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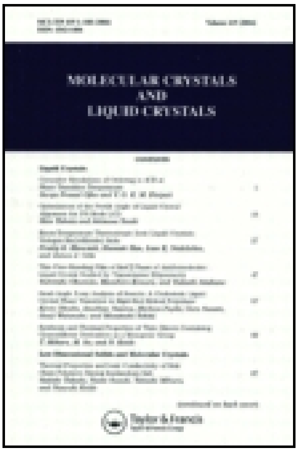

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Studies of Photoexcitations in Poly(Phenylene-Ethynylene-Silane)

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Version of record first published: 04 Oct 2006.

To cite this article: S. P. Huang , S. Jeglinski , X. Wei , Z. V. Vardeny , Y. W. Ding & T. J. Barton (1994): Studies of Photoexcitations in Poly(Phenylene-Ethynylene-Silane), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 513-518

To link to this article: http://dx.doi.org/10.1080/10587259408039284

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Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 513–518
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STUDIES OF PHOTOEXCITATIONS IN POLY(PHENYLENE-ETHYNYLENE-SILANE)

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Abstract A variety of optical probe techniques have been applied to films of poly(phenylene-ethynylene-silane) copolymers. We show that the σ-electron bands dominate the absorption and electro-absorption spectra, whereas the lower energy π-electron bands give rise to photoluminescence from singlet excitons and to long-lived triplet excitons, respectively.

INTRODUCTION

Poly(Phenylene-Ethynylene-Silane) (PPES) are novel polymers in which Si atoms with σ bonding are directly incorporated in the backbone structure with mostly π-bonding. As shown in Fig. 1 (inset), the PPES polymers consist of units of phenylene and methyl-silane, alternatively connected via carbon-carbon triple bonds, and thus they can be regarded as conducting polymers of the copolymer type. Weight average molecular weights ranged from 7000 to 17000 (~ 100-200 monomers/chain)[1]. The polymers are soluble in various organic solvents, easily cast into films and apparently quite stable in air[1]. Since PPES exhibit blue photoluminescence (PL), they have potential applications in the relatively new field of polymer-based light emitting diodes, in the blue spectral range[2].

In this work we have employed a variety of optical probe techniques to study the optical properties of PPES copolymers. These optical probes include absorption, photoinduced absorption (PA)[3], PL and their excitation spectra (ES)[4]. We have also used the absorption detected magnetic resonance (ADMR) technique[3] and

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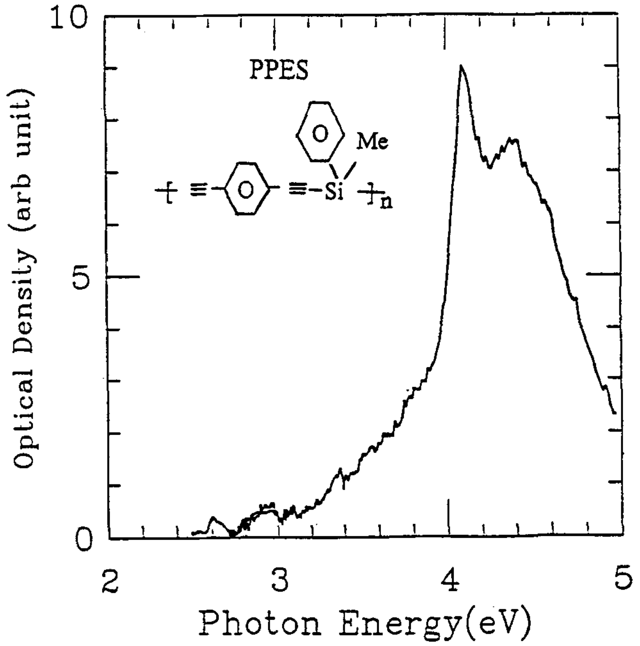

FIGURE 1 Absorption spectrum of a PPES film at 80K. The polymer backbone structure is given in the inset.

electroabsorption spectroscopy[4,5] to complement our measurements of PA and absorption spectra, respectively.

ABSORPTION AND ELECTRO-ABSORPTION

The optical absorption spectrum ($\alpha(\omega)$) of a spin cast thin film of PPES copolymer at 80K is shown from 2 to 5 eV in Fig. 1. Most of the oscillator strength is concentrated in an excitonic transition at 4.1 eV followed by a phonon side-band at 4.35 eV, suspected to be caused by strong electron phonon interaction with the c≡c stretching mode[6]. $\alpha(\omega)$ also shows a long tail absorption down to 2.7 eV with a lower oscillator strength.

The optical absorption spectrum is complemented by the electro-absorption (EA) spectrum shown in Fig. 2. The dominant feature of the EA spectrum is a derivative-like band with zero-crossings at 4.1 eV and 4.35 eV, respectively, which

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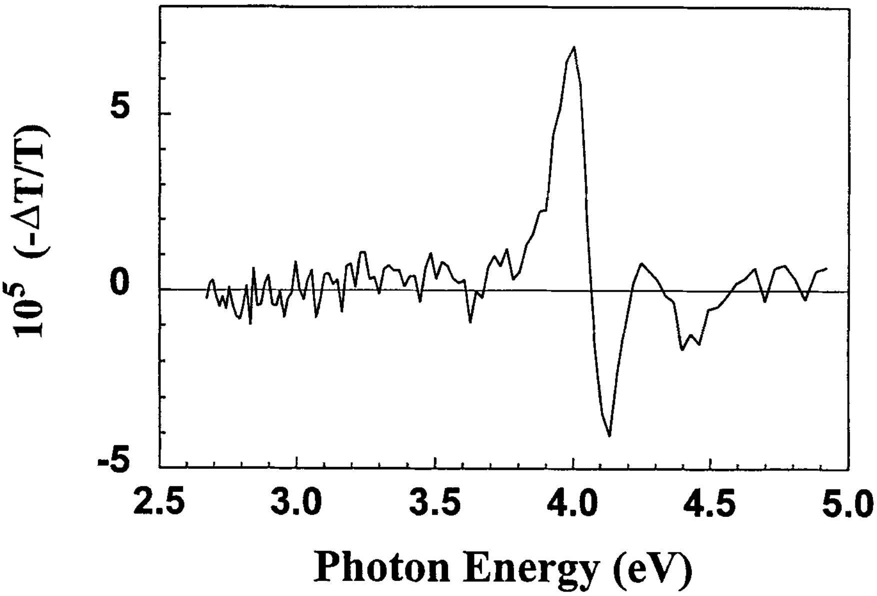

FIGURE 2 Electro-absorption spectrum of a PPES film at 80K, measured with field modulation of ≈5×10^4 volt/cm.

closely follows the spectrum of the absorption energy partial derivative ($\partial\alpha/\partial\omega$). The EA signal follows a quadratic dependence on the applied electric field F and therefore is due to second-order Stark effect[5]. The first derivative-like feature then shows that the dominating exciton at 4.1 eV (Fig. 1) is a Frenkel type exciton. Since the integration of the EA spectrum gives zero, this exciton apparently does not lose oscillator strength to the lower energy band at 2.8 eV upon application of electric field. Based on their energy location and EA properties we correlate the Frenkel exciton at 4.1 eV with the Si unit of the PPES backbone, whereas the spectral feature at 2.8 eV in $\alpha(\omega)$ is probably related to the phenylene unit (Fig. 1). The following studies of PA, PL, and their excitation spectra are in agreement with this assignment.

PHOTOEXCITATION SPECTROSCOPY

Photoluminescence Studies:

The PL spectrum of the PPES film shows a single band centered at 2.4 eV with no

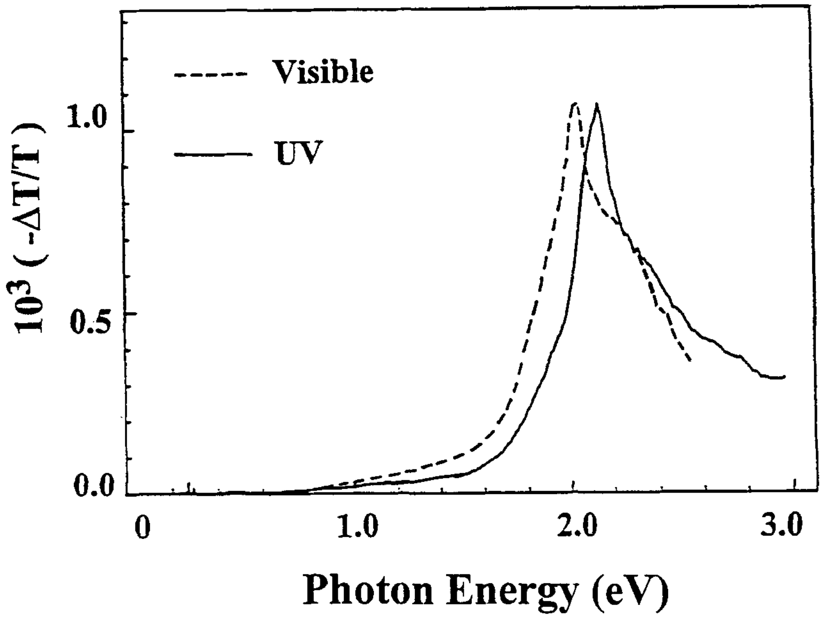

FIGURE 3 Normalized PA spectra (-ΔT/T) of PPES at 80K excited with 100 mW/cm^2 at 458 nm (dashed line) and 331 nm (full line).

phonon side bands[7]. Its high energy onset is at 3 eV, which coincides with the long absorption tail in $\alpha(\omega)$ (Fig. 1). The PL band in PPES is quite fast as deduced from the flat PL modulation frequency response up to 30 KHz. This shows that the PL is due to emission of singlet rather than triplet excitons. Since the PL band is closer in energy to emission bands of traditional π-conjugated polymers, such as poly(p-phenylene vinylene)[4], rather than to σ-conjugated polymers[8], we identify it as due to the phenylene units of the PPES structure. This is also in agreement with the PL excitation spectrum (PLE). PLE shows high quantum efficiency in the 2.4 to 4 eV spectral range which decreases thereafter[7], indicating that the PL band is not related to the σ-bond exciton at 4.1 eV.

Photoinduced Absorption Studies:

The PA spectrum of PPES at 80K is shown in Fig. 3. It consists of a single asymmetric PA band peaked at 2 eV. From its linear laser excitation dependence we conclude that the related photoexcitations undergo mono-molecular recombination

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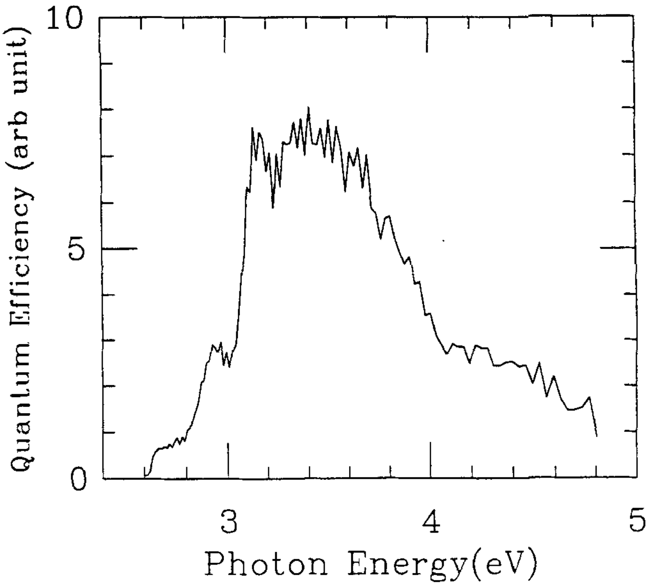

FIGURE 4 Normalized excitation spectrum of the PA band at 2 eV shown in Fig. 3.

kinetics. The magnetic field spectrum of ADMR at 2 eV shows[7] a correlated half-field resonance at H≈500 Gauss, identifying the PA band as due to optical transitions of triplet excitons[3]. These triplets are long-lived with lifetime in excess of 0.1 sec, as deduced from a steep PA modulation frequency (f) response for $f < 10$ Hz. We also note (Fig. 3) that the PA band blue shifts by 0.1 eV when excited at 3.3 eV compared to 2.7 eV excitation. This indicates that the PPES films are quite inhomogeneous, having a broad distribution of π-exciton energy levels[6], in agreement with the featureless absorption band tail below 4 eV (Fig. 1).

The PA excitation spectrum (PAE) is shown in Fig. 4; it has similar features as PLE[7]. It consists of an onset at 2.6 eV, a broad band centered at 3.4 eV, followed by a decreasing tail up to 5 eV. This again shows that the photogenerated triplets can be clearly associated with π-excitons (at 3-4 eV) rather than σ-excitons (above 4 eV). We believe then that the triplets are formed by intersystem crossing [4] from the π-exciton manifold. The σ-excitons are probably short-lived in PPES[8], and we also expect fast energy migration from the σ-manifold to the π-manifold due to the lower energy levels of the latter.

CONCLUSIONS

In conclusion, using a variety of optical techniques we could clearly separate the contributions of π-and σ-electron manifolds in PPES copolymer films. Whereas the σ-excitons dominate both absorption and EA spectra, the PL and PA bands are due to singlet and triplet excitons, respectively, associated with the π-electron manifold.

This work was supported in part by NSF grant No. DMR-92-22947.

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