emission of the disordered chains is observed at shorter wavelengths (λ_{em} = 553 nm). The excitation spectrum (λ_{em} = 660 nm) of the structured long-wavelength emission resembles the absorption spectrum of the aggregates with peaks at ∼500, 532, and 580 nm.[11]

The Stokes shift (E_S) between 0–0 transitions of absorption and emission in *n*-decanol is less than 90 meV (25 nm), indicating a small structural reorganization in the excited state. The small Stokes shift is close to the ones observed for other highly ordered polymers such as gel drawn blends of poly[2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylene vinylene] in ultra-high molecular weight polyethylene (UHMW-PE) and ordered

[†] Eindhoven University.
[‡] Leiden University.
(1) See, e.g.: *Proceedings of the International Conference on Science and Technology of Synthetic Metals*; ICSM: Seoul, Korea, 24–29 July 1994. *Synth. Met.* **1995,** *69,* 71.
(2) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995,** *268,* 1860 and references therein. (b) Charney, E. *The Molecular Basis of Optical Activity: Optical Rotatory Dispersion and Circular Dichroism*; Wiley-Interscience: Chichester, 1979. (c) Dekkers, H. P. J. M. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH Publishers: New York, 1994; p 121. (d) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986,** *86,* 1.
(3) (a) Elsenbaumer, R. L.; Eckhardt, H.; Iqbal, Z.; Toth, J.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1985,** *118,* 111. (b) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1988,** 659. (c) Kotkar, D.; Joshi, V.; Ghosh, P. K. *J. Chem. Soc., Chem. Commun.* **1988,** 917. (d) Anderson, M.; Ekeblad, P. O.; Hjertberg, T.; Wennerström, O.; Inganäs, O. *Polym. Commun.* **1991,** *30,* 546. (e) Bouman, M. M.; Havinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Mol. Cryst. Liq. Cryst.* **1994,** *256,* 439. (f) Delabouglise, D.; Garnier, F. *Synth. Met.* **1990,** *39,* 117. (g) Salmón, M.; Saloma, M.; Bidan, G.; Genies, E. M. *Electrochim. Acta* **1989,** *34,* 117. (h) Harlev, E.; Wudl, F. In *Conjugated Polymers and Related Materials. The Interconnection between Chemical and Electronic Structure,* Proceedings of the Eighty-First Nobel Symposium; Salaneck, W. R., Lundström, I., Rånby, B., Eds.; Oxford University Press: Oxford, 1993; Vol. 139. (i) Drake, A. F.; Udvarhelyi, P.; Ando, D. J.; Bloor, D.; Obhi, J. S.; Mann, S. *Polymer* **1989,** *30,* 1063. (j) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991,** *113,* 1704. (k) Havinga, E. E.; Bouman, M. M.; Meijer, E. W.; Pomp, A.; Simenon, M. M. J. *Synth. Met.* **1994,** *66,* 93. (l) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995,** *7,* 385.
(4) (a) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994,** *265,* 765. (b) Samuel, I. D. W.; Rumbles, G.; Collison, C. J. *Phys. Rev. B* **1995,** *52,* R11573 (c) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Göbel, E. O.; Müllen, K.; Bässler, H. *Chem. Phys. Lett.* **1995,** *240,* 373. (d) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995,** *261,* 376.

(5) Gronowitz, S. *Ark. Kemi* **1958,** *12,* 239.
(6) Hoechst, AG. German Patent DE 3804522 A1, 1989.
(7) The CD spectrum is found to be independent of the lateral or angular orientation of the sample with respect to the photomultiplier detector.
(8) (a) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci. Polym. Phys. Ed.* **1987,** *25,* 1071. (b) Salaneck, W. R.; Inganäs, O.; Thémans, B.; Nilsson, J. O.; Sjorgren, B.; Österholm, J.-E.; Brédas, J.-L.; Svensson, S. *J. Chem. Phys.* **1988,** *89,* 4613. (c) Roux, C.; Bergeron, J.-Y.; Leclerc, M. *Makromol. Chem.* **1993,** *194,* 869.
(9) Daoust, G.; Leclerc, M. *Macromolecules* **1991,** *24,* 455.
(10) In the discussions presented here, we do not distinguish interchain interactions between different polymer chains from those between two parts of a single, but folded, polymer chain.
(11) The absorption spectrum of PDMBT in *n*-decanol at 20 °C shows vibronically resolved transitions at 497, 531, and 581 nm.
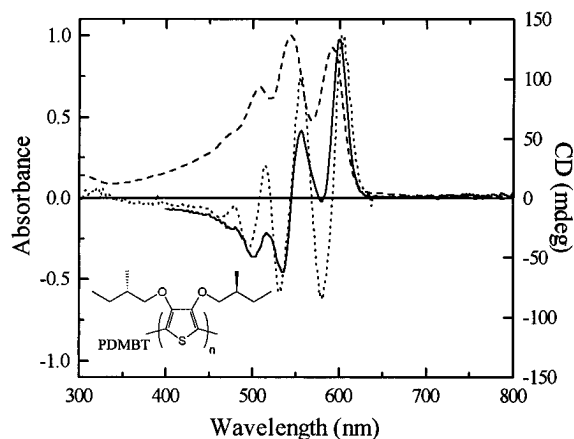
Figure 1. Normalized absorption (dashed line, left axis), first derivative of the absorption (dotted line, left axis), and CD spectrum (solid line, right axis) of PDMBT in dichloromethane at −30 °C.
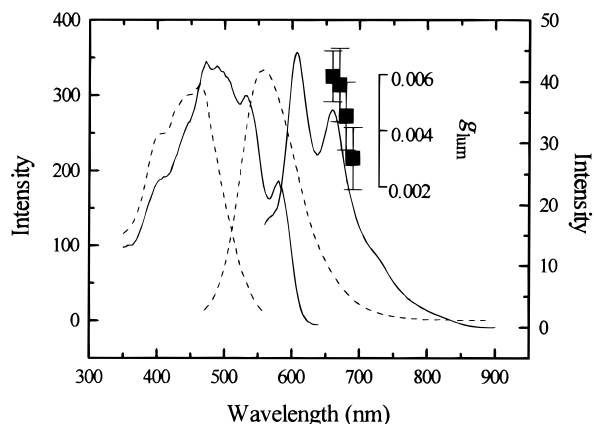
Figure 2. Emission and excitation spectra of PDMBT in *n*-decanol at 20 °C (solid line, right-hand axis, $\lambda_{ex} = 540$ nm, $\lambda_{em} = 660$ nm) and at 110 °C (dashed line, left-hand axis, $\lambda_{ex} = 450$ nm, $\lambda_{em} = 580$ nm). The inset shows the circularly polarized luminescence spectrum (■) at 20 °C of PDMBT in *n*-decanol recorded with excitation at 540 nm.

poly(*p*-phenylene vinylene) films where E_S ranges from 50 to 70 meV.[12,13] The linear polarization of the fluorescence in the aggregated phase is high, $p_{lum} \geq +0.3$, which indicates that the transition dipole moments in the long-wavelength absorption and emission are to a large extent parallel.

In addition to optical activity in absorption we find that the photoluminescence of PDMBT in the associated phase is also circularly polarized.[14] The degree of circular polarization in emission, defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, shown in Figure 2 has the same sign as g_{abs} on the high wavelength side. The magnitude of g_{lum} is on the order of $(+5.0 \pm 1.0) \times 10^{-3}$, a factor of 4 smaller than that in absorption. The exact cause of this difference is presently unclear, but might be related to very small conformational changes (quinoid form) upon photoexcitation or to emission from polymer chains that are defects in the lattice of the aggregate.[15]

The molecular origin of the strong CD effect, and especially the large g_{abs} value, must be ascribed to a highly ordered packing of the polythiophene chains in a chiral aggregate. The resemblance of the bisignate CD spectrum with the first derivative of the linear absorption spectrum is in full agreement with a splitting of the excited state into two exciton levels via a Davydov interaction.[16] The full width at half maximum of the first vibronic transition at −30 °C (~70 meV (20 nm), Figure 1) serves as an upper limit to the energy separation between these exciton levels. The oscillator strengths of the optical transitions to these exciton levels strongly depend on the orientation of the transition dipole moments and for a parallel orientation excitation to (and emission from) the lower level is formally forbidden.[16] Classical theory on exciton coupling using a point dipole approximation, however, cannot explain high g_{abs} values as are presently found for PDMBT with long conjugated segments.[17,18] Therefore, it seems necessary to include either a helical main chain conformation or a delocalization over more than two chain fragments into the theory. The circular polarization in the luminescence of the aggregated form proves that the chirality in conformation or packing is not destroyed by photoexcitation and is in agreement with the small Stokes shift. The relative weak emission observed from aggregates as compared to the optically inactive emission of free chains is a result of a more efficient radiationless decay in the ordered phase. The splitting into exciton levels with different dipole strengths which occurs in aggregates of conjugated polymers is expected to affect the luminescence efficiency and should be taken into account when comparing polymers in different environments (e.g. films vs solutions). Moreover, these results suggest that understanding interchain interactions is important in the design of highly luminescent conjugated polymers.[4]

In summary we have shown that PDMBT can be obtained in a highly ordered phase in solution. The optically active ordered phase of this chiral semiconducting polymer has been studied in detail using CD and CPL spectroscopy and was shown to exhibit a vibronically resolved and circularly polarized absorption and luminescence due to splitting of the excited state into two exciton levels.

(12) (a) Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652. (b) Halliday, D. A.; Burn, P. L.; Bradley, D. D. C.; Friend, R. H.; Gelsen, O. M.; Holmes, A. B.; Kraft, A.; Martens, J. H. F.; Pichler, K. *Adv. Mater.* **1993**, *5*, 40.

(13) The confinement parameter γ as determined by the ratio of the energies of the 0−0 transitions in emission and absorption, (ω_0/Δ_0), is given by $\gamma = (\omega_0/\Delta_0)\sin^{-1}(\omega_0/\Delta_0)/(1 - (\omega_0/\Delta_0)^2)^{1/2}$. For PDMBT we find $\gamma = 4.3$, a value larger than previous estimates of $\gamma \sim 1$ reported for 80% head-to-tail poly(3-alkylthiophene)s. (Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457.)

(14) For a description of the instrument, including a detailed analysis of the possible artifacts in the measuring technique, see: Rexwinkel, R. B.; Schakel, P.; Meskers, S. C. J.; Dekkers, H. P. J. M. *Appl. Spectrosc.* **1993**, *47*, 731.

(15) For poly{3-[2-((*S*)-2-methylbutoxy)ethyl]thiophene}, a chiral regioregular poly(3-alkylthiophene),[3e] we find a good agreement between circular polarization in absorption and emission: $g_{abs} = -10 \times 10^{-3}$ and $g_{lum} = -8.7 \pm 0.6 \times 10^{-3}$ ($\lambda_{ex} = 570$ nm, $\lambda_{em} = 660$ nm) in *n*-decanol at 20 °C.

(16) For randomly ordered transition dipole moments, on average the lower lying level will have lower oscillator strength: Knox, R. S. *J. Phys. Chem.* **1994**, *98*, 7270.

(17) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy. Exciton Coupling in Organic Stereochemistry*; Oxford University Press: Oxford, 1983.

(18) Classical dipole−dipole theory on exciton coupling of $\pi-\pi^*$ states shows that the two split levels have identical rotational strengths of opposite sign (ref 17). Within this model, the magnitudes of the rotational and dipole strengths are determined by the intrinsic dipole strength of the isolated chromophores and their orientation: $R^{\pm} = \pm(1/2)\pi\sigma_0 \, \mathbf{R}_{ab}(\boldsymbol{\mu}_{a0n} \times \boldsymbol{\mu}_{b0n})$; $D^{\pm} = \pm(1/2)(\boldsymbol{\mu}_{a0n} \pm \boldsymbol{\mu}_{b0n})^2$, where σ_0 and $\boldsymbol{\mu}_{0n}$ are the excitation energy and electric transition moment of transition $|0\rangle \to |n\rangle$, and $\mathbf{R}_{ab}$ is the interchromophoric distance vector. The exciton interaction energy scales with R_{ab}^{-3}. Using this theory, the maximum possible value of $g_{abs} = 4R/D = \pi\sigma_0 R_{ab}$ is independent of the value of the transition dipole moment. It is clear that a value of $g_{abs} = 8 \times 10^{-2}$ measured at 598 nm is irreconcilable with this exciton model as it would lead to $R_{ab} \approx 150$ Å and, hence, a vanishing small exciton interaction energy, resulting in a zero net CD effect.