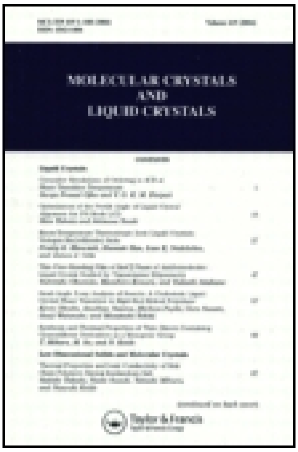

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Luminescence Excitation Spectroscopy in Poly(p-Phenylene-Vinylene) Derivatives: Implications for a Semiconductor Band VS. Exciton Model in Conjugated Polymers

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Version of record first published: 04 Oct 2006.

To cite this article: Duncan McBranch , Frederick H. Long , Thomas W. Hagler , Jeanne M. Robinson , Basil I. Swanson , Khashayar Pakbaz , Alan J. Heeger , Scott Schricker & Fred Wudl (1994): Luminescence Excitation Spectroscopy in Poly(p-Phenylene-Vinylene) Derivatives: Implications for a Semiconductor Band VS. Exciton Model in Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 499-505

To link to this article: http://dx.doi.org/10.1080/10587259408039282

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 499–505
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LUMINESCENCE EXCITATION SPECTROSCOPY IN POLY(*p*-PHENYLENE-VINYLENE) DERIVATIVES: IMPLICATIONS FOR A SEMICONDUCTOR BAND *VS.* EXCITON MODEL IN CONJUGATED POLYMERS

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Abstract High-resolution luminescence excitation spectroscopy (site-selective flourescence) results are presented for two soluble derivatives of poly(*p*-phenylene-vinylene): poly(2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV), and poly(2,5-bis(cholestanoxy)-*p*-phenylene vinylene) (BCHA-PPV). Measurements have been performed on both thin films of these polymers, and dilute blends in polyethylene oriented by tensile drawing. By examining the effects of oxygen exposure in cast films, and the energy-dependence of the luminescence anisotropy in the oriented blends, we provide evidence that the electronic states in the absorption tail arise from localized states in an amorphous semiconductor.

INTRODUCTION

Since the discovery that poly(*p*-phenylene-vinylene) (PPV) and its derivatives can serve as the active material in electroluminescent devices,[1,2] much research has been devoted to identifying the microscopic processes involved in charge injection. This attention has renewed a longstanding controversy over the nature of the electronic excited states in these and other conjugated polymers. In particular, much debate has centered on whether the strong optical absorption and the excited state dynamics should be modelled within the context of a quasi-one-dimensional π-π^*

band theory,[3,4] or of a tightly-bound molecular exciton model.[5,6] Luminescence excitation spectroscopy (site-selective fluorescence) results on PPV have been cited as providing definitive evidence for the latter model.[5,6] However, some ambiguity remains, since these results can be explained by the effects of extrinsic disorder in a band model.

In this work, we present the results of high-resolution luminescence excitation spectroscopy on two soluble derivatives of PPV: poly(2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV), and poly(2,5-bis(cholestanoxy)-*p*-phenylene vinylene) (BCHA-PPV). In addition, we have measured highly-oriented blends of these two PPV derivatives in polyethylene (PE), formed by tensile-drawing.[4] In particular, we look at the changes in position of the peaks in the photoluminescence spectra as the pump wavelength is tuned.

We find, as in previous studies,[5,6] that the position of the primary luminescence peak (zero-phonon line) is constant with changing pump energy until a threshold energy is reached, below which the position shifts linearly with pump energy. Upon exposure of pristine MEH-PPV cast films to oxygen, this threshold position moves up in energy, consistent with a disorder-induced mobility edge in a band model. In addition, the emission anisotropy in the tensile-drawn blends begins to decrease at the same threshold energy, indicating a decreased coherence length below this threshold. This result is consistent with a band model, in which the states below the mobility edge become progressively more localized; it cannot be explained within the context of the exciton hopping picture, since the lowest energy states in this model should be the longest chains with the longest coherence lengths.

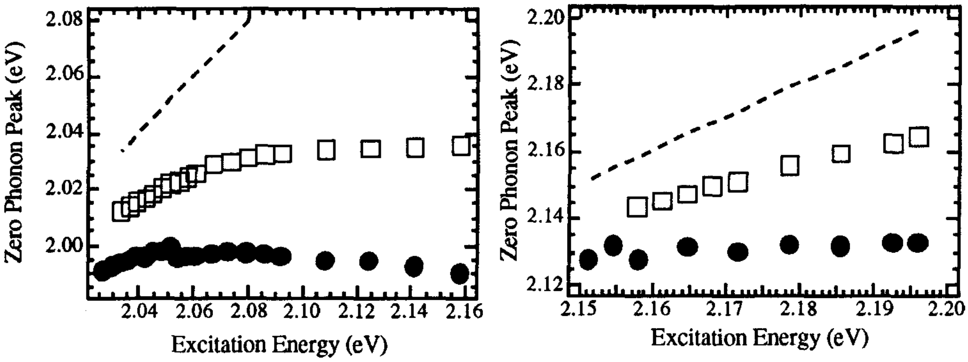
EXPERIMENTAL

Luminescence spectra were measured over a range of pump wavelengths on pristine cast films (d<500 Å) of both MEHPPV and BCHA-PPV. Highly oriented blends (1% PPV in polyethylene) were made as previously described.[4] Luminescence in the stretched blends was highly polarized along the stretch direction, with anisotropies of up to 50:1. Samples were cooled to either 77K in a liquid Nitrogen-dewar cryostat, or 12K using a closed-cycle Helium cryostat.

Excitation was performed with a CW dye laser (Coherent CR-599) using Rhodamine R6G dye. The broad flourescence backround of the dye laser was filtered before the sample. Emission was detected with a triple-grating monochrometer (Spex 1877, 0.6 m), which enabled the primary luminescence peak (zero-phonon line) to be distinguished for emission energies within 8 meV (65 cm^{-1}) of the laser. Spectra were corrected with a calibrated irradiance standard.

RESULTS

In Figure 1, the position of the zero-phonon line (ZPL) in emission is plotted for MEH-PPV and BCHA-PPV cast films before and after exposure to oxygen (T=77K). For the MEH-PPV cast films, a threshold value is observed in each case, below which the ZPL shifts linearly with decreasing pump energy. However, the position of the energy threshold shifts up upon exposure to oxygen, and the energy of the ZPL also shifts up. In the BCHA-PPV, very little shift is observed for the pristine film; however, a linear shift is seen upon oxygen exposure for all pump energies. Since the pump beam is far in the absorption tail, the threshold energy is above the range of accesable pump energies in the latter case.



(a) (b)

Figure 1: Zero phonon line peak position *vs.* excitation energy at 77K for pristine (solid circles) and oxygen exposed films (open squares): (a) MEHPPV cast film; (b) BCHAPPV cast film. Laser energy is indicated with dashed line.

A series of spectra taken for decreasing pump energies is shown for the MEH-PPV/PE blend in Figure 2 (T=12K). Upon decreasing the pump energy, similar shifts as in the cast films are observed. However, due to the enhanced microscopic order in these materials, additional features appear. First, a dramatic sharpening of the higher phonon peaks is observed. This behavior is sensible within either model: in each case, at the lowest energies only the local molecular environment is probed.

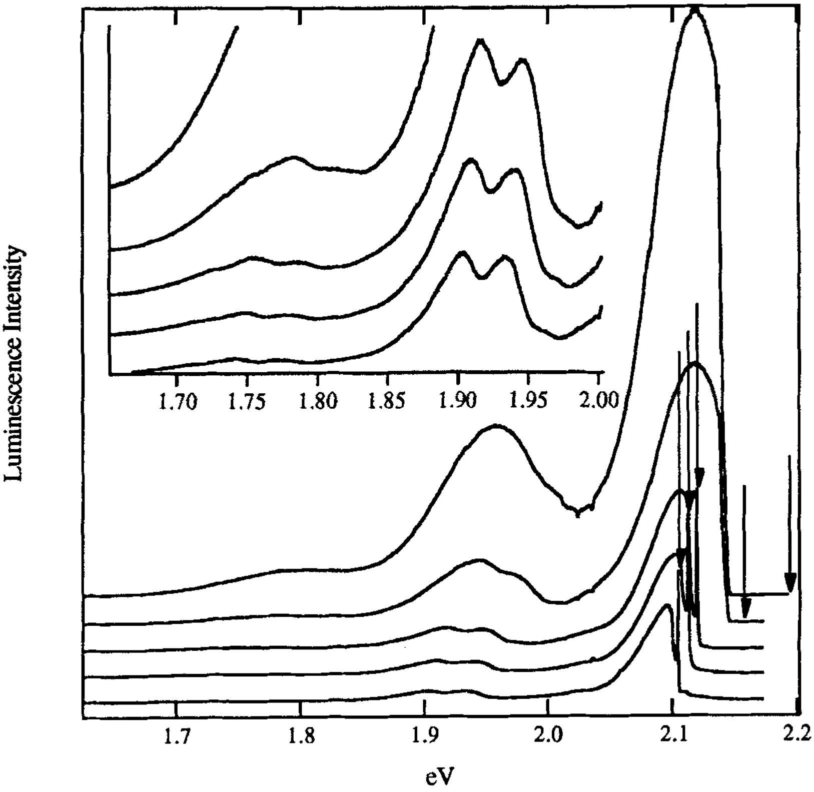


Figure 2: Luminescence spectra of MEHPPV/PE tensile-drawn blends for several laser pump energies (indicated with arrows). Inset: higher-order phonon lines on expanded scale.

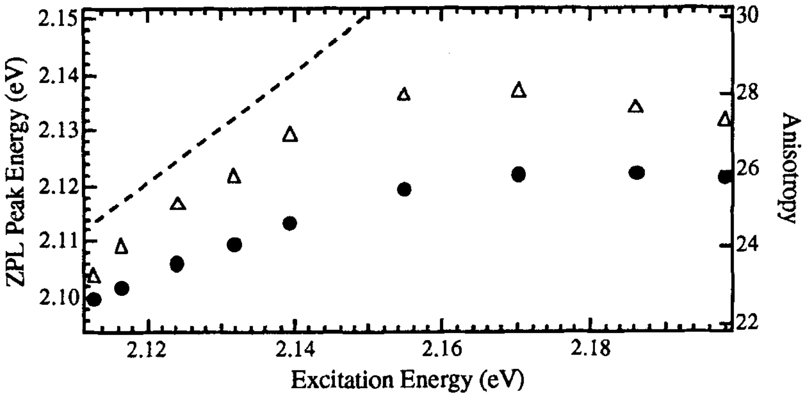


Figure 3: Zero phonon line peak position (solid circles) and emission anisotropy (open triangles) *vs.* excitation energy at 77K for MEHPPV/PE oriented blend

Second, the emission anisotropy evolves as the pump energy is lowered. The anisotropy of the ZPL (parallel peak value/ perpendicular peak value) is plotted in Figure 3 for MEH-PPV/PE. The anisotropy begins to decrease below the threshold energy, the same threshold for which shifts in the ZPL begin to appear. Hence, both the threshold in the ZPL position and the decrease in anisotropy arise due to extrinsic disorder.

DISCUSSION

The main results of these studies are twofold: first, for excitation energies in the main absorption band, the luminescence spectrum is independent of energy; second, as the excitation energy is moved to lower energy, a threshold is observed in the MEH-PPV cast films and oriented blends, below which the luminescence spectrum begins to shift, and the first and higher-order phonon peaks sharpen.[5] In the BCHA-PPV films and blends, no threshold behavior is seen prior to exposure to oxygen, indicating that this effect is sensitive to extrinsic disorder. The first observation provides evidence that subsequent to photoexcitation, rapid relaxation takes place to the bottom of the energy distribution. The second observation indicates that below this threshold energy, an inhomogeneously-broadened distribution is sampled, and further energy relaxation is only possible by dispersive transport. These deductions are bourne out by time-resolved measurements.[7]

However, these two deductions do not in themselves provide definitive evidence for either model. In a band model of a disordered semiconductor, one expects rapid energy relaxation within the band of delocalized states to the bottom of the band; further energy relaxation is only possible by hopping between localized states below the mobility edge.[8] In a tightly-bound molecular exciton model with a distribution of conjugation lengths, one expects rapid hopping to the tail region of the distribution, below which the probability of finding a lower energy chain segment within the radiative lifetime goes to zero.[5,6]

In the context of these two models, the results of the oxygen exposure measurements could be interpreted two ways. Oxidation certainly increases the microscopic disorder, and serves to shift the distribution of conjugation lengths to shorter chains. Hence, the changes seen upon exposure to oxygen are consistent with an increasing mobility edge due to microscopic disorder in an amorphous semiconductor, or consistent with a net reduction of the longest chains, and hence a reduction of available states at the lowest energies, in the exciton hopping model.

Although the two models predict similar relaxation phenomena as observed in the luminescence excitation spectra, an important qualitative difference exists in their picture of the excited state wavefunction. The amorphous semiconductor model predicts a delocalized wavefunction for states within the band, with a transition to localized states below this threshold.[8] By contrast, the exciton model predicts that lower energy states correspond to longer chain length segments, with progressively more delocalized wavefunctions. Within this model the threshold energy arises simply from a statistical point below which the hopping time is greater than the radiative lifetime. No threshold is predicted for the extent of localization. Since the degree of luminescence anisotropy in highly-oriented conjugated polymers correlates with the coherence length of the excited state wavefunction,[9] this provides a straightforward test of the two models: what is the behavior of the luminescence anisotropy in highly-oriented samples below the threshold energy?

The data in Figure 3 clearly demonstrates a decrease in the emission anisotropy below the threshold energy in the MEH-PPV/PE tensile-drawn blends. This implies that below this threshold, the coherence length of the excited state wavefunction decreases.[9] This is consistent with the presence of a mobility edge in an amorphous semiconductor, below which the electronic states are progressively more localized. This behavior is *inconsistent* with a model of tightly-bound excitons diffusing through a distribution of conjugation lengths, which predicts longer coherence lengths at the lowest energies. This suggests that the observed phenomena are strongly correlated with the degree of *extrinsic* disorder.

CONCLUSIONS

We have performed luminescence excitation spectroscopy (site-selective flourescence) on two soluble varieties of PPV. We observe a threshold energy below which the luminescence spectra shift and sharpen. This can be explained by either an exciton hopping model or an amorphous semiconductor model.

In addition, we observe that the emission anisotropy in highly-oriented blends begins to decrease below this threshold energy, implying that the transition corresponds to a mobility edge and that the electronic states below this edge have a decreased coherence length, consistent with increasing localization of the excited-state wavefunction. These results do not fit the predictions of a tightly-bound molecular exciton relaxing through a distribution of conjugation lengths.

ACKNOWLEDGEMENTS

DM, FHL, and TWH thank the Director's Postdoctoral Program at Los Alamos National Laboratory for support. We thank Ian Campbell for help in sample preparation and useful discussions.

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