The Photophysics of Thin Polymer Films of Poly-(*meta*-phenylene-co-2,5-dioctoxy-*para*-phenylenevinylene)

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Summary. We have investigated the effect of film preparation procedures on the photoluminescence efficiency of the luminescent co-polymer poly-(*m*-phenylene-co-2,5-dioctoxy-*p*-phenylenevinylene) (*PmPV*). The photoluminescence efficiency of *PmPV* films improved by up to 50% when the solution was degassed by bubbling argon gas through it prior to spin casting in an inert atmosphere and baking under vacuum. Photoinduced absorption and doping measurements show that this preparation method reduces polaron photogeneration, which reduces the photoluminescence (PL) yield through exciton quenching and excited state absorption. It is proposed that this sample preparation method increases interchain separation, reducing the formation of polarons and non-radiative quenching routes, thus resulting in increased PL efficiency.

Keywords. Photo-induced absorption; Polaron; Solid state; Efficiency; Fluorescence spectroscopy.

Introduction

Over the last decade polymers have been utilized successfully as luminescent materials in organic light emitting devices. Polymers with excellent carrier transport properties and high photoluminescence efficiency have been synthesized [1–3]. In recent years, these developments have led to the investigation of polymers as suitable materials for an electrically pumped organic laser [4, 5]. The question of whether polymers can be used successfully as a solid state laser material has raised numerous important issues in polymer science, one of which is excited state absorption by charged species [6]. The presence of a large excited state population with absorption close to the emission maximum will quench any lasing action and has been highlighted as a major problem in fabricating an electrically pumped organic laser.

In this work we have investigated the photophysics of the highly luminescent co-polymer poly-(*m*-phenylene-co-2,5-dioctoxy-*p*-phenylenevinylene) (*PmPV*) using photoinduced absorption (PA) spectroscopy. The structure of *PmPV*,

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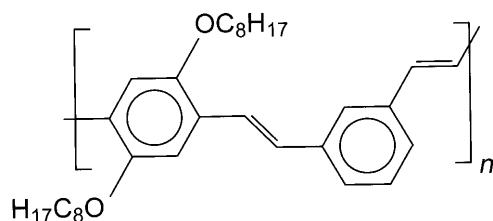
Fig. 1. Chemical structure of the co-polymer poly-(*m*-phenylene-co-2,5-dioctoxy-*p*-phenyleneviny-lene); the repeat unit molecular weight is 460.672 g/mol

synthesized by the authors [7] using the *Horner-Emmons* polycondensation reaction [8], is shown in Fig. 1. Previously, using a variety of different thin film preparation techniques, the photoluminescence (PL) efficiency and photostability of this polymer were increased by ∼50% [9]. The improvement in these properties directly correlates with increased film thickness, leading to speculation of improved interchain separation. Increased interchain separation can significantly enhance PL efficiency and reduce polaron formation [10]. A thin film formation technique that could enhance both of these polymer properties would have important implications for the future development of organic optical devices. In this work the relationship between film forming procedure and polaron formation is fully investigated.

Results and Discussion

Fluorescence spectra show a broadening of 7 nm towards the blue region for film T compared to film C, indicative of morphological changes such as reduced aggregate formation, which supports the argument for increased interchain separation in film T. PL efficiencies of 6.5 and 8.2% [11] were measured for five day old films of type C and T using an integrating sphere and an excitation wavelength of 354 nm from a He-Cd laser at $0.1 \, \text{mW/cm}^2$, giving an efficiency increase of 26%. Using stability curves for these films in air, an initial efficiency increase of ∼50% was calculated for film T over film C in good agreement with previous PL intensity measurements [9]. Matrix films have higher efficiencies than neat polymer films [10], but importantly there is a large improvement in efficiency for the film of type T, using specific processing procedures. The values obtained are somewhat lower than those of some poly-phenylene derivatives which range from 20 to 50% [12]. The reason for the poor efficiencies most likely relates to new non-radiative routes present in this polymer type.

The three types of film were studied by PA spectroscopy in order to understand the origin of the enhanced radiative yield in films T and M compared to film C. Interchain aggregation can enhance polaron photogeneration [13], which in turn will reduce the PL quantum yield. Polarons quench singlet excitons [14], and if the excited state absorption and PL spectra overlap, excited state absorption will also reduce the PL quantum yield. The absorption spectrum of polarons were determined by doping a dilute solution of *PmPV* ($1.25 \, \text{g/dm}^3$) in CH_2Cl_2 with a solution containing $FeCl_3$ at a concentration of $3.75 \, \text{g/dm}^3$ ($0.023 \, M$). Figure 2 shows the absorption spectra of a *PmPV* solution as successive amounts of $FeCl_3$
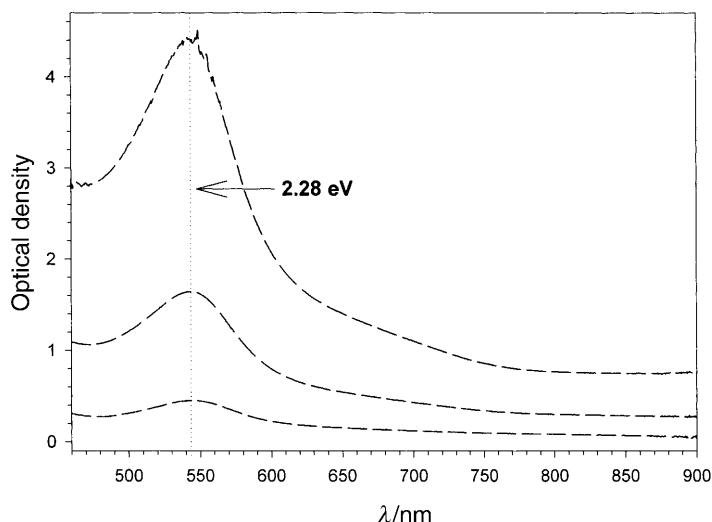
Fig. 2. Solution absorption spectrum of pure *PmPV* (solid line) and with increasing concentrations of FeCl$_3$ (dashed lines); the polaron absorption increases with increasing concentration of FeCl$_3$

solution are added. The polymer is oxidized by the dopant, and the absorption spectra show the formation of an absorption band with a peak at 543 nm (2.28 eV) due to positive polarons (cations) on the polymer chain. The lineshape of the doping induced absorption spectrum was independent of the dopant concentration, and we did not observe a second oxidation step which would indicate the formation of positive bipolarons. The polarons being formed result from charge transfer in solution, whereas the polarons formed by photoexcitation will be investigated by PA spectroscopy.

Figure 3 shows the PA spectra of films C, T, and M measured with the lock-in set 90° out of phase with the laser modulation (quadrature detection) to eliminate contamination of the PA spectrum by photoluminescence. The matrix-isolated sample (*M*) has a PA band with a maxima at 1.87 eV; films C and T have a second PA band with a maximum at 2.25 eV. This energy matches that of polaron absorption (Fig. 2), and we accordingly assign this PA band to photogenerated polarons. The polaron absorption band is significantly stronger in film C, which is consistent with a link between reduced photoluminescence efficiency and enhanced charge photogeneration.

We further investigated the nature of the PA bands at 1.87 and 2.25 eV by measuring the dependence of the PA signal on laser power and frequency. The rate equation for photoexcitations is given by Eq. (1):

$$\frac{dn}{dt} = G - Rn - Bn^2 \tag{1}$$

G is the generation rate (proportional to the laser flux), R is the monomolecular recombination rate, and B is the bimolecular recombination rate. The steady state excitation density is proportional to the laser power ($n_{SS} = G/R$) for monomolecular recombination and proportional to the square root of the laser power ($n_{SS} = \sqrt{G/B}$) for bimolecular recombination. This can be used to distinguish
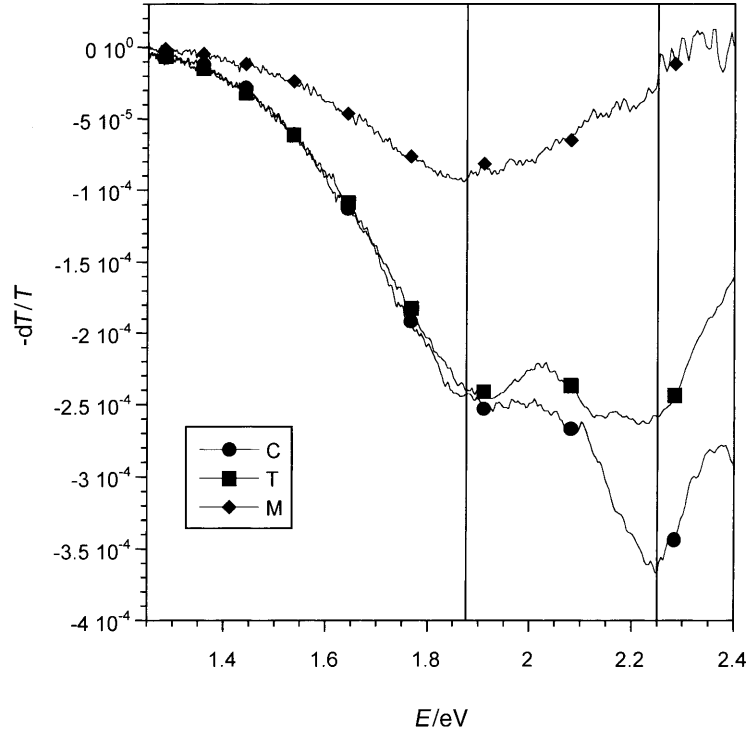
Fig. 3. PA spectra of films C, T, and M. The spectra were measured out of phase with the laser
excitation to eliminate PL from the PA spectrum

excitations, as triplet excitons show monomolecular recombination (except at high
excitation densities), whereas non-geminate polarons are characterized by bi-
molecular recombination. A power index between 0.5 and 1 indicates a combination
of monomolecular and bimolecular recombination, as would be the case for a
combination of polarons and geminate polaron pairs. The dependence of the PA
signal on laser power for the PA band at 1.87 eV in films C and T was linear, which
is consistent with triplet excitons. Combining these results with the PA
spectroscopic results we can assign the 1.87 eV PA band to triplet absorption.
Accordingly, the PA band at 2.25 eV is assigned to geminate polaron-pairs.

The dependencies of the PA bands at 1.87 eV and 2.25 eV in all three films upon
the pump modulation frequency were measured. For monomolecular recombina-
tion, the in-phase and quadrature PA signals depend on the modulation frequency f
according to Eqs. (2) and (3) where f is the pump modulation frequency and τ is
the excitation lifetime [15].

In-phase $\qquad\qquad\qquad\qquad \Delta T \propto 1/(1 + (2\pi f\tau)^2)$ $\qquad\qquad\qquad$ (2)

Quadrature $\qquad\qquad\qquad \Delta T \propto 2\pi f\tau/(1 + (2\pi f\tau)^2)$ $\qquad\qquad\qquad$ (3)

Table 1 shows the calculated values of τ(s) at 80 K. The lifetimes for both PA bands
are the same within the calculated errors (± 0.00002 s). Similar lifetimes for the
1.87 and 2.25 eV PA bands in films C, T, and M indicate that any changes in the PA

Table 1. Lifetimes (s) for the polaron (2.25 eV) and triplet (1.87 eV) species for in phase (X) and quadrature phase (Y); error: ±0.00002 s

| Film type	2.25 eV		1.87 eV	
	X	Y	X	Y
C	0.00046	0.00041	0.00044	0.00046
T	–	–	0.00044	0.00045
M	N/A	N/A	0.00046	0.00045

signal are due to different generation rates and not changes in polaron recombination rates.

The assignment of the feature at 2.25 eV to polaron-pair formation is in clear agreement with the results using $FeCl_3$ as a dopant. We observed no shift in energy of polaron absorption bands between solution and film. This is likely because the solvatochromic red-shift [16] is compensated by a blue-shift due to *Coulomb* interactions between correlated polarons [17]. Comparison of the PA spectrum of film M with those of films C and T provides further support of the assignment of these features. In film M we continue to observe the triplet feature but no polaron peak. This indicates that polarons in *PmPV* are predominately formed through interchain species and that separation of the polymer chains accordingly reduces the polaron population. The intensity of the triplet band in films C and T (Fig. 3) is the same as expected and has a reduced intensity in film M for the same spinning speed due to the incorporation of the PS matrix. As a consequence, we can directly compare the polaron peaks in film C and T.

These results give important information about the properties of films C and T. Comparison of the PA signals shows that there is a significant reduction (about 30%) in the polaron population of film T. This would indicate that there is increased interchain separation in this film, agreeing with the previous measurement of film T having an increased thickness of 31% [9]. Furthermore, this supports the increased PL efficiency measured.

Our results correlate reduced polaron photogeneration with enhanced quantum yield. This has important implications for the production of an electrically pumped polymer laser. The strong overlap of excited state absorption (ESA) of polarons in *PmPV* makes such an application unlikely for this material. The ESA band, measured by doping and photogeneration, occurs at a relatively high energy for a phenylene polymer. Figure 4 compares the PL and polaron peaks for a series of phenylene-based polymers: poly-(9,9-dioctyl fluorene) (*PFO*) [18], methyl-substituted ladder-type poly-(*para*-phenylene) (*m-LPPP*) [19], poly-(2,5-dibutoxy phenylene ethynylene (*DBO-PPE*) [20], poly-(2,5-dioctyloxy-*para*-phenylene vinylene) (*DOO-PPV*) [18], and *PmPV* (Figs. 2–3).

This result can be explained by the chemical structure of *PmPV*. Every polymer in Fig. 4 other than *PmPV* has C_{2h} symmetry. Consequently, molecular orbitals possess even (A_g) or odd (B_u) parity and optical transitions are allowed only between orbitals of opposite parity. Adding a charge to a conjugated chain causes a spontaneous distortion of the chain, drawing the highest occupied molecular orbital (HOMO) and the singly occupied molecular orbital (SOMO) into the optical gap
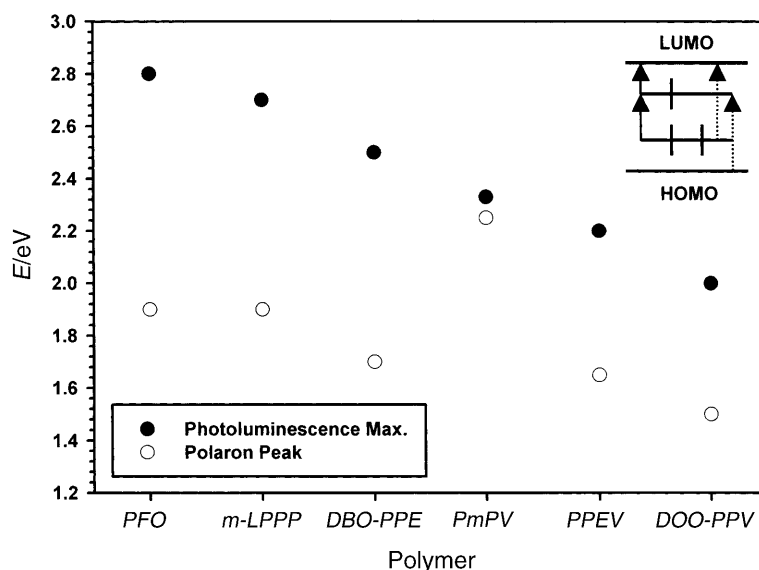
Fig. 4. The peaks of the PL spectra (solid circles) and high-energy polaron band (open circles) for a series of phenylene-based polymers; the inset shows a schematic diagram of the polaron orbital energy levels and possible optical transitions

(Fig. 4, inset). This results in two induced absorption bands shown by the vertical solid lines in Fig. 4 (inset). The dashed vertical lines show transitions that are permitted by occupation, but forbidden by dipole selection rules. However, this band is seen in the PA (Fig. 3) and doping-induced absorption (Fig. 2) spectra of *PmPV* as the presence of a *meta*-conjugated phenylene ring breaks C_{2h} symmetry. The absorption spectra of doped *PmPV* in Fig. 2 show a relatively weak band between 650 and 750 nm where one would expect to see a polaron absorption band. These results illustrate the effect of molecular structure on the photophysics of conjugated polymers.

Conclusions

In conclusion, the excited state absorbing species have been fully characterized for three types of *PmPV* films. Doping and photoinduced absorption studies have shown that there are excited state absorption bands at 2.25 eV for polarons and 1.87 eV for triplet excitons. This work shows that by controlling film processing properties the number of polarons formed in thin films of *PmPV* can be significantly reduced by increasing interchain spacing. Furthermore, this decrease in polaron formation increases the PL efficiency significantly and reproducibly, thus having important implications for understanding further the photophysics of luminescent polymers and more immediately in developing a successful polymer for use as an emissive layer in an electrically pumped organic laser.

Experimental

The absorption spectra were measured using a Shimadzu UV-2101PC absorption spectrometer. The PL spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer at a pump

wavelength of 458 nm. For PA measurements, the sample was excited by an amplitude-modulated pump beam, and changes in the transmission of a probe beam were measured by a photodetector and a lock-in amplifier. The 457.9 nm line of an argon ion laser at a power of 30 mW/cm^2 was used as the pump beam, and a monochromated tungsten white light source was used as the probe. The use of multiple detectors and gratings enabled the PA spectrum to be investigated between 0.7 and 3.0 eV. The pump beam was modulated at 120 Hz by an acousto-optical modulator. The films were tested under vacuum (2.7×10^{-3} torr) at 80 K. The PA spectrum, defined as the normalized change in transmission of the probe beam, is proportional to the photoexcitation density n. The lock-in amplifier simultaneously measures the in-phase and quadrature signals which can be compared to determine the excitation lifetime and to correlate different PA bands.

Three separate types of films were fabricated. Firstly, a control film, denoted as film C, was spun and baked in atmosphere from a non-degassed solution. A second film type with dramatically improved PL efficiency [9], denoted as film T, was spun in an inert atmosphere from a degassed 25 mg/cm^3 toluene solution of *PmPV* and then baked at 70°C for a minimum of two hours in vacuum (∼5 torr). The solution was degassed by bubbling with argon [9], and the removal of air from this film type was verified using *Fourier* transform infrared spectroscopy (FTIR). A further film with the polymer in an inert matrix, denoted as film M, was spun and baked in atmosphere from a non-degassed toluene solution containing *PmPV* at a concentration of 25 mg/cm^3 and polystyrene (PS) at a concentration of 15 mg/cm^3. Films C, T, and M were spun at 400 rpm onto Spectrosil B substrates.

Acknowledgements

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