

# Photophysics of thiophene based polymers in solution: The role of nonradiative decay processes

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An investigation has been undertaken of the photophysics of six thiophene-based polymers. This includes the measurement of fluorescence quantum yields, quantum yields for triplet formation, and determination of fluorescence and triplet lifetimes in benzene solution at room temperature. From the above-mentioned data, the overall set of rates for the deactivation processes (fluorescence, intersystem crossing, and internal conversion), has been evaluated. Mechanisms of nonradiative decay are discussed, and it is shown that both intersystem crossing and internal conversion are important in the decay of the lowest singlet excited state of isolated polythiophenes molecules in solution. Comparison of spectroscopic and photophysical properties of the polymers with analogous oligothiophenes shows that with the polymer, the  $S_1 \rightsquigarrow S_0$  internal conversion deactivation pathway plays a major role, in contrast to the behavior found with the oligomers where this internal conversion deactivation channel is essentially negligible. © 2003 American Institute of Physics. [DOI: 10.1063/1.1528604]

## I. INTRODUCTION

Conjugated organic polymers are gaining increased interest because of their enormous potential in several fields, such as video matrix displays or semiconductors, where it has been anticipated that they may substitute inorganic systems based on silicon and potentially reduce a computer to pocket size.<sup>1</sup>

In this field, thiophene based polymers have gained considerable interest, due to their chemical stability and potential for charge transport, nonlinear optics, and light emitting diode (LED) applications.

The study of the behavior of conjugated organic polymeric systems is obviously a highly complex matter, both for solids and solutions. One route to understanding these systems involves the oligomer approach,<sup>2</sup> in which the observed properties of a number of oligomers are extrapolated to an infinite number of units.<sup>3</sup> Alternatively, information has been obtained from the behavior of polymers substituted with alkyl or other groups, which both makes them soluble in common solvents, and also modifies the backbone structure or conformation, and hence has profound effects on the electronic and photophysical properties.<sup>4</sup>

Although the initial interpretation of the spectroscopic and photophysical behavior of conjugated polymer systems used a one-electron semiconductor band model, where the transitions are largely delocalized,<sup>5,6</sup> a number of experimental results are not consistent with this,<sup>7</sup> and suggest that for

the description of many of the properties of excited states of conjugated polymers, it is better to consider that excitation is localized within a relatively small conjugation length. Following this line of thought, it is clear that the use of the properties of the corresponding oligomers can provide fundamental information needed to characterize the polymer.

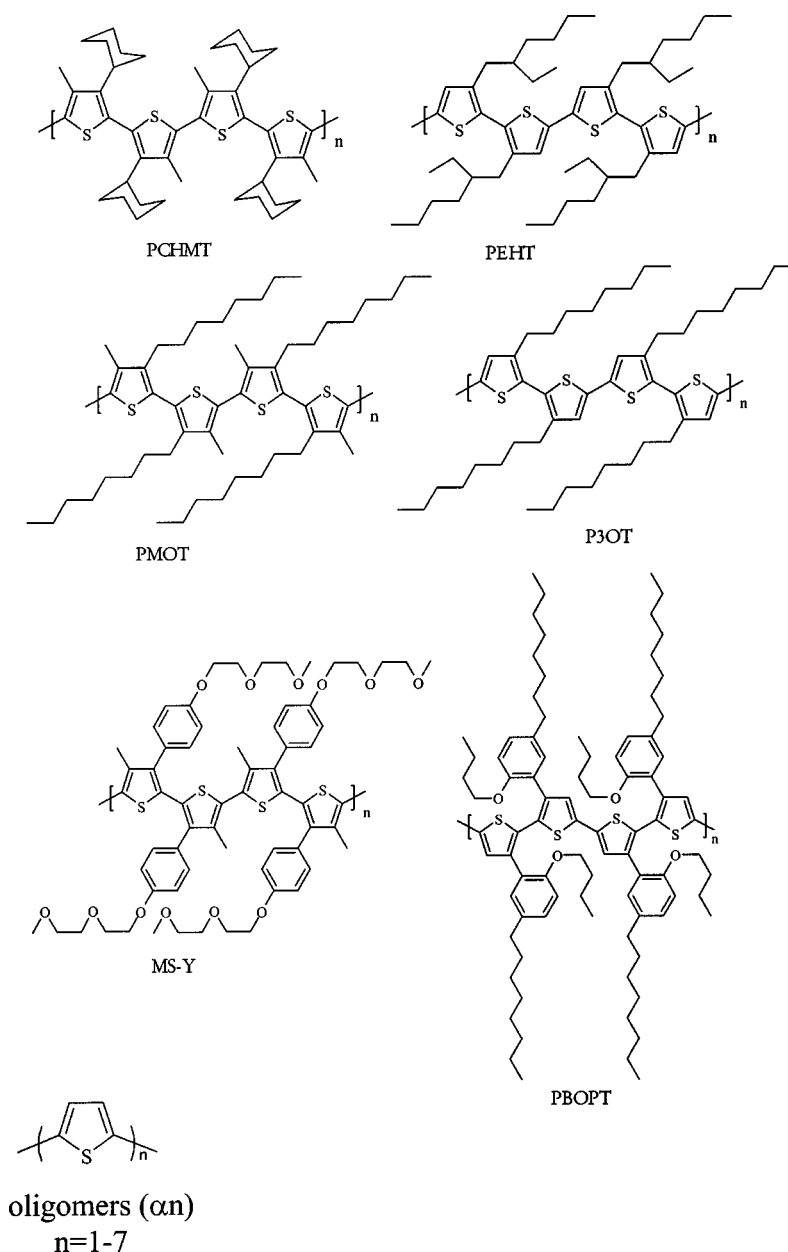
In this work, we will discuss the photophysical properties of six thiophene based polymers and compare the data with the known properties of the related oligomers (from two to seven units).<sup>3,8</sup>

The polymers studied here show different degrees of torsion between the thiophene units, which leads to variations in the effective conjugation length. This is in contrast to the behavior found for the oligothiophenes, where the addition of thiophene units increases the conjugation length.<sup>8</sup> From a comparison between the optical (absorption and emission maxima) and photophysical properties of both sets of compounds, it has been possible to establish the exact conjugation length for the polymers.<sup>3,9</sup> As a consequence of the success of that comparison, it is proposed that certain fundamental quantities of the oligomers, such as their molar extinction coefficients, can be used to further elucidate the photophysical parameters for the polymers (see Scheme 1).

## II. EXPERIMENT

Absorption and fluorescence spectra were recorded on a Shimadzu UV-2100 or Olis-Cary 14 (absorption) and a Jobin-Ivon SPEX Fluorog 3-22 (fluorescence) spectrometer, respectively. All the fluorescence spectra were corrected for the wavelength response of the system. Fluorescence quan-

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Scheme 1. Structures and abbreviations of the studied polymers and oligomers.

tum yields were measured using as standards terthiophene ( $\phi_F=0.07$  in benzene) and heptathiophene ( $\phi_F=0.36$  in benzene).<sup>8,10</sup>

The experimental setup<sup>11</sup> used to obtain triplet spectra and triplet yields consists of an Applied Photophysics laser flash photolysis equipment pumped by the third harmonic (355 nm) of a Nd:YAG laser (Spectra Physics). The laser light arriving at the sample consists of an unfocused beam, and the detection system is at right angles to this excitation beam. A pulsed 150 W Xe lamp is used to analyze the transient absorption. The signal obtained is fed into a HP digital analyzer and transferred to an IBM RISC computer where, with the appropriate software (Applied Photophysics), the optical density (OD) at different wavelengths and different time delays after the flash are collected. When triplet yields were measured special care was taken to have optically matched dilute solutions (abs  $\approx 0.2$  in a 10 mm square cell)

and low laser energy ( $\leq 2$  mJ) to avoid multiphoton and  $T-T$  annihilation effects. Absorption spectra were recorded every 5 or 10 nm averaging 10 shots per wavelength recorded. In all cases the signal was assigned to a triplet state because:

- (i) it was quenched by oxygen,
- (ii) it decayed by first-order kinetics,
- (iii) other possible transients, such as radical ions are generally not produced on photolysis in the nonpolar solvent benzene.

In support of these assignments, where comparison was possible the spectra were very similar to those reported from the triplet states using the pulse radiolysis/energy transfer technique.<sup>12,13</sup>

First-order kinetics were observed for the decay of the lowest triplet state in all cases. The transient spectra were

obtained by monitoring the optical density change at intervals of 5–10 nm over the 300–850 nm range and averaging at least 10 decays at each wavelength.

The triplet formation quantum yields of the thiophene polymers in benzene were determined by the singlet depletion technique followed by actinometry with benzophenone.

The  $\phi_T$  values were obtained by comparing the  $\Delta OD$  at 525 nm of a benzene solution of benzophenone (the standard) and of the polymer (optically matched at the laser wavelength) using<sup>14</sup>

$$\phi_T^{\text{polymer}} = \frac{\epsilon_{TT}^{\text{benzophenone}}}{\epsilon_{TT}^{\text{polymer}}} \cdot \frac{\Delta OD_{\text{max}}^{\text{polymer}}}{\Delta OD_{\text{max}}^{\text{benzophenone}}} \cdot \phi_T^{\text{benzophenone}}. \quad (1)$$

All measurements were carried out at  $20 \pm 2^\circ\text{C}$  and the solutions were degassed with argon.

Fluorescence decays were measured using a home-built TCSPC apparatus with a  $\text{N}_2$  filled IBH 5000 coaxial flash lamp as excitation source, Jobin-Ivon monochromator, Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA. Alternate measurements (1000 counts per channel) of the pulse profile at 337 nm and the sample emission were performed until  $1-2 \times 10^4$  counts at the maximum were reached.<sup>15</sup> The fluorescence decays were analyzed using the modulating functions method of Striker with automatic correction for the photomultiplier “wavelength shift.”<sup>16</sup> The fluorescence decays of MSY and P3OT were obtained with picosecond resolution in an apparatus described elsewhere.<sup>17</sup>

### III. RESULTS

Figure 1 shows the comparative absorption spectra for the polymers (a) and for the thiophene oligomers (b) in benzene solution. It is worth noting that, with the exception of PBOPT, the maxima for all the other polymers fit within the absorption region of the oligomers. With both polymers and oligomers there is a systematic redshift, which in the case of the oligomers is due to the increasing of the number of thiophene units and in the case of the polymers to changes in the steric distortion of the backbone which controls the effective conjugation length.

Although a similar redshift occurs in the fluorescence spectrum, it is much more pronounced in the case of the polymers. As a typical example of this difference, in Fig. 2 the absorption and fluorescence spectra of  $\alpha 2$  and PCHMT in benzene are shown. For similar absorption maxima a Stokes shift of 140 nm occurs for the polymer whereas the much smaller shift of 60 nm is observed with the oligomer. Very marked Stokes shifts with identical absolute values are observed with almost the entire set of polymers studied. The exception seems to be PBOPT, where the Stokes shift is  $\approx 92$  nm (Table I). However, even this is considerably larger than the values found for the oligomers.

Figure 3 shows the fluorescence spectra of PMOT, MSY, PEHT, PBOPT, P3OT and hepathiophene ( $\alpha 7$ ). It can be seen that the broad emission band of  $\alpha 7$  overlaps the maxima of all the polymers, except PMOT.

Figure 4 shows the triplet–triplet spectra of the six polymers studied in benzene solution at 293 K.

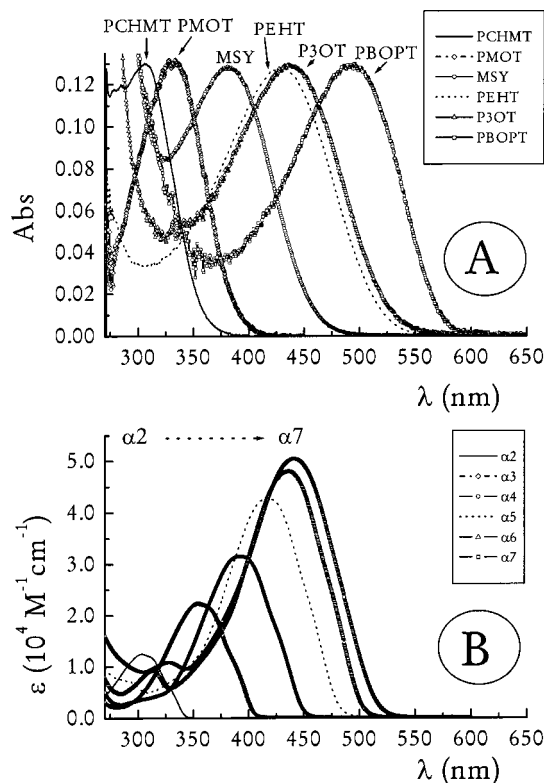


FIG. 1. Absorption spectra of the thiophene polymers (a) and oligomers (b) in benzene solution at  $T = 293$  K.

### IV. DISCUSSION

Since our goal is to extract information on nonradiative processes in polymers from the behavior of the corresponding oligomers, our first consideration will be to compare their absorption and fluorescence maxima. From Table I, it can be seen that comparable absorption maxima are observed for  $\alpha 2$  and PCHMT, for PMOT the value is between  $\alpha 2$  and  $\alpha 3$ , with MSY it is between  $\alpha 3$  and  $\alpha 4$ , for PEHT or P3OT the corresponding values lie between  $\alpha 5$  and  $\alpha 6$ ; and finally PBOPT and  $\alpha 7$  show very similar maxima. However, in the case of the fluorescence spectra, a different sequence of comparisons is found. Thus, the emission maximum for the first two polymers, PCHMT and PMOT, compare with  $\alpha 4$ , while

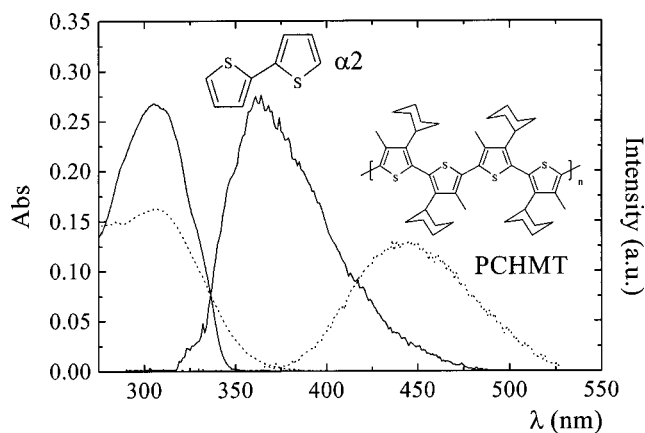


FIG. 2. Absorption and fluorescence spectra of  $\alpha 2$  (—) and PCHMT (···) in benzene at  $T = 295$  K.

TABLE I. Comparative spectroscopic and photophysical data of polymers and oligomers ( $\alpha n$ )<sup>a</sup> of thiophene in benzene solution at  $T=293$  K.

Polythiophene	$\lambda_{\max}$ (abs)	$\lambda_{\max}$ (fluo)	$\lambda_{\max}$ ( $T_1 \rightarrow T_n$ )	$\phi_F$	$\phi_T^b$ (SD)	$\phi_T^c$ (PAC)	$\phi_{\Delta}^d$	$\phi_{IC}$	$\tau_F$ (ns)	$\tau_T$ ( $\mu s$ )	$k_F$ ( $ns^{-1}$ ) ( $\phi_F/\tau_F$ )	$k_{ISC}^e$ ( $ns^{-1}$ )	$k_{IC}^f$ ( $ns^{-1}$ )	$\alpha n$	$\lambda_{\max}$ (abs)	$\epsilon$ ( $M^{-1} cm^{-1}$ )	$\lambda_{\max}$ (fluo)	$\lambda_{\max}$ ( $T_1 \rightarrow T_n$ )	$\phi_F$	$\phi_T$	$\phi_{IC}$
PCHMT	304	444	612	0.02 <sub>4</sub>	0.42 ( $\alpha 1$ )			0.55 <sub>6</sub>	0.23	14 <sup>g</sup>	0.10	1.83	2.42	$\alpha 2$	303	12440	362	385	0.02 <sub>6</sub>	0.99	$\approx 0$
PMOT	333	477	670	0.04 <sub>7</sub>	0.34 ( $\alpha 3$ )	0.66	0.69	0.61	0.52	62 <sup>h</sup>	0.09	0.65	1.18	$\alpha 3$	354	22080	426	460	0.07	0.95	$\approx 0$
MSY	382	524	742	0.06	0.17 ( $\alpha 4$ )	...	...	0.77	0.2 <sup>i</sup>	14 <sup>g</sup>	0.30	0.85	3.85	$\alpha 4$	392	31560	478	560	0.18	0.73	0.09
PEHT	428	567	830	0.26	0.18 ( $\alpha 5$ )	...	...	0.56	0.54	6.4 <sup>g</sup>	0.48	0.33	1.04	$\alpha 5$	417	42670	482	630	0.34	0.59	0.07
P3OT	438	576	825	0.27	0.21 ( $\alpha 6$ )	0.77	0.41	0.52 (SD)	0.2 <sup>i</sup>	8 <sup>g</sup> 21 <sup>h</sup>	1.35	1.05	2.6	$\alpha 6$	436	47910	502	685	0.44	...	...
				0.77 ( $\alpha 3$ )				$\approx 0$ (PAC)				3.85	$\approx 0$								
PBOPT	495	587	833	0.30	0.27 ( $\alpha 7$ )	0.47	0.54	0.43 (SD)	0.56	14 <sup>g</sup> 57 <sup>h</sup>	0.54	0.48	0.77	$\alpha 7$	441	50500	522	720	0.36	$\approx 0.6$	$\approx 0.04$
								0.23 (PAC)					0.41								

<sup>a</sup>Data from Refs. 8 and 10.<sup>b</sup>Intersystem crossing quantum yields obtained in this work by the singlet depletion technique (SD). In brackets is the oligomer used as "standard."<sup>c</sup>Data from Ref. 13 using time-resolved photoacoustic calorimetry (PAC) in conjunction with  $\phi_F$  and singlet and triplet state information.<sup>d</sup>Quantum yields for singlet oxygen formation, data from Ref. 20.<sup>e</sup>For the determination of the ISC rate constant ( $k_{ISC} = \phi_T/\tau_F$ ) the averaged value of the two fluorescence decay times was considered. In the case of PBOPT the two values correspond to the different values for  $\phi_T$  obtained with PAC and SD techniques.<sup>f</sup>For the determination of the IC rate constant, [ $k_{IC} = \phi_{IC}/\tau_F = (1 - \phi_F - \phi_T)/\tau_F$ ], when two values are presented, these correspond to the different values for  $\phi_T$  obtained with PAC and SD techniques.<sup>g</sup>This work.<sup>h</sup>Data from Ref. 12, based on pulse radiolysis experiments.<sup>i</sup>Averaged value for a double exponential decay behavior. See the text for more details.

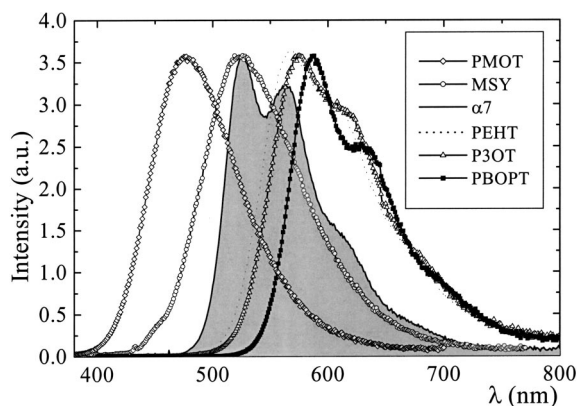
with the next two polymers (MSY and PEHT),  $\alpha 7$  is the equivalent oligomer. In all these cases there is a departure from the absorption analogy, where there was clearly a gradual, stepwise change of the absorption maxima of the polymer with the oligomer. For P3OT and PBOPT, the polymers emit at longer wavelengths than all the oligomers studied and there is no possible correspondence between their fluorescence wavelength maximum ( $\lambda_{\max}^{\text{fluo}}$ ). This situation is even more pronounced when we try to compare the  $T_1 \rightarrow T_n$  maxima, where only PCHMT has a corresponding oligomer:  $\alpha 5$ . With both fluorescence and triplet absorption this seems to reflect a situation where the polymer possesses much longer effective conjugation segments in the excited  $S_1$

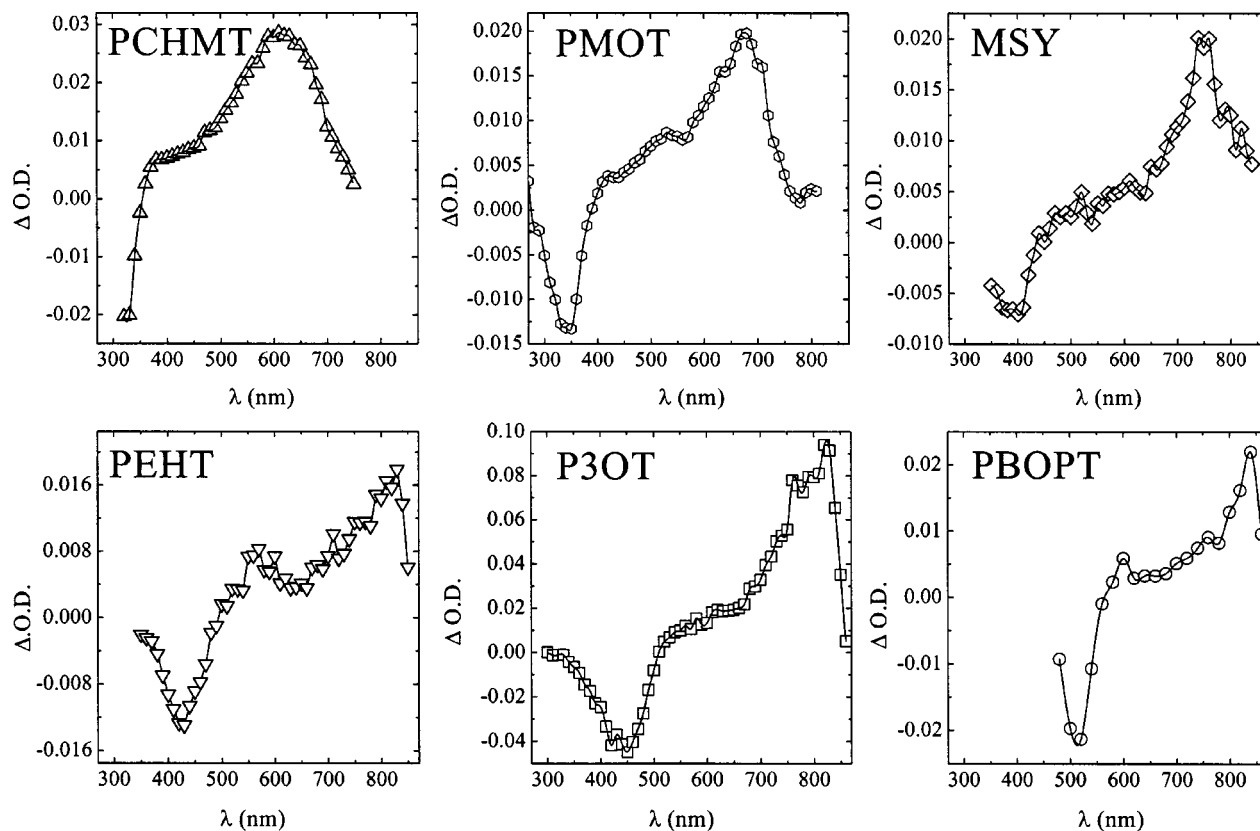
and triplet states than are displayed by the oligomers. Based on the above-mentioned comparisons, it is tempting to consider that, in photophysical terms, the  $\alpha 7$  oligomer already behaves truly as a polymer, since its absorption overlaps the maxima of all the polymers considered, and that, excluding P3OT and PBOPT, the same applies with its broad emission band.

We will now consider the determination of the singlet-triplet intersystem crossing yield for the polymers using data from the oligomers. PMOT will be used as a typical practical example. From the transient triplet absorption spectra shown in Fig. 4, we can observe depletion in the ground state absorption around 500 nm. Consequently, the singlet depletion technique can be used to obtain the extinction coefficient of the transient triplet transition for PMOT, according to the well-known relationship:<sup>18</sup>

$$\epsilon_{S_0 \rightarrow S_1} \times \Delta OD_T = \epsilon_{T_1 \rightarrow T_n} \times \Delta OD_S, \quad (2)$$

where  $\Delta OD_S$  and  $\Delta OD_T$  (obtained from the spectra in Fig. 4) are, respectively, the optical density changes in the singlet and triplet maxima in the transient spectra and the molar extinction coefficients for the ground state singlet absorption and the triplet to triplet transition are given by  $\epsilon_{S_0 \rightarrow S_1}$  and  $\epsilon_{T_1 \rightarrow T_n}$ . However, as will be discussed later the  $\epsilon_{S_0 \rightarrow S_1}$  value is unknown and difficult to define for the polymer. If we consider the absorption maximum for PMOT, as previously discussed we are led to the corresponding oligomer being between  $\alpha 2$  and  $\alpha 3$ . For the singlet depletion technique we can use the value for  $\alpha 3$  in benzene  $\epsilon_S$

FIG. 3. Fluorescence spectra of PMOT, MSY, PEHT, PBOPT, P3OT, and  $\alpha 7$  in benzene at  $T=293$  K.

FIG. 4. Transient triplet-triplet absorption spectra of the polythiophenes in benzene at  $T = 293$  K.

$= 22\,540\text{ M}^{-1}\text{ cm}^{-1}$ ,<sup>8,10</sup> which, by using Eq. (2), leads to  $\epsilon_T = 28\,980\text{ M}^{-1}\text{ cm}^{-1}$ . The use of the actinometer benzophenone and Eq. (1) then provides the  $\phi_T$  value for the polymer in question, which for optically matched solutions, with  $\epsilon_T^{\text{benzophenone}} = 7200\text{ M}^{-1}\text{ cm}^{-1}$  and  $\phi_T(\text{benzophenone}) = 1$ ,<sup>19</sup> leads to  $\phi_T(\text{PMOT}) = 0.34$ . This can be compared with the values obtained in benzene solution by photoacoustic calorimetry (PAC) of 0.66, and by sensitized singlet oxygen formation of  $\phi_\Delta = 0.69$ .<sup>20</sup>

Table I summarizes the values for all the other polymers. In parentheses are indicated the appropriate oligomers considered for the  $\epsilon_S$  values. Also shown are the  $\phi_T$  values obtained by PAC. It can be seen that there are some relatively large discrepancies between the values determined by these two different techniques. Some possible explanations will be discussed later.

*Some considerations on  $N_{\text{effective}}$ .* The effective number of double bonds involved in the  $\pi$ -electron delocalization has been considered previously.<sup>9</sup> This used a correlation for the oligomers based on a linear relationship between the peak absorbance and the number of repeat units.<sup>3</sup> Monkman *et al.*<sup>9</sup> suggested the direct comparison between the band edge wavelength of the polymer and the data obtained from this correlation for the thiophene oligomers<sup>3</sup> as a way of determining the “effective” conjugation length,  $N_{\text{eff}}$ , in polythiophenes. In practical terms  $N_{\text{eff}}$  is the number of double bonds. Using this procedure, they were able to predict an effective repeat unit number for any polymer under consideration. Since for both polymeric and oligothiophenes the absorption spectra appear to be Franck-Condon forbidden in

shape,<sup>21</sup> we have considered that this comparison is better if the wavelength maxima rather than band edges are used. The application of Franck-Condon band shape analysis to the inhomogeneously broadened bands of conjugated polymers is questionable, since these consist of the absorptions or emissions of conjugation segments of various lengths. However, with the systems studied the energy separation between the absorption edge and maxima is only  $\sim 25\%$  greater in the polymers than that in the oligomers, and the slight difference this will have on the choice of oligomer for a particular polymer will not significantly affect the values calculated for the triplet quantum yields. This change to using the maxima instead of the edge of the band<sup>9</sup> takes on a special meaning for the highly twisted polymers, since if we consider the band edge wavelength for the case of PMOT, we obtain an  $n_{\text{eff}}$  value of 2.8, corresponding to something in between a single thiophene and bithiophene, which does not appear likely.

Although the procedure of relating the polymers to corresponding oligomers has its limitations, since it reduces predictions to the use of a single property of the oligomers (the wavelength maxima), it is logical and appears applicable to the properties required from ground-state absorption spectra for determination of triplet quantum yields by the singlet depletion technique.

We now consider further aspects of the determination of  $\phi_T$  by using the singlet depletion method. As previously indicated, the comparison with the behavior of well-characterized oligomers provides a useful way to predict properties of the polymers.<sup>3</sup> For example, the determination of the extinction coefficient ( $\epsilon$ ) of a polymer is not a trivial



matter. As has been indicated previously,<sup>9</sup> because of the high molecular weights of typical conjugated polymers, the classical way using absorbance and molar concentration leads to impossible values greater than  $1 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ ! Other workers<sup>4</sup> have assumed that the monomer unit molecular weight should be used as the MW of the polymer for determining  $\epsilon$ . However, this is physically nonrealistic. It therefore seems to us much more reliable to use data from a related, well-characterized oligomer, having similar spectral characteristics and wavelength absorption maximum to the polymer.

We focus now on the way to obtain the correct oligomer based on the  $N_{\text{eff}}$  of the polymer. According to the  $N_{\text{eff}}$  obtained by Monkman *et al.*<sup>9</sup> we can see that PBOPT possesses an  $N_{\text{eff}}=19.7$ . This is equivalent to having  $\approx 20$   $\pi$  electrons, meaning that we have 10 double C=C bonds, i.e., the oligothiophene with 5 rings,  $\alpha 5$ . If this is the case, in the determination of  $\phi_T$  by the singlet depletion technique, we should use the  $\epsilon_S$  for  $\alpha 5$  ( $42\,670 \text{ M}^{-1} \text{ cm}^{-1}$ ),<sup>8,10</sup> which would then lead to a value of  $\epsilon_T=44\,610 \text{ M}^{-1} \text{ cm}^{-1}$  and consequently  $\phi_T=0.32$ . This can be compared with the value 0.27 determined with  $\alpha 7$  as “standard.” Within the 15% error normally observed for a  $\phi_T$  determination the two values are in excellent agreement. Using either of the values for  $\phi_T$  (0.27 with  $\alpha 7$  as “standard” or 0.32 with  $\alpha 5$  as “standard”) we obtain very similar values for  $\phi_{\text{IC}}$  of 0.43 or 0.38. This shows that internal conversion is a significant pathway with polythiophenes, in obvious contrast to the oligothiophene situation where  $\phi_T + \phi_F \approx 1$ .<sup>8</sup>

We will now address the nature of the other nonradiative channel for decay of the singlet excitations. As discussed by Beljonne *et al.* for oligothiophenes,<sup>22</sup> nonradiative decay can occur *via* internal conversion (IC) to the ground state, intersystem crossing (ISC) to the triplet manifold, singlet fission (SF), or charge separation (CS). SF has been observed for the two different phases of poly(diacetylene) in solution<sup>23</sup> and suggested for  $\alpha$ -sexithienyl in films.<sup>24</sup> However, this requires either biphotonic excitation or excitation at high energies, both of which are unlikely in our experiments. Further, SF leads to triplet state formation, which would be indistinguishable from ISC. CS is expected to be more important in films than in solution.<sup>22</sup> Further, if any charge separated species were formed, this would be expected to lead to long-lived absorption of radical cations in oxygenated solution. No long-lived transients were observed in flash photolysis studies of aerated solutions of the polythiophenes. We, therefore, favor ISC and IC as the nonradiative decay routes for the singlet excited poly(thiophenes) in solution.

In the oligothiophene case, the absence of the internal conversion deactivation process was attributed to the quinoidal-like structure of the  $S_1$  state, which then results in the absence of any significant coupling between the modes of the excited state, planar quinoidal-like structure, and the twisted, single-bonded ground state.<sup>8</sup> In the case of the polythiophenes, it is likely that a significant contribution of the alkyl chain will result in coupling of these modes of the  $S_1$  structure with the twisted single-bonded ground state. Based on the Franck–Condon forbidden shape of the absorption spectra and the large Stokes shifts observed, there appear to

be clear differences in geometries between the ground and first singlet excited states of the polymers. The  $S_1$  structure is likely to be similar to that found for the oligothiophenes. However, with the polymers the presence of the bulky substituent groups will probably mean that the excited state is less planar than with the oligomers. The alkyl chains will also induce an important effect on the nonradiative processes by adding new coupling modes that will allow the molecule to “deactivate” through internal conversion. This is not completely unexpected since with the  $\alpha 7$  oligomer (which is in fact the dibutylheptathiophene) the sum  $\phi_T + \phi_F$  was found to be less than 1,<sup>8</sup> indicating that the alkyl chains are potentially influencing the deactivation pathway of this molecule. Similar effects have previously been observed for small substituted aromatic molecules.<sup>25,26</sup>

From Table I, we can also see some differences in  $\phi_T$  values obtained with the techniques used. The photoacoustic calorimetric method<sup>13</sup> generally seems to give larger values than singlet depletion. We will compare two particular cases: P3OT and PBOPT. In the first case we match the  $\phi_T$  values with both techniques if we use  $\alpha 3$  as the “standard” for  $\epsilon_S$  of the polymer. In that case the quantum yield for internal conversion would be equal to zero. Based on the general pattern found for the other polymers, this does not seem very realistic. If we consider the “true standard,” i.e.,  $\alpha 6$ , we are led to a value for  $\phi_{\text{IC}}$  of 0.52. The other comparable situation occurs with PBOPT. If we consider the  $\phi_T$  obtained by SD we get  $\phi_{\text{IC}}=0.43$ , whilst if we consider the PAC data we get  $\phi_{\text{IC}}=0.23$ . In this case, again we are tempted to believe the value obtained by the SD technique is more reliable. This seems logical according to the energy gap law<sup>25</sup> where a smaller  $S_0-S_1$  energy gap will correspond a faster internal conversion process. From Table I, since the values of  $\phi_{\text{IC}}$  for the other polythiophenes are always  $\geq 0.52$ , it seems that the value of 0.43 for PBOPT is more trustworthy.

The calculation of nonradiative rate constants for the polymers requires use of the measured fluorescence lifetimes. With two of the compounds, MSY and P3OT, biexponential decays were observed (Table I). Nonexponential fluorescence decays have previously been reported in chloroform solution with certain polythiophenes having bulky substituents, and has been suggested to be associated with inhomogeneities with different conformations and lifetimes.<sup>4</sup> Nonexponential decay has also been reported in a photoinduced absorption study of the P3OT lowest excited singlet state.<sup>27</sup> This has been attributed to one-dimensional excitation diffusion to different quenching sites along the polymer chain. Neither of these explanations seems completely satisfactory and a detailed explanation awaits more detailed time-resolved emission spectral studies on well-defined polymers having different conjugation segments. One additional explanation might be found in the possible coexistence of *trans* and *cis* geometries of these polymers. For the thiophene oligomers it is quite well accepted that the *all-trans* geometry is adopted by the thiophene rings.<sup>8</sup> However for the oligomers of the corresponding polyfurans there is evidence that *cis* and *trans* geometries can coexist.<sup>28</sup> We are currently undergoing a study with trimer structures of PPV derivatives where small “contaminations” of the *cis* isomer coexist with the

major *trans* conformer. This will undoubtedly provide some evidence on the potential influence of the *cis* versus *trans* conformers and will be the subject of a forthcoming publication. However, as our primary goal was to determine the importance of nonradiative pathways in the decay of the excited singlet states of polythiophenes, we have used the weighted average of the lifetimes where nonexponential decays are observed to calculate the rate constants of internal conversion and intersystem crossing. The calculated values are also given in Table I. With aromatic molecules, the rate of radiationless decay between two electronic states depends on the energetic separation between them.<sup>26</sup> Similar energy gap correlations have recently been suggested for  $S_1-T_1$  (Ref. 20) and  $T_1-S_0$  (Ref. 29) intersystem crossing in conjugated polymers. To see if such behavior is applicable here, logarithmic plots were made of the rate constants for internal conversion and intersystem crossing against the appropriate energy gap. However, no correlations were observed. It is likely with the polythiophenes, as suggested earlier, that coupling with rotational modes of the substituent side chains also plays a major role in nonradiative deactivation.

## V. CONCLUSIONS

The photophysical characteristics of six thiophene polymers have been investigated in solution, with particular emphasis on the determination of the dominant pathways in the excited state decay. It was shown by using data for the equivalent oligomers that it is possible to obtain  $S_1 \rightarrow T_1$  intersystem crossing quantum yields. From these and fluorescence yields, information has been obtained on internal conversion. In contrast to what has been found with the oligomers, the  $S_1 \leadsto S_0$  internal conversion process is the dominant deactivation process in the polymers. This is suggested to be due to the efficient coupling promoted by the alkyl chains (present in the polymers), which add new coupling modes, thus allowing the molecule to deactivate via this channel. Although the behavior of conjugated polymers in thin film light emitting devices is likely to depend mainly on interchain processes, these results indicate that intrachain radiationless decay cannot be ignored in their overall luminescence efficiency.

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