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Polarized ultraviolet absorption of highly oriented poly(2-methoxy, 5-(2′-ethyl)-hexyloxy) paraphenylene vinylene

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Absorption spectra (2.0–6.1 eV) for poly[(2-methoxy, 5-(2′-ethyl)-hexyloxy) paraphenylene vinylene] oriented by gel processing in polyethylene show that the bands peaking at 2.5, 3.6, and 6 eV are polarized parallel to the draw direction, while the band at 4.7 eV is polarized off axis. Although the onset of absorption in oriented samples is redshifted from that in disordered, spin-cast films, indicating significantly higher conjugation lengths, the 3.6-eV band is present in both. Thus, the 3.6-eV band is an intrinsic feature of the electronic structure of the macromolecule and not a characteristic of oligomers or polymers with short conjugation lengths. [S0163-1829(99)09707-6]

I. INTRODUCTION

Recent debate on the electronic structure of luminescent, conjugated polymers such as poly paraphenylene vinylene (PPV) and its soluble derivatives has focused on the predictions of visible and ultraviolet (vis-UV) absorption spectra, which are readily compared with spectroscopic data. However, although the electronic structure of conjugated polymers is inherently anisotropic, relatively little is known from experimental studies about the polarization of the π-π^* absorption bands in these semiconducting polymers.

Although the optical properties of partially oriented conjugated polymers have been studied,[1] the anisotropy was not high enough to enable strong conclusions. Gel processing of blends of soluble conjugated polymers in ultrahigh molecular weight polyethylene (PE) produces highly oriented, chain-extended and chain-aligned conjugated macromolecules in an inert, transparent matrix.[2] Samples with draw ratios in excess of fifty demonstrated polarized absorption and emission. However, the earlier spectroscopic studies of conjugated polymers oriented in blends with PE by gel processing were restricted to the lowest energy absorption band.[3]

The success of the Su-Schrieffer-Heeger Hamiltonian[4] in describing the electronic structure of *trans*-polyacetylene implies that it is a useful starting point for modeling more complex, phenylene-based conjugated polymers. PPV and its soluble derivatives have eight conjugated atoms in the unit cell and are hence expected to have eight π-electron energy bands. As indicated in the schematic band structure[5,6] shown in Fig. 1, four of these bands are occupied in the ground state (three π bands with strong dispersion in which the states are delocalized, labeled $D1$, $D2$, and $D3$, and one localized π band, labeled L), and four are unoccupied (again, three delocalized π^* bands, labeled $D1^*$, $D2^*$, and $D3^*$, and one localized π^* band, labeled L^*).

More complete theoretical studies of the electronic structure of PPV and its soluble derivatives have followed a number of different paths. The band structure shown in Fig. 1, supplemented by the Coulomb interaction between electrons and holes (to form bound excitons), was shown to be capable of explaining the optical transitions observed in model five-ring oligomers.[5] Quantum chemical methods[7,8] and band models that treat the interaction between the electron and the hole when both are on the same phenyl ring[9,10] have also been successful in accounting for many of the observed spectral features. The quantum chemical approach provides a natural way to include and treat variations such as chemical substitution and finite chain length. However, such calculations cannot be extended to the long-chain limit needed for comparison with data obtained from high molecular weight conjugated polymers.

The different theoretical approaches lead to important differences in the predictions of the vis-UV absorption spectrum of oriented conjugated chains. The lowest energy absorption band (2.1–2.5 eV) is generally predicted to be polarized parallel to the chain direction, as is the higher energy band that peaks at approximately 6 eV. The third absorption band, peaked near 4.7 eV, is predicted to be polarized perpendicular to the chains. The fourth band, with maximum near 3.6 eV, has been ascribed to an exciton associated with the higher energy interband transition at 4.7 eV,[6] to symmetry breaking upon chemical substitution,[7,11] or to finite chain-length effects.[7,8,10,11] Thus, measurements of the polarization and conjugation length dependence of the

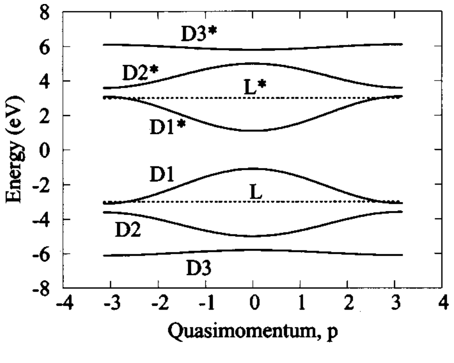

FIG. 1. Schematic one-electron band structure of PPV.

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3.6 eV peak can provide a valuable test of the various theories.

In this paper, we present absorption spectra of poly[(2-methoxy, 5-(2′-ethyl)-hexyloxy) paraphenylene vinylene] (MEH-PPV) oriented by gel processing in PE over the broad spectral range from 2.0 to 6.1 eV. The three absorption bands peaking at 2.5, 3.6, and 6.0 eV are polarized parallel to the mechanical draw axis. A fourth band at 4.7 eV is polarized off the draw axis, with perpendicular to parallel intensity ratio of approximately 2:1. We compare the polarized absorption spectra with predictions obtained from four different theoretical approaches.[6–8,10,11] The band model supplemented with Coulomb interactions[6] seems to be the only approach capable of providing a complete description of the observed spectra.

II. EXPERIMENTAL DETAILS

Oriented MEH-PPV/PE blends were prepared as previously reported[2] by tensile drawing of dried gel films at a temperature of 100 °C. Photoluminescence (PL) from the drawn films was in all cases polarized parallel to the chains with a polarization anisotropy of greater than 12:1. The data presented here were obtained from a film of 5% MEH-PPV in PE, drawn to a ratio of 100 and exhibiting polarized photoluminescence with intensity ratio of 15:1 (parallel to perpendicular). Spin-cast films were cast from xylene solution under nitrogen atmosphere onto UV-grade silica substrates and subsequently dried under vacuum for 36 h to remove residual solvent.

The oriented samples were mounted between plates of UV-grade silica, which shows no absorption in the relevant spectral range. Surface scattering was reduced by index matching the samples with *n* octadecane (Aldrich), which also shows no UV absorption below 6.5 eV. The octadecane is an ideal index-matching fluid for PE, since it is simply an oligomer with the same repeat unit as in polyethylene. Encapsulated samples were mounted on a rotating stage at the focus of the optics described below. Parallel orientation was defined as the orientation, which maximized the absorption in the lowest energy peak. In all cases, the optical axis coincided with the mechanical draw axis.

Light from a deuterium lamp was collimated and then polarized by Brewster angle reflection from UV-grade silica. The light, polarized vertically with respect to the optical table, was then sent through a McPherson monochromator equipped with a UV-blazed diffraction grating, mechanically chopped and focused onto the sample. Light was then collected and focused onto a McPherson photomultiplier tube and measured with a lock-in amplifier.

Several details of this setup are critical to the proper measurement of deep-UV-polarized absorption. First, since dichroic or beamsplitting polarizers are not commercially available for the deep UV, the light was polarized by Brewster-angle reflection from silica, which is only modestly dispersive below 6.5 eV. Using a dichroic sheet polarizer in the visible region of the spectrum, we determined the polarization ratio to be approximately 250:1, implying that the ratio in the deep UV is greater than 200:1. Second, diffraction gratings are notorious for polarizing the light that they transmit. Moreover, the polarization ratio is often not monotonic function of wavelength. For this reason, it is important to polarize and disperse the light before focusing it onto the sample because the sample itself is an optical element, which changes the polarization state of the transmitted light due to its birefringence and dichroism. Third, only reflective optics were used to avoid dispersion problems inherent in refractive optics; UV-coated aluminum mirrors were used in all measurements. Finally, surface scattering was greatly reduced by index matching with a UV-transparent fluid (*n*-octadecane; see above). Bulk scattering, however, is intrinsic to materials with mesoscale structure. From measurements on films of pure polyethylene, we estimate that the contribution to the optical density (the apparent absorbance) is approximately 0.1 at 2 eV, increasing monotonically to approximately 0.3 at 6 eV. Including MEH-PPV in the PE matrix might be expected to enhance the scattering over this spectral range since scattering is due to inhomogeneities in the optical properties of the material. However, since the MEH-PPV concentration was small (5%), the semiquantitative estimate of the scattering contribution given above is useful.

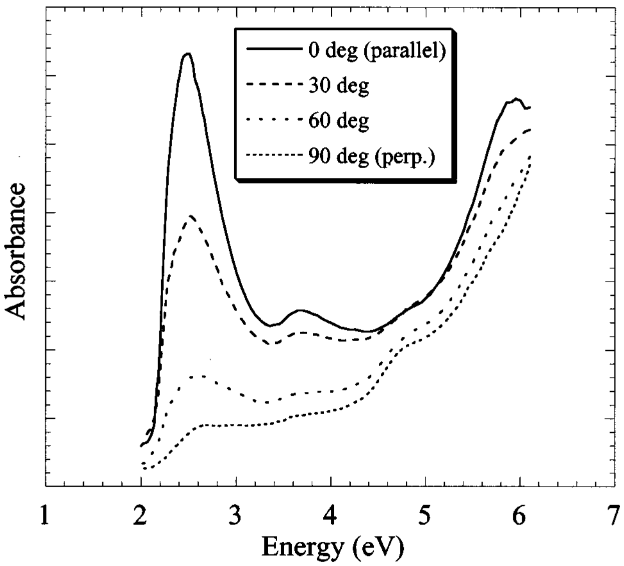

FIG. 2. Polarized absorption spectra for the oriented MEH-PPV/PE blend with four different angles between the electric-field vector of the light and the draw axis of the film. The four observable features peak at 2.5, 3.6, 4.7, and 6.0 eV.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra (room temperature) of the oriented MEH-PPV chains for four different angles between the electric-field vector of the polarized light and the draw axis. The draw axis was found to be a principal axis for all four absorption features, with absorption either at a maximum or a minimum for light polarized parallel to the stretch direction, consistent with the assumption that the films are uniaxially anisotropic.

Figure 3 shows the absorption spectra (room temperature) of the oriented MEH-PPV chains for light polarized parallel and perpendicular to the draw axis. The polarized spectra are directly compared with the absorption spectrum of a spin-cast film. The spectra all have the characteristically sharp onset of absorption near 2.1 eV. However, the onset of ab-

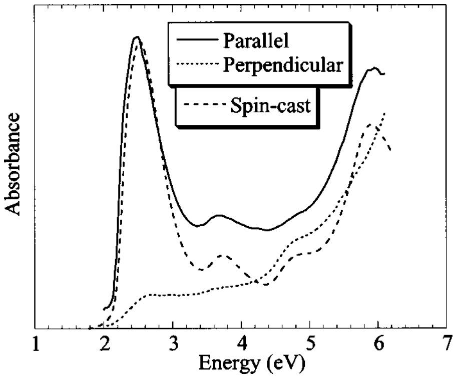

FIG. 3. Polarized absorption spectra for the oriented MEH-PPV/PE blend for light polarized parallel to and perpendicular to the draw axis. Shown also is the absorption spectrum of a disordered, spin-cast film of MEH-PPV.

sorption and the peak absorption in the oriented film are at slightly lower energies than the spin-cast film, indicating significant chain extension compared to the disordered film. The improved order in the highly oriented films was studied in detail by Hagler, Pakbaz, and Heeger.[3]

The data presented in Figs. 2 and 3 were obtained from a film with a peak optical density of about 0.8. The relatively low-optical density enables extension of the spectra deeper into the ultraviolet where much smaller light signals (primarily due to source brightness and mirror reflectance) prohibit accurate measurements of highly absorbing films.

Other, more concentrated blends have shown higher dichroic ratios and higher polarization ratios for the luminescence, indicating that subtleties in the processing can affect macroscopic anisotropy, and that the intrinsic anisotropy of the polymer chains is much higher. This is consistent with previous reports on optical measurements of oriented polymer films including PPV (Refs. 12–14) and MEH-PPV.[3]

The residual absorption in the oriented film for polarization perpendicular to the draw direction is not an artifact; the ‘‘perpendicular absorption’’ onsets at the same energy as the parallel feature but peaks approximately 0.2 eV higher in energy. The weak photoluminescence polarized perpendicular to the draw axis suggests that a small fraction of shorter chain segments are incompletely aligned; these same segments could be responsible for the blueshifted perpendicular absorption signal. However, since the blends are expected to be phase segregated, we cannot rule out an interchain absorption mechanism. The perpendicular ‘‘absorption’’ does not result from scattering; the dielectric mismatch between MEH-PPV and PE is higher at photon energies below the 2.5-eV transition, whereas the perpendicular optical density increases on going through the 2.5-eV transition.

The second absorption peak in the oriented MEH-PPV film at 3.6 eV is polarized parallel to the draw direction and is pronounced in both the spin-cast film and in the oriented film. Note that in the oriented film, the peak is again slightly redshifted from the peak in the spin-cast film, indicating significant participation by delocalized electronic states (D or D^*, see Fig. 1) in this transition.

The quantum chemical calculations of Cornil *et al.*[7] on oligomers of unsubstituted and alkoxy-substituted PPV indicated that in the unsubstituted case, this peak grew weaker with increasing chain length and was a superposition of two transitions, both of which involve purely delocalized states (D-D^*). For the substituted oligomers, the peak did not weaken with increasing chain length, and it was a superposition of four D-L^*/L-D^* transitions. The analytical model of Gartstein, Rice, and Conwell[11,15] predicts that for oligomers with finite chain lengths, the peak at 3.6 eV will have parallel polarization and the unrelated peak in the same spectral region that results from broken charge-conjugation symmetry will have perpendicular polarization.

Recent photoconductivity results on MEH-PPV (Ref. 8) were interpreted using the predictions of the quantum chemical calculations carried out for unsubstituted oligomers, with the conclusion that the 3.6-eV feature is D-D^* and should be polarized primarily parallel to the chain axis. Mixed interband transitions (D-L^* and L-D^*), on the other hand, are generally predicted by these calculations to have large off-axis transition dipole moments and to give rise to strong photoconductive response.

We conclude, therefore, that this second peak in the polarized MEH-PPV absorption spectrum is not an interband D-L^*/L-D^* transition caused by substitution effects, since that would imply an absorption feature perpendicular to the draw axis, which is not observed in the oriented polymer. In addition, we conclude that the 3.6-eV feature does not result from finite conjugation length, since it is present both in the spectrum obtained from the disordered spin-cast film and in the spectrum obtained from chain-extended MEH-PPV macromolecules in the oriented films. Thus, the 3.6-eV peak results from a transition intrinsic to the electronic structure of the long-chain polymer and is unrelated to symmetry-breaking chemical substitution on the phenyl ring.

Of the theoretical descriptions considered here, only the model discussed by Brazovskii *et al.*[5] includes such a transition. In this model, the 3.6-eV feature is an exciton associated with the interband D-L^*/L-D^* transition. This exciton can be thought of as a localized electron (hole) bound to a delocalized hole (electron) with a binding energy on the order of 1 eV and a spatial extent on the order of 10 Å. The existence of this molecular exciton follows naturally from the consideration of the electrostatic Coulomb attraction as a perturbation to the electronic band structure. We note, however, that the initial calculations predicted that this feature would be polarized perpendicular to the chain axis, contrary to our observations. However, parallel polarization could potentially be explained by recent qualitative arguments,[16] which take into account the resonance of the D-D^* continuum with the D-L^* exciton as well as the electron correlations on the phenyl ring. Configuration mixing of D-D^* transitions with the D-L^* transition for conjugated oligomers was shown numerically by Chandross *et al.*, but the result was optical coupling of a previously state to the ground state, rather than a change in the nature of an optically allowed transition.[10] Quantitative analysis of these considerations is necessary to properly predict the polarization of this excitonic feature.

Assignment of this 3.6-eV peak to a parallel-polarized exciton associated with the D-L^* transition simultaneously explains the following. (a) There are contributions from localized and delocalized states, as predicted by quantum chemistry,[7] (b) the photoconductivity feature observed in association with this transition is relatively weak,[8] and (c) this assignment accounts for the existence and parallel polarization of the absorption observed in oriented, chain-extended samples.

The third absorption feature, peaked near 4.7 eV, is polarized off the draw axis; the perpendicular to parallel intensity ratio is approximately 2:1. This is in qualitative agreement with data obtained from rubbed films of PPV derivatives,[1] and is accounted for by all of the present theories as a transition between localized and delocalized electronic levels (L-D^* and D-L^*). This absorption typically results in spatially separated electron-hole pairs, as evidenced by the large photoconductivity response typically measured in this region of the spectrum.[8] For this reason, it is sometimes termed a ''charge-transfer'' state.

Finally, at the highest energy accessible in our experiment, there is a peak at 6 eV polarized parallel to the draw axis. Although scattering adds a significant background to the spectrum (increasing as λ^{-4}), the 6-eV peak, polarized parallel to the draw axis, is clearly evident in the data. The 6-eV band is universally assigned to a transition between electron and hole states localized on the phenyl ring (L-L^*). This transition is a tightly bound Frenkel exciton in which the excitation is confined to a single ring.

Absorption features polarized perpendicular to the chains (of D-L^*/L-D^* character) at energies higher than presented here have also been predicted.[6,7] Thus, the steep rise in the perpendicular signal might result from an absorption feature at higher energy.

IV. CONCLUSION

The polarization of the four commonly observed absorption bands (2.5-, 3.6-, 4.7-, and 6.0-eV) was determined using polarized absorption spectroscopy on highly oriented MEH-PPV/PE blends. The 2.5, 3.6, and 6.0 eV peaks are polarized parallel to the chain axis; the 4.7-eV peak is polarized off axis with a 2:1 ratio (perpendicular to parallel). In addition, the behavior of each band upon chain extension was assessed by comparison with absorption in disordered, spin-cast films. The lowest energy absorption bands at 2.5 and 3.6 eV were redshifted in the ordered material (i.e., relative to the spin-cast films) consistent with chain extension in the drawn and oriented films. However, the relative intensities of the two peaks did not change, indicating that both are intrinsic to the electronic structure of the conjugated chain and not the result of finite conjugation length.

The data were compared with the predictions of all the theoretical methods/models. The model presented by Brazovskii *et al.* accounts for all the intrinsic features of the spectrum obtained for chain-extended conjugated macromolecules. Even in this case, however, the polarization of the 3.6-eV absorption band is not predicted correctly[6] without taking into account higher order effects such as the resonant interaction of the D-D^* continuum with the exciton and electron correlations on the phenyl ring.[16] The role of the latter effects in rotating the polarization from perpendicular (as predicted in the original theory)[6] to parallel must be confirmed through quantitative calculations.

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