ELSEVIER

Synthetic Metals 76 (1996) 47–51

SYNTHETIC METALS

Chromism and luminescence in regioregular poly(3-dodecylthiophene)

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Abstract

We report photoluminescence studies of poly(3-dodecylthiophene) (P3DT) in solution. In a good solvent the polymer exhibits luminescence with a high quantum efficiency and a decay time of 500 ps. In a poor solvent the emission is red shifted with a 20-fold reduction in quantum efficiency and a decay profile that is non-monoexponential, but has an average lifetime that is very similar to the good solvent environment. The data indicate a large increase in the natural radiative lifetime from approximately 1 ns in a good solvent to 20 ns in a poor solvent, which implies an emitting state that is different in the two situations. In the poor solvent the spectrum is almost identical to that of the thin film, suggesting that the polymer aggregates in the solution and the emitting species is the same in both environments. The data are consistent with the formation of an excited state that is not localized on a single chain but is delocalized over more than one chain.

Keywords: Chromism; Luminescence; Poly(3-dodecylthiophene)

1. Introduction

Poly(3-alkylthiophenes) have been shown to be good electroluminescent (EL) polymers that emit in the red region of the spectrum [1,2]. They were originally prepared by electrochemical methods [3,4], but more recently structurally homogeneous polymers have been made, where the coupling between adjacent 3-alkylthiophene units leads to a more regioregular arrangement of the alkyl side groups. This method of synthesis leads to polymer chains that have the solvating side groups in an alternating head-to-tail arrangement, and can produce regioregularities of up to 98% [4]. Increasing regioregularity leads to a shift in the absorption spectrum to lower energy, which is indicative of either a more delocalized excited state or larger absorbing chromophore. The large, bulky alkyl side groups provide the solubility that is desirable for the preparation of thin films, as required for EL devices. They also provide an opportunity to study the photophysics of isolated polymer chains in solution and, hence, to investigate the influence of polymer conformation on the excited state properties.

Several alkyl-substituted polythiophenes have been shown to exhibit solvatochromism and thermochromism in both solution and thin film states [5–8], in a similar fashion to soluble polydiacetylenes [9,10]. However, since the luminescence efficiencies of poly(3-alkylthiophenes) are much higher, these polymers are ideal for investigating the chromism phenomenon using luminescence spectroscopy [11].

In this article we report on some time-resolved and steady-state luminescence studies of two regioregular poly(3-dodecylthiophene) (P3DT) samples in both good and poor solvents, and compare the results to those obtained for thin films. The luminescence depends on both the degree of regioregularity of the polymer side groups and on the solvent quality, so we can investigate the influence of these factors on both the radiative and non-radiative decay channels of the excited state.

2. Experimental

The two regioregular samples of P3DT were prepared, purified and characterized, as described elsewhere [12], and were found to be 95% and 60% regiospecific[4,12,13]. Toluene and methanol were tested for extraneous luminescence

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and were used without further purification. All solvent mixtures are reported as a volume fraction of toluene versus total volume. Luminescence spectra were recorded on a photon-counting spectrometer (SPEX fluoromax) and were corrected for the wavelength response of the detection system. Luminescence quantum efficiencies were calculated by comparing spectra with those of a reference standard of rhodamine 101 in ethanol (quantum efficiency, $q_f = 1.0$). Luminescence decays were measured using time-correlated single-photon counting with pulsed laser excitation and a microchannel plate photomultiplier tube (PHOTEK PMT 413LJ) detector. The apparatus is described elsewhere [14] and produces an instrument response function of 70 ps (FWHM). Luminescence decays were analysed in terms of the sum of exponentials using a non-linear least-squares iterative reconvolution procedure and stringent statistical analysis [15].

3. Results

The absorption spectra of P3DT (95% regioregular) in a range of toluene/methanol mixtures at constant polymer concentration are given in Fig. 1. In neat toluene the absorption is structureless with a peak absorbance at 448 nm. With decreasing volume fraction of toluene (down to a minimum of 10%), the absorption spectrum red shifts, peaking at 520 nm and gains vibrational structure. The less regioregular

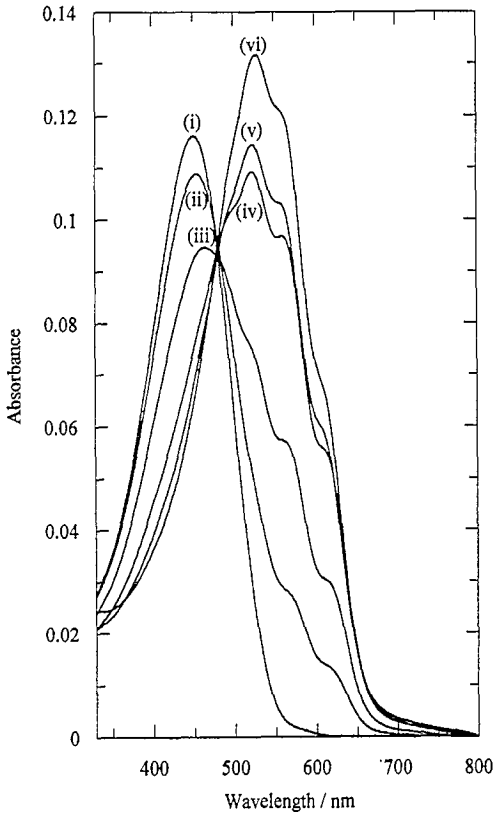

Fig. 1. Absorption spectra of P3DT (95% regioregular) in various toluene/methanol volume fractions, normalized to constant polymer concentration: (i) 100; (ii) 70; (iii) 63.5; (iv) 60; (v) 58 and (vi) 10% volume fractions of toluene.

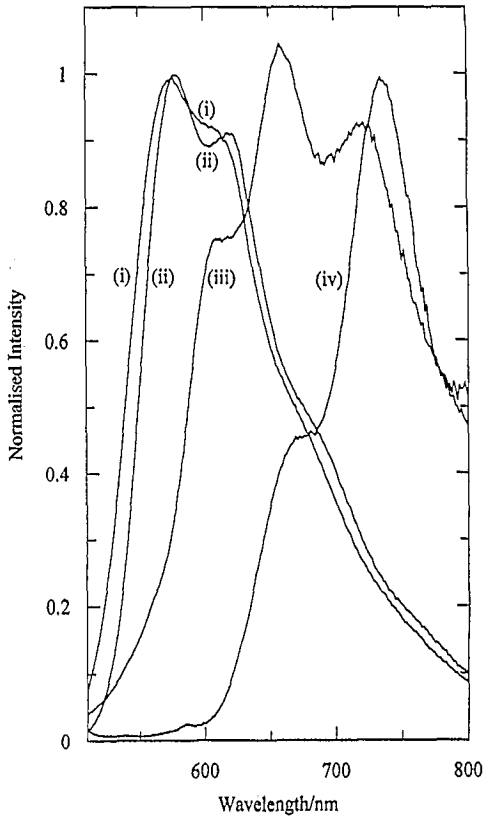

Fig. 2. Emission spectra ($\lambda_{ex} = 500$ nm) of two P3DT samples in toluene/methanol solution: (i) P3DT (60% regioregular) in 100% toluene; (ii) P3DT (95% regioregular) in 100% toluene; (iii) P3DT (60% regioregular) in 17% toluene; (iv) P3DT (95% regioregular) in 17% toluene.

P3DT (60% regioregular) exhibits a similar effect, although the red-shifted form is less structured and requires more methanol to reach the limiting case. The luminescence emission spectra of both P3DT samples at the two extremes of solvent conditions are given in Fig. 2. In toluene, the emission spectra show vibrational structure, that is more pronounced in the case of the regioregular sample, and both samples emit at approximately the same peak wavelength of 578 nm. In a 17% toluene solution the emission spectra, like the absorption spectra, bathochromically shift to longer wavelengths, peaking at 735 and 660 nm for the 95 and 60% regioregular samples, respectively. The P3DT (95% regioregular) emission spectrum is shifted further to the red than the 60% regioregular sample, but has the same general vibronic structure. The lack of detector sensitivity at wavelengths longer than 800 nm precludes the possibility of detecting emission at long wavelengths. However, comparison of the emission spectrum with that of the thin film, recorded on a different apparatus, suggests there is only a small amount of long-wavelength emission, as shown in Fig. 3.

The red shift, as the toluene fraction is decreased, is accompanied by a dramatic drop in luminescence quantum efficiency from 40 to about 2% and 30 to about 2%, for the 95 and 60% regioregular samples, respectively. Analysis of the luminescence decays in the neat toluene solution reveals a good monoexponential decay with an associated lifetime of

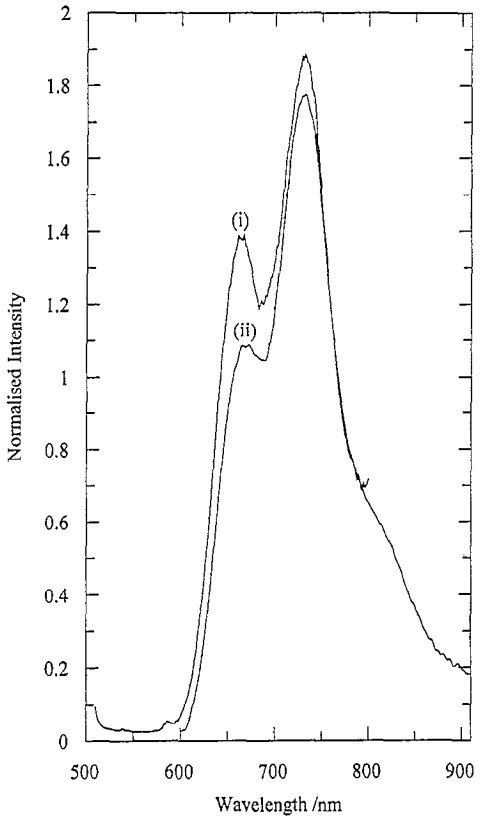

Fig. 3. Comparison of the P3DT (95% regioregular) emission spectrum in (i) a 17% toluene/83% methanol mixture ($\lambda_{ex}=500$ nm), with (ii) a thin film of the same sample ($\lambda_{ex}=488$ nm).

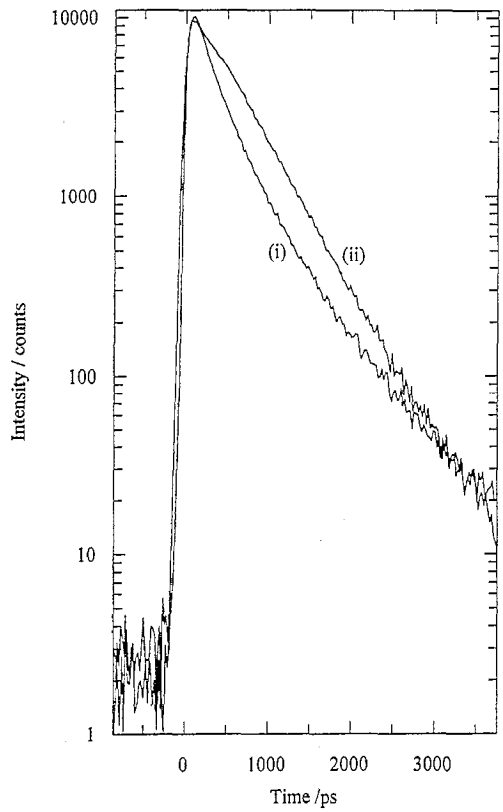

Fig. 4. Comparison of the fluorescence decay profiles of P3DT (95% regioregular) in (i) 17% toluene/83% methanol ($\lambda_{ex}=600$ nm) and (ii) 100% toluene ($\lambda_{ex}=560$ nm).

500 ± 20 ps that, like the emission spectra, is almost independent of the regioregularity of the sample. The decay associated with the red-shifted emission is more complex and can only be satisfactorily modelled by a tri-exponential decay function. However, the average 'lifetime' (of the three extracted decay times weighted by the relative yields) is only marginally shorter than that of the blue-shifted emission in neat toluene. This is far better visualized by a direct comparison of the two decays, as shown in Fig. 4. A summary of the quantum efficiency and decay time data is given in Table 1. Decay time data are not yet available for the red-shifted emission of the 60% regioregular sample or for the thin film samples.

4. Discussion

The luminescence quantum efficiency, q_f, of P3DT (95% regioregular) in neat toluene is 40% and combining this value with the measured luminescence lifetime, τ_f, using the relationship:

$$q_f=\frac{k_r}{k_r+k_{nr}}=k_r\tau_f \quad (1)$$

gives a natural radiative rate constant k_r of 7.9×10^8 s^{-1} (natural radiative lifetime, $\tau_r=1.3$ ns) and corresponds to a fully allowed radiative transition in this spectral region, in agreement with the intense absorption cross section. However, using the well-known Strickler–Berg [16] relationship to extract the natural radiative lifetime (τ_r) from the absorption profile is difficult for conjugated polymers, as the concentration of absorbing chromophores is unknown.

For the 60% regioregular P3DT sample, the emission spectrum and decay time are, within experimental error, the same as the 95% regioregular P3DT sample, although the luminescence quantum efficiency is reduced to 30%. These data indicate that the natural radiative lifetime has actually increased to 1.7 ns, which is marginally longer than for the 95% regioregular sample. Thus, the regioregularity of the polymer sample influences the natural radiative lifetime as well as the non-radiative decay processes.

In the poor solvent the luminescence quantum efficiency reduces to approximately 2% and the decay curves are, as mentioned above, non-exponential but can be modelled with a tri-exponential fitting function with three associated decay times. These decay times are sensitive to both the excitation and emission wavelength, but consistently produce an average decay time of 400 ± 100 ps, consistent with the form of the decays shown in Fig. 4. Although the decays are non-monoexponential the important point to note here is the small changes in the decays in spite of a 20-fold reduction in the luminescence quantum efficiency. A drop in quantum efficiency is often accompanied by an increase in the rate of luminescence decay, due to an increase in the non-radiative

Table 1
Luminescence efficiencies, decay times and deactivation rate constants for P3DT in good and poor solvents

	Luminescence quantum efficiency, q_f	Luminescence decay time, τ_f (ps)	Natural radiative lifetime, τ_r (ns)	Natural radiative rate constant, k_r ($\times 10^8\ s^{-1}$)	Non-radiative decay rate constant, k_{nr} ($\times 10^9\ s^{-1}$)
P3DT (95%) (100% toluene)	0.41 ± 0.04	520 ± 20	1.3 ± 0.1	7.9 ± 0.6	1.2 ± 0.1
P3DT (95%) (17% toluene/83% methanol)	~ 0.02	(400 ± 100) [a]	$\sim 20 \pm 5$	0.5 ± 0.1	2.5 ± 0.7
P3DT (60%) (100% toluene)	0.29 ± 0.03	500 ± 20	1.7 ± 0.1	5.9 ± 0.6	1.4 ± 0.1

[a] This value is the average decay time associated with a tri-exponential modelling of the decay profile. The three derived rate constants (and relative yields) are 60 ps (16%), 310 ps (52%) and 750 ps (32%).

processes, while the radiative rate constant remains unaffected [17,18]. The data here clearly suggest otherwise, and can only be explained by an increase in the natural radiative lifetime to approximately 20 ns. This observation is similar to that observed in thin films of a related cyano-substituted poly(*p*-phenylene vinylene) with hexyloxy side groups (CN–PPV), where the luminescence decay time is longer in the film than in the solution, although the luminescence quantum efficiency is actually lower [19].

The absorption spectra of the P3DT (95% regioregular) in a thin film and in a poor solvent appear to have large extinction coefficients and, hence, suggest a short natural radiative decay time [16], of similar magnitude to that observed in a good solvent. However, the measured natural radiative lifetime is substantially longer than would be expected for a fully allowed transition in this spectral region, and indicates an emitting state that is not the same as the initial photoexcited state. The luminescence spectrum of P3DT (95% regioregular) in a thin film and in a poor solvent (Fig. 3) are similar and indicate a similar species is emitting in each case. We propose that the polymer aggregates in the poor solvent and, hence, the local environment would be similar to the thin film, and would explain the similarity of the spectra. The data are consistent with a model of strong interchain interactions that lead to an excited state that is delocalized over more than one chain and is not strongly radiatively coupled to the ground state.

The measured data allow the rate constants for the non-radiative decay channel to be calculated and these are given in Table 1. Although the non-radiative route in P3DT is larger than that of the radiative route in both good and poor solvents, the difference between the two is small. The luminescence quantum efficiency of P3DT in different states is therefore determined predominantly by the natural radiative rate constant.

Soluble conjugated polymers are well known to exhibit solvatochromism and in many ways the spectral data reported here are very similar to those of soluble polydiacetylenes [9]: in good solvents the polymer adopts a disordered configuration to produce a yellow solution and in poor solvents it adopts a more ordered configuration to produce a red or sometimes even a blue solution. The nature of the ordered state is a subject of controversy: one opinion is that the effect is a result of single chains, another that it is an aggregate and more recently a compromise explanation that requires the polymer to fold and form an intramolecular aggregate [10]. If the P3DT in a poor solvent adopts a similar configuration to the polydiacetylene, then an aggregate model is more consistent with the data.

5. Conclusions

P3DT exhibits solvatochromism in both absorption and emission. By adding methanol to a solution of P3DT (95% regioregular) in toluene, the solution changes in colour from yellow to red. Similarly, the luminescence spectra show a shift to lower energy with an accompanying drop in the quantum efficiency, but with a less pronounced effect on the luminescence decay. This can be explained in terms of an increase in the natural radiative rate constant, due to the emission originating from a different state that is not as strongly coupled radiatively to the ground state as the originally excited state. Emission spectra in a poor solvent and a thin film are similar and indicate a common environment of the emitting species in the two cases. By combining these two observations we infer that the emitting species is an interchain excited state. Similar observations in CN–PPV indicate that interchain interactions are important in understanding the luminescence properties of thin films of conjugated polymers and will affect the molecular engineering of new electroluminescent polymers.

We have shown that both the natural radiative and non-radiative rate constants change among solution, aggregates and thin films, and so it is important that both luminescence quantum efficiencies and decay times are measured when trying to interpret the decay of excited states in conjugated polymers.

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