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Signatures of Melting and Recrystallization of a Bulky Substituted Poly(thiophene) Identified by Optical Spectroscopy

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S Supporting Information

ABSTRACT: As-cast and slowly crystallized films of conjugated polymers can contain (partially) ordered and less ordered (amorphous) regions with structural defects. Crystallization allows to generate chains with highly planarized backbones, embedded in structures exhibiting long-range order. In the present study, we used spatially resolved optical spectroscopy to quantify differences in the degree of order of a bulky substituted poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT). In particular, we compared absorption and photoluminescence (PL) measurements from large spherulitic crystals, and the same region rapidly recrystallized after melting, which allowed to identify characteristic features of ordered and less ordered regions. In addition, on the basis of temperature-dependent absorbance and PL measurements, we followed *in situ* melting and recrystallization processes, i.e., transitions between ordered and disordered phases. A multipoint analysis of absorption and PL spectra based on a modified Franck–Condon progression showed changes in for example the relative intensities of each peak, the excitonic bandwidth, and the vibronic energy as a function of temperature. Most importantly, at the phase transition temperature, a clear change in the positions of the peaks (i.e., their wavelengths, corresponding to the energy of the emitted photons) was detected. In particular, the relative absorption and PL intensities depended sensitively on the extent of order within PDOPT samples. Furthermore, on the basis of a comparison with calorimetric measurements, we have confirmed correlations between changes in the relative absorbance and PL intensities with variations in order/disorder occurring during melting and recrystallization.

■ INTRODUCTION

In order to understand optoelectronic properties of conjugated polymer systems and to establish ways for enhancing their performance in optoelectronic applications, previous studies have measured absorption and emission spectra as a function of packing and order in thin films.^{1–7} To a large extent, optical properties of conjugated systems are determined by intra- and interchain interactions,^{8,9} which also strongly influence energy and charge transfer. A conjugated polymer chain can be viewed as a system of many coupled chromophores. Although the contour length of a polymer chain may be more than 100 nm, the presence of disorder of different kinds leads to localization of the exciton wave function on a smaller sequence of the polymer chain, to the ultimate extent that each individual chromophore along a polymer chain may act as an (independent) emitter. For instance, in a solution of poly(phenylenevinylene) (PPV), excitons are localized on segments with a size range of 5–10 monomer units, corresponding to a typical length of ca. 3–6 nm.¹⁰ Hence, because of variations in

the degree of delocalization of the exciton along the chain, emission from a long polymer chain will generally have a broad spectrum resulting from a superposition of individual spectral lines.¹⁰ Depending on the extent of delocalization, emission ranges from rather short (blue) to long (red) wavelengths. In addition, the wavelength of emitted photons detected in a photoluminescence (PL) experiment is influenced by the nature of the morphology, solvent, concentration, and temperature.^{11–14} In particular, the formation of highly ordered structures is meant to planarize the chains and to reduce the number of defects, e.g., due to twisting of the backbone, and hence to increase the conjugation length.^{15,16} In addition, crystallization may cause a change of intermolecular distances and thus may affect the electronic and vibrational coupling of chromophores. Hence, crystallization may give rise to changes

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in the energy levels and energy transfer processes and thus in the optical properties of the conjugated polymer.

Having said that, large intermolecular spacing and correspondingly weaker intermolecular interactions may also have a significant influence on molecular ordering. Bulky side chains attached to conjugated polymers may separate the polymer backbones from each other, and this can lead to changes of the final optoelectronic properties of these materials. Except for a few recent reports,^{6,14,17–20} a clear understanding of the relationship between ordering of molecules with bulky side chains, the resulting morphology, and optoelectronic properties of conjugated systems having a large interchain separation distance (>1 nm), and thus no π – π interactions, has yet to emerge. Recently, large spherulites of poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT) were reported.^{1,19} According to previous studies, the bulky dioctylphenyl side groups separate the thiophene backbones of PDOPT by ca. 1.47 nm.^{1,6,17,19} Hence, π – π interactions do not play an important role in PDOPT.^{1,12,14} Moreover, the weakened interchain interactions in PDOPT lead to a much lower melting temperature as compared to poly(3-hexylthiophene) (P3HT)¹⁶ and most other polythiophenes.¹⁶ Large interchain separation can also strongly affect the photoluminescence quantum efficiency (PLQE), i.e., the ratio of the number of emitted photons to the number of absorbed photons, of conjugated systems.^{6,17,21,22} Polythiophenes for which the electronic energy gap is increased by steric hindrance show low PLQE, in both film and solution. This low PLQE originates from a nonradiative decay of excited states.^{17,22}

Morphology-induced thermochromism is a frequently encountered phenomenon in conjugated polymers. It was first observed when studying the fluorescence from polydiacetylene in solution.¹¹ In polydiacetylene, depending on temperature, the relative emission intensity was high either from a high-energy state (blue phase) or from a lower-energy state (red phase). Temperature-dependent PLQE of poly(9,9-dioctylfluorene) (PFO) films with different morphologies showed that PLQE depended on morphology.²

In most theoretical treatments of the electronic properties of polymer aggregates, it is assumed that every noninteracting chromophore can be represented by individual, well-defined ($S_0 \rightarrow S_1$) electronic transitions.²³ Vibronic progression peaks, observed in both absorption and PL spectra, accompany these electronic transitions. These vibronic progression peaks result from coupling to vibronic wave functions of the ground state and excited states. Often, the most intense peak is represented by the transition which takes place between the lowest energy level in the excited state and the zero vibronic level in the ground state for both emission and absorption (the so-called 0–0 transition).

If crystallites of conjugated polymers are formed, and thus interchain interactions (between chromophores) are considered, electronic excitations become delocalized over several chromophores; i.e., exciton manifolds form. As a consequence, both the absorption and emission spectra shift and the vibronic progression become distorted with respect to that of the spectra of the noninteracting chromophores.^{24–27} In the resulting emission spectra, the change of the 0–0/0–1 ratio characterizes the degree of order in the crystallites. In the absorption spectra, the corresponding peak ratio is a measure for the strength of the interchain interactions. Hence, the energy distribution in the excited state is a fundamental property of an ensemble of chromophores constituting an organic semi-

conductor, which is controlled by interactions between chromophores. Manifestations of the latter are changes in the optical spectra as well as modified charge and energy transfer rates that are of paramount importance to the operation of optoelectronic devices.²⁸

In this study, we performed temperature-dependent optical spectroscopy on as-cast thin films and spherulitic crystals of PDOPT in order to understand, in particular, the relationship between emission probability and changes in morphology from ordered crystalline regions to disordered molten chains. Specifically, we focused on properties of highly ordered polymer chains resulting from crystallization and the changes induced by melting. Crystallization of PDOPT is expected to planarize the backbone, thereby increasing the effective conjugation length. In our system, we observed distinct differences in optical spectra obtained from slowly formed spherulitic crystals and the same molecules after melting. In addition, we correlated PL spectra with calorimetric data in order to establish a relation between thermal and optical properties.

EXPERIMENTAL DETAILS

Materials and Preparation. Poly(3-(2,5-dioctyl phenyl)-thiophene) (PDOPT) (Figure 1) was synthesized through Kumada

Figure 1. Schematic representation of the chemical structure of poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT).

catalyst transfer polycondensation.¹ The weight-average molecular weight (M_w) of the PDOPT sample used was 28 kg/mol with a dispersity $\bar{D} = 1.86$. All studied samples were prepared from a 3.3 mg/mL PDOPT solution in toluene. To ensure complete dissolution, the vial was placed in an oil thermostat at an elevated temperature of 60 °C for 10 h. A thin film of thickness 200 nm was made by casting approximately 10 μ L of this hot solution of PDOPT on 1 cm² glass or silicon substrates, which earlier were carefully cleaned in an ultrasonic bath at 45 °C for 15 min using acetone, followed by a 30 min treatment in a UV-ozone chamber.

Isothermal Crystallization of Pristine PDOPT Films. Large spherulitic crystals were grown via isothermal crystallization from molten films. First, to erase memory effects, films were brought to a temperature well above the nominal melting temperature T_m of PDOPT ($T_m \approx 115$ °C), i.e., to 150 °C for ca. 2 min.¹ Sample temperature was controlled to a precision of ca. 0.1 °C by a hot stage purged with nitrogen (Linkam Scientific Instruments, UK). Then, the sample was cooled to selected crystallization temperatures T_c (e.g., to $T_c = 100$ °C) at a rate of 10 °C/min and isothermally crystallized for up to 50 h. Highly birefringent large spherulitic crystals (Figure 2a) were formed. The size of the spherulites varied from 10 μ m to more than 250 μ m in diameter, depending on when nucleation occurred during the crystallization process (see Figure S1a).

Optical Microscopy and Spectroscopy. To characterize the morphology of the spherulitic crystals formed, optical micrographs were taken using a Zeiss Axio 100 microscope. In order to gain insight into the origin of the optical properties, spatially resolved (with a diameter of 10 μ m for the detected area) absorption and PL spectra were recorded on different regions in as-cast films and spherulitic

Figure 2. Optical micrographs (a) under crossed polarizers (indicated by the white arrows) showing strong birefringence and (b) of absorption and (c) of emission upon excitation with polarized light (polarization direction is indicated by the horizontal white arrows) for a spherulitic crystal grown at 100 °C for 50 h in a molten thin film (ca. 200 nm) of PDOPT. All micrographs were taken after the sample was quenched to room temperature; i.e., the surrounding molten film was rapidly crystallized. The scale bar indicates a length of 50 μm .

Figure 3. First and third rows show the birefringence from a spherulitic crystal during heating from 30 to 125 °C. The second and fourth rows show the corresponding PL images, when the spherulite was excited by light polarized in the direction indicated by the white arrows. The crystal was grown at 100 °C for 50 h. The scale bar indicates a length of 20 μm .

crystals, enabling the identification of contributions from different regions of order and different morphologies to optical spectra. Absorption measurements with a USB 2000 Ocean Optics spectrometer and Ocean Optics optical fibers were performed in combination with the Zeiss Axio 100 microscope, allowing for such localized measurements. *In situ* photoluminescence spectra were taken as a function of temperature in order to gain insight into how a change from an ordered crystalline phase (spherulitic crystal) to a disordered molten phase is reflected in optical properties. As light source for PL measurements, we used an Ocean Optics TS-LED light source combined with a filter set having a band-pass for the incident light ranging from 450–500 nm, a long pass starting at 500 nm for the emitted light, and a beam splitter with 99% transmission above 500 nm (all filters were purchased from AHF analysentechnik AG, Tübingen, Germany). In this study, while absorption spectra were collected in transmission mode, PL spectra were collected in reflection mode using an optical fiber of diameter 200 μm and a 20 $\times$ objective of the Zeiss Axio 100 microscope (see also Figure S7).

RESULTS AND DISCUSSION

Morphology of PDOPT Crystals. When observed under crossed polarizers at room temperature, the spherulitic crystals showed the characteristic Maltese cross,²⁹ indicating a pattern of radially oriented crystalline lamellae (Figure 2a). The high

molecular order within the lamellae resulted in strong birefringence. The edges of the spherulitic crystals were not sharp but rather diffuse, indicating that lamellae grew in parallel but with some lag time. The absorption image (Figure 2b) clearly showed that only lamellae in the direction orthogonal to the polarization direction of the incoming light were strongly absorbing. Accordingly, emission was only observed in regions where absorption was occurring (Figure 2c). Interestingly, emission from the spherulitic crystal was less than from the surrounding quenched and thus rapidly crystallized film.

Melting: A Phase Transition from Order to Disorder. *Optical Microscopy.* PDOPT spherulites exhibited a clear anisotropy (see Figure 2), demonstrating that the transition dipole moment of PDOPT (along the chain, i.e., *c*-axis) in spherulitic crystals was perpendicular to the radius. Optical micrographs with crossed polarizers (i.e., birefringence images) taken during the heating process (Figure 3) also showed this anisotropy. However, the birefringence intensity from the spherulitic crystals decreased with increasing temperature and disappeared upon melting of the spherulitic crystal. The corresponding PL images in Figure 3 from the central spherulite showed an analogous behavior. Interestingly, at 30 °C, PL emission was more intense in the film surrounding the

spherulitic crystal. However, the relative intensity of emission from the spherulitic crystal increased with increasing temperature until it matched the intensity of the surrounding film at around 125 °C, when the spherulite was molten completely. This temperature-dependent change of optical properties, i.e., the thermochromic behavior observed in PL, can be directly mapped to melting of the spherulite, i.e., a change in morphology. Interestingly, fully consistent with the well-known Hoffman–Weeks relation of polymer crystals, i.e., the dependence of melting temperature of a polymer crystal on its crystallization temperature,³⁰ the film surrounding the spherulite (which crystallized upon quenching the sample to room temperature) showed the thermochromic change in the PL spectrum reflecting the melting process at a ca. 11° lower temperature.

Temperature-Dependent Absorption Spectra. To gain further insight into the influence of molecular conformation and order on the photophysical properties of PDOPT spherulites, we studied *in situ* changes in absorption spectra while heating the PDOPT spherulites from 30 to 150 °C and subsequently cooling of the melt back to 30 °C, both at a rate of 2 °C/min. The corresponding absorption spectra measured with 10 μm spatial resolution at the position of a spherulite are shown in Figure 4a for the heating process and in Figure 4c for the cooling process from the melt.

Figure 4. Optical absorption and PL spectra of a spherulitic crystal showing (a, c) absorbance and (b, d) emitted photons during (a, b) heating and (c, d) cooling at a rate of 2 °C/min. The numbers in blue represent temperature in °C (for curves measured at additional temperatures, see Figures S8 and S9). Note that during these measurements the number of molecules interacting with light was always constant.

The absorption spectrum of the spherulite at 30 °C (Figure 4a, black) showed three distinct peaks between 2.12 and 2.5 eV and a broad shoulder at higher energies around 2.6 eV. Upon heating the sample, the intensity of the lower-energy peaks dropped and peak positions shifted to higher energies. Above the nominal melting temperature of around 120 °C (see also Figure 3), only the higher-energy contribution survived. In the subsequent cooling process, absorption at higher energy prevailed down to about 75 °C. Below 75 °C, structured absorption features started to dominate once more at lower energies. The spectrum of the sample cooled back to 30 °C looked qualitatively very similar to the initial 30 °C spectrum before heating, but with significantly higher absorbance.

It should be noted that the spherulites were grown by slow isothermal crystallization of PDOPT and grew in the radial direction. The PDOPT chains arranged in a well-ordered fashion into radially growing lamellar crystals, with the polymer backbones being oriented perpendicular to the growth direction,^{6,19} giving rise to clearly observed anisotropy under crossed polarizers (see Figures 2 and 3). The space in between these lamellar crystals contained disordered chain segments (or chain ends).³¹ Both the shape of the 30 °C absorption spectrum of the PDOPT spherulite and the sample morphology (crystalline lamellae intertwined with disordered regions) were similar to that found for semicrystalline films of the prototypical poly(3-hexylthiophene).^{32–34} Hence, we attribute the 30 °C spectrum from a PDOPT spherulite to a superposition of absorption from a lower-energy (2.12–2.5 eV) crystalline phase with reasonable interchain interactions that features a distorted vibronic progression with a peak spacing of about 170 meV and a broad unstructured absorption from a disordered phase, dominating at higher energies around 2.6 eV. Upon heating, the spherulitic structure of PDOPT disappeared above ca. 120 °C. At higher temperatures, exclusively the spectrum from the disordered melt prevailed, which closely resembled that of a dilute solution (see later, Figure 9), suggesting a loss of significant interaction between PDOPT chains. After rapid cooling from the melt, PDOPT recrystallized at around 75 °C, as evidenced by the reappearance of the corresponding peaks at lower energies in the absorption spectrum. Yet, formation of macroscopic spherulites did not occur, as demonstrated under polarized illumination (see Figure S1c), where no significant anisotropy in PL was observed. Hence, a semicrystalline film was formed containing randomly oriented nanometer-sized crystallites embedded in a matrix of disordered polymers.

The similarity between PDOPT and P3HT with respect to the spectral shape and position of the crystalline absorption (relative to that of the disordered contribution) suggested that PDOPT crystallites form H-type aggregates both in isothermally grown spherulites and in semicrystalline films after rapid cooling from the melt. At first glance, this observation might be surprising as in contrast to P3HT, there is no π – π stacking in PDOPT, suggesting that crystallization was driven by side-chain interactions.^{6,19} The crystal structure of PDOPT features a distance of 1.47 nm between backbones in π – π stacking direction, while the smallest backbone–backbone distance is about 0.55 nm, measured perpendicular to the stacking direction of backbone planes.^{6,19} However, it is important to realize that the appearance of H-type spectra does not require π – π stacking. The transition dipole moments that are oriented along the PDOPT backbone only have to be arranged in a parallel fashion with respect to each other to give rise to a positive interchain interaction characteristic of H-type structures.³⁵ For PDOPT, the interchain coupling is therefore almost exclusively determined by the smallest backbone–backbone distance perpendicular to the π – π stacking direction. Hence, using the framework for H-type spectra put forward by Spano and co-workers,^{36,37} an analysis of the contribution to the absorption resulting exclusively from crystalline regions was possible (see also Figure S4).

Such quantitative analysis of the absorption spectra required a “deconvolution” of the contributions from disordered and crystalline regions. In short, we assumed that absorption at 125 °C (or at higher temperatures T) stemmed solely from disordered chains in the melt. Scaling this contribution to the

absorption spectrum to the high-energy tails of the spectra measured for $T < 120$ °C (for a heating run) and $T < 70$ °C (for a cooling run), and subtracting this so-adjusted contribution, allowed us to extract the part of the absorption spectrum resulting from the crystalline regions, as illustrated in Figure 5.^{32–34}

Figure 5. Extraction of the contribution to the measured spectrum (black) resulting from the aggregated phase of PDOPT at 30 °C. The spectrum of the disordered, molten film at 125 °C (red) was scaled to the high-energy tail of the 30 °C spectrum (black). The difference curve (blue) is taken for further fitting.

To comply with Spano's notation, the peaks of this latter spectrum were labeled A_i ($i = 1, 2, 3, \dots$) in order of increasing energy. The crystalline absorption was then fitted by a modified Franck–Condon (FC) progression (see eq 1) put forward by Spano and co-workers.^{36,37}

$$\begin{aligned} \frac{A(E)}{nE} &\sim \left(1 - \frac{We^{-S}}{2E_d} \left(\sum_{n \neq m} \frac{S^n}{n!(n-m)} \right) \right)^2 \\ &\times \exp \left(-\frac{(E - E_{A_1})^2}{2\sigma_{A_1}^2} \right) \\ &+ \sum_{m=1} \frac{S^m}{m!} \left(1 - \frac{We^{-S}}{2E_d} \left(\sum_{n \neq m} \frac{S^n}{n!(n-m)} \right) \right)^2 \\ &\times \exp \left(-\frac{(E - E_{A_1} - mE_d)^2}{2\sigma^2} \right) \end{aligned} \quad (1)$$

Here, $A(E)$ is the intensity of absorption, S is the Huang–Rhys parameter of disordered chains ($S = 0.7$), and the vibrational energy $E_d = 167$ meV (1350 cm^{−1}) of the effective carbon-stretching mode was extracted from solution spectra with a standard FC progression (see Figure S3). The remaining free parameters are the vibrational quantum number m , the free exciton bandwidth W (related to the interchain electronic coupling J by $W = 4J$), the transition energy E_{A_1} of the lowest-energy peak A_1 , and the width σ_{A_1} of the Gaussian line shape functions. Note that we used a modified version of the fitting function proposed by Spano et al. in order to allow for a different (narrower) Gaussian line width σ_{A_1} of the absorption peak A_1 compared to the line width σ of the absorption peaks A_i ($i > 1$). As shown in detail in Figure S4, this modification significantly enhanced the quality of the fits. This modified Franck–Condon progression was fitted to all deconvoluted crystalline absorption spectra, for both heating and cooling runs. The resulting temperature-dependent evolution of the

relevant fitted parameters is displayed in Figure 6a–c, i.e., the free exciton bandwidth W , the center energy E_{A_1} and width σ_{A_1} of the A_1 peak versus temperature (red symbols: heating; blue symbols: subsequent cooling).

Figure 6. Results of the fits to the temperature-dependent contribution of crystalline domains to the absorption spectra: (a) Free exciton bandwidth W , (b) energy E_{A_1} and (c) line width σ_{A_1} of the A_1 peak, evaluated for 30–120 °C for heating (red symbols) and for 30–70 °C for cooling (blue symbols). (d) Heat flow curve for heating and cooling spherulitic crystals at a rate of 2 °C/min, prepared in an aluminum cap by crystallizing the molten polymers at $T_c = 100$ °C for 50 h (see Figure S6). The red and the blue curves represent heating and cooling, respectively.

During the process of heating PDOPT spherulites, the free exciton bandwidth W , the A_1 peak position E_{A_1} , and its line width σ_{A_1} increased rather steadily from 50 to 87 meV (W), from 2.109 to 2.142 eV (E_{A_1}), and from 53 to 56 meV (σ_{A_1}), respectively. These changes in absorption from the crystalline regions clearly indicated an increasing degree of structural and electronic disorder up to the melting temperature (reached at ca. 120 °C, for the spherulite).⁶ It has been shown that the backbones of PDOPT chains in crystallites are fully planar at room temperature.⁶ Increasing temperature activates torsional degrees of freedom of the backbone, and thus deviations from planarity become more and more evident. For an isolated and disordered chain, this effect gives rise to a localization of the wave function of intrachain electronic excitations. In an H-type crystalline arrangement, this temperature-activated localization results in a stronger interchain electronic interaction and thus in a larger free exciton bandwidth (W).^{38,39} Upon heating, thermal expansion of the crystalline lamellae in the spherulite gives rise to an increasing interchain distance and thus a decreasing W . In a previous work, upon heating the interchain distance was found to increase by $\approx 3\%$.¹⁷ Hence, this effect can be neglected. Importantly, our value for the free exciton bandwidth W of around 50 meV at 30 °C is substantially smaller than the value found for crystalline P3HT at room temperature, which is up to 120 meV, depending on processing

conditions.^{4,33,37} This substantially larger value of W for P3HT is related to the smaller backbone–backbone distance as compared to PDOPT (0.38 nm for π – π stacked P3HT and 0.55 nm for PDOPT).

The blue-shift in the A_1 peak position E_{A_1} was partly caused by the increase in W from 50 to 87 meV (from 30 to 110 °C) because the upper (absorbing) exciton state in the lowest energy exciton band shifts to higher energy with larger W . However, this effect was not large enough to account for the observed peak shift of 32 meV (from 2.109 to 2.141 eV) because the width of the lowest exciton band is given by $W \cdot e^{-S}$,²⁶ with the Huang–Rhys factor $S = 0.7$ for an isolated, disordered chain. A further contribution to the blue-shift of E_{A_1} arises from the increasing localization of intrachain wave functions due to increasing structural disorder, as discussed above. Moreover, upon heating the sublattice of the dioctyl-phenylene side groups will eventually melt as well and thus lose its perfect order. As a consequence, the local dielectric environment for the polymer backbones changes. The resulting different local polarization energy may contribute to the shift of E_{A_1} to higher energies (similar to a recent observation for P3HT³⁴).

In addition to this increasing intrachain (and thus intracrystallite) disorder that modified W and E_{A_1} as a function of temperature, the line width σ_{A_1} of the A_1 peak increased continuously up to 70–80 °C and then reached a plateau. This inhomogeneous width σ_{A_1} is determined by disorder between different crystallites probed in our measurement, implying that intercrystallite disorder did not change anymore above ca. 80 °C (despite high spatial resolution of 10 μ m, we still probe many crystalline lamellae within the detected area inside the spherulite).

The temperature-dependent absorption spectra upon heating suggested that the melting of a spherulite—or more precisely of the crystalline lamellae arranged within the spherulite—is a rather continuous process over a wide temperature range, in which the structural and thus electronic order is being continuously reduced until it is lost completely at the melting temperature of ca. 120 °C.

Upon cooling from the melt, signs of absorption from crystalline regions reappeared at around 75 °C. However, no (macroscopic) spherulites but many randomly arranged small crystallites were formed. Below 75 °C, both W and E_{A_1} were consistently higher with respect to the corresponding values at the same temperatures upon heating the spherulite. This difference suggests that the crystallites formed upon cooling from the melt did not possess the same degree of structural perfection as the crystalline lamellae in the initial spherulite, slowly grown at 100 °C for 50 h. Caused by the rather fast cooling process, chains did not have enough time to re-form the better ordered macroscopic spherulitic structure. In fact, the higher energy E_{A_1} after cooling is consistent with the recent observation of a more blue-shifted absorption of as-cast semicrystalline (rapidly quenched) PDOPT films as compared to the spherulite absorption,¹⁹ which further supports our interpretation of the formation of less perfectly crystalline films upon rapid cooling and recrystallization. The inhomogeneous line width σ_{A_1} is identical before and after melting, implying that disordered segments between lamellar crystals in a spherulite

are not differing much from disordered segments between lamellar crystals in rapidly crystallized films.

It is now interesting to compare the changes in these spectra with the corresponding variations in thermal properties as determined by differential scanning calorimetry (DSC) (Figure 6d). Upon heating (red curve), a cold crystallization peak appeared around 80 °C. This peak indicates that even after 50 h at $T_c = 100$ °C not all parts of the sample were completely crystallized (see also Figures 2 and 3, where the spherulites are surrounded by regions which only crystallized upon quenching the sample to room temperature). Alternatively, some reorganization of molecules, which may not have been aligned appropriately in the spherulite structure, may have occurred. Such reorganization is consistent with the observed plateau in the σ_{A_1} line width (i.e., the constant intercrystallite disorder) above 70 °C. At around 115 °C, DSC indicated the melting of the spherulites. The melting peak from DSC agreed with the disappearance of the crystalline absorption; i.e., any long-range order and thus electronic interchain interactions were lost upon melting. Upon cooling, the DSC curve (Figure 6d, blue line) showed the recrystallization peak at around 50 °C. This low temperature may appear to be in conflict with the higher recrystallization temperature of ≈ 70 °C observed in the absorption spectra (appearance of a low-energy peak at around 2.14 eV). Tentatively, this difference may be attributed to a higher (re)nucleation probability in the region of molten spherulites, as randomization of chain conformations requires time and some polymers may “remember” their ordered states for times longer than the characteristic relaxation time.^{40,41} Correlations between thermal and optical properties in crystalline regions are probably related to the rather long-range nature of electronic interchain interactions between thiophene backbones, as demonstrated recently,^{38,42} that have a strong impact on the shape and position of optical spectra. Hence, spatially resolved optical spectroscopy can be used to study melting and recrystallization of polythiophenes.

Temperature-Dependent Photoluminescence Spectra. To gain further insight into the influence of molecular conformation and order, we additionally studied *in situ* changes in emission spectra when increasing or decreasing temperature at a rate of 2 °C/min, focusing in particular on the processes of melting of spherulites grown via isothermal crystallization at 100 °C (Figures 2 and 3) and their subsequent recrystallization. The emission spectra from a PDOPT spherulite measured with nonpolarized light in reflection mode with a spatial resolution of 10 μ m are shown in Figures 4b and 4d. During heating and cooling, a spectrum was recorded after typically a temperature change of 5 °C. At room temperature, the emission spectra allowed to identify clearly three peaks,^{4,34} with a suppressed 0–0 emission peak which is characteristic for PL of H-type crystallites that could be associated with a distorted single Franck–Condon progression.⁴³ With temperature increasing up to 120 °C, we observed a significant increase of the overall intensity, followed by a (small) decrease in intensity and the emergence of new peaks in higher energy regions at higher temperatures. These high-temperature spectra closely resemble PL from solution (see later, Figure 9) with its dominating 0–0 emission, in agreement with the loss of order in the melt. Furthermore, from Figures 4b and 4d, we can observe a significant broadening of the PL peaks at elevated temperatures.

Melting of the spherulitic crystal led to a significant increase of emission intensity of the PDOPT structures (Figure 4b).

Above 120 °C, there is increased PLQE due to increasing disorder (decreasing H-type character). It should be noted that disorder breaks the symmetry of (weakly) interacting molecules, allowing for 0–0 emission.²⁵ For ideal H-aggregates at 0 K, 0–0 emission is forbidden by symmetry rules of emission.^{25–27,44} Increasing disorder (e.g., by increasing temperature) allows for 0–0 emission and thus gives rise to an overall increase in PL intensity. The spectra of Figure 4b showed that for increasing temperature the emission intensity increased, with a bias toward higher energies, a signature which we tentatively attribute to increasing disorder,^{14,18,45,46} in agreement with the absorption data presented above.

In order to determine more quantitatively the corresponding changes in the PL spectra with temperature and to identify the origin of the PL peaks, in an approach fully consistent with the discussion on absorption data, we used the framework of analysis developed by Spano and co-workers.⁴ In the deconvolution of absorption spectra, it was argued that analysis of the contributions from crystalline regions (aggregates) in PDOPT was only possible using the H-aggregate type spectra. For the analysis of the emission spectra, we therefore also adopted the H-type model. The peaks of the emission spectra were labeled from highest energy to the lowest energy as L_i ($i = 1, 2, \dots$). Each emission spectrum was therefore fitted with the modified Franck–Condon progression (see eq 2) as suggested by Spano and co-workers.⁴

$$L(\omega) \sim (\hbar\omega)^3 n_f^3 e^{-S} \left\{ \alpha \Gamma(\hbar\omega - E_{L_1}) + \sum_{m=0}^{S^m} \frac{S^m}{m!} \Gamma(\hbar\omega - (E_{L_1} - mE_d)) \right\} \quad (2)$$

where n_f is the real part of the refractive index, $\hbar\omega$ is the photon energy, $L(\omega)$ is the intensity of emission, m denotes the vibrational quantum number, S is the Huang–Rhys factor for the dominant carbon bond stretch mode of disordered chains ($S = 0.70$), E_{L_1} is the 0–0 transition energy, $E_d (= E_{L_1} - E_{L_2})$ is the C=C symmetric stretching vibration coupling of electronic transition (ca. 0.16 eV), Γ is the line shape function (Gaussian with constant width), and α gives the “suppression” factor for the 0–0 emission peak. Note that for simplicity we used eq 2 also to fit the high-temperature PL spectra above 120 °C, although there was no emission from H-type crystallites anymore. In this situation α approaches 1, yielding a nearly undistorted vibronic progression as expected for the emission of a disordered ensemble.

Based on eq 2, the modified Franck–Condon progression was fitted to all PL spectra for both heating and subsequent cooling (see Figure S5). Figures 7a–d represent the resulting temperature-dependent evolution of some of the fitted parameters, i.e., the peak position E_{L_1} and the width σ_{L_1} of the L_1 peak, the variation of the vibronic energy E_d (C–C stretching mode), and amplitude I_{L_1} of the L_1 peak during the heating and cooling cycle.

A closer look at the evolution of these parameters with temperature (E_{L_1} , σ_{L_1} , E_d , and amplitude of I_{L_1}) showed a steady increase from 2.024 to 2.117 eV (E_{L_1}), from 47 to 83 meV (σ_{L_1}), from 0.154 to 0.1705 eV (E_d), and from 0.314 to 0.66 (I_{L_1}), as temperature increased from 30 to 150 °C (Figure 7a–

Figure 7. Results of the fits to the temperature-dependent PL spectra. (a) Peak position E_{L_1} and (b) line width σ_{L_1} of the L_1 peak, (c) vibronic energy E_d , (d) relative amplitude I_{L_1} of the L_1 peak for the heating (red symbols) and cooling (blue symbols) cycle, respectively, and (e) heat flow curve for heating (red) and cooling (blue) spherulitic crystal (see also Figure 6d and Figure S6).

d). Figure 7d revealed a steady increase of the intensity I_{L_1} up to around the nominal melting temperature of PDOPT. This could be attributed to an increasing degree of thermally induced structural disorder, in line with the absorption data.⁴⁷ The peak position E_{L_1} (Figure 7a) increased steadily and changed only by 20 meV up to ca. 110 °C, where a steep increase was observed, shifting the peak by ca. +70 meV, which reflects the transition from crystalline H-type to amorphous (solution-like) PL spectra. Likewise, during the cooling process (Figure 7a), a reverse transition could be observed at ca. 70 °C, where the peak positions also changed by ca. –70 meV. It should be noted that the observed transitions at ca. 110 °C and ca. 70 °C were at temperatures close to the nominal melting and crystallization temperatures, in agreement with absorption data (Figure 6). The variations in vibronic energy E_d during heating and cooling cycles could be associated with the varying degree of order of the emitting crystalline lamellae.^{48,49} The relative increase in emission intensity of the 0–0 peak L_1 with temperature is a typical characteristic of disorder in H-aggregates systems.²⁵ The line width σ_{L_1} (Figure 7b) increased steadily with temperature increasing from 30 to 150 °C and followed a reverse trend during the cooling cycle. The increasing (decreasing) line width σ_{L_1} during heating (cooling) is a signature of increasing (decreasing) disorder. Interestingly, at room temperature, both before the heating and after the cooling cycle, E_d and σ_{L_1} were quite similar, indicating that the degree of disorder of the emitting crystallites is very similar in both situations, as explained above.

A comparison of peak positions and maximum intensity of all the peaks L_1 , L_2 , L_3 , and L_4 showed that at temperatures below the melting transition all peaks hardly changed their position (only a rather small increase by about 20 meV could be observed). However, at temperatures above ca. 120 °C, there was a clear change in position by over +70 meV (Figure 8a,b). This confirms that the energy of a peak is a function of

Figure 8. Results of the fits to the temperature-dependent PL spectra. (a) Peak positions (E_{L_i}), (b) maximum intensities of peaks (I_{L_i}), and (c) peak intensity ratio $R = I_{L_1}/I_{L_2}$ for the heating (full symbols) and cooling (open symbols) cycle.

temperature. The maximum peak intensity of L_2 dropped relative to L_1 , with the peak intensity ratio $R = I_{L_1}/I_{L_2}$ changing from $R < 1$ for temperatures less than ca. 110 °C to $R > 1$ for temperatures above ca. 120 °C during the heating cycle (Figure 8b,c).

Comparing Optical Properties of PDOPT As-Cast Thin Films and Spherulitic Crystals. Figure 9 compares spatially

Figure 9. Absorbance (dotted curves) and photoluminescence spectra (solid curves) of PDOPT from solution (black), an as-cast film (blue), and a spherulitic crystal (red) grown at 100 °C for 50 h in a molten thin film (ca. 200 nm), taken at room temperature at an area of a diameter of 10 μm and an integration time of 5 s, measured with nonpolarized light. For comparison, we also added results for a dilute PDOPT solution in toluene.

resolved (detecting a small circular area having a diameter of 10 μm) absorption and PL spectra, collected at room temperature from an as-cast film and from a region within a spherulite. We observed qualitatively similar spectra for both samples, characterized by broad peaks and a small red-shift of ca. 0.02 eV in absorbance spectra for the spherulite with respect to the as-cast film. Interestingly, this shift was similar to that between the spectra acquired from a spherulite before heating and from the same area taken in the semicrystalline film obtained after cooling the molten spherulite down to 30 °C (see Figure 6b). Hence, the small shift in absorbance spectra indicated that the crystalline structures formed in as-cast films did not possess the high structural order observed for the crystalline lamellae grown during slow isothermal crystallization in spherulites, as discussed above. Yet, the structured low-energy contribution

to the absorbance spectra still indicates the formation of excitons delocalized over several chromophores in the crystalline regions of the as-cast film. From the same data, it was observed that the spherulite had lower absorption and emission relative to the film. This could be attributed to the interdigitation of side chains during slow crystallization of the spherulites, reducing the intermolecular distance and hence reducing the quantum yield.¹⁷ At room temperature, emission from the spherulitic crystal showed a number of vibronic peaks. It was interesting to note that at room temperature the emission intensity from the film was almost a factor of 2 higher than from the spherulitic crystal. Besides low emission from the spherulitic crystal, we observed a small red-shift (ca. 0.02 eV), just like in absorbance spectra.

At room temperature, owing to thermally induced structural disorder, vibronic peaks were rather broad. In the PL spectra taken at room temperature, three clearly identifiable peaks were observed at 2.02 ± 0.02 , 1.87 ± 0.02 , and at 1.76 ± 0.02 eV for both the as-cast film and the spherulitic crystal. The solution of PDOPT in toluene also had two peaks and a big blue-shift relative to the spherulitic crystal. We attribute the first two peaks to the 0–0 (L_1) and 0–1 (L_2) transitions.³⁹ To precisely identify the vibronic peaks due to contributions from more ordered spherulitic crystal and less ordered as cast film and to quantify differences in the spectra, we used a set of four Gaussian functions for a deconvolution of the spectra (Figures 10a and 10b) without imposing any constraints on the fit

Figure 10. PL spectra measured at room temperature (same as in Figure 3), decomposed into four Gaussian functions, for (a) an as-cast film and (b) a spherulitic crystal. (c) Bar chart of the intensity of the individual Gaussians for the film and the spherulitic crystal. The energy E of the emitted photons is decreasing from peak L_1 to peak L_4 , as can be seen also in (a) and (b).

parameters. In addition to three clearly visible peaks, a fourth but very small Gaussian peak close to 1.6 eV was included in the fitting procedure to ensure that the width of the peak at ca. 1.75 eV was comparable to the width of the other peaks. From Figure 10a–c, we can find the energy gap between E_1 and E_2 to be ca. 0.145 eV, which is within a margin of error for the typically observed energy for C–C stretching modes in substituted polythiophenes (0.16 ± 0.02 eV).³⁹

In the following discussion, we rely on the sensitivity of photoluminescence spectra with respect to changes in order and morphology.^{5,14,23} By using a series of four Gaussian functions, we simulated the vibronic progressions of the 0–0,

0–1, 0–2, and 0–3 peaks. Energy gaps of most conjugated systems show a vibronic progression as a result of symmetric vinyl stretching modes.^{14,23,25,39,45} Fourier transform infrared spectroscopy results for PDOPT have shown that electronic transitions couple strongly to the aromatic carbon-bond stretching of the thiophene ring within an energy range from 0.148 to 0.20 eV and a strong peak at 0.18 eV (Figure S2). Absorption and emission spectra of virtually all phenyl- and thiophene-based conjugated molecules reveal vibronic progressions, mainly due to symmetric ring breathing stretching modes or a group of such modes.²⁷

The comparison of results (Figures 9 and 10) from such a spectral analysis of the emission spectra for as-cast films and spherulitic crystals at room temperature showed that the positions of the four peaks (in terms of their emission energy) were (almost) independent of morphology (Figure 10a–c). Interestingly, while peak positions matched, intensities clearly differed. For the highly ordered structures within spherulitic crystals, the relative emission intensities were higher in the low-energy region while for the less ordered PDOPT molecules in as-cast thin films intensities were more pronounced in the high-energy region (Figure 10c). This observation is corroborated by the fact that in crystalline regions PDOPT chains are better ordered. Crystallization of the bulky 2,5-dioctylphenyl side groups of PDOPT could assist in planarizing the polymer backbone. Local molecular order and changes in conformation also affect the exciton radiative recombination probability and thus the resulting photoluminescence intensity.² Relative changes in PL intensity of the emitting species, taken at a given wavelength, for different morphologies may differ due to changes in intermolecular and intramolecular interactions.^{14,50} Tentatively, the difference in spectral PL intensity between as-cast film and spherulitic crystal may be attributed to an improved planarized thiophene backbone induced by crystallization,⁵ i.e., due to different degrees of order and hence differences in quantum efficiency as seen in temperature-dependent experiments above.

CONCLUSIONS

We have demonstrated that crystallization and melting of poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT) were accompanied by significant changes in optical properties. The change in morphology, i.e., changing from an ordered to a disordered state, induced by melting of a spherulitic crystal was accompanied by particular changes in emission and absorption spectra, reflecting a change in color and an increase of emission intensity. Furthermore, upon melting, birefringence was completely lost due to a loss of preferential orientation of the transition dipole moments within the crystalline structure. We observed that well-ordered spherulitic crystals emit less than the same polymers when rapidly recrystallized after being molten. Moreover, molten polymers showed a significantly higher emission probability although the absorbance rather decreased. Thus, characteristic changes in absorption and emission spectroscopy on samples of substituted polythiophenes allow to follow melting and recrystallization processes and to establish relations between optical properties and the corresponding changes in molecular conformations and order.

ASSOCIATED CONTENT

Supporting Information

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Figures S1–S9 (PDF)

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Notes

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