

## Polarized ultraviolet absorption by a highly oriented dialkyl derivative of poly(paraphenylene vinylene)

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We present polarized ultraviolet absorption spectra obtained from films of poly[2-butyl-5-(2' ethyl)-hexyl paraphenylene vinylene], BuEH-PPV, in polyethylene; the films were oriented by gel processing to high draw ratios. The spectra show three strong features between 2 and 6.2 eV. The lowest-energy absorption is peaked at 2.9 eV and is strongly polarized parallel to the draw axis. At 4.8 eV, there is a sharp onset for perpendicular absorption, indicative of a transition from a localized state to a delocalized state (or vice versa). Finally, there is a predominantly parallel-polarized absorption band at 5.8 eV that we attribute to excitations localized on the phenyl ring. Since the aliphatic side chains have only weak electronic interactions with the conjugated polymer backbone, the dialkyl-substituted PPV's are excellent model systems for studying the electronic structure of PPV.

Although luminescent conjugated polymers are emerging as important materials for use in applications such as light-emitting diodes<sup>1,2</sup> and biosensors,<sup>3</sup> the details of their electronic structure have been difficult to extract from available data. When obtained from oriented samples, polarized ultraviolet absorption and/or reflection spectra can provide detailed information about the quasi-one-dimensional electronic energy bands. Oriented poly(paraphenylene vinylene), PPV, is typically too thick for transmission measurements; the spectral dependence of the optical constants has been obtained by Kramers-Kronig analysis of reflectance data.<sup>4</sup> Although processable derivatives of PPV have been studied extensively, data on highly oriented samples are available in the literature only for alkoxy-substituted derivatives.<sup>5,6</sup>

We present polarized absorption spectra over the spectral range between 2 and 6.2 eV of poly[2-butyl-5-(2' ethyl)-hexyl paraphenylene vinylene], BuEH-PPV, oriented by gel processing in polyethylene (PE). The molecular structure of BuEH-PPV is shown in Fig. 1. The data show strong anisotropy in all absorption bands, including parallel-polarized absorption bands peaking at 2.9 and 5.8 eV and a perpendicular-polarized band peaking at 4.8 eV. Dialkyl substitution on the phenyl ring of the repeat unit is expected to interact only weakly with the  $\pi$  electrons; this is in contrast to alkoxy substitution, in which the oxygen atom donates significant electron density to the  $\pi$  system, thus destabilizing both the valence and conduction bands.<sup>7</sup> As a consequence, the dialkyl PPV's are good model systems for studying the PPV electronic structure. Since the dialkyl PPV's are soluble, they can be gel processed in polyethylene into highly oriented films suitable for transmission measurements.

The BuEH-PPV polymer was obtained from the UNIAX Corporation and used as received. The synthesis of BuEH-PPV is described by Andersson *et al.*<sup>8</sup> Oriented BuEH-PPV/PE blends were prepared by tensile drawing of dried gel films at 100 °C, as previously reported for MEH-PPV.<sup>9</sup> The data presented here were obtained from an oriented film containing 30% (by weight) of BuEH-PPV. The oriented films

had a draw ratio of 50 and exhibited polarized photoluminescence with an intensity ratio of 48:1 (parallel to perpendicular).

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 decane, which also shows no UV absorption below 6.5 eV. Decane is an ideal index-matching fluid for PE, since it is an oligomer with the same repeat unit as polyethylene. Encapsulated samples were mounted on a rotating stage at the focus of the optics. Parallel orientation was defined as the orientation that maximized the absorption in the lowest-energy peak. The optical axis was observed to coincide with the mechanical draw axis to within  $\sim 2^\circ$ .

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. Quantitative analysis of the polarization is presented elsewhere;<sup>6</sup> the importance of each of the following was emphasized: (a) polarization by reflection, (b) polarization by the monochromator, (c) reflective optics, and (d) scattering of light by the sample.

In Fig. 2, we show the room-temperature absorption spectra of the oriented BuEH-PPV/PE blend for light polarized

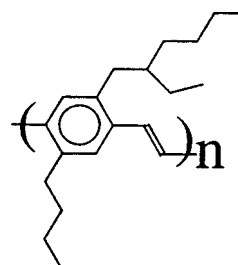


FIG. 1. Molecular structure of BuEH-PPV.

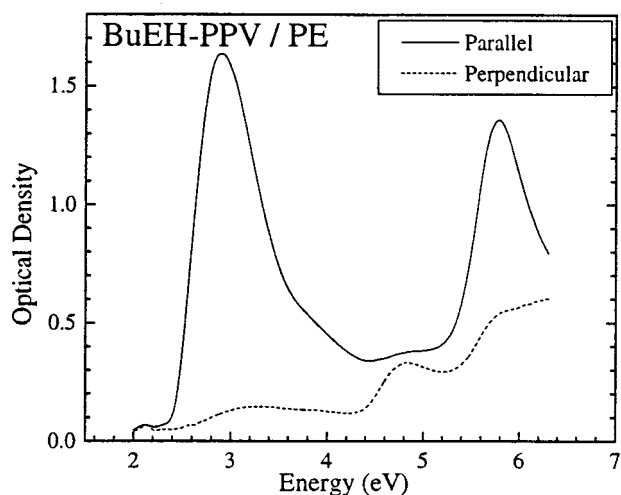


FIG. 2. Polarized absorption spectra of highly oriented BuEH-PPV/PE blend. Light is polarized parallel (solid line) or perpendicular (dashed line) to the draw axis.

parallel (solid line) and perpendicular (dashed line) to the mechanical draw axis. The lowest-energy absorption peak is at 2.9 eV and is polarized approximately 16:1 parallel to the chain. This strongly anisotropic absorption is the transition between the dispersive  $D1$  and  $D1^*$  bands, as shown in the schematic band diagram in Fig. 3, adapted from Kirova *et al.*<sup>10</sup> At 3.7 eV is a weak shoulder to the parallel absorption feature; this shoulder is commonly observed in unsubstituted PPV. It has no distinguishable component in the perpendicular spectrum. The lowest-energy perpendicular-polarized feature, at 4.8 eV, is attributed to  $L$ - $D1^*$ / $D1$ - $L^*$  transitions. The highest-energy feature observed in this study is at 5.8 eV and is strongly parallel polarized. We assign this feature to the  $L$ - $L^*$  transition, in which both the electron and the hole are localized on a single phenyl ring.

Other theoretical studies of the electronic structure of PPV and its alkoxy derivatives<sup>11-13</sup> have successfully predicted polarized absorption features similar to those observed in Fig. 2. In these calculations, the perpendicular polarization of the 4.8 eV peak is widely considered to be due to the localized-delocalized nature of the electronic states involved. The shoulder at 3.7 eV is seen in alkoxy derivatives, such as MEH-PPV, as a separate peak. It has been ascribed to symmetry breaking caused by chemical substitution, splitting of the degeneracy of the  $L$ - $D1^*$ / $D1$ - $L^*$ , or a weak exciton of the 4.8 eV transition.<sup>10</sup> The electron-hole asymmetry in BuEH-PPV should be similar to that in unsubstituted PPV, due to the inactive alkyl sidechains, whereas the asymmetry is enhanced in alkoxy derivatives. This may explain why a split degeneracy would have a weaker signature in alkyl PPV's than it does in the alkoxy PPV's.

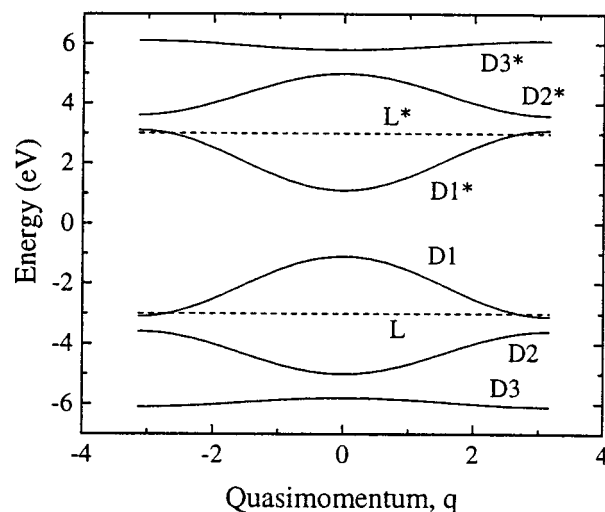


FIG. 3. Schematic band diagram for PPV.

Few studies of dialkyl PPV's have been published. Fahlman *et al.*<sup>14</sup> performed photoelectron spectroscopy and also carried out detailed calculations on PPV as well as its dialkyl and dialkoxy derivatives. They concluded that in highly ordered material, dialkyl substitution affects only the localized bands, shifting them toward the center of the gap by approximately 0.3 eV relative to PPV. Hybridization of the carbon side chain with the  $\pi$  electrons is weak compared to the dialkoxy case in which both the localized and delocalized bands are significantly destabilized.

Movement of the  $L/L^*$  bands by 0.3 eV would be evident in optical spectra as (a) a shift to lower energy of the perpendicular-polarized  $L$ - $D^*$ / $D$ - $L^*$  transition and (b) a smaller separation between the perpendicular feature and the lowest-energy parallel absorption. In our data, however, the perpendicular-polarized transition is at 4.8 eV, very similar to unsubstituted PPV. We note also that in the case of less-well-ordered material, the results of Fahlman *et al.*<sup>14</sup> imply even closer spacing of the  $D$ - $D^*$  and  $L$ - $D^*$  transitions. In this context, it appears that mechanical alignment of the BuEH-PPV/PE blend also induces planarization of the rings and increased dispersion of the delocalized  $\pi$ -electron bands.

These observations along with the recently published data obtained from oriented PPV (Ref. 4) provide a basis for refining the calculations of the band structure of PPV. The polarization of the three strong bands is a robust feature of the electronic structure that must be accounted for in any viable theory of the electronic structure.

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