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Communications


Chiroptical Properties of Poly[2,5-bis[(S)-2-methylbutoxy]-1,4-phenylene vinylene]**

By Emiel Peeters, Ann Delmotte, René A. J. Janssen, and E. W. Meijer*

The use of poly(p-phenylene vinylene), PPV, and its derivatives as the active layer in light emitting diodes (LEDs)** has generated considerable interest in the element photoexcitations of these systems and their decay behavior.[11-14] In several recent reports, it has been demonstrated that optical properties in absorption and luminescence of π-conjugated oligomers and polymers are considerably modified when isolated or molecularly-dissolved polymer chains aggregate in mesoscopic assemblies and polymer films.[15] These changes result from interactions between the π-conjugated chains as they appear in the solid phase. For physical dimers and molecular crystals of organic molecules, it is well established that this interaction leads to a splitting of the excitation level into two states (Davydov splitting).[16] For a parallel orientation of polymer chains, delocalization of the photoexcitation over several chains leads to the formation of low-energy non-radiative states.[17-18] The magnitude of the Davydov interaction is an important parameter, since a large splitting in the excited state is detrimental to luminescence quantum efficiency. Therefore, the luminescent properties of π-conjugated polymers in solid films will critically depend on the mesoscopic structure and three-dimensional packing of chains.

Various studies on chiral π-conjugated polymers substituted with enantiomerically pure pendant groups or chiral dopants demonstrate a strong optical rotation and circular dichroism (CD) of the π-π* transition.[13-19] In general, a CD spectrum is observed with positive and negative curves at the wavelength of the π-π* band. This bisignate character is consistent with the presence of two close-lying π-π* excited states with opposite rotational strengths resulting from a Davydov coupling of the transition dipole moments of two polymer chains which are differently directed in space.[19] Therefore, chiroptical studies of chiral semiconducting polymers may give important information with respect to interchain interactions.[15]

Despite extensive (electro)optical studies on PPV and its derivatives in recent years, only few reports have addressed PPVs substituted with enantiomericallypure-chiral pendant groups.[12,13] Here, we present the (chiro)optical properties of optically active poly[2,5-bis[(S)-2-methylbutoxy]-1,4-phenylene vinylene] (MBM-PPV) and demonstrate that a bisignate CD spectrum is associated with aggregated chains. We show that distinct emission spectra can be obtained for molecularly dissolved and aggregated polymer chains. The latter show a significant red-shift and more pronounced vibronic coupling, while being less intense. The chiroptical and luminescent properties of BMB-PPV are discussed in terms of a coupled oscillator mechanism.

The choice to study BMB-PPV was motivated by the expectation that by introducing two identical chiral side-chains, aggregation of polymer chains is more likely because a regioregular and stereoregular polymer is obtained which may exhibit enhanced three-dimensional ordering in the solid state. The synthesis of optically active BMB-PPV is outlined in Figure 1 and described in the Experimental section. The polymer is fully characterized using FT-IR and 1H-NMR spectroscopy.[21] Well-resolved 1H-NMR spectra are recorded in chloroform-d and hot o-dichlorobenzene-d4 (ODCB-d4), while broad resonances are observed when the spectra are recorded in ODCB-d4 at ambient temperature, indicative for association of polymer chains (see below). The GPC analysis of BMB-PPV turned out to be unreliable due to association.[22]

Linear absorption and CD spectroscopy of BMB-PPV in chloroform and o-dichlorobenzene (ODCB) at 20°C (Fig. 2) reveal that two different forms of BMB-PPV can be present in solution.[23] In diluted chloroform solution (15 mg/L), where λ max = 496 nm, the polymer chains are conformationally disordered. No optical activity for the
Fig. 1. Synthetic route leading to optically active BMB-PPV.

\[ \text{\( \pi-\pi^* \) transition is observed using CD spectroscopy in this case. For dilute solutions of BMB-PPV in ODCB at room temperature, the absorption is red-shifted to } \lambda_{\text{max}} = 514 \text{ nm as a result of chain aggregation.}\]

For this aggregated phase, a strong bisignate Cotton effect is found in the CD spectrum at the position of the \( \pi-\pi^* \) band. The degree of circular polarization in absorption, defined as \[ g_{\text{abs}} = \frac{G_{\text{L}} - G_{\text{R}}}{G_{\text{L}}} \], is high for a \( \pi-\pi^* \) transition. Typically \[ g_{\text{abs}} = -1.2 \times 10^{-3} \] is found for BMB-PPV in ODCB at 20°C, although the actual value depends on sample preparation and history.

The UV/vis and CD spectra of BMB-PPV solutions in ODCB recorded at several temperatures show that a transition from the aggregated phase to conformationally-disordered polymer chains can be accomplished by increasing the temperature (Fig. 3). During this transition, a blue-shift and narrowing of the absorption band occurs. The presence of an isosbestic point at 510 nm provides evidence that two different phases exist in solution. Simultaneously with the changes in the linear absorption, the increasing temperature induces a strong decrease of the CD intensity, which is completely lost at 110°C. The thermochromism of BMB-PPV is not accompanied by the appearance of a series of well-resolved vibronic transitions on the \( \pi-\pi^* \) band, as found for highly-ordered polythiophenes and polydiacetylenes under similar conditions.\[132, 252\] Considering the fact that vibrational bands have been observed for highly-ordered PPV and gel-drawn blends of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) in UHMW-PE,\[127\] we conclude that the present BMB-PPV aggregates are partly ordered.

Fig. 2. a) UV/vis and b) CD spectra of BMB-PPV in ODCB (solid line) and chloroform (dashed line) at 20°C.

Fig. 3. a) Variable temperature UV/vis and b) CD spectra of BMB-PPV in ODCB.
The thermochromic behavior, as found in linear absorption and CD spectroscopy, is accompanied by dramatic changes in the fluorescence spectra (Fig. 4). These changes give further proof for the existence of two different forms of BMB-PPV in solution. Photoexcitation at $\lambda_{ex} = 550$ nm of aggregated BMB-PPV chains in ODCB solution (O.D. $< 0.1$ at $\lambda_{max}$) at 29°C gives an emission maximum at $\lambda_{em} = 597$ nm, with a vibronic shoulder at about 645 nm. Photoexcitation of the same solution at slightly higher energy ($\lambda_{ex} = 475$ nm), however, produces a different fluorescence spectrum with a clear shoulder at 560 nm, attributed to the emission of free chains. Apparently, selective photoexcitation of aggregated chains of BMB-PPV in ODCB can be accomplished by increasing the excitation wavelength beyond the onset of the $\pi-\pi^*$ transition of the molecularly dissolved polymer chains. Increasing the temperature, while exciting at 550 nm, results in a gradual loss of the emission at 597 and 645 nm, consistent with the increasing interchain separation. Concurrent with the loss of the emission of aggregated chains, the intensity of the emission spectra recorded with photoexcitation at $\lambda_{ex} = 475$ nm increases and a prominent emission at 554 nm coming from free chains in solution is observed. At the highest temperatures, this emission dominates the spectrum and the total intensity has increased by a factor of about 3 as compared with the spectrum at room temperature.

Further evidence of the thermal transition from aggregated to free polymer chains in solution comes from the fluorescence excitation spectra (Fig. 4). The variation with temperature of the fluorescence excitation spectrum recorded at an emission wavelength of 645 nm is similar to thermochromic behavior of the linear absorption (Fig. 3), and reveals an isosbestic point at 523 nm. In contrast, excitation spectra recorded while monitoring the emission at 560 nm exhibit an increasing intensity with temperature, but show almost no change in shape. This indicates that the emission at 560 nm is predominantly from the well-dissolved conformationally disordered polymer chains.

Thin films of BMB-PPV, spin-coated from chloroform solution, exhibit similar chiroptical properties as observed for the aggregated phase in solution. The linear absorption of the films peaks at $\lambda_{max} = 502$ nm and a strong bisignate CD effect is observed in the CD spectrum ($\Delta_{\alpha\lambda} = -6 \times 10^3$). With photoexcitation at 450 or 470 nm, the emission maximum is found at 603 nm with a shoulder at about 645 nm.

The weaker emission from aggregated BMB-PPV chains as compared to molecularly-dissolved polymer chains, is the result of a more efficient radiationless decay. Recent reports show that for several $\pi$-conjugated polymers, the luminescence lifetime is of the same order of magnitude for the aggregated phase (or film) and the molecularly dissolved polymer, while the quantum efficiency in the aggregated phase is significantly lower. Hence, the natural radiative lifetime in the aggregated phase is much longer, indicating that emission is from a different species than that of a molecularly-dissolved polymer. This species has been assigned to an interchain dimer, for which exciton coupling results in the formation of a non-emissive low-energy state. The present chirooptical results on BMB-PPV are in full agreement with this result and the CD spectrum gives direct spectral evidence for the presence of two photoexcited states in BMB-PPV, with an opposite sign for their rotational strength as expected for the two exciton levels created via a Davydov interaction.

In conclusion, we have demonstrated that two different forms of poly[2,5-bis[(S)-2-methylbutoxy]-1,4-phenylene vinylene] can be present in solution depending on the solvent. CD spectroscopy proved to be very powerful in detecting the association of the polymer, because in this form the chiral chains induce a large optical activity in the $\pi-\pi^*$ transition of the conjugated backbone. In addition, we have shown that aggregation of BMB-PPV chains results in a distinctively different fluorescence spectrum as compared to molecularly dissolved chains. In our view, control over interchain interactions in solid films is an important aspect in the optimization of photoluminescent and electroluminescent properties of conjugated polymers.

Fig. 4. Emission and excitation spectra of BMB-PPV in ODCB at different temperatures; a) emission spectrum recorded with photoexcitation at $\lambda_{ex} = 550$ nm, excitation spectrum recorded for emission at $\lambda_{em} = 645$ nm; b) emission spectrum recorded with photoexcitation at $\lambda_{ex} = 475$ nm; excitation spectrum recorded for emission at $\lambda_{em} = 550$ nm.

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A Williamson ether reaction of hydroquinone with (S)-2-methylbutoxybenzene, 1, in 74% yield after column chromatography. Subsequent chloromethylation of 1 with HCl and 36% formaldehyde in 1,4-dioxane yields pure 1,4-bis(chloromethyl)-2,5-bis[(S)-2-methylbutoxy]benzene, 2. Polymerization of 2 is carried out with K' BuO in dry refluxing 1,4-dioxane for 2h. The polymerization is stopped by addition of acetic acid and BMB-PPV is isolated by filtration of the reaction mixture, washing, and drying.

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Simulation of Layered Double Hydroxide Intercalates**

By A. Michael Aicken, Iain S. Bell, Peter V. Convery,* and William Jones

Layered double hydroxides (LDHs) offer potential applications in a diverse range of areas including catalysis, medicine, molecular sieving, electrochemistry and oil-field exploration. A great deal of experimental work has been performed to achieve the synthesis and characterization of LDHs containing an extensive range of incorporated organic and inorganic guests.1 In the area of clay minerals, it is recognized that computational techniques are now to support as well as extend experimental observations.1,2,3 However, for other two-dimensional materials, such as LDHs, comparatively little work has been reported to date. Here we demonstrate that computer simulations yield values for the gallery heights in LDHs which agree well with those observed experimentally. The presence of intercalated water is shown to serve as a principal factor in controlling interlayer repeat distances. The modelling approach which we employ in this paper is more sophisticated than previous, unsuccessful, attempts at LDH simulations.4

To understand the structure of hydroxide-like compounds (HTCs), it is first necessary to consider the structure of brucite, Mg(OH)2, where octahedra of Mg²⁺ (6-fold coordinated to OH⁻) share edges to form infinite sheets. The sheets stack on top of each other forming a layered solid. Mg²⁺ ions can then be substituted by a trivalent cation of similar radius (Al³⁺ in the case of hydrotalcite itself), resulting in an overall positive charge on the metal-hydroxyl sheet. This charge is compensated for by anions (CO₃²⁻ in hydrotalcite) occupying positions in the interlayers between the sheets, with water of crystallization also being present.

[24] 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.

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[21] FTIR: characteristic peaks of trans-vinylene: 3059 cm⁻¹ (CH stretch) and 967 cm⁻¹ (out-of-plane C=H). 1H-NMR (CDCl₃): δ 7.35 (2H, PhH), 7.30 (2H, CH₃–CH=), 5.54 (2H, OCH₃), 3.87 (2H, OCH₃), 2.05–1.91 (2H, 2H–CH₂–CH₃), 1.68 (2H, 2H–CH₂–CH₃), 1.38 (3H, 2H–CH₃–CH=), 1.13 (6H, CH₃), 1.03 (6H, 6H–CH₃–CH=). Attempted recording of 13C-NMR spectra (100.46 MHz) was not successful due to extremely low solubility of BMB-PPV in chloroform-d (0.05 mg/ml).
[22] GPC analysis of BMB-PPV in either THF or chloroform with an PLgel column (5 μm, 10^5 A, 300 x 7.5 mm) showed uninterpretable results due to aggregation on the column. The strong tendency of BMB-PPV to aggregate is a result of the relatively short sidechains in combination with a highly symmetrical and regular polymer chain. Currently, less-symmetrical chiral co-polymers consisting of differently substituted PPVs are being synthesized and characterized to overcome this problem.

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