

Polarized doping-induced infrared absorption in highly oriented conjugated polymers

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Received 30 March 2000; in final form 24 October 2000

Abstract

We present polarized, doping-induced absorption spectra obtained from conjugated polymers oriented by gel-processing in ultrahigh molecular weight polyethylene. Upon doping with iodine vapor, both poly(2-methoxy, 5-(2'-ethyl)-hexyloxy) paraphenylene vinylene), MEH-PPV, and poly(3-octyl thiophene), P3OT, show absorption features in the mid-infrared (the infrared-active vibrational (IRAV) modes and the low energy electronic absorption) that are strongly polarized parallel to the chain axis. All observed features have predominantly parallel polarization. We suggest that carrier-induced and electrode-induced losses in electrically pumped waveguide structures could be greatly reduced by using highly oriented films, with molecular axes orthogonal to the electric field polarization of the waveguide mode. © 2001 Elsevier Science B.V. All rights reserved.

Conjugated polymers have been widely studied as novel electronic materials for use in applications ranging from batteries to light-emitting devices. Recent work [1–3] has shown that luminescent semiconducting polymers are promising as high gain optical media for use in solid-state lasers. However, a number of problems have been identified that must be solved to enable the realization of electrically pumped polymer-based diode lasers. One particular feature of conjugated polymers is that self-localization of the charge carriers (electrons and holes) in polaronic states on the chain introduces broad absorption bands below the π - π^*

gap. Such absorption in the transport layers or in the gain layer of a polymer-based laser introduces losses and thereby raises the threshold for lasing. If too large, these carrier-induced losses could prevent electrically pumped polymer diode structures from lasing.

In this work, we present polarized, doping-induced infrared measurements on oriented samples of poly(2-methoxy, 5-(2'-ethyl)-hexyloxy) paraphenylene vinylene) (MEH-PPV) and poly(3-octyl thiophene) (P3OT), each blended with ultrahigh molecular weight polyethylene (PE). The spectra show that upon exposure to iodine vapor, carrier-induced absorption is highly polarized parallel to the chain axis over a wide range of doping levels. As a possible application of these structures we propose lasers with charge transport layers oriented orthogonal to the polarization of the

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waveguide mode, thus greatly reducing carrier-induced absorption in the thicker transport layer.

Highly oriented MEH-PPV/PE and P3OT/PE blends were prepared as previously reported [4] by tensile drawing of dried gel-films at a temperature of 100°C with concentrations between 1% and 5% as reported earlier [4,5]. 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 dichroism at the $\pi - \pi^*$ absorption peak was typically 7:1. The bright red MEH-PPV samples were observed to turn dark brown upon doping with iodine, indicating a strong absorption band developing below the $\pi - \pi^*$ edge; doping also quenched the photoluminescence. After a few days under flowing nitrogen, however, doped films of MEH-PPV regained their original color, and the doping spectroscopy could be repeated and the spectra monitored quantitatively during the doping process.

Oriented blends of poly (2-butyl-5-(2'-ethyl-hexyl) *para*-phenylene vinylene) (BuEH-PPV) and poly (9-hexyl-9-(2'-ethyl-hexyl)-fluorene-2, 7-diyl) (HEH-PF) in PE did not show color change when exposed to iodine. Evidently these two higher bandgap conjugated polymers could not be oxidized (nor doped) by iodine.

For infrared measurements, samples were mounted in a sealed transmission cell with ZnSe windows. Iodine crystals were added to the cell at the beginning of the experiment, and doping took

place in the saturated iodine vapor. Spectra were taken with a Bruker IFS-66/S FTIR spectrometer at time intervals ranging from 10 to 30 s. All spectra were normalized to a reference spectrum taken just prior to doping. For polarized absorption measurements, two reference spectra (one parallel and one perpendicular) were taken prior to doping; the polarizer was then rotated by 90° between measurements so that parallel and perpendicular spectra could be taken in situ on the same sample.

The doping-induced spectra for MEH-PPV and for P3OT obtained after 2 min of exposure to iodine vapor are shown in Fig. 1a and b, respectively. In both cases the parallel-polarized absorption is greater than the perpendicular-polarized absorption by a factor of about five. This is comparable to the anisotropy of the $\pi - \pi^*$ absorption peak in the 2–3 eV range for the same samples. The interference fringes are a result of multiple reflection in the film and are indicative of the high optical quality of the sample surfaces; fringes are seen in the direct single-beam spectra. The fringes shift slightly upon doping due to small changes in the index of refraction. As a result, the fringes in the difference spectra are 90° out of phase with those in the single beam spectra.

For both polymers, the induced absorption shows infrared-active vibrational (IRAV) modes below 1600 cm^{-1} and a broad electronic absorption centered near 4000 cm^{-1} . The electronic absorption feature is characteristic of that expected

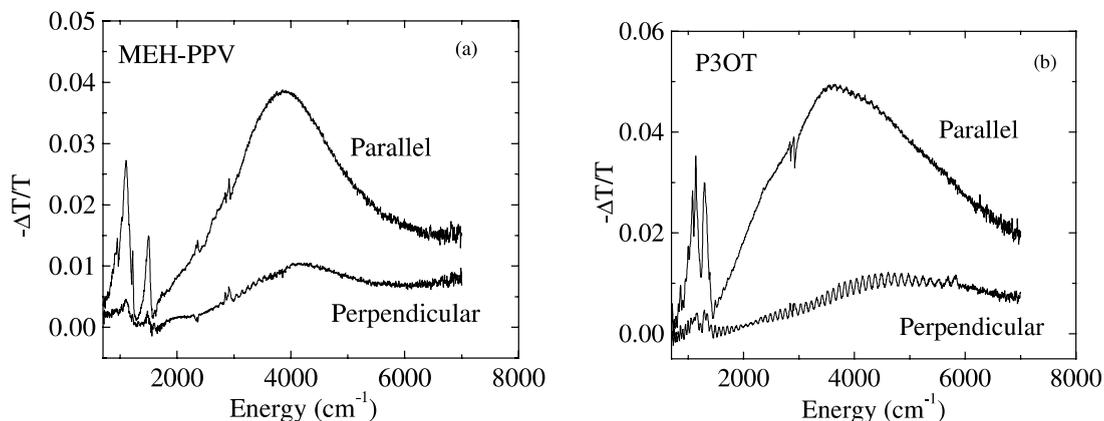


Fig. 1. Early time doping-induced spectra of oriented (a) MEH-PPV/PE and (b) P3OT/PE.

for self-localized charges (polarons) on the polymer chain [6]. Polaron absorption spectra are routinely observed in doping-induced [7] and photo-induced [8,9] experiments on cast films.

Calculations of the electronic absorption bands for polarons and bipolarons have typically been done for purely one-dimensional chains. However, the aromatic rings of MEH-PPV and P3OT introduce absorption features that are polarized perpendicular to the chain axis. Recent theoretical and experimental work on polarized ultraviolet absorption [5,10,11] suggests that localized electronic bands are confined to the rings and that these bands contribute to perpendicular-polarized absorption bands in the ultraviolet. Since none of the features observed in Fig. 1 has a perpendicular polarization, we conclude that the polaron states are indeed quasi-one-dimensional in nature, and that they involve hybridized orbitals at the linkage sites on the phenylene or thiophene rings. The weak blue shift of the perpendicular signal as compared to the signal recorded for parallel polarization may be indicative of the residual interactions between not completely isolated chains.

The parallel and perpendicular spectra evolve together, increasing in intensity monotonically with doping time. The co-evolution of the parallel and perpendicular spectra in the MEH-PPV/PE sample are shown clearly in Fig. 2, with each polarization normalized to the electronic absorption intensity after 20 min of doping. No spectral shift was observed with time during our 20 min experiment. This implies that in the range of doping concentrations studied, there is no crossover from one charged species to another (e.g., polarons to bipolarons, bipolarons to polaron lattice, or 1-d to 3-d crossover). In comparison to iodine doping of bulk P3OT thin film samples, an important difference is observed. For thin film bulk samples, the spectral shift of the doping-induced features (IRAV as well as polaron absorption) with doping degree is strongly expressed [12,13]. It is therefore safe to conclude, that the doping-induced spectral shift observed in bulk samples mirrors the co-evolution of charged species located on single chains (1-d) with charged species influenced by polymer interchain interactions (3-d).

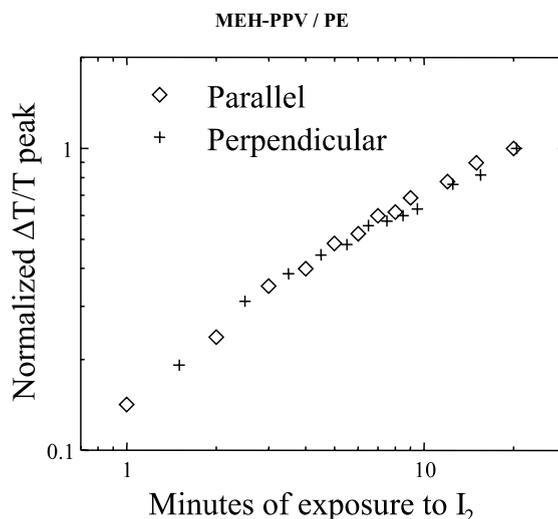


Fig. 2. Time evolution of mid-IR doping-induced absorption in MEH-PPV/PE.

For waveguide-based polymer lasers such as distributed feedback (DFB) and distributed Bragg reflector (DBR) lasers, the active layer must be isolated from the metal contacts by layers that satisfy stringent requirements. Transport studies on highly doped P3OT/PE gel composites yielded conductivity in the range of 10^{-2} – 10 S/cm [14,15] and meet therewith the requirements on the charge transport. Further, the layers must have very small absorption coefficients and lower indices of refraction than the active layer. The low indices of refraction serve to define the waveguide and confine the mode primarily in the active layer; inevitably, though, some radiation will propagate in the transport layers, thus requiring low absorption in those materials. Carrier-induced absorption has been demonstrated in polymer LED's, [16] and it is expected to be a problem in designing polymer-based diode lasers. We have shown, however, that orienting the transport polymers with their axes perpendicular to the polarization of the waveguide mode is a promising avenue for reducing carrier-induced absorption. A schematic diagram of this layered waveguide structure is shown in Fig. 3, with the electric field of the waveguide mode perpendicular to the orientation axis in the transport layers.

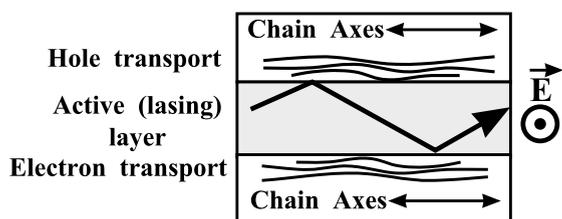


Fig. 3. Proposed structure for low-loss waveguide.

In conclusion, it was experimentally proven for P3OT and for MEH-PPV that chemical doping with iodine introduces self-localized charges on the conjugated polymer chains, yielding highly polarized doping-induced infrared spectra for stretch-oriented composites with PE gels. Evaluation of the polarized infrared measurements on oriented samples shows that absorption due to polaronic carriers on single chains is highly polarized parallel to the chain axis. Further, for isolated polymer chains of P3OT or MEH-PPV no spectral shift of the IR/V bands with doping ratio is observed, in difference to results from thin film bulk samples. This strongly implies the absence of crossover from polarons to another charged species like bipolarons or interchain polarons with doping degree for isolated chains of conjugated polymers. Suggestions are presented on the use of highly oriented thin films of doped polymers as charge injecting layers in diode lasers as a promising approach for reducing carrier-induced absorption in layered waveguide structures such as those proposed for polymer-based diode lasers.

Acknowledgements

This work was performed within the Christian Doppler Society's dedicated Laboratory for Plastic Solar Cells funded by the Austrian Ministry of Economic Affairs and Quantum Solar Energy Linz Ges.m.b.H. Financial support from Austrian Foundation for Advancement of Science (FWF P12680 CHE), from the European Commission

JOULE III Programme (JOR3-CT98-0206) and the Magistrat Linz are gratefully acknowledged. E. Kirk Miller was a visiting scientist funded by the Stabstelle für Auslandsbeziehungen at the Johannes Kepler University in Linz. We would like to thank Dr. Cuiying Yang for preparation of the P3OT/PE blend films. Work at UCSB was supported by the National Science Foundation through NSF-DMR9730126.

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