THE JOURNAL OF CHEMICAL PHYSICS **125**, 164701 (2006)

Polarized optical spectroscopy applied to investigate two poly(phenylene-vinylene) polymers with different side chain structures

Lars-Olof Pålsson,[a] Helen L. Vaughan, and Andrew P. Monkman
Photonics Materials Institute, Department of Physics, Durham University, South Road, DH1 3LE Durham, United Kingdom

(Received 6 December 2006; accepted 18 August 2006; published online 23 October 2006)

Two related poly(phenylene-vinylene) (PPV) light-emitting polymers have been investigated by means of polarized optical spectroscopy. The purpose of the investigation was to investigate the nature of the interactions in thin films and to examine what impact the difference in side chain structure and molecular weight in poly(2′-methoxy-5-2-ethyl-hexoxy)-1,4-phenylene vinylene (MEH-PPV) and poly(2-(3′,7′-dimethyloctyloxy)-5-methoxy-1,4-phenylene-vinylene) (OC_1C_{10}-PPV) has on the electronic and optical properties of the two polymers. Aligning the polymers by dispersing them in anisotropic solvents and stretched films shows that the side chains have an impact on the relative orientations of the transition dipole moments. In anisotropic solvents the linear dichroism is larger for MEH-PPV than for the related polymer OC_1C_{10}-PPV, while in stretched films the opposite situation prevails. A lower polarization of the luminescence from OC_1C_{10}-PPV, relative to MEH-PPV, was also obtained independent of alignment medium used. The data therefore suggest that while mechanical stretching may align the OC_1C_{10}-PPV to a greater degree, the emitting species is distinct from the absorbing species. The circular dichroism (CD) spectra of both polymers undergo dramatic changes when the liquid phase and the solid state (film) are compared. The solution CD spectra shows no evidence of interchain interactions; instead the spectra of both systems indicate a helical conformation of the polymers. The CD spectra of films are dramatically different with the strong Cotton effect being observed. This points to the formation of an aggregate in the film, with an associated ground state interaction, an interchain species such as a physical dimer, or a more complex higher aggregate. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2354473]

INTRODUCTION

An important and very attractive feature of organic light-emitting polymers (LEPs) is the possibility of tuning the electronic properties of the system. A way to achieve this is through the introduction and modification of the side chains/functional group structure, which in turn results in an impact on the optical and transport properties. This is best exemplified with the various LEPs within the poly(phenylene-vinylene) (PPV)[1–3] and the polyfluorenes[4–6] that have been synthesized to date. With structural variations within these two classes of polymers, markedly different transport properties have been observed.[7–12] In addition, it should also be mentioned that side chains play an important role in increasing the solubility and thus ease the processing of the LEP, which is significant in the engineering process of the device. The best example here is the PPV system for which the solubility was improved significantly by the addition of side chains/functional groups.[2,13,14]

The key objective has therefore been to enable the control of the interactions, but in this context it is of utmost importance prior to this to first understand the character of the interactions. There are several different proposals regarding the nature of the interactions in the solid state, i.e., thin films. These include polaron pairs and excimers, but also aggregates with an associated ground state interaction (physical dimers) have been considered.[15–22] The basis for the physical aggregate is a sufficiently strong interchain interaction predominantly via a dipole-dipole interaction. If this interaction is strong enough, there will be a significant impact on the electronic transition ($1A_g \rightarrow 2B_u$) leading to a Davydov splitting of the absorption band.[23] In some cases this splitting can be unraveled through the appearance of a new absorption band as was observed in Refs. 24 and 25. In general it is, however, very difficult to study and distinguish these new bands using the linear absorption spectra of complex systems such as the LEPs. This is due to the fact that there is extensive inhomogeneous broadening of the electronic transition resulting in relatively broad and featureless absorption bands. It is therefore not uncommon that the Davydov splitting is hidden under the broad and structureless profile.

An alternative approach is therefore needed, and a powerful method in this context is to probe the absorption spectra using circular dichroism (CD) spectroscopy. For a review on CD spectroscopy and related techniques we refer to the texts.[26,27] CD spectroscopy has been successfully used in examining the light-harvesting complexes of photosynthetic systems of plants and bacteria. For instance, the organization and relative orientation of the chromophores (bacteria chlo-

---

[a] Author to whom correspondence should be addressed. Fax: +44-(0)191-3343585. Electronic mail: lars-olof.palsson@durham.ac.uk

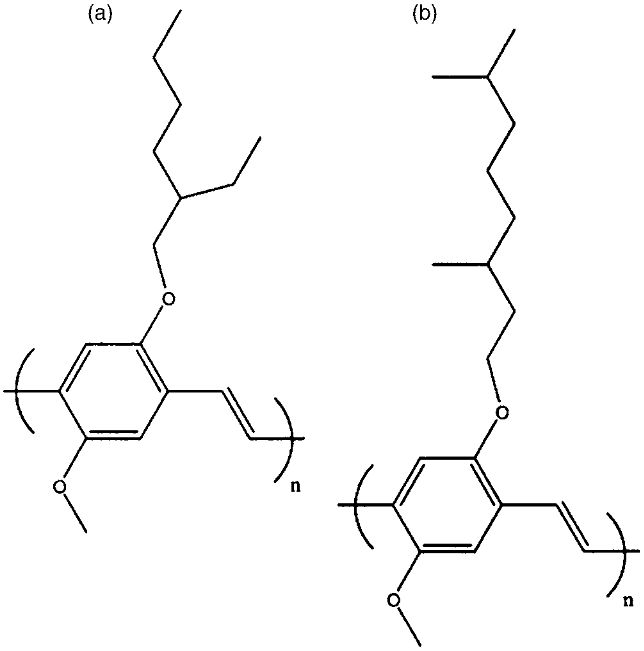

FIG. 1. The two LEPs used in this study. Polymer (a) is MEH-PPV while polymer (b) is OC_1C_{10}-PPV.

rophylls *a* and *b*) in the bacterial light-harvesting complex LH 2 was determined using a combination of CD and linearly polarized spectroscopies.[28] In addition, experimental spectra have been analyzed using a framework of exciton theory, resulting in a detailed understanding of the optical properties of these systems.[29,30] CD spectroscopy on LEPs has also been used in a few cases. These studies have indicated strong interactions and exciton delocalization, mainly in the solid state (films).[31–34]

The PPV polymer was the first material used that successfully produced electroluminescence in thin films.[1] The PPV system has very intriguing properties, for instance, an unusually high nonlinear response, and the system has accordingly been studied extensively within a range of experimental optical techniques, among them are site-selection luminescence and electroabsorption, etc.[35–40] However, there are still unresolved questions regarding the nature of the interactions, particularly the interchain type, and the strength of the interactions. With this in mind two related PPV LEPs were investigated using CD spectroscopy in combination with polarized linear spectroscopy: linear dichroism (LD) and polarized luminescence (PL). We observed that the side chain structure has a clear impact on the alignment of the polymer system. The most significant result is that CD spectroscopy clearly indicates that the interchain interactions lead to the formation of a physical dimer with an associated ground state interaction.

MATERIALS AND METHODS

The LEPs were obtained from Covion and investigated without further modifications. Figure 1 shows the structures of the two materials. The molecular weights of these two polymers are markedly different; for poly(2′-methoxy-5-2-ethyl-hexoxy)-1,4-phenylene vinylene (MEH-PPV) the upper limit is ~300 000 g/mol, while for poly(2-(3′,7′-dimethyloctyloxy)-5-methoxy-1,4-phenylene-vinylene) (OC_1C_{10}-PPV) the molecular weight can be as high as 1 900 000 which corresponds to ~7000 repeat units.[41,42] Dry powder was dissolved under stirring in toluene. For films the concentration was ~5 mg/ml, and films were made by spin coating at 1500 rpm/30 s deposition on a glass plate. For linearly polarized spectroscopy, the LEPs were oriented using an anisotropic solvent or stretched polyethylene (PE) films. The anisotropic solvent used was the nematic liquid crystal (LC) BL001 (Merck Pool Ltd.), and the LEP/LC mixture (~1% % w/w) (stirred for ~24 h) was filled into cells with antiparallel alignment layers by capillary force. The PE films were prepared by a method adapted from a previous work.[35] 80 mg of spectrophotometric grade PE (Aldrich) was added to 85 g of fresh o-xylene (Aldrich) in a conical flask left uncovered so any water in the solution could evaporate. This mixture was heated to ~120 °C in an oil bath and stirred vigorously until the PE had dissolved (~1 h). The temperature was reduced to ~90 °C, and a solution of o-xylene containing 4 mg of polymer was added and allowed to mix thoroughly (~10 min). The hot solution was poured into clean glass petri dishes cooled by an ice-water bath and upon cooling formed either a gelatinous or crystalline film. Strips of the film were carefully heated (to ~100 °C) over the edge of a hot plate and manually stretched to more than ten times their original length. The resulting stretched film had good optical properties.

Absorption spectra were measured using a Lambda 19 Perkin Elmer spectrophotometer, and PL was measured with a Jobin Yvon Horiba Fluoromax 2 equipped with Glan-Thomson polarizers. Polarized luminescence emission spectra (F_{ijk}) were obtained, where the notations *i*, *j*, and *k* denote two different orientation directions: *V* (vertical) or *H* (horizontal) as follows: *i* is the polarization of the excitation, *j* is the orientation of the alignment direction, and *k* is the emission polarization. The CD and LD measurements were performed on a home built system. Monochromated light (Bentham monochromator) from a tungsten halogen lamp (ORIEL), linearly polarized by a Glan-Thomson polarizer, was used as the probe light in a transmission experiment. The modulation of the polarization of the light was achieved with a photoelastic modulator (Hinds, PEM). The linearly polarized light for LD was accordingly produced through a half wave ($\lambda/2$) modulation, and the circularly polarized light for CD was produced through a quarter wave ($\lambda/4$) modulation. The transmitted light was detected using a home built amplified photodiode detector. Transmission spectra were subsequently obtained by normalization to a blank lamp spectrum. The signal was detected using a lock-in amplifier (Ortec 5210) through the well-known field modulation lock-in technique. The experimental setup was controlled by a personal computer (PC) through the general purpose interface bus (GPIB) interface with a LABVIEW 7.0 program. The transmission spectra were subsequently converted to absorbance spectra in accordance with the Beer-Lambert law.

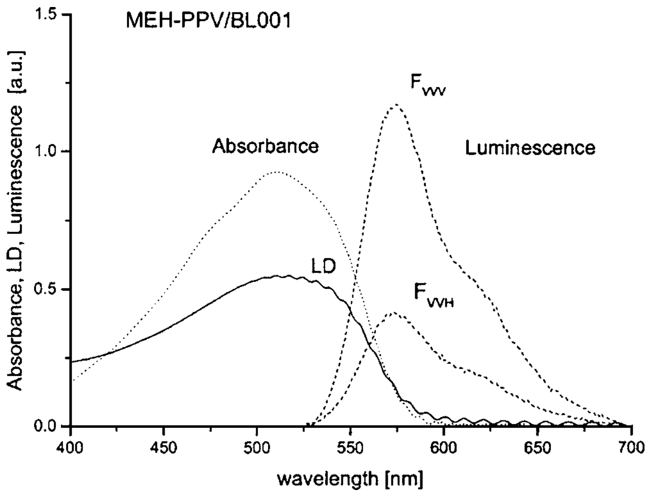

FIG. 2. Absorption, luminescence, and LD for MEH-PPV in the anisotropic host, the LC mixture BL001. For the luminescence the excitation wavelength is 490 nm.

RESULTS AND DISCUSSION

Linear dichroism and polarized luminescence

The LD of the two LEPs in anisotropic host showed a clear difference in magnitude as is evident from Figs. 2 and 3. The LD is given by the difference in absorption parallel and perpendicular to an alignment direction,

$$\mathrm{LD} = A_{\parallel} - A_{\perp}. \tag{1}$$

An LD > 0 means accordingly that the transition dipole moments are aligned along the orientation direction rather than perpendicular to it. The data show that when normalized to the isotropic absorption, the LD > 0 of MEH-PPV is clearly larger than that which was obtained for $\mathrm{OC_1C_{10}}$-PPV (Fig. 2 and 3). From the LD data an average orientation angle θ of the transition dipole to the alignment direction can be calculated using the relation[43]

$$\left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle \Phi = \frac{\mathrm{LD}}{A_{\mathrm{iso}}}, \tag{2}$$

where A_{iso} is the isotropic absorption, $A_{\mathrm{iso}} = (1/3)(A_{\parallel} + 2A_{\perp})$. Φ is an order parameter of the medium, in this case the anisotropic solvent. For nematic LCs it has been demonstrated that Φ takes a range of values, $0.5 \leqslant \Phi \leqslant 0.7$.[44] Using a value of $\Phi = 0.7$ for the anisotropic solvent we obtain the upper limit of the orientation, and for MEH-PPV an angle of $\theta = 25°$ is obtained, while for $\mathrm{OC_1C_{10}}$-PPV, we obtained $\theta = 41°$. The difference in orientation angle must be due to the difference in side chain structure between the two LEPs, and there can be two possible explanations for this difference. Firstly, the more extended side chain in $\mathrm{OC_1C_{10}}$-PPV has an impact on the overall alignment of the polymer backbone. It is not unlikely that the more extended side chain in $\mathrm{OC_1C_{10}}$-PPV can have isomers, which in turn can affect chain packing and alignment. Secondly, it is possible that the side chain has an impact on the charge distributions and thus affects the direction of the transition dipole moment although we regard this as a less likely explanation of the observed effect. An impact on the alignment due to the molecular weight is an unlikely factor in this context. The impact on the difference in molecular weight is mainly seen in the large difference in the number of repeat units of these two LEPs. For both systems of this study, this number is much larger than the spectroscopic unit; it is therefore unlikely that the molecular weight has an impact on the optical properties.

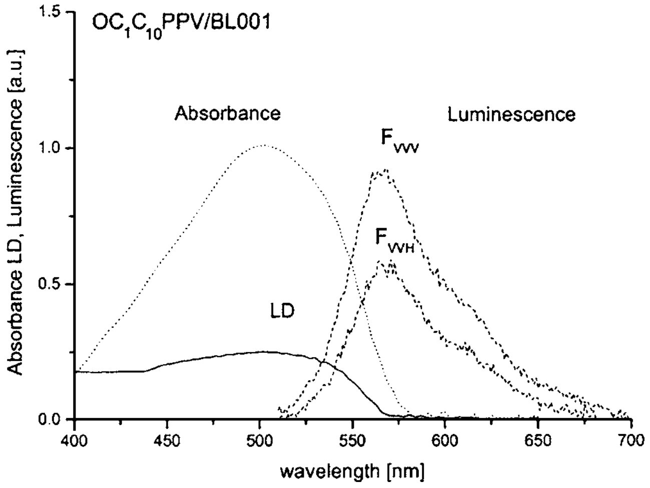

FIG. 3. Absorption, luminescence, and LD for $\mathrm{OC_1C_{10}}$-PPV in the anisotropic host, the LC mixture BL001. For the luminescence the excitation wavelength is 490 nm. See text for details.

Figures 2 and 3 also show the PL of the LEPs dispersed in anisotropic solvents. For both systems there clearly is a polarization of the emission. A measure of the degree of luminescence polarization can be appreciated from the dichroic ratio of the two PL components, F_{VVV}/GF_{VVH}, where G is an instrumental correction factor, $G = F_{HVV}/F_{HVH}$.[45] Calculating the luminescence anisotropy for ordered systems is not possible as the value of the denominator, $F_{VVV} + 2GF_{VVH}$, does not reflect the total intensity, which in turn makes normalization impossible.[45,46] The dichroic ratio for the LEPs dispersed in the LCs is calculated at the luminescence maximum (575 nm), returning a value of 2.55 for MEH-PPV, while $\mathrm{OC_1C_{10}}$-PPV/BL001 returned a value of 1.45. In comparing the dichroic ratio of the two LEP systems, we note that the data are in conjunction with the LD data which also revealed a higher degree of alignment relative to the orientation direction for MEH-PPV as compared to $\mathrm{OC_1C_{10}}$-PPV. A control measurement comparing F_{VVH} to F_{VHV} was also performed and this revealed that $F_{VVH} \neq F_{VHV}$ (data not shown). From this observation we conclude that the loss in polarization is not due to absorbing and emitting dipoles being nonparallel, even when alignment is good. Instead it must be due to electronic energy transfer to a small population of emitting sites in the reddest part of the inhomogeneous distribution function.

Figures 4 and 5 show the result of stretched PE films, doped with the LEP systems. As the film is manually stretched the long chains of the inert PE align along the stretching direction, so do the LEP chains.[26] This is independent of an internal interaction, whereas alignment in LCs is governed by a guest-host interaction. The LD of both LEPs

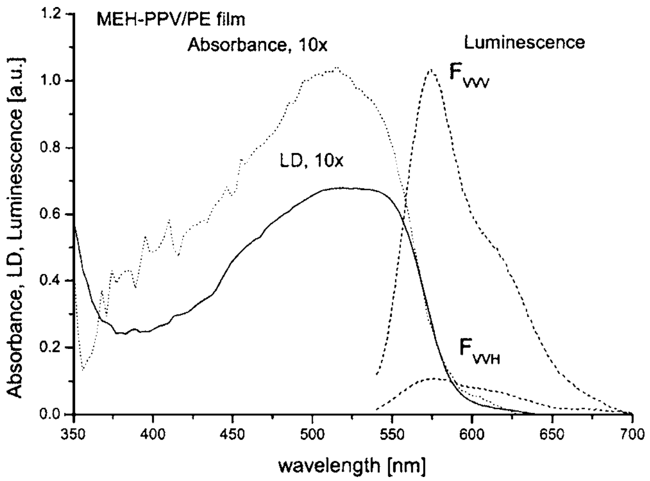

FIG. 4. Absorption (dotted line) and LD (solid line) for stretched PE films. Normalized luminescence at $\lambda_{exc}=525$ nm from MEH-PPV in a stretched PE film. See text for details.

in PE films had a magnitude larger than that which was observed in the anisotropic solvent, which in turn points to a better alignment. The trend was different though, with OC_1C_{10}-PPV showing a slightly higher LD as compared to MEH-PPV. This result was supported by polarized excitation spectra of both LEPs (data not shown) which showed a higher polarization for OC_1C_{10}-PPV. The data therefore suggest that for mechanical alignment, the side chain structure of OC_1C_{10}-PPV is possibly more flexible and can be more easily aligned along the polymer backbone. It can be seen in Figs. 4 and 5 that the degree of polarization of the luminescence is higher in both LEP PE films as compared to the anisotropic solvent. As was observed in the anisotropic host, the polarization of the luminescence is larger for MEH-PPV/PE films as compared to OC_1C_{10}-PPV/PE films as judged by the dichroic ratios. For MEH-PPV/PE film we obtained a dichroic ratio of 9.45, while for OC_1C_{10}-PPV/PE film the returned value was 5.75.

Finally we note that all LD spectra (Figs. 2–5) follow the absorption profiles quite well in the red tail of the LD spectra. Dividing the LD with the isotropic absorption also resulted in a wavelength dependent profile resembling the observed LD (data not shown). This fact points to a more random orientation of the absorbing species with the lowest energies in the broad inhomogeneous distribution function. For the opposite to prevail, no difference on the orientation of the dipoles in the red tail of the absorption band, a wavelength independent plateau is expected,[47] which is clearly not observed in this study. It is very likely that these low energy sites also are responsible for the luminescence and that these are in the receiving end of an electronic energy transfer process. The slightly less polarized luminescence of these species is therefore consistent with the lower polarization at the tail of the LD spectra.

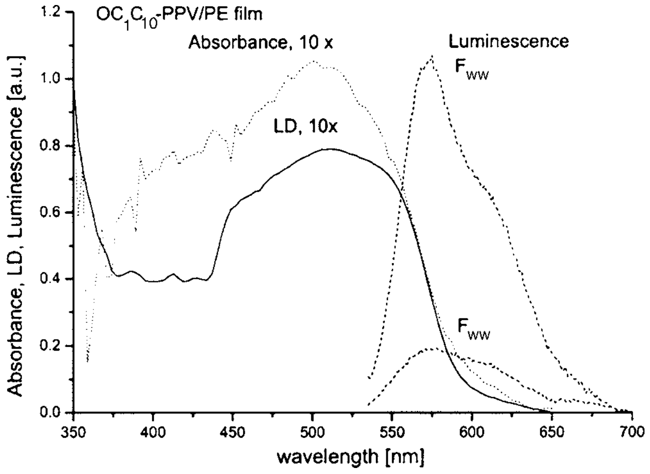

FIG. 5. Absorption (dotted line) and LD (solid line) for stretched PE films. Normalized luminescence at $\lambda_{exc}=525$ nm from OC_1C_{10}-PPV in a stretched PE film. See text for details.

Circular dichroism

CD is the difference between left hand and right hand circularly polarized light. The result is accordingly an optical rotation which is quantified as a rotational strength and is in turn related to an experimental observable. Via the Rosenfeld equation there is a formalism that connects the microscopic property to the experimental observable.[26,27] The Rosenfeld equation has various forms, and we refer to the texts cited here for more detailed reading.[26,27] In this context the relevant system is the physical dimer with an associated ground state interaction. This interaction is described by two interacting dipoles (a,b) and is given by,

$$V_{ab}(R)=\frac{\bar{\mu}_a\cdot\bar{\mu}_b}{R^3}-\frac{3(\bar{\mu}_a\cdot\bar{R})(\bar{\mu}_b\cdot R)}{R^5}. \tag{3}$$

If the interaction is sufficiently strong the result will be a split of the energy levels, i.e., a Davydov splitting.[23] For the simple case of a homodimer these energies are $E_\pm=E_{a,b}\pm V_{ab}/2$. The rotational strength is directly affected by the dipole-dipole interaction, and it can be shown that the rotational strength of ground to excited state transition for a degenerate dimer is [26]

$$R_{ge}\propto-\frac{E_aE_b}{\hbar(E_a^2-E_b^2)}\left\{\frac{\bar{\mu}_a\cdot\bar{\mu}_b-3(\bar{\mu}_a\cdot\bar{R}_{ab})(\bar{\mu}_b\cdot\bar{R}_{ab})}{R_{ab}^2}\right\}$$
$$\times\{\bar{\mu}_a\bar{\mu}_b\cdot\bar{R}_{ab}\}. \tag{4}$$

According to this formalism the measured spectrum will take the shape of a bisignate transition with the opposite sign of each component, which in turn will depend upon the relative orientation and interaction of the two dipoles. We remark that while this formalism strictly applies to a heterodimer, the interchain species could clearly meet this criterion. There is significant inhomogeneous broadening in these polymer systems to justify this assumption. In addition, at the point of the strongest interactions chain deformations could clearly affect the site energies.

Figures 6 and 7 show the CD spectra of the two LEPs dispersed in an isotropic solvent. Both spectra have similar shapes with an asymmetric and weak Cotton effect in the 450–600 nm region. In both systems the high energy component has a stronger absorption and this could in principle be due to an exciton splitting, presumably then from an in-

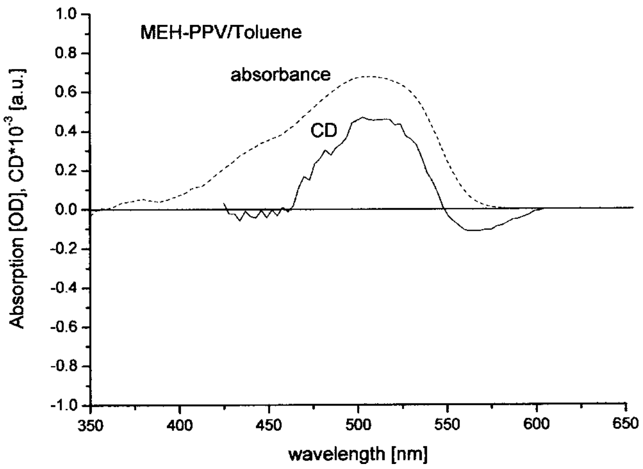

FIG. 6. Circular dichorism (solid line) and absorption (dot) for MEH-PPV in an isotropic solvent.

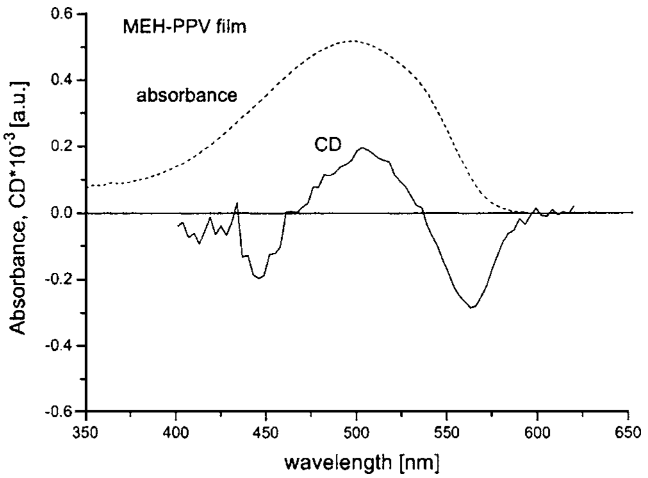

FIG. 8. Circular dichorism (solid line) and absorption (dot) of the MEH-PPV spin coated film.

trachain aggregate. The impact on the CD spectra of a polythiophene due the medium was investigated by Langeveld-Voss *et al.*,[31] and the result of their study is that a CD spectrum with a strong bisignate Cotton effect only is obtained for what is considered to be a poor solvent (mixture) for this particular polymer, and Oda *et al.*[32] made the same observations for a polyfluorene. Both these authors therefore concluded that the medium had forced the polymers into an aggregated state.

Regarding the observations in this study, an alternative explanation for the CD spectra in Figs. 6 and 7 is instead that the shape of the spectra is due to the conformation of the polymer rather then being indicative of exciton splitting. The main basis for this conclusion is the weak bisignate Cotton effect which makes it difficult to attribute the CD spectra of the solutions to an aggregated state. Using a theoretical approach it can be shown that a CD spectrum with a positive or negative signal originates from a helical conformation of the polymer system.[27] For instance, Sato *et al.* have examined polysilenes in solution and obtained CD spectra with a positive signal only, thus attributing their observation to the helical conformation of the system.[48] We can also refer to studies using x-ray scattering techniques applied to some LEP systems showing that the polymer chain adapts a helical conformation.[49] In addition, this hypothesis was backed up by density functional theory calculations on a semiconducting polymer.[50]

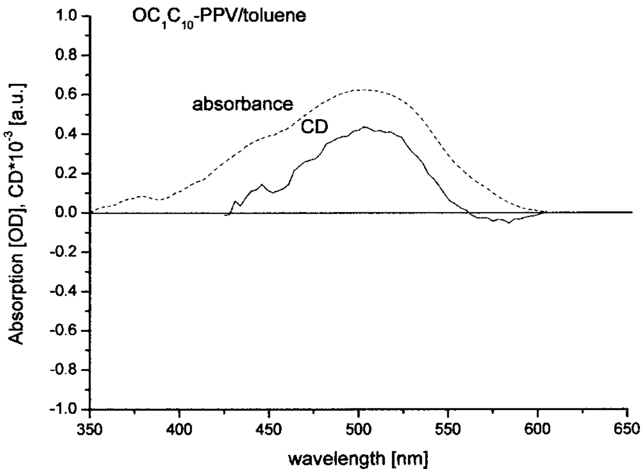

FIG. 7. Circular dichorism (solid line) and absorption (dot) for OC$_1$C$_{10}$-PPV in an isotropic solvent.

Furthermore, in a study on oriented LEPs (MEH-PPV) in a nanoscale architecture it was observed that the electronic energy transfer is more efficient between individual polymer chains then along the chain.[51] As the rate of energy transfer is directly related to the coupling strength[52] the conclusion of that study is that interchain interactions are stronger than the intrachain interactions. This could in turn explain the absence of the bisignate Cotton effect (indicative of a dipole-dipole interaction) in the CD spectra of the LEPs in the isotropic solvent (Figs. 6 and 7). Hence, we argue that the helical conformation of the polymer is the dominating factor in the shape of the CD spectra obtained for the LEPs in the isotropic solvent (Figs. 6 and 7). In the same context these data also suggest that electronic energy transfer between chain segments in solution is not as efficient as in the solid state, in agreement with what was observed in Ref. 51.

The CD spectra of the films are dramatically different in comparison to the solutions as can be seen in Figs. 8 and 9. The change in shape of the CD must accordingly be attributed to the formation of an interchain aggregate in accordance with what was observed by Langeveld-Voss *et al.*[31] and Oda *et al.*[32] In this scenario we assume that the $2B_u$ state has been split into the two states given by the linear combination with energy eigenvalues $E_{\pm}=E_{2B_u}\pm V_{ab}/2$. As for the symmetry of the system, we note that the PPV systems can in principle be described by C_{2h} symmetry,[36,53] although this assumes an ideal conformation of the polymer chain. The reality is, however, different; experimental data suggest that structural disorder breaks up the symmetry.[53] For the dimer, at the point of closest contact, the situation may be different. The local symmetry at this point could clearly be described by a C_{2h} symmetry and in that case the transitions ($1A_g \rightarrow 2B_{u^+}, 2B_{u^-}$) would be allowed by symmetry. The observed CD spectra of Figs. 8 and 9 suggest that this is indeed the case.

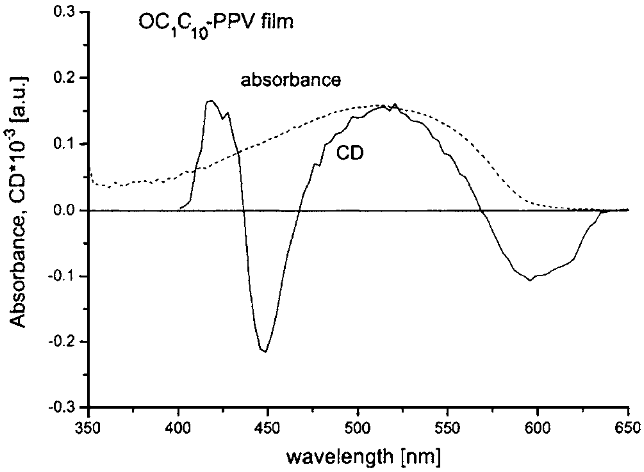

FIG. 9. Circular dichorism (solid line) and absorption (dot) of the OC_1C_{10}-PPV spin coated film.

While it would be reasonable to assume that a physical dimer is formed between two adjacent polymer chains, at the point of the closest contact providing a maximal strength in the dipole-dipole interaction, the CD spectra of the two LEP systems show a complexity beyond what would be expected of the molecular hetero/homodimer. In such a case one would expect that the linear absorption spectrum would convert into a bisignate Cotton effect of the CD spectrum. It is therefore not unlikely that the obtained CD spectra, in fact, are due to aggregates of different coupling strengths. Particularly, OC_1C_{10}-PPV shows a complexity in its CD spectrum that suggests that this might be the case.

We note that in following the CD spectra from long wavelengths towards shorter ones, the progression of the Cotton effect is different as compared to what has been observed for polythiophene polymers and polyfluorene.[32–34] However, for the polyfluorene system it was concluded that intrachain interactions as well as interchain interactions contribute to the CD signal which in turn complicates the interpretation of the data.[32] As the CD signal is sensitive to the dipole-dipole interaction, it will also be affected by the relative (mutual) orientation of the interaction dipoles. This would, in principle, imply that the relative orientations of the interaction species are different in this case. This impact will appear in the spectra through the progression of the Cotton effect.[26,27] If the rotational strength, in going from long wavelength regions towards shorter ones, has a progression $R<0\rightarrow R>0$ it would mean that the interacting dipoles have a mutual orientation angle less than 90° (with the precondition that the dipoles are coplanar).[26,27] We note that both polymers follow this progression for the red part of the absorption spectrum or wavelengths in the region of 650–500 nm (as seen in Figs. 8 and 9). This accordingly suggests that the dipole moments are oriented in a coplanar close to parallel fashion. With respect to the dipole-dipole interaction [Eq. (3)] such a configuration is not the optimal one. The most favorable case is a head-to-tail configuration, but this is an unlikely arrangement for an interchain aggregate. In passing we note that a perpendicular (mutual) arrangement would result in $V=0$ and a vanishing CD signal, but this is clearly not the case for the LEPs studied here.

CONCLUSIONS

We conclude that the suggested arrangement of the dipoles in a near coplanar parallel configuration, based upon the CD spectra, fits well with the LD data. These experiments clearly suggest that the preferential orientation of the dipole moments is along the polymer backbone. The overall picture is that for the two LEPs in anisotropic solvents, the absorption dipoles are better aligned as compared to the emitting dipoles. The data suggest that luminescence originates from a localized distinct state on the longest segments. For MEH-PPV/PE films this state is oriented closer to parallel to the alignment direction than is the case for OC_1C_{10}-PPV (in both PE films and anisotropic solvents). Finally, in comparing these LEPs it appears as if there is no major difference in the strength of the intermolecular interactions although they are more complex in OC_1C_{10}-PPV. For these two LEPs it appears that the only significant impact the side chains have on the system is the overall alignment, with OC_1C_{10}-PPV having a larger deviation relative to the polymer backbone as compared to MEH-PPV, when dispersed in the anisotropic solvent. However, this detrimental effect is to some extent overcome in the stretched films. It has been suggested using ellipsometry that the polymer backbone of MEH-PPV is relatively stiff.[54] This is clearly a contributing factor for the degree of alignment possible for the LEPs (unfortunately there are no data for OC_1C_{10}-PPV, which therefore prevents a comparison).

The results obtained in this present work provide a better understanding of the nature of the interactions in LEP systems. For the PPV systems, in particular, this topic has been debated extensively. Based on studies of the PL, it has been suggested that the aggregate formed when going from liquid to the solid state is an excited state species only, i.e., an excimer.[16] The main argument in favor of excimer formation is the strong redshift of the PL of films as compared to solutions.[13,22] However, alternative interpretations of the photophysics of PPV systems suggested instead that there are indeed ground state interactions.[55] Nguyen *et al.* concluded that for MEH-PPV films, a red edge in the absorption spectrum is related to an interchain aggregate.[7,8] Furthermore, the observations of large nonlinear responses would suggest relatively strong interactions and this is inconsistent with a scenario of excimer formations.[36–38] The data in this present study clearly show that there are very strong interactions in the ground state of films. The transformation of the CD spectra in going from solutions to films can only be explained by this fact. It is also apparent that linear spectroscopies are insufficient in this context, mainly due to the broad absorption of the PPV based systems. With the transformation of the CD signal in both the LEP systems of this study, in going from liquid to solid state, we have accordingly obtained a very strong argument against a scenario in which excimers are the main source of the PL in these two LEPs. In view of the results of this study and previous work, it is therefore clear that physical dimers are the prevailing type of interaction in these systems, in agreement with observations made on other LEP systems.[31–34] This work also shows that CD spectroscopy is a powerful approach in addressing questions of this character.

ACKNOWLEDGMENTS

Financial support from CENAMPS, One North East (ONE) and SONY Deutschland, MSL, Stuttgart, Germany, is gratefully acknowledged. We also acknowledge Jonathan Christer for performing some of the preliminary experiments of this study.

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[2] D. Braun and A. J. Heeger, Appl. Phys. Lett. **58**, 1982 (1991).
[3] E. M. Conwell, in *Primary Photo Excitations in Conjugated Polymers*, edited by N. Serdar Sacrifti (World Scientific, Singapore, 1997).
[4] T. Pauck, R. Hennig, M. Perner, U. Lemmer, U. Siegner, R. F. Mahrt, U. Scherf, K. Müllen, H. Bässler, and E. O. Göbel, Chem. Phys. Lett. **244**, 171 (1995).
[5] M. Redecker, D. D. C. Bradley, K. J. Baldwin, D. A. Smith, M. Inbasekaran, W. W. Wu, and E. P. Woo, J. Mater. Chem. **9**, 2151 (1999).
[6] J. Teetsov and M. A. Fox, J. Mater. Chem. **9**, 2117 (1999).
[7] T.-Q. Nguyen, I. B. Martini, J. Liu, and B. J. Schwartz, J. Phys. Chem. B **104**, 237 (2000).
[8] T.-Q. Nguyen, K. Doan, and B. J. Schwartz, J. Chem. Phys. **110**, 4068 (1999).
[9] S. A. van Syke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160 (1996).
[10] G. G. Malliaras and J. C. Scott, J. Appl. Phys. **83**, 5349 (1998).
[11] C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, J. Appl. Phys. **90**, 5048 (2001).
[12] H. L. Kwok, Rev. Adv. Mater. Sci. **5**, 62 (2003).
[13] R. Jakubiak, Z. Bao, and L. Rothberg, Synth. Met. **114**, 61 (2000).
[14] N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, Nature (London) **365**, 628 (1993).
[15] M. Yan, L. J. Rothberg, E. W. Kwock, and T. M. Miller, Phys. Rev. Lett. **75**, 1992 (1995).
[16] S. A. Jenekhe and J. A. Osaheni, Science **265**, 765 (1994).
[17] J. P. M. Hsu, M. Yan, T. M. Jedju, L. J. Rothberg, and B. R. Hsieh, Phys. Rev. B **49**, 712 (1994).
[18] J. M. Leng, S. Jeglinski, X. Wei, R. E. Brenner, Z. V. Vardeny, F. Gou, and S. Mazumudar, Phys. Rev. Lett. **72**, 156 (1994).
[19] M. B. Sinclair, D. McBranch, T. W. Hagler, and A. J. Heeger, Synth. Met. **49–50**, 593 (1992).
[20] D. D. C. Bradley, R. H. Friend, F. L. Pratt, K. S. Wong, W. Hayes, H. Lindenberger, and S. Roth, in *Electronic Properties of Conjugated Polymers*, Springer Series in Solid State Sciences Vol. 76, edited by H. Kuzmany, M. Mehring, and S. Roth (Springer, New York, 1987), p. 113.
[21] E. M. Conwell, J. Pearlstein, and S. Shaik, Phys. Rev. B **54**, R2308 (1996).
[22] I. D. W. Samuel, G. Rumbles, and C. J. Collison, Phys. Rev. B **52**, R11573 (1995).
[23] A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
[24] L.-O. Pålsson, C. Wang, D. L. Russel, A. P. Monkman, M. R. Bryce, G. Rumbles, and I. D. W. Samuel, Chem. Phys. **279**, 229 (2002).
[25] D. D. C. Bradley, M. Grell, X. Long, H. Mellor, A. Grice, M. Inbasekaran, and E. P. Woo, Proc. SPIE **3145**, 254 (1997).
[26] A. Rodger and B. Norde'n, *Circular Dichroism & Linear Dichroism* (Oxford University Press, Oxford, UK, 1997).
[27] E. Charney, *The Molecular Basis of Optical Activity: Optical Rotatory Dispersion and Circular Dichroism: Principles and Applications* (Wiley, Chichester, USA, 1979).
[28] J. M. Kramer, J. D. Pennoyer, R. Van Grondelle, W. H. J. Westerhius, R. A. Niederman, and J. Amesz, Biochim. Biophys. Acta **767**, 335 (1984).
[29] V. Liuola, L. Valkunas, and R. Van Grondelle, J. Phys. Chem. B **101**, 7343 (1997).
[30] V. I. Novoderezhkin and A. P. Razjivin, Photochem. Photobiol. **62**, 1035 (1995).
[31] B. M. W. Langeveld-Voss, R. A. J. Jansen, and E. W. Meijer, J. Mol. Struct. **521**, 285 (2000).
[32] M. Oda, H.-G. Nothofer, U. Scherf, V. Ŝunjić, D. Richter, W. Regenstein, and D. Neher, Macromolecules **35**, 6792 (2002).
[33] K. P. R. Nilsson, J. Rydberg, L. Baltzer, and O. Inganäs, Proc. Natl. Acad. Sci. U.S.A. **100**, 10170 (2002).
[34] K. P. R. Nilsson, M. R. Andersson, and O. Inganäs, J. Phys.: Condens. Matter **14**, 10011 (2002).
[35] T. Hagler, K. Pakbaz, K. Vossm, and A. Heeger, Phys. Rev. B **44**(16), 8652 (1991).
[36] S. J. Martin, D. D. C. Bradley, P. A. Lane, H. Mellor, and P. L. Burn, Phys. Rev. B **59**, 15133 (1999).
[37] M. Leiss, S. Jeglinski, Z. V. Vardeney, M. Ozaki, K. Yoshino, Y. Ding, and T. Benton, Phys. Rev. B **56**, 15712 (1997).
[38] U. Raicher, H. Bässler, D. D. C. Bradley, and M. Hennecke, Phys. Rev. B **42**, 9830 (1990).
[39] S. Heun, R. F. Mahrt, A. Greiner, U. Lemmer, H. Bässler, D. A. Halliday, D. D. C. Bradley, P. L. Burns, and A. B. Holmes, J. Phys.: Condens. Matter **5**, 247 (1993).
[40] H. Bässler and B. Schweitzer, Acc. Chem. Res. **32**, 173 (1999).
[41] S. S. Sartori, S. De Feyter, J. Hofkens, M. Van der Auweraer, F. De Schryver, K. Brunner, and J. W. Hofstraat, Macromolecules **36**, 500 (2003).
[42] Y.-L. Fan and K.-F. Lin, J. Polym. Sci., Part A: Polym. Chem. **43**, 2520 (2005).
[43] H. van Amerongen, H. Vasmel, and R. Van Grondelle, Biophys. J. **54**, 65 (1988).
[44] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, UK, 1993); C. Booth and P. Raynes, Phys. World **10**, 33 (1997).
[45] J. Michl and E. W. Thulstrup, *Spectroscopy with Polarized Light. Solute Alignment by Photoselection in Liquid Crystals, Polymers, and Membranes* (VCH, Deerfield Beach, FL, 1995); J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum, New York, 1999).
[46] M. Hennecke, T. Damerau, and K. Müllen, Macromolecules **26**, 3411 (1993).
[47] J. A. I. Oksanen, V. M. Helenius, P. H. Hynninen, H. Van Amerongen, J. E. I. Korppi-Tommola, and R. Van Grondelle, Photochem. Photobiol. **64**, 356 (1996).
[48] T. Sato, K. Terao, A. Teramoto, and M. Fujiki, Polymer **44**, 5477 (2003).
[49] M. Knaapila, R. Stepanyan, M. Torkkeli *et al.*, Phys. Rev. E **71**, 041802 (2005).
[50] J. P. Foreman and A. P. Monkman, J. Phys. Chem. A **107**, 7604 (2003).
[51] T. Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz, and S. H. Tolbert, Science **288**, 652 (2000).
[52] T. Förster, Ann. Phys. **2**, 55 (1948).
[53] S. Wachsmann-Hogiu, L. A. Peteanu, L. A. Liu, D. J. Yaron, and J. Wildeman, J. Phys. Chem. B **107**, 5133 (2003).
[54] M. Tammer and A. P. Monkman, Adv. Mater. (Weinheim, Ger.) **14**, 210 (2002).
[55] R. Chang, J. H. Hsu, W. S. Fann *et al.*, Chem. Phys. Lett. **317**, 142 (2000).