

# Photophysics of Substituted Polythiophenes

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We have measured the photoluminescence quantum yield and photoluminescence lifetime for a series of polythiophenes, in solution, and the quantum yield for the same polymers in thin films. Depending on the different substituents, quantum yields ranged between 0.38 and 0.01 for polymers dissolved in chloroform; for spin-coated films, quantum yields as high as 0.24 were measured. We observe that increasing the bulkiness of the substituent increases the quantum yield in solution. For spin-coated films an increased ordering can either increase or decrease the quantum yield, depending on the separation of the conjugated backbones. Polythiophenes in which the electronic band gap is increased by steric hindrance show very low quantum yield, both for film and solution. This low quantum yield originates from a fast nonradiative decay.

## Introduction

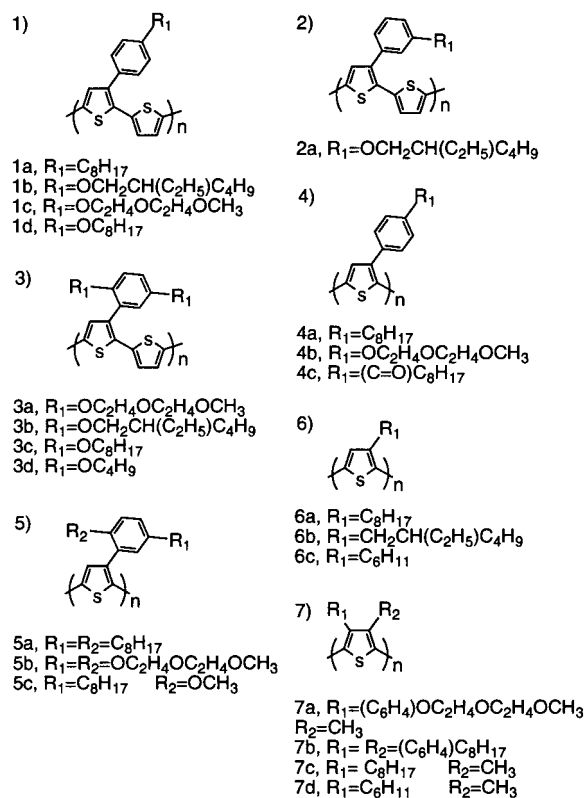
Conjugated polymers have attracted great interest due to their electrooptical properties. Polythiophenes (PT) constitute one class of conjugated polymers that has been incorporated in electroluminescent devices such as polymer LEDs,<sup>1</sup> microcavities,<sup>2</sup> solar cells,<sup>3</sup> and recently, optically pumped lasers.<sup>4</sup> Oligothiophenes (OT) have also been studied extensively due to their high third-order nonlinearity<sup>5</sup> and well-defined chemical structure which make them well suited for molecular electronics.<sup>6</sup> Introducing side chains on the PT backbone makes the polymer soluble and processable. Furthermore, side chains have a profound influence on the properties of the polymer such as the band gap and the yield of photoluminescence (PL). In PL the excitations are singlet excitons which can decay to the ground state radiatively, and the PL yield is decreased from unity by different competing nonradiative losses of singlet excitons. For PT, intersystem crossing (ISC) from singlet to triplet states reduces the PL yield; the transition between triplet state and ground state is dipole forbidden or weakly allowed. The back transition rate from triplet to singlet is slow due to the low energy of the triplet level relative to the first excited singlet level. Experimentally it has been shown that the triplet yield decreases with increasing length of OTs, in solution, and reaches a constant level for 5 repeating units.<sup>7</sup> The PL lifetime of sexithiophene has been reported, 1.0 ns,<sup>7</sup> 0.88 ns<sup>8</sup> together with the PL yield, 0.44,<sup>7</sup> 0.42<sup>8</sup> whereas for regioregular (95%) poly(3-dodecylthiophene) (P3DT) a PL lifetime of 0.5 ns and a PL yield of 0.41 is reported.<sup>9</sup> The ISC lifetime of regiorandom poly(3-octylthiophene) (P3OT), regioregular poly(3-hexylthiophene) (P3HT), as well as 12 repeat unit oligothiophene was measured to be 1.2 ns from the rise of the photoinduced absorption (PA) of the triplet,<sup>10</sup> independent of the regularity of the polymer/oligomer. In the poly[*p*-phenylene–vinylene] (PPV)-system Gettinger et al. have shown that the more rigid polymers had a longer intrinsic persistence length, and longer

persistence length gave a higher PL yield than short persistence length.<sup>11</sup> Measurement of the intrinsic persistence length of polyalkylthiophenes (P3OT and P3HT) showed values around 2.1 nm,<sup>12</sup> corresponding to 5–6 repeating thiophene units, which is shorter than an estimated conjugation length of P3HT, of 10 repeating units,<sup>13</sup> from the red-shift of OT spectra with increasing numbers of thiophene units.

For thin films, additional quenching occurs due to increased mobility of the exciton. A great number of measurements have been made to understand these dynamical properties of the exciton in thin films of conjugated polymers, by time-resolved PL,<sup>14</sup> time-resolved photoinduced absorption,<sup>15,16</sup> and combined with theoretical simulations.<sup>17,18</sup> The packing of chains is of great importance for the mobility of the excited state; in addition it may influence the electronic structure in the solid film. In sexithiophene films, crystallographic data support a close-packed arrangement of the molecules and the transition dipoles of the molecular crystal will interact, splitting the exciton levels and affecting the transitions between the ground state and the excited state.<sup>19,20</sup> When such dimers are formed between molecules with parallel dipoles, the transition to one of the levels will be forbidden. In conjugated polymers and molecules the exciton may form excimers<sup>21,22</sup> where one excited chromophore interacts with a nonexcited chromophore to form an excited-state complex. If the excimer has low PL yield the excimer formation lowers the PL yield of the material.

We report on the quantum yield, in solution and thin films, for polythiophenes with different substituents. In the following, we have organized the text to follow the different classes of substitution. Together with the optical absorption and emission we trace the effects of different substituents on the PL yield. We have grouped the polymers according to their substituents as shown in Figure 1. Most of the polymers are substituted with phenyl groups which make further substitution on the phenyl ring much more diverse than by substituting directly on the polymer backbone. We will show that the position of the substituent on the phenyl ring strongly influences the morphology of the ordered phases (crystal structure) of the polymer. In

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**Figure 1.** Molecular structure of polythiophenes used in this study. All side chains not assigned are hydrogen atoms. The side chains for polymers **7a** and **7b** are attached at the para position of the phenyl group. Polymers **6c** and **7d** have cyclohexyl side groups.

groups **1–3** we find poly-bithiophenes which are substituted at position 3 of the bithiophene unit; hence no head-to-head coupling of the substituents will occur in these polymers. With random coupling of the bithiophene units the polymer will also be irregular and thin films made of these polymers will therefore be amorphous. Polymers in group **1** are substituted only at position 4 of the phenyl group and group **2** is substituted at position 3, whereas group **3** is substituted both at positions 2 and 5 of the phenyl group. With substituents on every thiophene unit the polymer will not necessarily be amorphous and the degree of crystallinity will depend on the regularity as well as the nature of the substituents. The conditions of preparation of the film will also influence the crystallinity. In groups **4** and **5** we have polythiophenes with analogue substituents to the poly-bithiophenes in groups **1** and **3**. Polymers in group **4** are close to amorphous when spin-coated from chloroform but they show quasi-thermo-chromic properties, an irreversible transition to a more ordered and red-shifted phase as a result of annealing or exposing the film to chloroform vapor. These transitions are studied, considering how the PL yield is altered when the transitions occur. For polymers in group **5** the ordered phase generally has much higher PL yield than for polymers in group **4**, which can be explained by the different substitution. In group **6** we find not only P3OT but also two other polythiophenes with different substitutions which prevent the polymer from forming an ordered phase in the thin film. Finally, in group **7**, four polythiophenes substituted at both positions 3 and 4 of the thiophene unit are shown to have very low PL yield due to some nonradiative process related to the twisted backbone.

## Experimental Section

Molecular structures of the polymers used in this work are shown in Figure 1. Polymerization of the monomers was done

by adding  $FeCl_3$  and then carefully dedoping with  $NH_4OH$  and EDTA. More detailed description of the synthesis can be found elsewhere (**1a**, **7d**),<sup>1</sup> (**1b–d**, **2a**, **3a–d**, **4b,c**, **5c**, **7b**),<sup>23</sup> **4a**,<sup>24</sup> **6c**.<sup>25</sup> Absorption spectra were measured on a Perkin-Elmer  $\lambda 9$  spectrometer, and emission spectra were measured with an Oriel Instaspec IV diode matrix spectrometer. PL yields and spectra were measured with the polymer dissolved in chloroform with concentrations adjusted to give an optical density 0.2 or lower in a 10 mm optical glass cell. Thin films were spin coated from chloroform solutions, 5–10 mg/mL, on  $24 \times 40$  mm<sup>2</sup> quartz substrates giving optical densities of 0.1–0.3. Time-resolved PL experiments are made with a photon-counting streak camera in synchroscan mode, and all samples were excited with 300 fs pulses from a frequency-doubled Ti:Sapphire laser with a repetition frequency of 75 MHz. All samples were excited at 380 nm, and detection was made with magic angle polarization. Average excitation power in the time-resolved PL measurements was approximately 100 mW, and a spot-size diameter of around 3 mm was used. To avoid contact with air polymer thin-films were sandwiched between glass substrates. Solutions were not de-gassed before experiments because the PL quantum yield do not change for de-gassed samples, but quantum yields were measured before and after the time-resolved PL measurements to make sure that no photodegradation occurred during the experiment. The response of the system was 20 ps, and the decay curves were deconvoluted with an exponential decay giving a time resolution of 20 ps. The radiative lifetime,  $\tau_{rad}$ , is calculated from the following well-known relations:

$$\tau^{-1} = \tau_{rad}^{-1} + \tau_{nrad}^{-1} \quad (1)$$

$$Q = \tau \cdot \tau_{rad}^{-1} \quad (2)$$

where  $\tau$  is the PL lifetime,  $\tau_{nrad}$  is the nonradiative lifetime, and  $Q$  is the PL quantum yield. If the PL decay is nonexponential, a sum of exponentials is used for fitting the measured decay. With a nonexponential decay, the radiative lifetime can be calculated by calculating an average PL lifetime (weighting respective lifetimes by their amplitudes) which would give a correct value if the radiative lifetime is constant, i.e., no emission from aggregates occurs and the quantum yield of forming intrachain excitons is equal to unity. Hence, the nonexponential decay must be caused by a nonexponential nonradiative decay or by several different nonradiative decay channels.

Quantum yields were measured in a custom-built integrating sphere made by Labsphere. The sphere has a diameter of 4 in. and an input port (1 in.) at the equator. Samples are mounted in a sample holder which can be put in two positions: one is located where the excitation beam (monochromatized light from a halogen lamp) impinging through the entrance hole will hit the sample directly, and another where the sample is out of the excitation beam. The sample holder can be rotated around the north pole so that the sample can be tilted at an angle ( $10^\circ$ ) and light reflected at the sample will not escape out of the entrance hole. Light is detected through an output port (0.5 in.) at the south pole protected from direct illumination from the sample and from the backside of the sphere, where the excitation beam hits the sphere wall, with a baffle. The output port of the sphere is connected to an Oriel Instaspec IV diode matrix spectrometer with a liquid light guide. The spectra recorded with the spectrometer are corrected for the spectral response of the system, and then converted from intensity to photon quanta per channel by dividing each channel by the photon energy of the same channel. The number of quanta is then the area under the recorded spectra.

A calibrated 45 W halogen lamp from Optronic Laboratories is used for measuring the spectral response of the sphere light guide spectrometer as one system. In the blue region of the spectrum, compensation for the stray light inside the spectrometer is necessary since the calibrated lamp has low intensity in that region. Stray light compensation is done by measuring the spectrum of the lamp with a LWP-filter and then subtracting the stray light measured in the spectral region where the LWP-filter cutoff (wavelength 395 nm) from a spectrum measured without the LWP-filter.

Photoluminescence quantum yield is defined as the ratio of the number of emitted quanta to the number of absorbed quanta. We calculate the absorption in the sample by measuring the number of quanta at the exciting wavelength when the excitation hit the sample directly,  $L_i$ , and the number of quanta at the excitation wavelength when the excitation first hit the sphere wall,  $L_o$ , and the absorption is then given by<sup>26</sup>

$$A = \left(1 - \frac{L_i}{L_o}\right) \quad (3)$$

The number of absorbed quanta, when the excitation beam hits the sample, is  $A$  times the number of quanta in the excitation beam with no polymer in the sphere,  $L_e$ . To obtain a correct value for the absorption, no changes of sphere geometry are made between the measurement with and without polymer inside the sphere. Therefore, when measuring on an empty sphere, we use an empty optical glass cell filled with solvent in the sample holder if we measure solutions and a quartz substrate if we measure thin films. One advantage of measuring the absorption inside the sphere is that light scattered in the polymer is collected by the sphere walls. The number of emitted quanta we take as the area under the emission spectrum (compensated for the stray light originating from the exciting light scattered in the spectrometer). Correcting for indirectly absorbed light (from the sphere walls) the quantum yield is given by<sup>26</sup>

$$Q_{PL} = \left(\frac{E_i - (1 - A)E_o}{L_e A}\right) \quad (4)$$

where  $E_i$  is the number of quanta emitted when the excitation beam hit the sample directly, and  $E_o$  is the number of quanta emitted when the excitation beam hit the sphere-wall first.

The advantage with using the CCD array with a monochromator is that one measures both absorption and emission simultaneously, and thereby minimizes errors due to degradation, and also avoids the use of cut-off filters which may fluoresce and/or be insufficiently absorbing.

Errors in the quoted PL yield originate from imperfections in the sphere; caused by the sphere being quite small, and a different material being used in the sample holder, which has lower reflectance than the sphere walls. Further errors originate from uncertainties in the spectral correction and stray light inside the spectrometer. With thicker films, self-absorption due to waveguiding in the film may be a problem if the absorption and emission spectra overlap. Errors due to fluctuation of excitation light and to differences in position of the sample inside the sphere are minimized by repeating the measurement several times. Some degradation of the material is seen for the thin films during the measurement even though the exciting intensity is low (less than  $50 \mu\text{W}/\text{cm}^2$ ). To avoid degradation, PL yields are measured on samples directly after the preparation. We estimate the errors for the PL yields to be 1/5 of the measured value if the yields are above 5% and 2/5 of the measured value

if the yields are 5% and lower. It should be noted that the relative yields of PL for different polymers are much more accurate than the absolute values.

## Results and Discussion

The common aspect for all the different polythiophenes in this study are due to the creation of an excited state by optical absorption, followed by radiative and nonradiative transitions to the ground state. In sequence, these processes are reflected in a well-structured or nonstructured absorption spectrum and also in the emission spectrum. Structureless absorption is consistent with a low barrier of torsional rotation around the C–C bond between adjacent thiophene dyads, for the ground state, which makes the distribution of conjugation lengths broad and thereby broadens the absorption spectrum. In the excited state, the more quinoid electronic structure of the main chain stiffens the C–C bond between subsequent thiophene units and thereby decreases torsional motion and therefore, vibronic structure can be discernible in the emission spectrum but not necessarily so in the absorption spectrum. In some cases, when the chains are fixed in an ordered thin-film structure, vibronic structure can be well pronounced in thin film absorption spectra as well.

Measuring the PL decay of the red polymers, with low Stokes shift, dissolved in chloroform we find that the PL lifetime is around 0.6 ns and is not changed by the substituents (Table 3). When the backbone is twisted, by bulky substituents substituted in 3-, or 3- and 4-positions of the thiophene ring, the PL decay is faster and nonexponential. The origin of the nonexponential decay is not clear, but in such polymers there will be inhomogeneities with different conformations and different lifetimes, as well as transport of the excitation to segments with low energy. We cannot rule out isomerization around twisted segments giving a nonexponential decay. Fast components in solution have also been found by Kraabel et al. in regiorandom P3OT in xylene which showed fast components in the photo-induced absorption signal ( $t < 50$  ps).<sup>10</sup> They could model the decay as a one-dimensional diffusion among randomly distributed quenching sites, but the origin of these quenching sites still remains unclear.

Absorption and emission spectra for thin films have the same spectral shape as for solution, but both emission and absorption spectra are red-shifted when going from solution to thin film. The physical origin of the red-shift can be a different conformation of the polymer chains in the film causing a different electronic structure, or it may be due to overlapping of the wave functions on adjacent chains causing changes of electronic structure due to splitting of orbitals. It may also be a consequence of changing the refractive index giving rise to a solvatochromic shift. The refractive index of the solvent is  $n = 1.44$ , and that of the polymer film is typically higher than 1.9 at both emission and absorption wavelengths, and is influenced by the number of side chains.

When comparing the kinetics of PL in film and solution, not only is the change of electronic structure possible, but also the probability of excitation transfer is much increased.

The high reduction of the PL quantum yield found for films of the polymers in groups 1–3 when going from solution to thin film seems to be caused by the fast, highly nonexponential PL decay of the thin film (Figure 3).

Such complex behavior of the decay in conjugated polymer films has been well described by exciton migration in an inhomogeneously broadened density of states.<sup>17,18</sup> In such models the transport of excitons is modeled by Förster transfer



**TABLE 1: Absorption and Emission Data and Quantum Yields in Solution, Molecular Dispersion Data, as well as Regularity of Thiophene Polymers**

polymer	absorption eV (nm)	FWHM <sup>a</sup> eV	$\epsilon^b$ (10 <sup>4</sup> l/mol cm)	emission eV (nm)	$Q_{PL}$	$M_n$ (10 <sup>3</sup> )	$M_w$ (10 <sup>3</sup> )	regularity
1a	2.62 (474)	0.80	0.86	2.12 (585)	0.25	23	52	
1b	2.62 (474)	0.74	0.80	2.13 (583)	0.26	2.9	8.3	
1c	2.65 (469)	0.74	0.77	2.14 (579)	0.28	2.7	16.3	
1d	2.59 (479)	0.73	0.87	2.13 (581)	0.25	2.9	19	
2a	2.63 (470)	0.76	0.77	2.13 (582)	0.31	3.2	9.7	
3a	2.51 (495)	0.62	1.01	2.12 (584)	0.38	13.6	42	
3b	2.59 (480)	0.70	0.86	2.14 (579)	0.36	3	7.3	
3c	2.49 (497)	0.62	1.04	2.13 (581)	0.31	24.5	105	
3d	2.54 (488)	0.66	0.95	2.13 (581)	0.37	6	62	
4a	2.68 (463)	0.84	0.71	2.11 (587)	0.18	8	50	0.91
4b	2.69 (461)	0.74	0.76	2.12 (585)	0.20	7.8	25	0.85
4c	2.77 (447)	<i>c</i>	0.69	2.11 (587)	0.14	9.4	27	
5a	2.48 (499)	0.64	0.91	2.12 (585)	0.37	36	70	>0.90
5b	2.55 (486)	0.75	0.83	2.11 (587)	0.27	20.6	135	
5c	2.67 (464)	0.74	0.83	2.13 (581)	0.29	46	160	0.95
6a	2.86 (431)	0.85	0.74	2.15 (576)	0.27	35	110	0.77
6b	2.92 (425)	0.94	0.72	2.18 (569)	0.26			
6c	2.92 (425)	0.80	0.80	2.17 (571)	0.27	6	56	0.77
7a	3.33 (372)	<i>c</i>	0.62	2.37 (523)	0.034			
7b	3.57 (347)	<i>c</i>	0.53	2.42 (512)	0.011	21	63	1
7c	3.77 (329)	<i>c</i>		2.60 (477)	0.032			
7d	4.12 (301)	<i>c</i>		2.74 (453)	0.013	26	72	

<sup>a</sup> FWHM of absorption band. <sup>b</sup> Extinction coefficients are measured at absorption maximum and quoted as the molar concentration of thiophene units. <sup>c</sup>  $\pi$ – $\pi^*$  transitions overlap extensively with phenyl group or other higher transitions making the fwhm hard to estimate without peak fitting.

**TABLE 2: Absorption and Emission Data and PL Quantum Yields in Thin Film**

polymer	absorption eV (nm)	emission eV (nm)	$Q_{PL}$
1a	2.41 (513)	1.98 (627)	0.04
1b	2.51 (495)	1.99 (622)	0.015
1c	2.49 (498)	1.97 (629)	0.04
1d	2.45 (506)	1.97 (629)	0.05
2a	2.50 (496)	1.98 (625)	0.10
3a	2.42 (512)	2.05 (606)	0.08
3b	2.54 (488)	2.08 (596)	0.08
3c	2.43 (510)	2.07 (598)	0.04
3d	2.50 (497)	2.06 (603)	0.07
4a	2.57 (482)	1.83 (677) <sup>b</sup>	0.09
4a <sup>a</sup>	2.23 (555)	1.62 (764) <sup>c</sup>	0.03
4b	2.61 (476)	2.01 (616)	0.08
4b <sup>a</sup>	2.25 (552)	1.58 (783) <sup>c</sup>	0.010
4c	2.73 (454)	1.94 (638)	0.10
4c <sup>a</sup>	2.23 (555)	1.57 (795) <sup>c</sup>	0.09
5a	2.34 (530)	2.07 (599)	0.24
5b	2.39 (519)	2.03 (611)	0.09
5c	2.64 (470)	2.10 (590)	0.11
6a	2.45 (506)	1.70 (729) <sup>c</sup>	0.04
6b	2.67 (464)	2.09 (593)	0.09
6c	3.06 (405)	2.16 (574)	0.09
7a	3.26 (380)	2.33 (532)	0.028
7b	3.58 (346)	2.46 (504)	0.010
7c	3.80 (326)	2.65 (468)	0.022
7d	4.09 (303)	2.80 (442)	0.008

<sup>a</sup> Annealed samples. <sup>b</sup> Not 0–0 phonon transition, see Figure 5. <sup>c</sup> Not 0–0 phonon transition. All these polymers have emission spectra similar to the red-shifted emission shown in Figure 5.

between conjugated segments with different band gaps. With the low density of side chains in these polymers, the transfer distance between different segments will be short and exciton transport to quenching sites will be efficient.

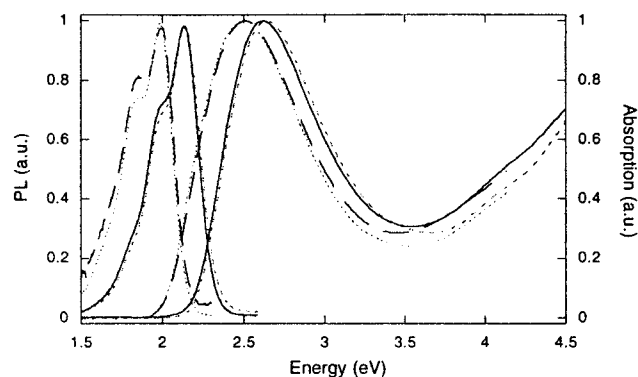
The presence of nonemissive states in the solid state has been advocated for the PPV system, such as intermolecular bound polaron pairs–excimers detected in MEH–PPV.<sup>27</sup> On the other hand strongly emissive excimers are found in CN–PPV even though the radiative lifetime of the excimer is very long. The different behavior of the excimers found in CN–PPV and MEH–PPV has been shown to be caused by the stronger

**TABLE 3: PL Lifetimes, Quantum Yields, as well as Calculated Radiative and Nonradiative Lifetimes of the Polymers Dissolved in Chloroform**

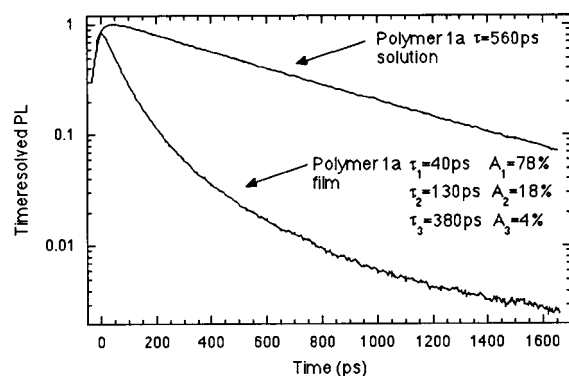
polymer	$\tau_1$ (ns)	$a_1$	$\tau_2$ (ns)	$a_2$	$\tau$ (ns)	$Q_{PL}$	$\tau_{rad}$ (ns)	$\tau_{nrad}$ (ns)
1a	0.56 <sup>a</sup>				0.56	0.25	2.2	0.75
1b	0.58 <sup>a</sup>				0.58	0.26	2.2	0.78
1c	0.58 <sup>a</sup>				0.58	0.28	2.1	0.81
1d	0.56 <sup>a</sup>				0.56	0.25	2.2	0.75
2a	0.59 <sup>a</sup>				0.59	0.30	2.0	0.84
3a	0.60 <sup>a</sup>				0.60	0.38	1.6	0.97
3b	0.64 <sup>a</sup>				0.64	0.36	1.8	1.00
3c	0.59	0.83	0.19	0.17	0.52 <sup>b</sup>	0.31	1.7	0.76 <sup>b</sup>
3d	0.60 <sup>a</sup>				0.60	0.36	1.7	0.94
4a	0.49	0.75	0.14	0.25	0.40 <sup>b</sup>	0.18	2.2	0.49 <sup>b</sup>
4b	0.45	0.89	0.09	0.11	0.41 <sup>b</sup>	0.20	2.1	0.52 <sup>b</sup>
4c	0.40	0.71	0.10	0.29	0.31 <sup>b</sup>	0.14	2.2	0.36 <sup>b</sup>
5a	0.59 <sup>a</sup>				0.59	0.37	1.6	0.93
5b	0.49 <sup>a</sup>				0.49	0.27	1.8	0.67
5c	0.55 <sup>a</sup>				0.55	0.29	1.9	0.78
6a	0.52 <sup>a</sup>				0.52	0.27	1.9	0.71
6b	0.54	0.83	0.16	0.17	0.47 <sup>b</sup>	0.26	1.8	0.64 <sup>b</sup>
6c	0.55	0.83	0.15	0.17	0.47 <sup>b</sup>	0.27	1.8	0.65 <sup>b</sup>
7a	0.29	0.21	0.07	0.79	0.12 <sup>b</sup>	0.034	3.5	0.12 <sup>b</sup>
7b	0.20	0.13	0.05	0.87	0.07 <sup>b</sup>	0.011	6.4	0.07 <sup>b</sup>
7c	0.20	0.22	0.06	0.78	0.09 <sup>b</sup>	0.032	2.8	0.09 <sup>b</sup>

<sup>a</sup> Appears to be single exponential. <sup>b</sup> Effective lifetimes.

coupling of chains in CN–PPV leading to shorter interchain distances which in turn give rise to a larger matrix element for emission.<sup>28</sup> In aggregates or crystals of oligothiophenes, where the interactions between close-packed molecules are large, the PL quantum yield is orders of magnitude lower than in solution<sup>29</sup> due to the formation of dimers or exciton bands. These make the radiative lifetime much longer than in solution, and nonradiative quenching dominates the exciton decay. For pristine PPV films a quantum yield of singlet intrachain generation close to unity is reported<sup>30</sup> but chemical defects such as oxygen bound to the conjugated backbone have been found to be an important quenching mechanism in PPV.<sup>30,31</sup> For poly(3-butylthiophene) (P3BT) fast generation of free polarons was detected in the PA spectra within 5 ps by Frolov et al.<sup>32</sup> and on longer time scales triplets were found. From the time-resolved PL data of polymer **1a** only, we cannot define the nature of the quenching sites,



**Figure 2.** Absorption and emission spectra of polymer **1b** dissolved in chloroform (solid line) and thin-film absorption and emission spectra for the same polymer (broken line). For comparison, the absorption and emission spectra of polymer **2a** dissolved in chloroform (dashed line) and thin-film absorption and emission spectra for the same polymer (dotted line) are shown.



**Figure 3.** Time-resolved PL for polymer **1a** dissolved in chloroform and PL decay of a spin-coated film of the same polymer.

intrinsic or not. As no rise of an excimer signal corresponding to the fast decay in the PL signal is observed in the time-resolved PA spectra, such a nonradiative decay channel can be ruled out. This is expected as the random coupling of the bithiophene units in these polymers will not likely allow any crystals and they could therefore be considered amorphous. Also, no formation of free polarons on these time scales (polarons are formed only at subpicosecond time scales) matching the fast decay in the PL is observed in the PA spectra (preliminary data), thus ruling out exciton splitting at defects such as the carbonyl groups found in PPV. The lack of spectral signature in the PA spectra suggests a fast decay to the ground state at the quenching sites.

Extrinsic chemical impurities left from synthesis, like residual  $\text{FeCl}_3$ ,<sup>33</sup> could act as quenching sites where energy/electron transfer to the impurity occur or the chemical impurities give rise to unintentional doping of the polymer which in turn quenches singlet excitons. Excitons will readily be transferred to the polaron state by Förster transfer as the absorption of the polaron matches the emission spectra of the exciton. The excess energy of the excited polaron will most likely be dissipated by internal conversion to the polaron ground state. When we add doping ions in the form of iron tosylate to the solution from which we spin coat a polymer film, the PL quantum yield is quenched by an order of magnitude when the added iron atoms are between one in every hundred and one in every thousand thiophene units. These are quite low levels of dopant ions which cannot easily be detected as a change in the linear absorption spectra of spin-coated films.

If the quenching is of intrinsic nature, quenching at conformational defects via internal conversion is one possibility which

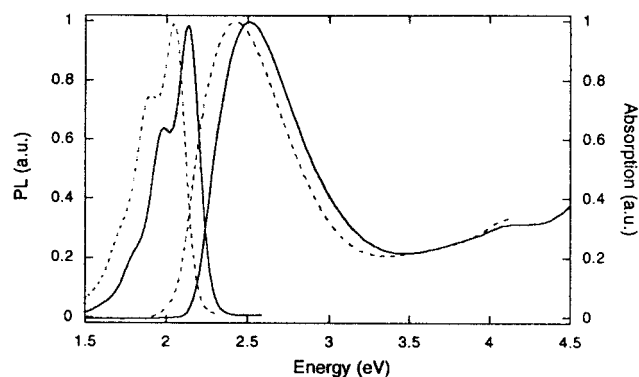
would give the observed behavior in the time-resolved PL and PA. The importance of triplets in films will be low if the ISC time is the same in film and solution due to the fast PL decay observed in this polymer (Figure 3). On the other hand, one could think of an enhanced ISC rate due to the heavy sulfur atoms of the surrounding polythiophenes in the film. Unfortunately very little work has been done on estimating the absolute triplet yield in films.

In the following sections we discuss the influence of the substituents on the PL and absorption, group by group. In this way we hope that the presentation will be easier to follow as the number of polymers is quite high.

**Polymer 1a–d.** These four PTs have different sidegroups attached on the para position of the phenyl group (Figure 1). All these polymers have a structureless  $\pi$ – $\pi^*$  absorption in the blue-green region of the spectrum, and the emission spectra show vibronic structure with the 0–0 vibronic transition being the most pronounced, see Figure 2 depicting absorption and emission spectra of spin-coated films of polymer **1b** and spectra of the same polymer dissolved in chloroform. PL quantum yields in solution are 0.25 (**1a**), 0.26 (**1b**), 0.28 (**1c**), and 0.25 (**1d**).

Spectral characteristics and quantum yields are very similar among these polymers, and this is expected since the steric interaction between the substituent and the thiophene backbone is not altered; the substituents have approximately the same length and weight, and therefore torsional motion should not be affected. Furthermore, the effect of the different strength of the electron-donating sidegroups attached to the phenyl group does not alter the absorption spectra, indicating a small electron donation to the main chain. Still, there are small differences in the absorption and emission maxima of the different polymers. In the case of polymer **1c**, there is a subset of chains which are shorter than the conjugation length and therefore the emission and absorption are slightly blue-shifted compared to the other. From the time-resolved PL measurements, which appear to be single exponential, when probed at the emission maxima, we obtain PL lifetimes (Table 3) of 0.56–0.58 ns and from formula 2 we calculate radiative lifetimes of typically 2.2 ns and nonradiative lifetimes of 0.75 ns.

Absorption and emission spectra for thin films have the same spectral shape as for solution, but both emission and absorption spectra are red-shifted by more than 0.1 eV going from solution to thin film. PL quantum yields for the films are 0.04 (**1a**), 0.015 (**1b**), 0.04 (**1c**), and 0.05 (**1d**). Compared to the values of the PL yields in solution, thin-film PL yields are very low. It can be seen from the PL decay of polymer **1a** in thin film as compared to solution (Figure 3), that the thin-film decay is much faster at short time scales. We have to use a sum of three exponentials with lifetimes 40 ps (78%), 130 ps (18%), and 380 ps (4%) to get an acceptable fit to the observed decay in the film. This fit should not be taken as a physical model; rather it is a mathematical description of the complex decay in the film. We can estimate the radiative lifetime in the film using the fit and calculating an effective lifetime as explained in the Experimental Section. We can justify this as the emitting species must be the same during the decay. The emission spectrum is almost identical to the one observed in solution, and at long time scales the decay in film and solution is quite similar, as can be seen in Figure 3. With an effective lifetime of 70 ps and a PL quantum yield of 0.04 the radiative lifetime is 1.7 ns, in reasonable agreement with the value 2.2 ns calculated for the same polymer in solution (Table 1). In this calculation we have assumed that the singlet exciton yield when absorbing photons is equal to one, even though it is known from PA measurements



**Figure 4.** Absorption and emission spectra of polymer **3a** dissolved in chloroform (solid line) and thin film absorption and emission spectra for the same polymer (dashed line).

on the same polymer that polarons are formed on subpicosecond time scales. Hence the real radiative lifetime must be shorter than the calculated value. The nonexponential decay of this polymer indicates a decay by exciton diffusion to exciton quenching sites as discussed in the previous section. We cannot get a good fit when modeling the decay as a simple one-dimensional diffusion among randomly distributed quenchers. The failure of such models is most likely due to diffusion between different chains, altering the dimensionality of the diffusion motion. The low PL quantum yield of **1b** is rather surprising, but a possible explanation is found when measuring the absorption in the band gap of highly concentrated solutions which reveal a small amount of absorption states extending up to 0.67 eV which is not found for the other polymers in this group. This can be considered to be due to a high amount or residual dopant ions giving rise to polarons.

**Polymer 2a.** This polymer has the same chemical structure as polymer **1b** except that the 2-ethyl-hexyloxy group is attached to the meta position of the phenyl group. Absorption and emission spectra of polymer **2a** are almost identical to the spectra of **1b** both for solution and thin film (Figure 2), but the PL yield is higher both in solution (0.31) and in film (0.10). Time-resolved PL measurements reveal that the PL lifetime in solution of **2a** (0.59 ns) is within the error margin of the value obtained for polymer **1b** (0.58 ns), but from the PL quantum yield we calculate a radiative lifetime of 2.0 ns and a nonradiative lifetime of 0.84 ns. A lower amount of quenching defects could explain the observed increase of the PL yield in the film but as the quenching mechanism is not well-known, we cannot rule out a different morphology of the film.

**Polymer 3a–d.** Attaching two sidegroups symmetrically on the ortho and meta positions on the phenyl ring gives polymers with more narrow electronic transitions (fwhm) and lower Stokes shift, both in solution and thin film, compared to those polymers with a sidegroup in the para position of the phenyl group, see Figure 4. The reason for this must be the substitution pattern where the phenyl group is turned out of coplanarity with the thiophene ring, which in turn influences the ground-state geometry of the whole polymer (more planar). Although the Stokes shift is lower with two side groups on every phenyl group, the electronic transition from the excited state down to the ground state occurs at the same energy for both groups of polymer (Table 1) which means that increasing the bulkiness of side chains mostly influences the ground-state conformation due to the lower barrier for rotation in the ground state. High values of the PL yield in solution are measured in these polymers: 0.38 (**3a**), 0.36 (**3b**), 0.31 (**3c**), and 0.36 (**3d**). These

are high if one compares them the values reported on sexithiophene, 0.44,<sup>7</sup> or highly regular (95% regioregular) P3DT, 0.41.<sup>9</sup>

PL lifetimes of these polymers (around 0.6 ns) are about the same as for the polymers in groups **1** and **2**. Hence the higher PL yield of these polymers is due to a shorter radiative lifetime as well as a slower nonradiative lifetime, 1.6 ns and 0.97 ns, respectively, for polymer **3a**. Assuming the same ISC as for poly(alkylthiophenes), 1.2 ns,<sup>10</sup> the major nonradiative decay path in these rigid polymers would be ISC. Polymer **3c** has a lower PL yield than the other polymers with similar substitution. This indicates some extrinsic quenching center which does not break the conjugation since only a slight difference can be seen in the absorption spectra between polymers **3c** and **3a** in solution. The presence of a quenching center is confirmed by the time-resolved PL measurements, where the **3c** decay is not a single exponential. Assuming the same nonradiative decay rate of **3a** and **3c** we can calculate the quantum yield of **3c** in the absence of the fast decay caused by the quenching center and the obtained value is 0.37, a value that fits well among the other polymers with similar side chains. Polymer **3b** has a blue-shifted absorption compared to the other polymers in the same group and the emission spectrum has a blue tail which must be due to short segments (shorter than the conjugation length). Extraction of the short segments is difficult due to the good solubility of this polymer. The absorption spectrum of polymer **3d** is broader and more blue-shifted than that of the other polymers with two substituents on the phenyl group, consistent with the shorter and lighter substituents which makes the polymer less rigid. Still, **3d** has a lower Stokes shift than the polymers in groups **1** and **2** discussed above which have substituents as heavy as **3d**.

Thin-film spectra display a smaller red-shift of absorption and emission spectra, relative to solutions, than the polymers substituted only in the para position of the phenyl group. A smaller shift is the result of the increased number of side chains, which dilutes the polymer and decreases the backbone interchain interaction in the thin film and, hence, the polymer becomes more solution-like. PL yields in thin films are 0.08 (**3a**), 0.08 (**3b**), 0.04 (**3c**), and 0.07 (**3d**). The lower value of the PL yield of **3c** relative to the other, in solution, now shows up as a reduced PL yield in the film consistent with the assumption of a higher quenching site density in **3c**. The higher reduction of the PL yield in the film (50% compared to the reduction of PL yield in solution, 20% relative to polymer **3a** and **3b**) is consistent with a higher mobility of excitons in thin film. The yield of **3b** is not affected by the short segments since excitations on these segments is transferred to longer segments very quickly and therefore the emission spectrum of the film does not have any blue tail. This is not seen in the emission spectrum of the solution where the transport of excitons is prohibited by the separation of the polymer chains.

Comparing the thin-film PL yield of these polymers (**3a**, **3b**, **3d**) with the polymers in group **1** the PL yield increases as the number of side chains increases and hence interchain interaction decreases as the separation of chains increases due to longer hopping distances. On the other hand the PL yield of polymer **2a** is higher even though the density of side chains is lower than for the polymers in group **3**. This might again be due to a lower concentration of quenching sites of polymer **2a**.

**Polymer 4a–4c.** Stokes shifts in solution are higher in these polymers relative to their bithiophene analogues (if they exist), see Table 1. This can be caused by low regularity or increased steric interactions with substituents on every thiophene unit. The

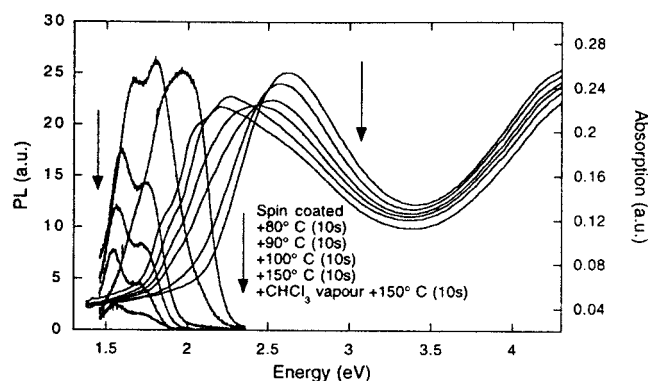


high regularity of these polymers, **4a** (94%), suggests that it is more plausible that steric interactions causes the blue-shift. Despite the high regularity of polymer **4a** the PL yield of the polymer dissolved in chloroform is low (0.18) and polymer **4b** has similar PL yield (0.20) whereas polymer **4c** has higher Stokes shift and even lower PL yield (0.15). Note that the Stokes shift follows the rigidity of the side chain, the oligoethyleneoxide chains are more flexible than the octyl chain and the carbonyl group attached to the side chain of polymer **4c** increases the rigidity. Also, the PL yield follows the same trend with lower yield for those with higher Stokes shift. All three polymers have a fast component in the PL decay. Taking the fast component into account and calculating the radiative lifetime of these polymers we see that they are almost the same as for their bithiophene analogues but the nonradiative pathways are much more efficient, even in the absence of the fast component. One interpretation of the change of the lifetimes is that it could be due to deactivation of the excitation by internal conversion (IC), a deactivation path indeed present in dye molecules<sup>34</sup> with phenyl group attached to the emitting chromophore which are not prevented from rotating. The extended conjugation between the phenyl group and the carboxyl group for polymer **4c** can be seen as a red-shift and as an enhancement of the phenyl group absorption around 4.4 eV. The phenyl group absorption is also extending down to 3 eV and overlaps more with the  $\pi$ - $\pi^*$  absorption than for the other polymers with similar substituents. This effect cannot be used for increasing the absorption in the blue and UV region of the spectrum since the excitation spectrum shows a lower PL yield for excitation where the phenyl group absorbs (not shown).

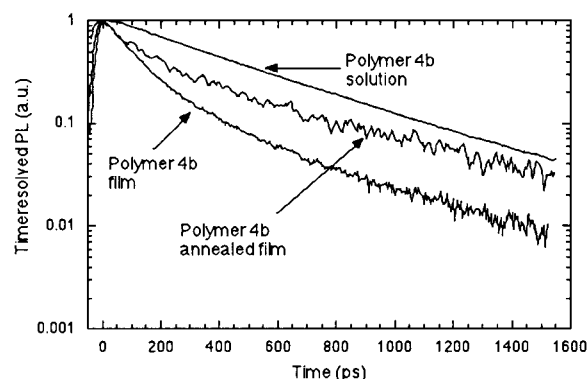
It has been shown that spin-coated films of polymer **4a** (from chloroform solution) are amorphous, which can be correlated to the structureless absorption. The emission spectrum has a rather different shape from the one seen in the solution and consists of a mixture of two phases, one red-shifted more ordered material and a more solution-like high-band-gap material. In absorption we mostly probe the high-band-gap material but since the excitation migrates to low-band-gap material this part becomes more pronounced in the emission spectrum. The PL yield of these materials in thin film, 0.09 (**4a**), 0.08 (**4b**), and 0.10 (**4c**), have the opposite trend relative to the solution as the most disordered material with the most rigid side chain has the highest PL yield. Compared to the bithiophene analogues the yield is about twice as large and the density of side chains is also twice as large which seems to be quite general for these red polythiophenes; when the density of side chains increases the PL yield increases. The reduction of the PL yield in film relative to solution is low, indicating either a low density of defects or a short diffusion range (which is expected due to the broad absorption spectrum, which will give a broader density of states). Furthermore if there are contributions from IC in solution it would be lower in the thin film as the rotational flexibility of the phenyl group is reduced.

Exposing the thin film to chloroform vapor or annealing at an elevated temperature, a transition to a partly crystalline phase occur. The crystal structure has been settled for polymer **4a** by X-ray diffraction<sup>35</sup> and the chains are arranged with their backbones parallel to each other, with a stacking distance of 5.06 Å, and the backbones are fully planar with the phenyl groups turned out of coplanarity with the backbone.

We can follow different stages of crystallization in the film by successively annealing a thin-film sample of polymer **4b** at increasing temperature (Figure 5). Between each annealing we let the sample cool and measure the absorption and emission



**Figure 5.** Absorption and emission spectra of spin-coated film of polymer **4b** and spectra of the same film after successive annealing at 80, 90, 100 and 150 °C for 10 s each, and the last spectrum is taken after treating the film with chloroform vapor followed by annealing at 150 °C at 10 s.



**Figure 6.** Time-resolved PL for polymer **4b** dissolved in chloroform and PL decay of a spin-coated film and the same film treated with chloroform vapor and annealed at 150 °C.

spectra. With increasing temperature the conversion to the ordered phase becomes more and more complete. By holding the sample in chloroform vapor at room temperature the conversion can be taken even further (Figure 5). As can be seen the absorption spectra seems to have an isosbestic point, but a closer inspection reveals that this is not really the case. When the annealing temperature is increased the part of the absorption spectra originating from the ordered phase does not only increases but also is red-shifted. This is in agreement with crystal growth in polymers; with increasing temperature, the size (thickness) of the crystallites increases. As the polymer chains extend through the crystallites, a thicker crystallite would give a longer conjugation length.

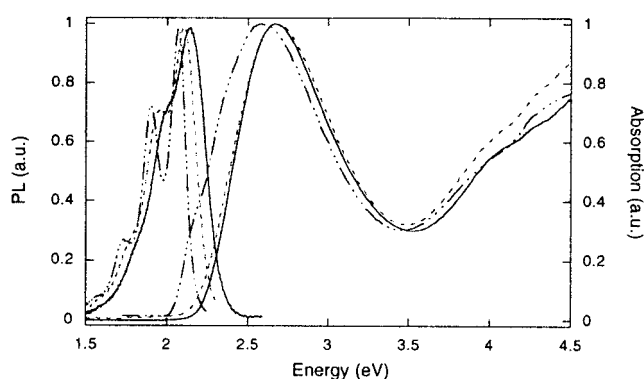
Measuring the PL spectra we excite the sample at 2.42 eV and the difference in absorption is at the most 10% for the different annealing temperatures, thus the intensity of the PL spectra reflects the PL yield of the sample. Even at the lowest annealing temperature (80 °C) the emission spectra displays a huge shift toward the red side of the spectra but still a blue tail originating from incomplete transfer can be seen. Further annealing results in a complete transfer to the ordered phase. With increasing annealing there is a red-shift of the emission spectra which is consistent with the red-shift observed in the absorption spectra. In addition to the red-shift there is also a shift of the weight of the vibronic peak from the first to the second vibronic peak. The most striking feature about the PL when annealing the thin film is the strong reduction of the PL yield. In Figure 6 the time-resolved PL of polymer **4b** in solution, thin film as well as annealed film (150 °C) are shown. It is apparent that the large reduction of the PL yield is not a

consequence of a faster nonradiative decay rate as the PL decay of the annealed film is not that much faster than the decay of the spin-coated film. Actually, the long-time component is even slower than in spin-coated film and solution. Using the fitted data of the annealed film, 70 ps (39%), 470 ps (61%), together with a PL quantum yield of 0.01 we estimate the radiative lifetime to be 31 ns, which is approximately 15 times longer than the one found in solution, 2.1 ns, as well as the radiative lifetime of the spin-coated film, 1.9 ns, which was calculated using the fitted data, 90 ps (77%), 360 ps (23%). These measurements are similar to the measurements on P3DT, done by Rumbles et al.,<sup>9</sup> which showed that the radiative lifetime was much longer (20 ns) if the polymer were in a bad solvent where the molecules aggregated, compared to the one of P3DT in a good solvent (1.3 ns). As the overall absorption spectra do not lose any absorption strength these results suggest an interchain species existing in the excited state with a low dipole strength. As the PL decay for the different stages of annealing does not change too much (not shown) from the one of the annealed film shown in Figure 6, the different PL yields originate from a continuous increase of the radiative lifetime as the conjugation length in the aggregate increases.

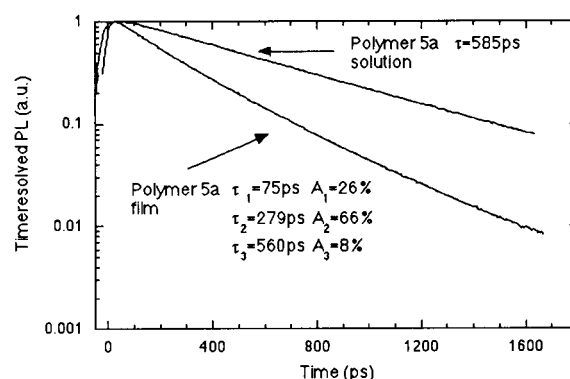
The different substitutions of the polymers in this group influences the behavior of the annealed films. In Table 2 the PL yield of the different polymers is shown after annealing at 200 °C for 5 min. If the side chain is more rigid the resulting PL yield is higher. With different side chains the flexibility of the polymer is affected by its melting temperature and glass transition temperature, and the same treatment may therefore result in a different morphology, which also includes the crystal structure. For example, when annealing polymer **4c** for 5 min at 200 °C the emission comes only from the low-energy segments and the absorption spectrum is shifted to the red but only small signs of vibronic structure can be seen in the absorption spectrum. If instead of annealing the sample we expose it to chloroform vapors, the absorption spectrum has pronounced vibronic structure and the PL yield is 0.06 compared to 0.09 for the annealed sample, which is quite different behavior from polymer **4b**.

**Polymer 5a-c.** These polythiophenes have two side groups attached on the meta and ortho positions of the phenyl group, and the resulting polymers exhibit rather different behavior in solution and film. Polymer **5a** has a PL yield of 0.37 in solution, a narrow absorption spectrum (fwhm) and small Stokes shift like the bithiophenes with the same substitution pattern (group **4**) indicating a very low sterical hindrance for this substitution. The **5a** lifetimes are also very similar to the bithiophene analogues. Changing the octyl chains of polymer **5a** to oligo-ethyleneoxide chains (polymer **5b**) the absorption spectrum becomes broader and the Stokes shift larger. PL yield is also decreased to 0.27. The polymer **5c** absorption spectrum (Figure 7) is broad and blue-shifted as for the polymers in group **4** discussed above with one phenyl group on every thiophene unit, see Figure 6. The short side chain of polymer **5c**, with oxygen attached at the ortho position of the phenyl group, is not able to planarize the backbone as efficiently as for polymer **5a**.

Spin-coating polymer **5a** dissolved in chloroform gives a film that is very well ordered (measurement on powder shows a partial crystallinity  $\approx$  40%). In contrast to the polymers in group **4**, the crystallization does not need to be induced by thermal treatment as the chains in solution are much more planar than those in group **4**. The crystalline part of the polymer gives rise to a well-resolved vibronic structure in the absorption spectrum. The emission spectrum has the same spectral weight for the vibronic peaks as for the same polymer dissolved in chloroform,



**Figure 7.** Absorption and emission spectra of polymer **5c** dissolved in chloroform (solid line) and thin-film absorption and emission spectra for the same polymer (dashed line). Also shown are the absorption and emission spectra of a film spin-coated from dichlorobenzene and chloroform vapor-treated film (solid-dashed line).



**Figure 8.** Time-resolved PL for polymer **5a** dissolved in chloroform, and PL decay of a spin-coated film of the same polymer.

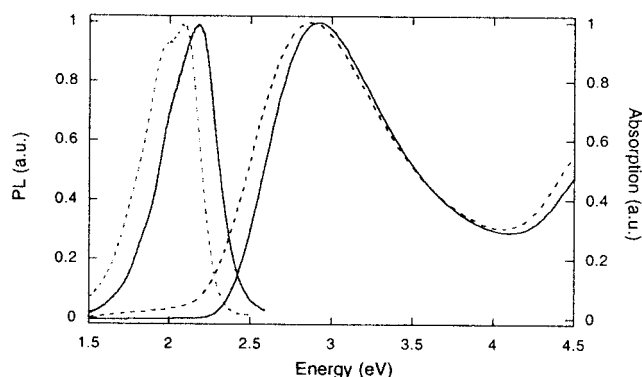
but the transitions are much narrower for the film, indicating an exciton diffusion to the crystalline parts of the polymer which has lower band gap. The Stokes shift of polymer **5a** between the  $S_1 \rightarrow S_0$  0-0 transition and the  $S_1 \leftarrow S_0$  0-0 transition (from second negative derivative) is only 0.07 eV; hence, a very small rearrangement of the backbone between the ground and excited states of the ordered phase occurs. The PL yield of this film, 0.24, is very high and must be due to a well-ordered polymer backbone that is separated from neighboring chains, making the interchain interaction small. Preliminary results on X-ray diffraction support this assumption as the smallest stacking distance is over 10 Å in this material. This is achieved with the substitution of octyl groups on the ortho position of the phenyl group which will, if the phenyl group is turned out of the plane of the backbone, fall over the  $\pi$ -orbitals and thereby separate the backbones from each other. Separating the chains might be more efficient in the ordered phase since in batches of the same polymer where no ordering occurs (no vibronic structure appears in the thin-film absorption spectrum) the PL yield is as low as 0.14, even though the solution absorption and emission remained unaltered. The increased PL yield in the crystalline film could be understood as any kind of defect such as chain terminations, cross-links, or twists of the backbone and impurities will be concentrated in the amorphous part of the polymer and hence reducing the nonradiative decay channel. The time-resolved PL (Figure 8) show a nonexponential behavior which is fitted with a sum of three exponentials with time constants 75 ps (26%), 280 ps (66%), and 560 ps (8%). Calculating the weighted-average PL lifetime, 230 ps, and using eq 2, a radiative lifetime of 960 ps is obtained which is much shorter than the radiative lifetime in solution, 1600 ps. The difference can be due to the



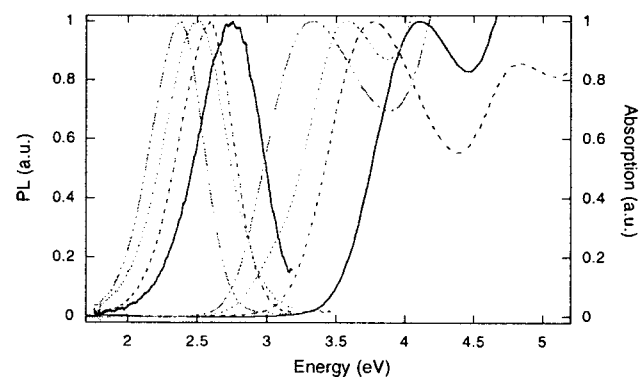
different measurement conditions of the time-resolved PL (higher excitation density) and PL quantum yield measurement but as seen from the trend in solution; the more rigid polymers with smaller Stokes shift show a shorter radiative lifetime and here the ordered thin films have an extremely small Stokes shift. From photoinduced absorption measurements done on this polymer a long-lived stimulated emission is observed with a lifetime of 90 ps,<sup>16</sup> in agreement with the time-resolved PL; more important, no other photoinduced absorptions appear in the band gap of the polymer, which is consistent with the line narrowing of the emission spectrum observed at high pump intensities and the report of lasing<sup>4</sup> in a microcavity using this material.

The PL yield of spin-coated polymer **5b** is as low as 0.09, rather disappointing since the structure is so similar to Polymer **5a**. From the absorption spectrum of the thin film we observe that the vibronic structure of this polymer is not at all as pronounced as for polymer **5a**, indicating a different morphology in the film. The faster, nonradiative lifetime observed in solution of polymer **5b** might be one reason for the low PL yield in the film. In the case of polymer **5c** the thin film absorption spectrum has no vibronic feature (Figure 7) and is similar to the solution. The PL yield, 0.11, is close to the values measured for the spin-coated polymers in group 4 which resembles similar structural and spectral features. Changing the solvent to dichlorobenzene increases the PL yield of the spin-coated film to 0.15, and some vibronic features can be resolved in the absorption spectrum; by treating the polymer film with chloroform vapor the order can be increased even further. Vibronic features in the absorption spectrum (Figure 7) are then much like the one seen for polymer **5a**, but the absorption spectrum is broader which indicates that there is a large portion of the polymer which still is in the amorphous phase. The emission spectrum of polymer **5c** in the well-ordered phase is almost identical to the emission spectrum of the well ordered polymer **5a** but the PL yield has decreased, compared to the film spin-coated from dichlorobenzene, to 0.13. Obviously, the properties of the regular polymers in this group when ordering and crystallization occur is very different from those in group 4, and the reason must be the different substitution pattern on the phenyl group, where the side chains on the phenyl group in this group prevent the interchain distances of the ordered phase from being small and thus prevent interchain interaction.

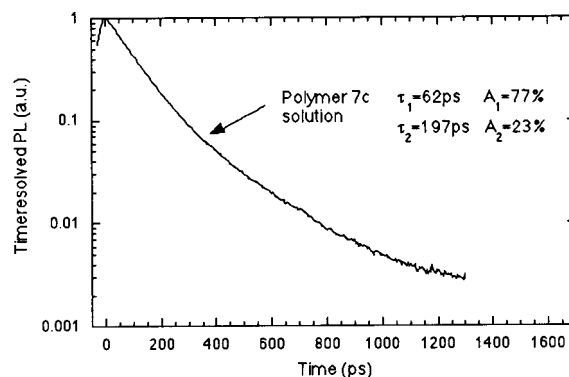
**Polymer 6a-c.** The most commonly studied soluble PTs are the polyalkylthiophenes, which have a quite low PL yield in thin film, especially if the regularity is high and the polymer does crystallize. In solution, on the other hand, the PL increases with increasing regularity.<sup>36</sup> Our P3OT (**6a**) has rather low PL yield in solution, 0.27, which is consistent with the low regularity of this polymer. PL yields of polymers **6b** and **6c** are 0.26 and 0.27. PL decay of polymers **6b** and **6c** are not single exponential but have a fast decay. Radiative and nonradiative lifetimes are similar for all three polymers. Thin films of P3OT have low yield, 0.04, but this is still higher than previously reported values of P3OT<sup>37</sup> (0.018–0.02). The P3OT absorption and emission spectra are red-shifted, which indicate a high interchain interaction as for the annealed polymers in group 4. Polymer **6b** does not shift so much to the red (more yellow than red emission) (Figure 9), and the PL yield in the film is more than twice as high (0.08) as for P3OT. From the blue-shift of the absorption and emission spectra of polymer **6b** relative to P3OT, in solution, polymer **6b** has more steric interactions (possibly due to lower regularity) which prevents it from aggregating in film. Polymer **6c** has a bulky cyclohexyl group substituted to the backbone. When going from solution to film the emission spectrum does not shift at all and the



**Figure 9.** Absorption and emission spectra of polymer **6b** dissolved in chloroform (solid line), and thin-film absorption and emission spectra for the same polymer (dashed line).



**Figure 10.** Absorption and emission spectra of polymer **7a** (solid-dotted line), **7b** (dotted), **7c** (dashed), and **7d** (solid) dissolved in chloroform.



**Figure 11.** Time-resolved PL for polymer **7c** dissolved in chloroform.

absorption spectrum is even blue-shifted compared to the solution. The PL yield is 0.08 for the film and again, as we increase the steric hindrance the main chain can not planarize in the film and the PL yield increases.

**Polymer 7a-d.** One route of making PTs with high band gap has been to use steric hindrance of head-to-head coupled substituents to twist the thiophene backbone out of planarity. By choosing the bulkiness of the substituent the emission can be tuned from the red to the blue region of the spectrum<sup>1</sup>. Emission spectra of these polymers, in solution (Figure 10), are broad and have no sign of vibronic structure. This is related to a large inhomogeneous broadening due to disorder in the material and a reduction of the  $\pi$ -overlap of the neighboring thiophene dyads not being able to make the backbone as rigid as the more planar PTs. Turning the backbone out of planarity decreases the PL yield in solution to low values: 0.03 (**7a**), 0.01 (**7b**), 0.03 (**7c**), and 0.01 (**7d**). All these polymers have a

strongly nonexponential decay. We observe an increased radiative lifetime for these polythiophenes compared to the ones substituted only at the 3-position, especially **7b** having a radiative lifetime of over 6 ns, but the error margins both in the PL yield measurement and the PL lifetime measurement start to be large for the extreme values measured here. The most important effect decreasing the PL yield is the fast nonradiative components. In a model compound made of randomly copolymerized 3-alkylthiophene and a 3,4-dialkylthiophene the measured time-resolved PL<sup>38</sup> revealed an increasing nonradiative decay when the 3,4-dialkylthiophene content and the twisting of the backbone increased in the copolymer, and this nonradiative path was assigned in PA<sup>39</sup> measurements which showed an increasing signal from both triplets and polarons. Comparing this with the trend seen among the OT, where the inter system crossing is becoming faster with a shortening of OT, the same trend appear in PTs as well, when the conjugation length has been decreased by steric hindrance. Twisting the backbone has also been found to increase the IC in some CN-substituted oligo-(*p*-phenylenevinyls). We do not observe the general trend with decreasing PL yield with increasing blue-shift, and we believe that the flexible phenyl group attached to **7a** and **7b** introduces additional IC or increased ISC in those polymers. As observed for thiophenes substituted only at the 3-position, the PTs with a phenyl group attached to backbone have faster nonradiative lifetimes when being nonplanar compared to those without phenyl group (for example P3OT).

With a high steric hindrance between each thiophene unit, the backbone is prevented from planarizing when going from solution to film, and only a very small red-shift, or even a blue-shift, of the absorption and emission spectra is observed. In thin films the PL yield is also low: 0.03 (**7a**), 0.01 (**7b**), 0.02 (**7c**), and 0.008 (**7d**), indicating similar decay routes as in the solution. The transport of excitons should be very low due to the disorder. The large Stokes shift giving a low spectral overlap between absorption and emission spectra will localize the excitons to sites with low energy very fast, and together with the short PL lifetime observed in solution, cause a short diffusion length.

## Summary/Conclusions

We have presented PL quantum yield measurement for a wide range of PT both in solution and thin film. For bithiophenes, where no head-to-head defects are present, the PL yield in solution is correlated to the rigidity of the main chain which appears as a reduction of the Stokes shift and a narrowing of the electronic transitions (fwhm). We observe that substituting the thiophene ring in both the 3- and 4-position twisting the main chain out of planarity, makes the PL yield low both in film and solution. The reduction of the PL yield originates from more than one nonradiative process.

Amorphous thin-films show higher PL yield when the density of side chains increases. We have observed the formation of aggregates in thin-films of regular conjugated polymers. If the conjugated chains form aggregates where the main chains are close-packed, the formation of aggregates reduces the PL yield due to formation of interchain species. For regular polymers, where the main chains are separated by bulky side chains, interchain interaction is prevented and we observe an increased PL yield when aggregates are formed.

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