PHYSICAL REVIEW B **70**, 195213 (2004)

Triplet exciton state and related phenomena in the β-phase of poly(9,9-dioctyl)fluorene

C. Rothe, S. M. King, F. Dias, and A. P. Monkman
Department of Physics, University of Durham, Durham DH1 3LE, England

(Received 23 April 2004; revised manuscript received 2 August 2004; published 22 November 2004)

Using both time-resolved emission and cw photoinduced absorption spectroscopy as a function of temperature, the aggregation phenomena (β-phase formation) observed in poly(9,9-dioctyl)fluorene is studied. All spectra of the β phase, including absorption, prompt and delayed fluorescence, phosphorescence, and photoinduced triplet absorption feature very narrow linewidths, which are unique within the class of conjugated polymers. From the comparison of the latter data with amorphous polyfluorene, poly(9,9-diethylhexyl)fluorene, as well as with the fully planar ladder-type poly(paraphenylene), we conclude that the origin of the β phase cannot simply be an extended intrachain conjugation, but interchain interactions are involved. Furthermore, the β phase acts as an energetic trap for both singlet and triplet excitons initially created on amorphous chain segments. The delayed fluorescence kinetics of the β phase were measured at different temperatures. From the analysis of these decays within the framework of dispersive triplet migration in a Gaussian density of states distribution, further evidence is provided that the delayed fluorescence originates from triplet-triplet annihilation. At room temperature, it is clear that triplet excitons migrate over large distances, exceeding that of singlet excitons. Also, the segregation time between dispersive triplet migration and classical thermally activated hopping, is in the case of β-phase containing samples, dependent on the separation of the β-phase domains.

DOI: 10.1103/PhysRevB.70.195213 PACS number(s): 78.47.+p, 78.55.−m

I. INTRODUCTION

After a decade of intensive research efforts the first commercial applications equipped with displays based on conjugated light emitting polymers are now emerging on the consumer markets.[1] This, however, might merely be the first step on account of the large number of advanced "potential" applications. These justify the ongoing, intense research efforts on the fundamental properties of light emitting conjugated polymers. A topic of current interest is the ability of certain conjugated polymers to self organize to some extent. In this context, the most prominent representative is the blue emitter, poly(9,9-dioctyl)fluorene (PFO), which was studied extensively, especially by the Sheffield group.[2–11] Applying certain treatment protocols to PFO thin films, such as annealing at high temperature, cooling and reheating to room temperature or exposure to certain solvent vapors modifies part of the films into a different structure, which has been termed a "β phase." The primary photophysics of this modified polyfluorene structure are characterized by sharp absorption and emission lines, redshifted compared to the amorphous PFO spectra. The β phase is also observed in solutions made of poor solvents and, interestingly, the induced state is conserved upon using such solutions to produce thin films. On account of the similarities of these induced spectra with the fully planar ladder-type poly(paraphenylene) (LPPP), it has been conjectured that twists between neighboring rings towards a more planar backbone conformation are the underlying microscopic origin of the β phase.[6] However, *in situ* experiments show a grow-in of the new spectral features, i.e., they appear at a fixed position in energy—the peak position is not smoothly changing from amorphous PFO towards the modified structure.[6,8] Also, as rather different treatment protocols cause the same changes, they must emanate from a certain well defined modification, which is characterized by its own absorption and emission spectra and average conjugation length. The latter (measured in terms of the singlet energy) is intrinsically limited, as in LPPP's, and is certainly shorter compared to the size of the modified structure itself.[6]

Initially, relying on experiments on 1% PFO blended into a polystyrene matrix, the β phase was explained solely as an intrachain process.[6] However, at such concentrations the polymer chain can by no means be considered as isolated but phase segregation will occur.[12] Furthermore, the formation of the modified structure in solution requires a minimum polyfluorene concentration.[6,13] Recently, experiments on a series of polyfluorene derivatives having different length side chains clearly demonstrated that interchain interactions of the linear side chains cause the observed changes in the backbone structure.[13–15] Thus, it is an interchain phenomenon, giving rise to unique spectral characteristics, compared to common excimer or dimer luminescence. It is still an open question what, on a microscopic level, exactly causes these alternations in the polymer chain structure.

Since its first application by Romanovskii *et al.*,[16] studies using the technique of time gated emission spectroscopy have provided major contributions to our knowledge and understanding of conjugated polymers. We refer in particular to phosphorescence (Ph) spectra, which still represent the only direct way to obtain information on the polymer triplet state.[16–19] Along with this usually very long-lived emission, all conjugated polymers exhibit delayed fluorescence (DF), emission from excited states whose lifetime is considerably longer than the typically 400 ps radiative lifetime of a regular singlet state.[16–19] Thus, gated spectroscopy should provide a powerful tool to gain insight in the photophysics behind the aggregated PFO. Further, quasi-cw photoinduced absorption spectroscopy has already shown the existence of several long-lived excitations including triplet excitons[9,20] and possibly polarons,[20] associated with the β phase.

This contribution is divided into three parts. First we report singlet absorption, transient triplet absorption as well as

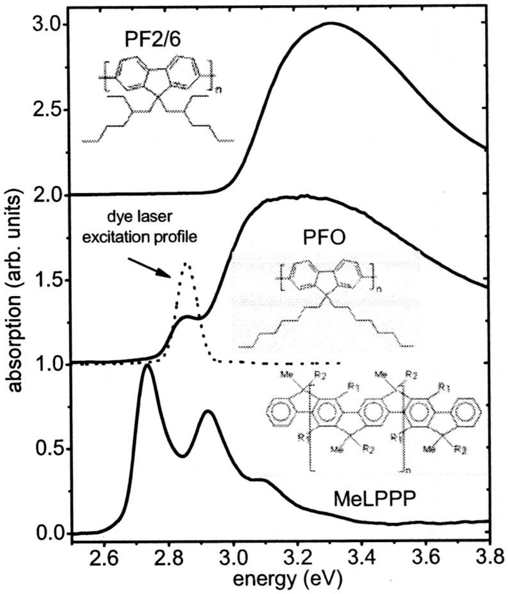

FIG. 1. Compendium of room temperature, solid-state absorption spectra including PFO, PF2/6, and MeLPPP. All spectra are normalized and offset for clarity. The coumarin 120 dye laser profile for selective excitation of the β phase is shown as dashed line. The insets show the chemical structures of the polymers investigated ($R_1 = n$-C_6H_{13}; $R_2 = 1,4$-C_6H4-n-$C_{10}H_{12}$).

prompt, delayed fluorescence and phosphorescence spectra of the β phase of PFO at different temperatures. These absorption and emission data are compared to corresponding data obtained for an all-amorphous polyfluorene derivative and the fully planar ladder-type polymer poly(paraphenylene) (MeLPPP). In the second part temperature-dependent time-resolved luminescence spectra obtained after exciting both, the β and the amorphous phase of PFO, are analyzed. These data qualitatively prove that the β phase within the amorphous polymer matrix acts as low-energy traps for both the singlet and the triplet exciton. In the third section, decay kinetics of the β-phase delayed fluorescence are given and analyzed within the framework of dispersive triplet hopping, which results in the observed, dispersive decay of the triplet-triplet-annihilation type delayed fluorescence.

II. EXPERIMENT

In order to produce PFO thin film samples, which partly exhibit the β phase, 10^{-2} wt. % of the polymer was dissolved at 60 °C in the moderately good solvent methylcyclohexane (MCH). Clear films of high quality were obtained by spin coating the latter, still warm, solution onto previously cleaned spectrosil disks at 2500 rpm for one minute. Using similar protocols the reference thin film samples of the all-amorphous polyfluorene, poly(9,9-diethylhexyl)fluorene (PF2/6) and the ladder polymer MeLPPP were prepared. All chemical structures are included in Fig. 1. Additionally, 10^{-5} wt. % solutions using either MCH or toluene, which were degassed by three freezing thaw cycles, have been prepared as well. Only for PFO, cluster formation has been observed if the 10^{-5} wt. % MCH solution was allowed to settle at ambient temperature. In some cases those solutions were used to drop cast films of high absorbance but poor quality, which nevertheless showed identical behavior to the above spin coated PFO thin films.

For the time-resolved photoluminescence studies, excitation in the amorphous polyfluorene absorption band at 3.5 eV (355 nm) was provided by the frequency-tripled output of a 160 ps pulsed Nd:yttrium aluminum garnet laser. For selective excitation of the β phase at 2.86 eV (434 nm) the latter Nd-YAG laser was employed to pump a home built single pass coumarin 120 dye laser (excitation profile is depicted in Fig. 1). The luminescence emitted by either the liquid or solid sample was passed through a spectrometer and detected by our intensified CCD camera (4 Picos, Stanford Computer Optics). In all cases spectra are measured, being characterized by two tunable time periods: the time between pulsed excitation and the start of the light detection (delay or gate time) and the duration of the light detection (integration time). The latter can be chosen as short as 200 ps. In order to obtain decay kinetics each spectrum was integrated over the desired energy region and plotted in a double logarithmic fashion versus the appropriated time (delay time plus half the integration time). A temperature controlled displex helium cryostat additionally allowed to vary the temperature of solid samples between room temperature and 11 K. By means of several spectral lamps the overall spectral resolution of the whole setup was measured to be better than one nanometer. Further information about the time-resolved luminescence setup is given in Ref. 12.

For the quasi-cw photoinduced absorption measurements either the liquid or solid sample was excited using our 3.1 eV (400 nm) blue laser diode module (Laser2000), modulated by the in-phase reference output of the lock-in amplifier (EG&G 7520). The probe beam was provided by a conventional tungsten lamp, which was monochromated after passing through the sample and subsequently detected by a Si-pin diode attached to a transimpedance amplifier. For temperature-dependent measurements a liquid nitrogen cryostat was used. The spectral resolution of this setup is ~5 nm.

III. RESULTS AND DISCUSSION

A. Primary photophysics of the β phase

In the recent literature a fully planar chain configuration has been conjectured as the microscopic origin of the β phase.[11] To test this notion it would be interesting to compare the β phase with the ladder-type polymer MeLPPP, which is by its chemical structure forced to be fully planar. On the other hand the branched side chain polyfluorene derivative PF2/6 never adopts the β phase. This was tested as we applied some of the treatment protocols outlined in the Introduction, namely, cycling at low temperature, annealing at 160 and 230 °C and preparing a thin film sample from the poor solvent (MCH), to PF2/6 thin films—none of the typical β-phase features could be detected. Therefore, only polyfluorene derivatives having linear, aliphatic side chains form

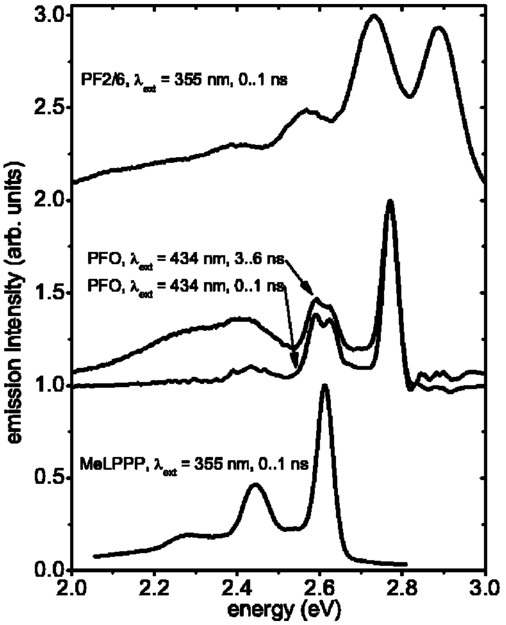

FIG. 2. Normalized prompt fluorescence spectra of PFO, PF2/6, and MeLPPP obtained with thin film samples at 11 K using one nanosecond integration time. The PFO β phase was selectively excited at 2.86 eV. A three nanosecond delayed β-phase spectrum is shown as well.

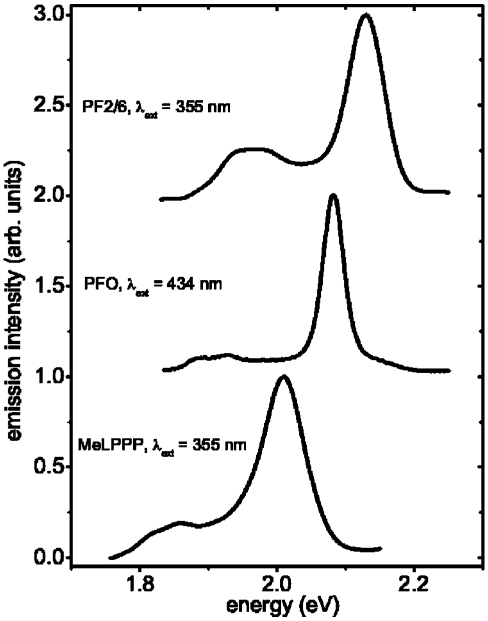

FIG. 3. Thin film phosphorescence spectra of the three polymers investigated. All spectra were obtained at 11 K upon integrating the delayed emission from 10 to 90 ms; PFO was excited selectively in the β phase at 2.86 eV. For the ease of evaluation the data are shown normalized and offset.

the β phase;[14,15] PF2/6 will hereafter be referred to as all amorphous. Therefore, by comparing PF2/6 with PFO spectra allows identifying typical β-phase features by distinguishing them from amorphous polyfluorene. In this section the singlet and triplet absorption and emission spectra of the β phase shall be compared to those of MeLPPP and PF2/6.

Figure 1 shows a compendium of typical room temperature, thin-film absorption spectra, including PFO, PF2/6, and MeLPPP, on a common energy scale. For the ease of comparison, the spectra are arbitrarily scaled and offset to each other. Consisted with literature data, and compared to the rather unstructured absorption of amorphous polyfluorene[18] the β phase features a new, low-energy absorption band, whose first peak appears at 2.84 eV (437 nm) followed by a vibronic satellite at 3.04 eV, which for our data only appears as a shoulder on the amorphous polyfluorene absorption band.[6,10,13] As can be seen from the included laser profile, the two excitation energies used throughout the study, 3.5 and 2.86 eV, enable selective excitation of the amorphous polyfluorene and the β-phase structure, respectively.

Normalized low temperature fluorescence spectra, obtained upon selectively exciting the β phase at 2.86 eV, are shown in the center part of Fig. 2. The prompt emission, which was detected over the first nanosecond after excitation, is characterized by a sharp transition at 2.77 eV followed by broader vibronic replicas at 2.59 and 2.41 eV. With our spectrometer we are able to resolve two subtransitions underneath the 0–1 band at low temperature; however, using higher spectral resolution at least three separate contributions can be distinguished.[11] At room temperature selective excitation of the β phase reveals the peak position at 2.800 eV (data not shown). Thus, the 300 as compared to the 11 K fluorescence is 30 meV shifted to the blue spectral region, which is a typical value for conjugated polymers. The low-temperature three nanosecond delayed spectrum is distorted by the occurrence of an additional broad yellow emission band centered at 2.3 eV, which is caused by unavoidable keto defect states. These will be discussed in more detail in the following section. No further striking differences between prompt and delayed fluorescence spectra are observed. For the sake of comparison, normalized low temperature prompt fluorescence spectra of PF2/6 and MeLPPP, which were obtained after exciting at 3.5 eV, are depicted in Fig. 2 as well. The $0 \leftarrow 0$ transitions are centered at 2.61 and 2.89 eV for MeLPPP and PF2/6, respectively; therefore the β phase emits at an intermediate energetic position.

Thin film phosphorescence spectra, including the all-amorphous PF2/6, the selectively excited β phase of PFO and the fully planar MeLPPP, are shown in Fig. 3 on a common energy scale. All spectra were obtained at 11 K using 10 ms gate and 80 ms integration time. As with the data shown in Figs. 1 and 2, these spectra are offset and normalized for clarity. The phosphorescence of both MeLPPP and PF2/6 are consistent with the spectral shape and position previously measured.[16,21] From the long lifetime of this emission as well as its spectral appearance the observed delayed β-phase emission is self-evidently assigned to phosphorescence from the first excited triplet state. The latter emission spectrum consists almost entirely of a very sharp $0 \leftarrow 0$ transition located at 2.08 eV, thereby following the general trend in conjugated polymers that phosphorescence spectra are dominated by the leading mode compared to corresponding fluorescence spectra, indicative of very similar ground and excited state chain (chromophore) geometries. Nevertheless, likewise for the fluorescence, at the energetic

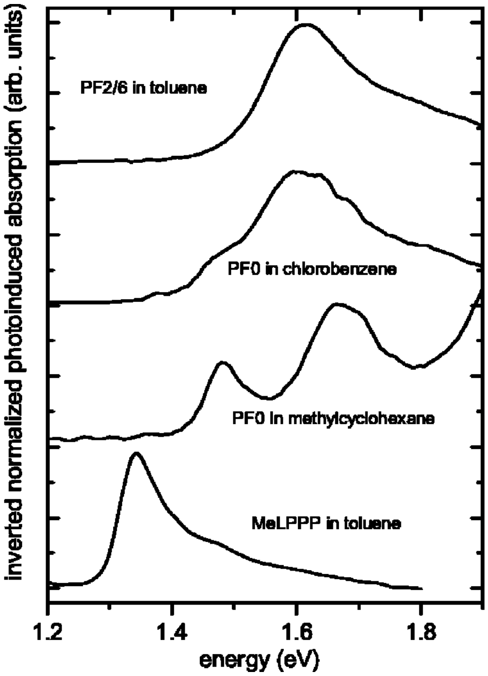

FIG. 4. Compendium of photoinduced quasi-cw transient absorption spectra. All data were measured on 10^{-5} wt. % solutions (solvent as indicated) at room temperature, excitation was made at 3.1 eV; the chopping frequency was 72 Hz.

position where the $1 \leftarrow 0$ transition is expected, ~1.9 eV, there are two weak bands just about visible. The singlet-triplet splitting is for all three polymers of order 700 meV. The redshift of the β-phase phosphorescence compared to the amorphous one amounts to 70 meV, which is an expected value considering the corresponding singlet shift of 120 meV.

Quasi-cw photoinduced transient absorption (PIA) spectra are shown in Figs. 4 and 5. This time the β phase could not selectively be excited due to the lack of an appropriate cw laser, all data are obtained after excitation at 3.1 eV. A compendium of such data for the three polymers in dilute room-temperature solution (all 10^{-5} wt. %) is shown in Fig. 4. Spectra similar to the ones shown here for MeLPPP and PF2/6 have been assigned to transient triplet absorption.[12] In the center part of the figure the PIA spectra of PFO dissolved in a good (chlorobenzene) and a poor (methylcyclohexane) solvent are shown. The PIA spectrum of PFO in the good solvent clearly resembles that of the all-amorphous PF2/6 and hence is attributed to triplet-triplet absorption originating from non-β-phase amorphous domains (from now we refer to such triplet excitons as "amorphous triplets"). The slight (10 meV) redshift of the PFO spectrum compared to PF2/6 is likely due to the different solvents polarities, which will have an enhanced effect on higher excited states. Upon using the poorer solvent MCH, the PFO PIA spectrum splits into two clearly distinct contributions. Because it is absent in the all-amorphous spectrum of PF2/6, the sharp feature centered at 1.44 eV is assigned to triplets located on the β phase. Since in this experiment the triplet excitons (formed via intersystem crossing) are not selectively excited in the β phase, there is also a contribution of amorphous triplet absorption in the PIA spectrum. Again the blueshift of the latter spectral component is attributed to the reduced polarity of MCH compared to toluene and chlorobenzene. Note, the increasing signal above 1.8 eV is due to prompt fluorescence. Apparently, even for the good solvent for PFO there is a shoulder just about visible around 1.46 eV, which indicates that any film made of PFO will contain a fraction of β phase. Due to efficient triplet exciton migration, which will be discussed in detail in the following two sections, it appears that the triplets readily migrate to the β phase allowing cw PIA to sensitively detect this latter component.

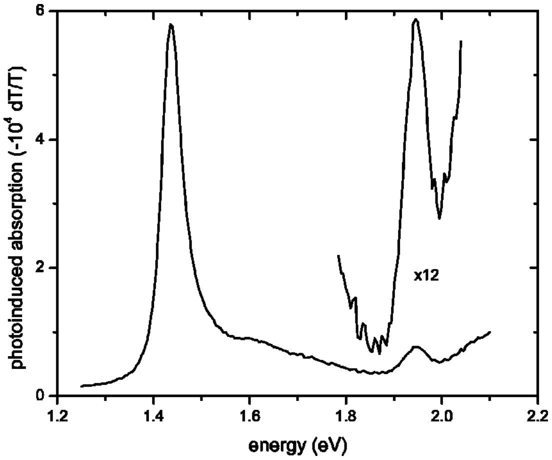

FIG. 5. 77 K photoinduced transient absorption spectrum of a PFO thin film sample. The sample was excited at 3.1 eV; the chopping frequency was 72 Hz. The area around 2 eV is shown on a magnified scale.

Independent of temperature (in the accessible range between 77–300 K), using thin PFO films the solid-state PA spectrum is dominated by β phase triplet absorption. A typical dataset, obtained at 77 K, is shown in Fig. 5. In addition to a small broad contribution around 1.6 eV, which is likely due to a residual amorphous triplet absorption, two further peaks can clearly be distinguished, a strong one at 1.44 and a ~12 times weaker one at 1.95 eV. Apparently the linewidth of both peaks is identical. Furthermore, the relative intensity of both peaks is independent of the chopping frequency used to detect the PIA spectrum (i.e., the decay kinetics for both features are identical), and also independent of temperature. In light of these experimental observations the assignment of the low-energy peak to triplets but the high-energy to peak polarons by Wohlgenannt *et al.*, who observed a similar solid-state PIA spectrum using PFO samples, appears very unlikely.[20] Much more probable is that both signals are caused by triplet transitions but to different higher lying, symmetrically allowed triplet levels, which consistently explains the above observations as both absorptions originate from the same excited species, the β-phase triplet exciton. To our knowledge this is the first conjugated polymer that shows such a double PIA spectrum, though other polymers might feature similar behavior but it would be harder to observe due to the spectrally broader transitions.

A reevaluation of the spectra shown in Figs. 1–5 yields some general trends and relationships between the three polymers under investigation. First, considering energetic position, the β phase lies at intermediate values between amorphous polyfluorene and fully planar polyparaphenylene. From this one concludes an increased conjugation length compared to polyfluorene, which, however, is not as long as that of MeLPPP. Further, all β-phase transitions are very narrow, which is unique within the class of conjugated polymers. This suggests a reduced dispersity of conjugation length, resulting in a narrower width of the density of energy states (DOS) (either for the singlet or for the triplet). From a simple extended conjugation length picture one expects a similar DOS compared to MeLPPP. The electronic transitions, relatively to MeLPPP, are dominated by the $0 \leftarrow 0$ transition, which is most obviously seen in Fig. 3. Furthermore, the Stokes shift of the β phase is the smallest within the class of conjugated polymers.[13] Both these observations are very interesting, as they point to more excited state (geometric) relaxation for the fully planar MeLPPP as compared to the β phase, though only the latter in principle has the freedom of ring rotations. Finally, we note the high luminescence anisotropy value only for the β phase.[13] The above experimental observations indicate that the β phase is more ordered than the fully planar ladder-type polymer MeLPPP. Additionally the driving force for the occurrence of the β phase has an intermolecular origin.[13–15] Both the higher ordering as compared to MeLPPP as well as the intermolecular origin provide indirect evidence that the excitations of the β phase itself are located in interchain as opposed to intrachain orbitals that are forced into an extended planar backbone conformation by the close packing of the polymer chains. Though final evidence is lacking, the interchain picture is much better suited to consistently explain the dissimilarities between MeLPPP and the β phase.

B. Singlet and triplet energy transfer from the amorphous to the β phase

In the following we do not speculate about the microscopic nature of the aggregated phase but make use of the miscellaneous character of any PFO thin film for exciton migration studies, by considering the β phase as an emissive low-energy trap within the amorphous PFO matrix. In this framework, the β-phase sensitizes the fluorescence and delayed fluorescence of singlet and, indirectly via triplet-triplet annihilation (TTA), triplet excitons, originally excited in the amorphous PFO manifold at 3.5 eV. Upon measuring the β-phase emission contribution in the prompt and delayed fluorescence spectra, one is able to draw qualitative conclusions about singlet and triplet migration, respectively. Representative results, itemized by prompt (PF) and delayed fluorescence (DF) and also by room and low temperature, are shown on a common energy axis in Fig. 6. For the PF, four nanoseconds integration time and zero gate time was chosen, the DF was detected from one to ten microseconds after excitation. The room temperature PF is dominated by amorphous polyfluorene emission, although an unresolved, small fluorescence contribution from the β phase (expected from room-temperature site selective measurements at 2.800 eV) just appears as a broadening on the blue side of the second vibrational mode of the amorphous fluorescence. This remaining β phase luminescence could either result from direct β phase absorption, at 3.5 eV or, more likely, it originates from direct singlet energy transfer such as Förster transfer. A somewhat reverse situation is observed for the one microsecond delayed room temperature emission. Apart from the broad defect emission contribution that peaks at 2.3 eV and which will be considered below, now the emission from the β phase with its prominent peak at 2.800 eV clearly dominates the spectrum—only leaving a small contribution of the amorphous polyfluorene delayed fluorescence visible. Keeping this important dissimilarity between the 300 K prompt and delayed fluorescence in mind, we pass to low temperature. Here, the vibronic structure of the spectra is generally much better resolved compared to the ones obtained at ambient temperatures. A redistribution of emission strength between the first and second vibronic mode of the amorphous polyfluorene emission is observed when comparing the room- with the low-temperature fluorescence spectrum. However, this is not caused by the β phase but is observed in conjugated polymers in general, i.e., also in branched side chain polyfluorene derivatives, which do not form aggregated structures at all, such as PF2/6.[22] Quantum-chemical modeling generally shows that such a redistribution towards the leading $0 \leftarrow 0$ vibrational mode originates from an increased conjugation length.[23,24] A small (25 meV) shift of the fluorescence to lower energies upon cooling the film is also observed.[9] Most importantly and at variance to the room temperature results, both prompt *and* delayed fluorescence are now dominated by the amorphous polyfluorene emission. However, in both cases the β phase fluorescence contribution at 2.770 eV is better resolved and appears as a pronounced shoulder on the blue edge of the second amorphous vibronic replica rather than just causing broadening. Further, both low temperature spectra (PF and DF) appear identical in spectral shape, i.e., there is no redistribution between the amorphous and β phase luminescence contribution when observing either the prompt or delayed fluorescence, respectively. This clearly indicates that prompt and delayed singlet exciton emission arises from identical sites.

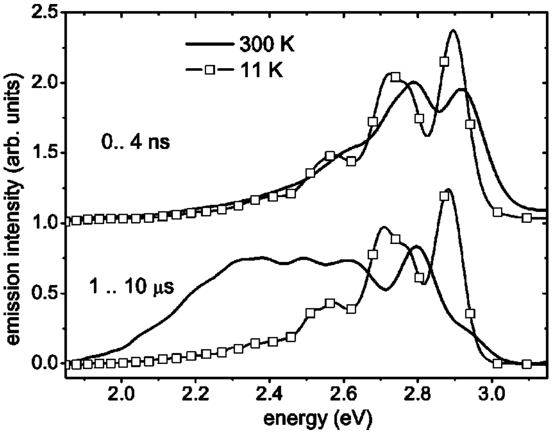

FIG. 6. Normalized prompt (upper part) and one microsecond delayed (lower part) emission spectra of a PFO thin film sample, either obtained at ambient or at low temperature after excitation in the amorphous PFO absorption at 3.5 eV.

In order to discuss the above experimental results we shall reiterate recent findings about triplet excitons and their migration in conjugated polymers. The delayed fluorescence observed in thin films, covering the vast majority of conjugated polymers, originates from triplet-triplet annihilation (TTA). Upon analyzing laser dose dependencies and transient triplet absorption kinetics, this, in particular, was shown for films of the all-amorphous polyfluorene derivative PF2/6.[12,18,19] The migration of the triplet is not solely an intrachain process, but interchain diffusion must occur. This fact was confirmed, since for a typical laser excitation dose of 100 $\mu J/cm^2$ on average less than one triplet is created on a single polymer chain.[12]

In view of this background knowledge we shall summarize and interpret the above experimental findings: nearly independent of temperature, for excitation in the amorphous phase, most of the prompt fluorescence is also emitted from the amorphous phase, thus in our samples the majority of singlet excitons do not reach the low-energy β phase during their radiative lifetime, ~300 ps. This implies that intersystem crossing mostly occurs on amorphous polymer segments—initially the majority of the triplet excitons reside on the amorphous phase. At low temperature the delayed fluorescence exactly matches the prompt fluorescence in spectral shape, which indicates that on average the triplets (prior to their annihilation) and the initially created singlets are located in the same environment. Thus, we conclude that in the absence of thermal activation triplet energy migration is inefficient and the triplets remain within close proximity to their parent singlet exciton. Whereas at ambient temperature, in contrast to the prompt fluorescence, the *delayed* fluorescence is dominated by sharp emission originating from the β phase. Using the above argument again: the PF mainly originates from the amorphous phase whereas the triplets encounter each other on the β phase, giving rise to the observed strong β-phase component in the delayed fluorescence spectrum. Note, singlet exciton Förster transfer to the β phase followed by intersystem crossing can safely be ruled out, because the prompt fluorescence shows no significant β-phase contribution. A straightforward explanation is that the triplet excitons, during their rather long existence compared to the singlet lifetime, manage to populate the β phase and any subsequent diffusion is only possible within this (low-energy) β-phase trap. This does not imply that the triplet hopping rate itself is equal or higher as compared to that of the singlet excitons, since the lifetime of the latter is much shorter. These experimental results clearly prove that at room temperature the absolute distance traveled by the triplet exciton clearly exceeds that of the singlet—at least in the case of polyfluorene. The general assumption of efficient Förster transfer for the singlet excitons compared to inefficient triplet transfer by the Dexter mechanism is an oversimplification of the situation. Further and common with earlier results,[12] the triplet migration is thermally activated rather than being caused by direct transfer mechanism, because no delayed fluorescence from the β phase is observed at low temperature. This interesting conclusion is fully consistent with the lack of room-temperature intrinsic phosphorescence in every conjugated homopolymer investigated so far. In the competition between radiative decay with long lifetime and encountering another triplet or a nonradiative decay site, the rather high mobility of the triplet exciton favors the latter possibilities. Unfortunately, the exact spatial distribution of the β phase embedded in the thin PFO film is unknown. Most likely, the β phase is rather inhomogeneously distributed, forming islandlike structures.[25] However, without this knowledge a serious estimate of the absolute distance traveled by the triplet is impossible. We are currently performing combined spatial and temporal resolved measurements on PFO thin films, which hopefully shine some light on this important issue.

Above it has been established that the amorphous triplet excitons in polyfluorene are essentially immobile at 11 K, but do efficiently migrate at room temperature. There is indeed further evidence for this notion. Upon measuring the temperature dependent phosphorescence intensity, we previously found that the average amorphous polyfluorene triplet trap depth is ~4.5 meV, thus roughly speaking the triplets are mobile above 50 K and trapped otherwise.[21] Therefore detecting the photoinduced transient triplet absorption spectrum at 77 K probes mobile triplets, which in the case of PFO populate the β phase. Further, so called “as spun” films are not completely β-phase free, which is proven by Fig. 4, because their parent polymer solution also shows signs of aggregation, even for supposedly good solvents such as toluene and chlorobenzene. Such interchain interactions would be even more pronounced in the solid state. As a result, any film made of PFO will contain some β-phase fraction. Keeping in mind the quasi-cw technique used to detect the PA signals, the mobile triplet excitons will have enough time (~ms) to occupy whatever low density of β-phase traps exist in the film, which explains why any cw-PA spectrum of PFO is dominated by β-phase signals.

Using this background knowledge we can also understand the initial cw photoinduced absorption spectra of the β phase published by Cadby *et al.*[9] and again by Wohlgenannt *et al.*[20] At 80 K the authors found a very sharp triplet absorption signal located at 1.44 eV, both for the presumably all-amorphous (as spun) and β-phase (thermally treated) PFO film. Their spectra are identical in spectral shape and position to the one shown in Fig. 5. However, from our own measurements on the truly all-amorphous derivative PF2/6 (Ref. 12) as well as on PFO in chlorobenzene, we locate a rather broad amorphous triplet signal of amorphous polyfluorene at 1.63 eV. Undoubtedly, the above authors simply measured the β-phase triplet signal in both cases, either with low (untreated) or high (thermally treated) β-phase content films. In the latter case the authors further observed a five- to tenfold reduced signal intensity. This observation is a consequence of enhanced triplet migration between β-phase domains, accompanied by more triplet-triplet annihilation events leading to an accelerated triplet decay. With low β-phase content, isolated β-phase traps greatly reduce the probability of triplet migration between traps, NB. The triplets cannot migrate between β-phase domains by hopping back onto the amorphous chains.

Within this study we tried to show the effect of freezing-in of the triplet migration on the photoinduced absorption spectrum after excitation in the amorphous phase as well. From the above said, we expected a substantial change between a 11 K compared to the 77 K spectrum for excitation in the amorphous absorption. Unfortunately we have not succeeded in doing so because small sample vibrations in our closed cycle helium cryostat prevented its use for PIA measurements.

Finally, we shall make some comments on the observed broad emission, which almost dominates the one microsecond delayed room temperature spectrum of Fig. 6. After a long debate about this issue, it has now been firmly established that this emission does not originate from excimers but from an emissive on-chain defect state, i.e., fluorene units that have been oxidized at the remote nine position to fluorenone.[26,27] The tendency to form these keto defect states in polyfluorene derivatives is very high if linear side chains (PFO) or hydrogen is attached;[26] it is reduced for branched side chains (PF2/6) and spirobifluorene is virtually inert against oxidation. Accordingly, PFO emission spectra are often accompanied by the broad keto signal, i.e., compare Figs. 2 and 6 or Refs. 4 and 14. Recently, it has been shown that these defect sites can either be directly excited at around 2.8 eV, which was essentially done in Fig. 2 or they can be populated via thermally activated singlet exciton migration.[27] This is why after excitation at 3.5 eV only the room temperature, one microsecond delayed spectrum of Fig. 6 shows a strong keto signal, but not the corresponding low temperature one. Note, a lack of keto emission in fluorescence spectra does not at all prove that these states are absent in the investigated polymer. In fact, none of our prompt fluorescence spectra show any keto emission contribution. However, using time-resolved spectroscopy it is very easy to detect even weak signals that are not visible in cw experiments, provided that the lifetime is different from other strong emission components. In the present case, gating out the prompt fluorescence enables us to observe the keto emission, which decays with a monoexponential lifetime of 5.8 ns,[27] i.e., ~ 20 times longer compared to the prompt fluorescence. Essentially, this was done in Fig. 2 if one only compares the β-phase spectra. Experience in our laboratory shows that *any* PFO sample contains keto defect sites—it is only the level that varies. Due to population via thermally activated interchain singlet migration the defect states will most likely show up at room temperature in solid samples. Additionally, keto emission is easily observed in electroluminescence devices, because fluorenone is an electron trap and thus acts as a recombination center in a working device.

C. Decay kinetics of the β-phase delayed fluorescence

One of the observations described in the previous sections is the occurrence of delayed fluorescence, which is identical in spectral shape and energetic position to the β-phase prompt fluorescence. Independent of temperature, only the latter DF is observed, provided that excitation is selectively made in the β phase of PFO. In this section we shall elucidate the selectively excited β-phase fluorescence decay kinetics and compare it to the kinetics previously observed in the all-amorphous polyfluorene PF2/6. The measurements were done on thin solid films and we state again that here the DF is caused by triplet-triplet-annihilation.[12] Since delayed fluorescence arises via triplet migration, it yields valuable information about this, otherwise dark, excited state. In order to understand the DF results it is helpful to first discuss the characteristics of the underlying triplet migration, which is rate limiting for the TTA. For this we draw heavily on earlier work about triplet-triplet annihilation in a disordered polyfluorene;[12] we shall not attempt to reproduce this work in detail, but highlight important findings.

At low temperature, it is reasonable to neglect the monomolecular decay contributions (both radiative and nonradiative) and in doing so to assume that annihilation is the dominating decay mechanism for the triplets in the time domain much shorter than the triplet lifetime, i.e., for $t < 100$ ms:

$$DF \sim \frac{dn_T}{dt} = -\gamma_{TT} n_T{}^2 \tag{1}$$

with n_T being the time-dependent triplet density, γ_{TT} denotes the triplet-triplet-annihilation "constant." Within the field of disordered materials, such as conjugated polymers, the only successfully applied theory to date describes the triplet diffusion as a series of incoherent jumps within a material dependent density of localized energy states (DOS). After pulsed excitation the diffusion of the triplet excitons, which for photoexcitation experiments have to be formed via intersystem crossing from the singlet manifold,[28] evolves in two fundamentally different migration regimes. First, motion is governed by fast energy relaxation towards low-energy sites inside the DOS. For the migrating triplet, neighbor sites that qualify for the next jump, i.e., of lower energy, become fewer with the elapse of more and more time after excitation. This renders the diffusion (and concomitantly γ_{TT}) time-dependent or dispersive, respectively, which itself asymptotically decays proportional to t^{-1} for any Gaussian-type DOS.[29–31] Furthermore, time-resolved transient triplet absorption studies prove that during the dispersive time regime the triplet density itself is nearly constant,[12] thus, the triplet-triplet annihilation does not substantially reduce the initially created triplet exciton reservoir. Therefore, the second, quadratic term in Eq. (1) is constant and the decay of the observed delayed fluorescence directly reflects the deceleration of the triplet diffusion, $\gamma_{TT}(t)$ and consequently obeys an algebraic law with an exponent close to -1. After a temperature dependent segregation time t_s, defined as

$$t_s(T) = t_0 e^{(c\delta/k_B T)^2} \tag{2}$$

with t_0 being a material constant and $c \sim 1$, the mean energy has settled $-\delta^2/k_B T$ below the center of the DOS, characterized by a width δ. At this (temperature dependent) delay time the diffusion due to thermalization within the DOS equalizes thermal activated hopping. Now the nondispersive, classical, regime is attained, which is described by a time-independent, but temperature-dependent diffusion constant. According to Eq. (1) with time-independent γ_{TT} the DF obeys an algebraic decay law with exponent -2, which reflects the bimolecular depletion of the triplet reservoir. Concomitantly, the triplet density n_T decays with a slope of -1.[12] Within this theory of migration in an energetic DOS, the observed redshift of the PF upon cooling is partly a consequence of the temperature-dependent energy relaxation within the DOS. A special case applies at zero temperature. Because of the lack of ther-

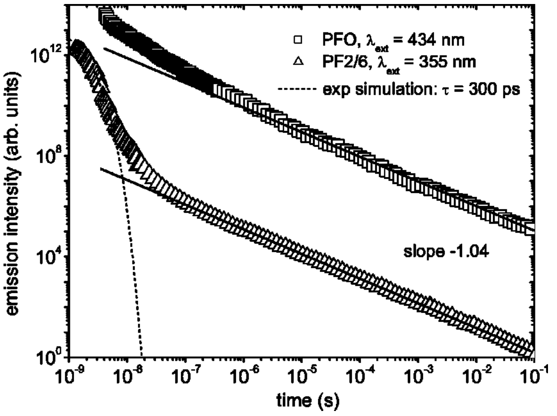

FIG. 7. Comparison of the PFO (directly excited in the β phase at 2.86 eV) and all-amorphous PF2/6 delayed fluorescence decay at 11 K using thin film samples. In this double logarithmic presentation the solid lines refer to power law decays, characterized by an exponent of −1.04. The exponential decay of the prompt fluorescence of PF2/6 is simulated using a lifetime of 300 ps. Note, the relative emission intensity between both curves is arbitrary.

mal activation energy only diffusion due to thermalization is possible, therefore the classical time-independent regime is never achieved. Already at moderately low temperature (typically <100 K), depending on the width of the DOS the segregation time t_s might be longer than the lifetime of the hopping exciton. This hopping theory with its major features, time-dependent exciton migration and energy relaxation, has been successfully applied on conjugated polymers covering both, singlets,[32] and triplet excitons.[12] In particular for the DF due to TTA in amorphous polyfluorene, the two successive time regimes, characterized by decays proportional to t^{-1} and t^{-2}, respectively, could clearly be distinguished.[12] This material independent, universal decay pattern is the fingerprint of triplet-triplet annihilation in a Gaussian distribution of states.

In Figs. 7 and 8 the fluorescence decays of PFO and PF2/6 thin films are shown together at 11 K and ambient temperature, respectively. In these double logarithmic plots each data point represents an integrated fluorescence spectrum, which was recorded upon accumulating spectra over 50 laser shots. Both PFO decays were excited selectively in the β phase at 2.86 eV, therefore exciton migration from the amorphous towards the low energy β phase does not interfere with the measurements. Since we are mainly interested in the delayed fluorescence kinetics, the initial nearly exponentially decaying prompt fluorescence has been omitted in all but the low-temperature curve of PF2/6. The latter dataset is rather unique for conjugated polymers as it covers the time span of eight orders in logarithmic time and the signal decays by 13 orders of magnitude in intensity. The low temperature DF kinetics itself are rather simple. Up to a few nanoseconds the emission is dominated by the tail of the nearly exponentially decaying prompt fluorescence, here only simulated for PF2/6 using 300 ps lifetime, the radiative singlet lifetime of the β phase is slightly shorter.[13] Subsequently, for both polymers the decay of the DF due to TTA asymptotically approaches an algebraic law with exponent of −1.04. Consistent with Eq. (1) and assuming a nearly constant triplet density, the latter (universal) exponent reflects the decaying triplet diffusion in a Gaussian density of state. Within the time period spanned by the graph, 100 ms, no further turning point in the kinetics is observed. Therefore, the classical equilibrium triplet migration regime is not realized within these 100 ms at low temperature and diffusion is achieved by thermalization towards low-energy states of the DOS only. For further increased delay times both DF curves feature an accelerated decay compared to the algebraic one (not shown), which reflects the reduced triplet-triplet-annihilation activity due to the monoexponential radiative triplet decay, which for both polymers is of the order of one second.[12]

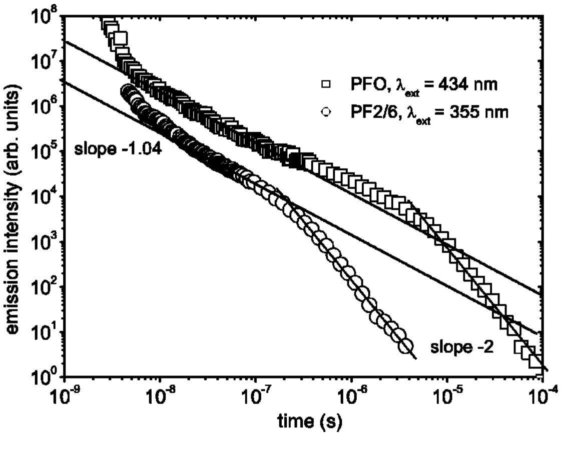

FIG. 8. Decays of the spectrally integrated, room-temperature fluorescence of PFO ($\lambda_{exc}=2.86$ eV) and PF2/6 ($\lambda_{exc}=3.5$ eV) thin films. The solid lines refer to power law decay kinetics with slope of −1.04 and −2, respectively. The data are arbitrarily scaled to each other.

Next, we pass over to the more complex kinetics observed at ambient temperature. For the sake of comparison in Fig. 8 identical conditions (except of the temperature) as in Fig. 7 have been used. Again, after the prompt fluorescence decay, the typical slope of −1.04 is observed at intermediate times in both cases, which is caused by triplet energy relaxation—even at room temperature. Subsequently, after dissimilar delay times, each of the decays accelerates now obeying an algebraic law with slope −2, which reflects the depletion of the triplet reservoir according to Eq. (1). Note, in order to realize the sudden depletion of the number of triplets as soon as the triplet diffusion approaches a constant value, one needs to think of the number of triplet jumps per unit time that occur, which in a logarithmic plot rapidly increases once equilibrium diffusion is attained, i.e., once the retarding effect of the decaying triplet diffusivity vanishes. For both polymer films thermally activated equilibrium triplet migration is achieved at room temperature but after dissimilar segregation times t_s. The time it takes to approach equilibrium triplet diffusion increases from 250 ns to 10 μs for the amorphous and the β phase, respectively. What is the significance of the dissimilar segregation times? Apparent from Eq. (2), two further variables influence t_s in addition to the temperature, the width of the DOS σ, and the prefactor t_0. In fact, from Fig. 3 the β-phase triplet DOS is obviously narrower compared to the amorphous DOS and therefore cannot account for the observed longer segregation time. The material dependent prefactor of Eq. (2) describes the time that is needed for a jump between two isoenergetic sites separated by R_{ij}

$$t_0 = [6\upsilon_0 e^{(-2\alpha R_{ij})}]^{-1} \tag{3}$$

with α being the inverse localization length of the triplet exciton and υ_0 the attempt-to-jump frequency. If we assume that α and υ_0 are identical for the β and the amorphous triplet phase, it follows that the average site spacing for triplet jumps in the β phase must be larger compared to the amorphous one. It is certainly misleading to assume that the site spacing in the supposedly well-ordered β phase itself is larger than in corresponding amorphous polymer films. However, the β phase does not form large connected areas but rather isolated domains of 25–30 nm diameter within the PFO film, which was recently shown by near field scanning optical microscopy.[25] Within such domains the triplet migration might be highly efficient. However, *rate limiting* for the observation of long-lived delayed fluorescence due to triplet-triplet annihilation is the triplet jump between separated β phase domains embedded in an amorphous PFO matrix. Obviously, on account of its higher triplet energy, the amorphous PFO matrix cannot participate on the β phase triplet migration, and therefore acts as an energetic barrier. To summarize the above, the increased time it takes to approach equilibrium triplet diffusion qualitatively reflects the larger average separation of individual β-phase domains when compared to the site spacing in an all-amorphous polymer film. Concomitantly, the segregation time is a qualitative measure of the β-phase level within the PFO film and in this way is sensitive to the sample preparation protocol. Of course a hypothetical polymer film that consists only of the β phase will show a very short dispersive diffusion regime, due to its reduced disorder, when compared to common conjugated polymers.

IV. CONCLUSIONS

In this contribution PFO β-phase spectra, including singlet, transient triplet absorption, fluorescence, and phosphorescence are presented and analyzed, most have been measured using the selectively excited β phase. Within the class of conjugated polymers, the uniquely narrow transitions accompanied by very little excited state relaxation, together with the intermediate energetic spectral positions between amorphous polyfluorene and the fully planar polyparaphenylene suggest an interchain extension of the conjugated π orbitals as opposed to just a simple increase in intrachain conjugation length.

It is also clear that the β phase acts as an energetic trap for both singlet and triplet excitons, originally photoexcited on non-β-phase, amorphous, chain segments. Photoinduced cw triplet absorption is found to be a very sensitive tool to probe the β fraction in either liquid or solid PFO samples. Using the latter technique it has been established that any PFO thin film, even the so called “as spun” samples, contain a certain amount of β phase, which is partly already preformed in solution. Further, using the β phase as an emissive trap that sensitizes delayed emission from triplet-triplet annihilation, we have shown that triplet as compared to singlet migration is equally active at room temperature. For that reason it has to be in general carefully checked whether Förster transfer is the dominating population mechanism in guest-host systems based on conjugated polymers. Thermally assisted exciton migration could also be the rate-limiting step.

Finally, the temperature-dependent delayed fluorescence kinetics of the selectively excited β phase have been given and analyzed within a well-established framework of triplet-triplet annihilation in a broad distribution of localized states. Consistent with foregoing work on different polyfluorene derivatives, we confirm that triplet migration is a thermally activated hopping process. Further, the triplet migration is dispersive for any delay time after excitation that is smaller than a temperature-dependent segregation time. Time-independent classical triplet migration is approached for longer delay times. In β-phase containing films, the segregation time, between dispersive and thermally activated migration, is strongly dependent on the separation between β-phase domains and indicates that β-phase content grows in via further nucleation of sites as opposed to growth of larger domains.

ACKNOWLEDGMENTS

We would like to thank Dr. Batsanov (Chemical Department of the University of Durham) for synthesizing the PFO. Further, we are grateful to EPSRC for funding (GR/R19687) and One North-East via the County Durham Sub-regional Partnership. C.R. acknowledges a Royal Philips Electronics CASE studentship.

---

[1] Philips released a shaver equipped with a two color display based on polymer light emitting diodes.

[2] K. S. Whitehead, M. Grell, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, Synth. Met. **111**, 181 (2000).

[3] T. Virgili, D. G. Lidzey, M. Grell, S. Walker, A. Asimakis, and D. D. C. Bradley, Chem. Phys. Lett. **341**, 219 (2001).

[4] B. Schartel, V. Wachtendorf, M. Grell, D. D. C. Bradley, and M. Hennecke, Phys. Rev. B **60**, 277 (1999).

[5] M. Grell and D. D. C. Bradley, Adv. Mater. (Weinheim, Ger.) **11**, 895 (1999).

[6] M. Grell, D. D. C. Bradley, G. Ungar, J. Hill, and K. S. Whitehead, Macromolecules **32**, 5810 (1999).

[7] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, and A. Yasuda, Adv. Mater. (Weinheim, Ger.) **11**, 671 (1999).

[8] M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. In-

basekaran, E. P. Woo, and M. Soliman, Acta Polym. **49**, 439 (1998).

[9] A. J. Cadby, P. A. Lane, H. Mellor, S. J. Martin, M. Grell, C. Giebeler, D. D. C. Bradley, M. Wohlgenannt, C. An, and Z. V. Vardeny, Phys. Rev. B **62**, 15 604 (2000).

[10] M. Ariu, D. G. Lidzey, and D. D. C. Bradley, Synth. Met. **111**, 607 (2000).

[11] M. Ariu, M. Sims, M. D. Rahn, J. Hill, A. M. Fox, D. G. Lidzey, M. Oda, J. Cabanillas-Gonzalez, and D. D. C. Bradley, Phys. Rev. B **67**, 195333 (2003).

[12] C. Rothe and A. P. Monkman, Phys. Rev. B **68**, 075208 (2003).

[13] F. B. Dias, A. L. Macanita, J. Morgado, H. D. Burrows, and A. P. Monkman, J. Chem. Phys. (to be published).

[14] J. Teetsov and M. A. Fox, J. Mater. Chem. **9**, 2117 (1999).

[15] P. Blondin, J. Bouchard, S. Beaupre, M. Belletete, G. Durocher, and M. Leclerc, Macromolecules **33**, 5874 (2000).

[16] Y. V. Romanovskii, A. Gerhard, B. Schweitzer, U. Scherf, R. I. Personov, and H. Bassler, Phys. Rev. Lett. **84**, 1027 (2000).

[17] C. Rothe, S. Hintschich, A. P. Monkman, M. Svensson, and M. R. Anderson, J. Chem. Phys. **116**, 10 503 (2002).

[18] C. Rothe, R. Guentner, U. Scherf, and A. P. Monkman, J. Chem. Phys. **115**, 9557 (2001).

[19] D. Hertel, H. Bassler, R. Guentner, and U. Scherf, J. Chem. Phys. **115**, 10 007 (2001).

[20] M. Wohlgenannt and Z. V. Vardeny, Synth. Met. **125**, 55 (2002).

[21] C. Rothe and A. P. Monkman, Phys. Rev. B **65**, 073201 (2002).

[22] C. Rothe, S. I. Hintschich, L. O. Palsson, A. P. Monkman, R. Guentner, and U. Scherf, Chem. Phys. Lett. **360**, 111 (2002).

[23] S. Karabunarliev, M. Baumgarten, E. R. Bittner, and K. Mullen, J. Chem. Phys. **113**, 11 372 (2000).

[24] S. Karabunarliev, E. R. Bittner, and M. Baumgarten, J. Chem. Phys. **114**, 5863 (2001).

[25] J. Teetsov and D. A. Vanden Bout, Langmuir **18**, 897 (2002).

[26] L. Romaner, T. Piok, C. Gadermaier, R. Guentner, P. S. de Freitas, U. Scherf, G. Cerullo, G. Lanzani, and E. J. W. List, Synth. Met. **139**, 851 (2003).

[27] S. Hintschich, C. Rothe, S. Sinha, and A. P. Monkman, J. Chem. Phys. **119**, 12 017 (2003).

[28] H. D. Burrows, J. S. de Melo, C. Serpa, L. G. Arnaut, A. P. Monkman, I. Hamblett, and S. Navaratnam, J. Chem. Phys. **115**, 9601 (2001).

[29] M. Grunewald, B. Pohlmann, B. Movaghar, and D. Wurtz, Philos. Mag. B **49**, 341 (1984).

[30] B. Movaghar, B. Ries, and M. Grunewald, Phys. Rev. B **34**, 5574 (1986).

[31] B. Movaghar, M. Grunewald, B. Ries, H. Bassler, and D. Wurtz, Phys. Rev. B **33**, 5545 (1986).

[32] S. C. J. Meskers, J. Hubner, M. Oestreich, and H. Bassler, Chem. Phys. Lett. **339**, 223 (2001).