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Host Matrix Dependence on the Photophysical Properties of Individual Conjugated Polymer Chains

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ABSTRACT: By means of fluorescence single molecule spectroscopy, it is shown that the conformation of high molecular weight conjugated polymers in thin films depends on the nature (chemical composition and molecular weight) of the host matrix. When a high molecular weight poly(*p*-phenylenevinylene) derivative (OC_1C_{10}-PPV) is dispersed in a thin polyvinylbutyral-*co*-vinyl alcohol-*co*-vinyl acetate (PVB) film, the spectroscopic properties suggest that OC_1C_{10}-PPV is in a highly coiled conformation. On the other hand, in a thin polystyrene film (PS) of low molecular weight, the OC_1C_{10}-PPV chains adopt a more extended conformation. Increasing the molecular weight of polystyrene leads to increased coiling of the OC_1C_{10}-PPV chains, related to poor solvation. The film preparation conditions (spin-coating or drop-casting) have no effect.

Introduction

Conjugated polymers form a very active area of research since their electronic and optical properties in combination with their processability make them excellent candidates for application as active materials in photodiodes,[1] photovoltaics,[2] and light-emitting diodes.[3] Since the application of conjugated polymers is still very much in its infancy, many fundamental questions regarding their functional properties are still unanswered.

The conditions of film preparation may significantly influence the photophysical properties of the conjugated polymers. For industrial applications, it is therefore of utmost importance to control the sample preparation conditions and know their impact on the optoelectronic material properties. In this respect, it is of great interest to know how drop-casting (ink-jet printing) changes the spectroscopic properties of the conjugated material as compared to the conventionally applied application by spin-coating.

It is indeed becoming increasingly clear that the properties of conjugated polymers are greatly influenced by interactions, e.g., due to $\pi-\pi$ stacking of conjugated segments.[4−6] It is well-documented that the chain conformation of a conjugated polymer in solution is retained after solvent evaporation.[5,7,8] Furthermore, the morphology and electrooptical properties of spin-cast polymer films are sensitive to the preparative processing: the solvent and polymer concentration, solution processing (stirring and heating), spin speed, and treatment of the film after deposition. The morphology of the films affects not only the optoelectronic properties of films but also the degree and ease of photooxidation leading to the creation of luminescence quenching sites and a decrease of the conjugation length.[7−12]

To get insight into the chain conformation and its effect on intrachain interactions, approaches on the single polymer chain level are especially appealing. Barbara et al. have elucidated the electronic energy transfer processes of a conjugated polymer and their relation to the individual polymer chain conformation in an inert polymer host film.[13−17] The single-molecule fluorescence spectroscopy of a multichromophoric polymer revealed for some preparation conditions single-step photobleaching kinetics and acute jumps in fluorescence intensity, which were attributed to efficient intramolecular electronic energy transfer to a localized fluorescence-quenching polymer defect. Huser et al. showed by using single molecule confocal fluorescence microscopy that the chain conformation has significant impact on conjugated polymer photophysics. They demonstrated that the choice of solvent leads to distinctive changes in the spectroscopy of the individual polymer chains.[18,19] Other groups investigated the spectral properties of short chain luminescent conjugated polymers.[20,21]

In this contribution, we have investigated the effect of optically inert polymers (called host polymers) on the spectroscopic and conformational properties of individual OC_1C_{10}-PPV (poly(2-methoxy-5-(2′,6′-dimethyloctyloxy)-*p*-phenylenevinylene) polymer chains (Figure 1, inset). The effect of an optically inert host polymer on the conformational and spectroscopic properties of the PPV chains is investigated in a toluene solution and compared with films containing isolated PPV polymer chains in the host polymer. Two polymers with different polarity were selected as host: polystyrene (PS) as the apolar matrix and polyvinylbutyral-*co*-vinyl alcohol-*co*-vinyl acetate (PVB) as the polar matrix. Toluene is a good solvent for OC_1C_{10}-PPV and PS but is a poor solvent for PVB. Not only the influence of the host polymer and its molecular weight has been explored but also the effect of different sample preparation condi-

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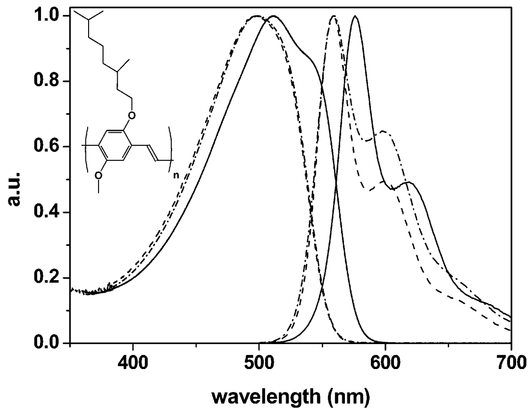

Figure 1. Absorption and emission spectra (λ_{ex} = 488 nm) of OC_1C_{10}-PPV solutions in toluene (dashed dot line), in toluene/PS (dashed line), and in toluene/PVB (solid line). The concentration of OC_1C_{10}-PPV is 0.0015% w/w and the concentration of PS (M_w = 44 000) or PVB (M_w = 105 000) is 0.3% w/w. Note that the content of PVB is an overestimation due to its low solubility in toluene.

tions, i.e., spin-coating or drop-casting. The latter mimics the conditions of ink-jet printing, now widely investigated for manufacturing of full-color displays.[22]

Experimental Section

OC_1C_{10}-PPV polymer (mass-averaged molecular weight (M_w) ~ 1 900 000 (~6600 monomer units) and polydispersity ~ 5.7) was dissolved in toluene by heating for 1 h at 50 °C and subsequently stirring for at least 12 h at room temperature after bubbling argon through the solution. For single molecule investigations, a drop of this stock solution (0.025% w/w) was then added to a 50 mL toluene solution (0.3% w/w) of polyvinylbutyral-*co*-vinyl alcohol-*co*- vinyl acetate (PVB, M_w = 105 000) or PS ("low" M_w: 4500 or 44 000; "high" M_w: 240 000). The host polymer solutions were bubbled with argon for 15 h before mixing with PPV. The mixed solutions were then sealed and stirred overnight. For the spectroscopic studies in solution, the mass ratio of OC_1C_{10} in toluene measured 0.0015% w/w and of the host polymer in toluene 0.3% w/w. Note that in the case of PVB the host polymer content given is an overestimation as PVB only dissolves in part in toluene. The solutions were at all times kept in the dark to avoid photoinduced degradation. The spectroscopic measurements and film preparation were always done with freshly prepared solutions. Films for single molecule investigations have been prepared by spin-coating the blend solution on a thin cover glass of 1.5 × 1.5 cm^2 at spin speeds ranging between 500 and 3000 rpm for 60 s to yield thin polymer films of different thickness (~20–500 nm). For the drop-casting experiments, a drop of the solution was applied on the glass substrate and left to dry. To reduce oxygen diffusion into the films, some samples have been covered by a poly(vinyl alcohol) (PVA) cover layer, spin-coated at 1000 rpm for 60 s from a 0.6% w/w solution in water. The permeability for molecular oxygen in PVA is about 3 orders of magnitude lower than for polymers like polystyrene.[23] The sample preparation included careful cleaning of the glassware used for sample preparation as well as cleaning of the cover glasses by sonication in acetone, sodium hydroxide (10%), and Milli-Q water prior to spin-coating or drop-casting. Before use, the cover glasses were put in an UV-ozone cleaner for 20 min. To minimize any degradation effects, the films were investigated immediately after preparation.

The simulations were performed using Microsoft Excel. For a given system (number of chromophores) and for each independent calculation (total is 64), the orientation of each of the chromophores in the *xy* plane was set by using a random number generation procedure. So, for each independent calculation, the orientation of the chromophore(s) was different. Each independent calculation gives a value for the polarization, and a polarization histogram was constructed by 64 of these independent calculations.

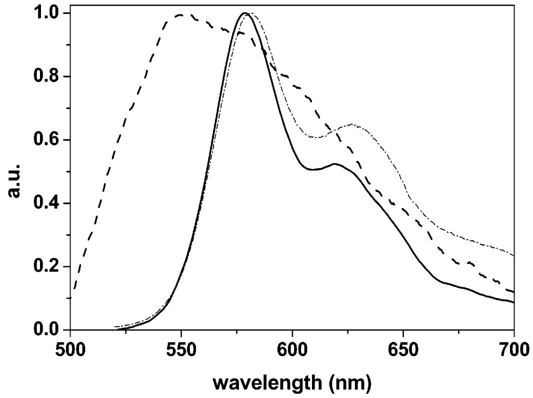

Figure 2. Emission spectra of spin-coated films: OC_1C_{10}-PPV film (dashed-dot line). Sum of every first emission spectrum of 39 fluorescence transients of OC_1C_{10}-PPV/PS (M_w = 4500) (dashed line) and of 39 single molecules of OC_1C_{10}-PPV/PVB (thick solid line).

Equipment. Absorption spectra were measured with a Perkin-Elmer Lambda-6. Fluorescence spectra were recorded on a SPEX Fluorolog 1680.

The fluorescence of the single molecules was detected using a confocal microscope with an oil immersion lens (NA 1.4). Notch filters (488 nm) were used to prevent excitation light from reaching the detectors. All fluorescence intensity transients were measured with a dwell time of 5 ms. The fluorescence spectra were measured with a liquid nitrogen cooled, back-illuminated CCD camera coupled to a polychromator using 5 s integration time. The recorded spectra were corrected for the background. The molecules have been excited with circularly polarized light at a wavelength of 488 nm, which is close to the absorption maximum. The excitation power density at the sample was typically ~50 W/cm^2. Single fluorescence spots were isolated in the polymer film at an areal density of 0.6–0.9 spots/μm^2.

Results

Solution. Steady-state absorption and fluorescence spectra of OC_1C_{10}-PPV in toluene are shown in Figure 1. The spectral properties of OC_1C_{10}-PPV in toluene and in PS/toluene are similar and independent of the molecular weight of the PS used (not shown). The absorption spectrum is featureless and broad with a maximum at 505 nm. The fluorescence spectrum is more structured, showing vibronic progressions at 558 and 600 nm. In the presence of PVB, the absorption spectrum shows in addition to the absorption maximum, which is slightly red-shifted (512 nm), a shoulder at 540 nm. The relative contribution of this shoulder depends on the concentration of the PVB polymer added. The emission spectra (emission maxima at 576 and 620 nm) are bathochromically shifted. The excitation spectra of a given solution reflect the absorption spectra and are independent of emission wavelength.

Films: Single OC_1C_{10}-PPV Chain Photophysics. A. OC_1C_{10}-PPV/PVB Films. Typical fluorescence intensity trajectories (transients)—that is, the fluorescence intensity as a function of the irradiation time—of single OC_1C_{10}-PPV polymer chains spin-coated from a OC_1C_{10}-PPV/PVB/toluene solution (see Experimental Section) are shown in Figure 3. Ninety-five molecules were investigated. On top of the transient in Figure 3a, the spectral mean ($\int I(\lambda)\lambda \, d\lambda / \int I(\lambda) \, d\lambda$) and the spectral maximum are given as a function of the irradiation

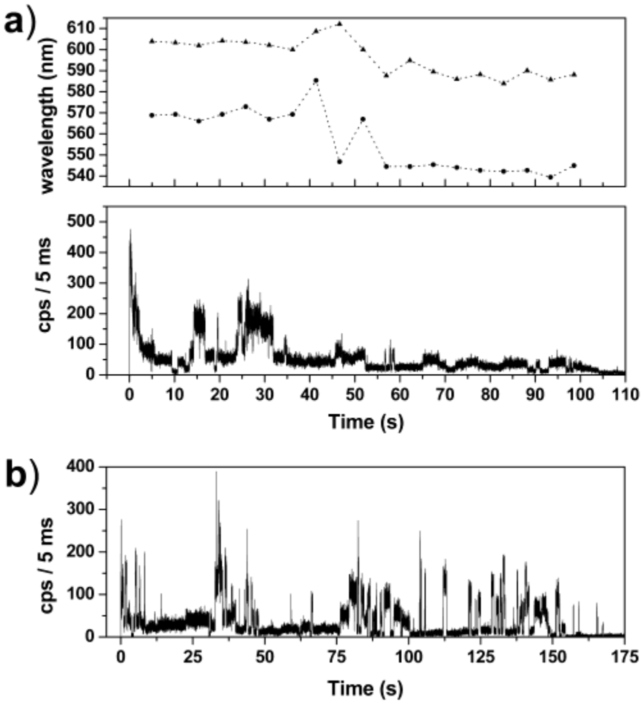

Figure 3. (a) Fluorescence intensity transient of a single OC_1C_{10}-PPV polymer chain in PVB. The upper line in the upper panel is the spectral mean. The lower line in the upper panel is the spectral maximum. (b) Fluorescence intensity transient of a single OC_1C_{10}-PPV polymer chain in PVB showing pronounced on/off behavior.

time. The transients show substantial fluctuations in the fluorescence intensity before irreversible photobleaching takes place. The polymer backbone is not chemically inert, and upon illumination in the presence of oxygen, it is known that the polymer will undergo chemical changes, which finally lead to complete photobleaching (signal reaches a constant noise level). The important feature in these fluorescence intensity trajectories is the presence of abrupt changes in fluorescence intensity. Such intensity changes are typical for single molecules containing only one chromophore and are surprising for polymer chains, which contain hundreds of “chromophores”: the optical coherence length for such a PPV derivative is typically ~10−17 monomer units.[24] For a large number of noninteracting chromophores, a gradual decrease in intensity is expected.

The spectral evolution shows some general trends (Figure 4). The spectra, which are taken every five seconds, exhibit vibrational fine structure as they do in solution. Over time, however, the spectra shift hypsochromically, often maintaining the same overall shape. In addition to the overall spectral blue shift, sometimes a blue “shoulder” appears. This extra blue component often appears and disappears as shown in Figure 4, which presents the fluorescence spectra taken every 5 s of the molecule shown in Figure 3a. Because of the low solubility of PVB in toluene, varying the concentration of the PVB host polymer in a controlled way or changing the film height by changing the spin-coating conditions did not succeed. Drop-casting did not affect the spectral properties.

The sum of the first spectrum of every fluorescence transient in the OC_1C_{10}-PPV/PVB system is shown in Figure 2. The spectrum is similar to the one in solution and has a maximum around 575 nm.

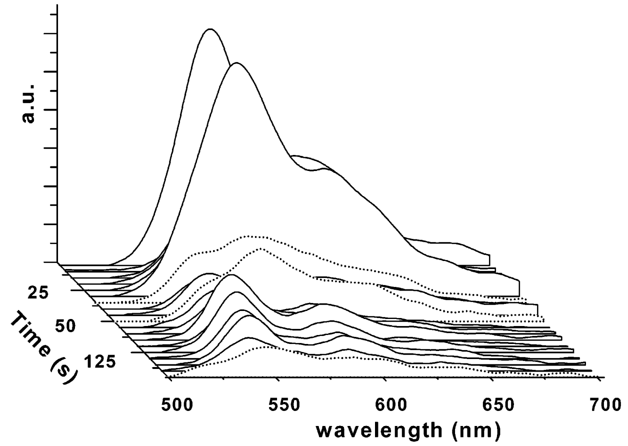

Figure 4. Spectral evolution of the transient in Figure 3a. The spectra are recorded every 5 s. Those spectra which clearly contain an additional blue shoulder are indicated as heavy solid lines.

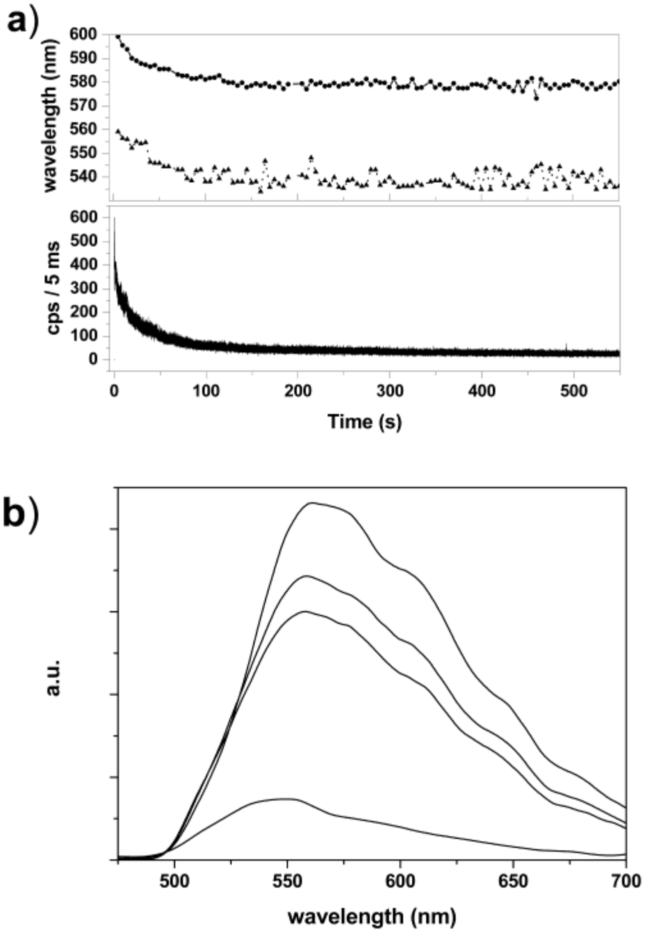

Figure 5. (a) Fluorescence intensity transient of OC_1C_{10}-PPV in a PS ($M_w = 4500$) film (prepared by drop-casting). The upper line in the upper panel is the spectral mean. The lower line in the upper panel is the spectral maximum. (b) Spectral evolution at 5, 10, 15, and 215 s after the start of the irradiation (intensity decreases).

B. OC_1C_{10}-PPV/PS Films. B.1. Experiments with Low Molecular Weight PS ($M_w \leq 44\,000$). A typical transient of the fluorescence intensity of a single OC_1C_{10}-PPV polymer chain in PS ($M_w = 4500$, 103 molecules investigated) is shown in Figure 5a. The sample was prepared by drop-casting, and its spectroscopic properties do not differ significantly from those prepared by spin-coating (not shown). Samples prepared with PS ($M_w = 44\,000$, 210 molecules investigated) show

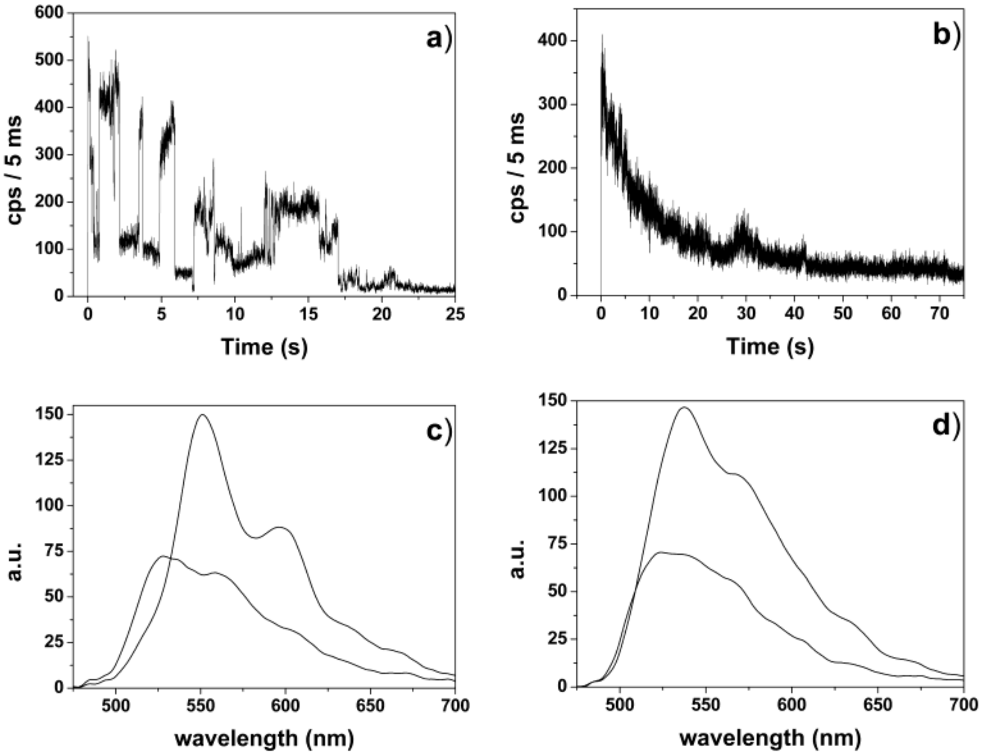

Figure 6. (a, b) Fluorescence transient and (c, d) spectral evolution of a spin-coated OC_1C_{10}-PPV/PS film (M_w = 240 000). (a, c) The host polymer solution is not sonicated. The fluorescence trajectory reflects the behavior of ~80% of the molecules. ~20% of the molecules show a transient such as shown in (b). (b, d) The host polymer solution is sonicated leading to a shortening of the PS chains. The fluorescence trajectory reflects the behavior of ~50% of the molecules. The other molecules display a behavior as shown in (a). The spectra are taken after 5 and 10 s.

similar behavior. In contrast to PVB blends, the transients in low molecular weight PS are characterized by a monotonic decrease in intensity (also at binning times of 0.5 ms), very occasionally with jumps to higher fluorescence intensity levels, until complete photobleaching occurs. The fluorescence spectra are broad, centered around 560 nm, and do not show any fine structure. As a function of the irradiation time, the spectra of most molecules undergo a slight hypsochromic shift (Figure 5b). The sum of the first spectrum of every single molecule in PS is presented in Figure 2. The sum fluorescence spectrum is very broad with a maximum around 545 nm and shows a pronounced blue shift compared to solution spectra or to the fluorescence spectrum of a pure OC_1C_{10}-PPV film.

B.2. Experiments with High Molecular Weight PS (M_w = 240 000). In contrast to the low M_w PS samples, a large fraction (81%: 60 out of 74 molecules) of the molecules investigated in spin-coated samples containing higher M_w PS (M_w = 240 000) do show pronounced intensity fluctuations, including on/off behavior. A typical spectrum is shown in Figure 6a. Part of the spectral evolution is shown in Figure 6c. Interestingly, the spectra show vibronic progressions, and as a function of illumination time, the spectra undergo a hypsochromic shift. The spectroscopic behavior of 19% of the molecules (14 out of 74) reflects the behavior found for low M_w PS systems. To relate this difference to the M_w of PS, the PS host solution was sonicated in order to increase the content of polymer chains with lower M_w.[25] After sonication and the addition of OC_1C_{10}-PPV, the samples were prepared in the same way as described in the Experimental Section. Figure 6b shows such a transient obtained after sonication of the solution. It is characterized by an overall smooth decrease in fluorescence intensity except for slight changes in intensity at 30 and 40 s. The initial spectrum (Figure 6d) is broader and shows less fine structure compared to the spectra in Figure 6c. A lot of molecules of which the fluorescence intensity decays smoothly are characterized by even broader emission spectra. In analogy with the other systems investigated, the sum fluorescence spectrum of the first spectrum of every molecule was constructed. Prior to the summation, the spectra recorded for the samples prepared from sonicated and nonsonicated high M_w PS were sorted on the basis of the transient type (quasi-monotonic decrease or intensity fluctuations). The first spectra of all molecules characterized by the same type of transient were summed, and no distinction was made if the spectra were recorded on samples prepared from a solution with sonicated PS or not. The sum spectrum of those transients showing pronounced intensity fluctuations is more structured (emission maximum at 567 nm) compared to the sum spectrum (emission maximum at 545 nm) of the transients showing a smooth decrease in fluorescence intensity as a function of illumination time. These results are very similar to the ones obtained for OC_1C_{10}-PPV in PVB and OC_1C_{10}-PPV in PS low M_w (Figure 2).

C. Polarization-Dependent Fluorescence Transients. For both PVB and PS systems, also polarized fluorescence transients have been obtained. The detection conditions are such that the emitted light was split and collected by two detectors sensitive to the orthogonal polarization components of the emitted light. The excitation light is circularly polarized. Figure 7 depicts a fluorescence transient and the corresponding polarization trajectory acquired for a “single” OC_1C_{10}-PPV chain in a OC_1C_{10}-PPV/PVB spin-coated film (Figure 7a) and

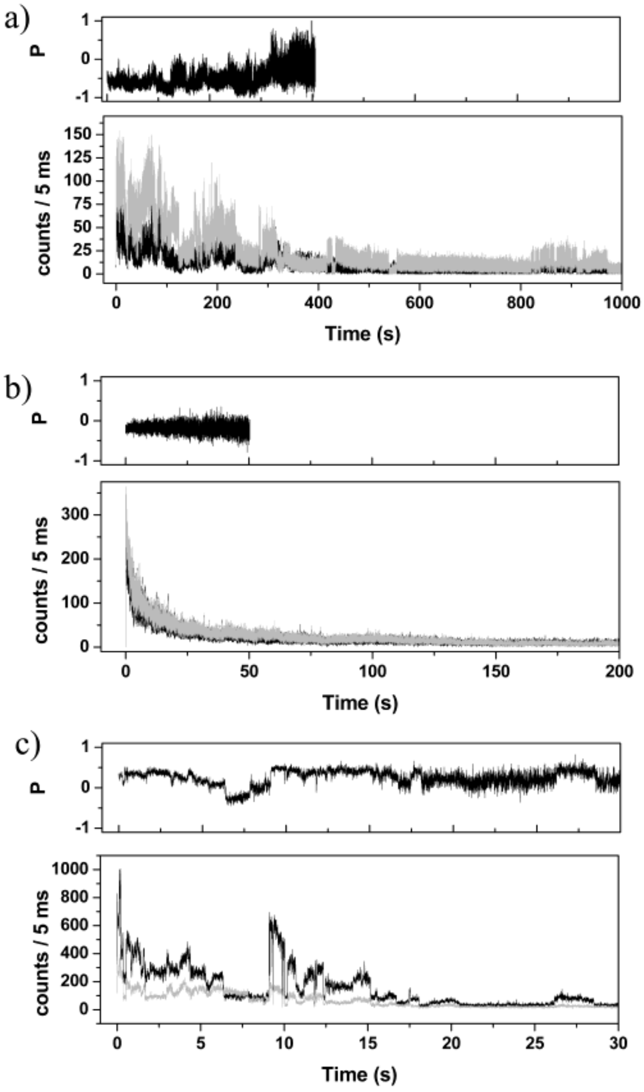

Figure 7. Polarization fluorescence transients and polarization trajectory (upper panel) of (a) a single OC_1C_{10}-PPV chain in PVB (b) and PS low molecular weight ($M_w = 44\,000$) (c) and PS high molecular weight ($M_w = 240\,000$). The polarization values have been corrected with a *g* factor, which accounts for differences in detection sensitivity between both detection channels.

in a OC_1C_{10}-PPV/PS spin-coated film ($M_w = 44\,000$) (Figure 7b). Figure 7c shows the fluorescence intensity and polarization trace of isolated OC_1C_{10}-PPV chains in a high molecular weight PS (240 000) spin-coated matrix (nonsonicated). The polarization (P) is defined as $(I_1 - gI_2)/(I_1 + gI_2)$ and ranges between -1 and $+1$. I_1 and I_2 are the intensities recorded by the corresponding detectors. The polarization has been corrected for differences in detection sensitivity between detection channels, expressed by the so-called "*g*"-factor. During the survival time of a single molecule—defined as the time it takes before irreversible bleaching occurs—it was found that the polarization value changes for the PVB and high molecular weight PS systems, while for the low molecular weight PS the polarization remains fairly constant. Histograms of the polarization recorded during the first 5 s of a transient for all molecules measured in a certain matrix are shown in Figure 8. Interestingly, the fwhm of the histogram in PS (105 molecules: Figure 8b) ($M_w = 44\,000$) is much smaller than for PVB (116 molecules: Figure 8a). The histogram in PS ($M_w = 240\,000$) (97 molecules: 70 show intensity fluctuations, 27 show a smooth decrease of fluorescence intensity) (not sonicated) is broad and resembles the one in PVB (not shown).

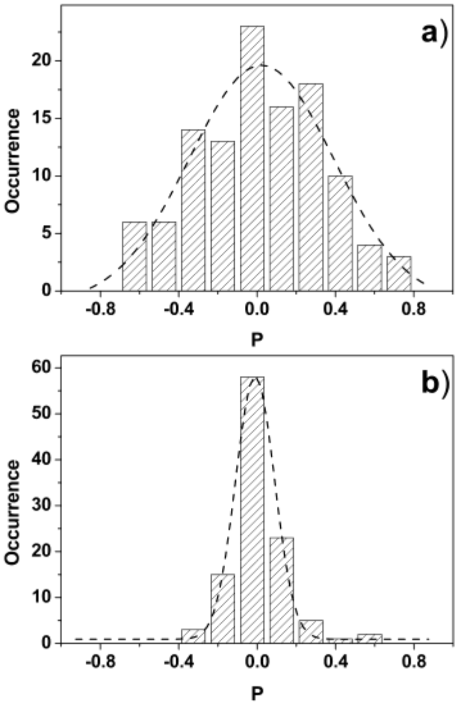

Figure 8. Polarization histograms based on the average polarization (P) recorded during the first few seconds (before any significant photodegradation occurs) of every transient and Gaussian fit for (a) OC_1C_{10}-PPV in PVB (b) and OC_1C_{10}-PPV in low molecular weight PS ($M_w = 44\,000$).

D. Effect of Sample Preparation Conditions. As film thickness could have an effect on the single chain photophysics, the spin-coating conditions were changed in a systematic way or the concentration of the host polymer with low M_w was varied in the case of PS. No significant effects could be observed. For most of the PS containing systems investigated, the film thickness is some tens of nanometers. When special effort was taken to increase the film thickness, no spectral changes were observed. Moreover, also drop-casting, resulting in films with a thickness of several hundreds of nanometers, has no effect on the characteristics of the transients, except for a lengthening of the survival time. A similar lengthening of the survival time was observed upon spin-coating a "protective" PVA layer on top of the OC_1C_{10}-PPV/PS blends.

Discussion

The absorption spectra in solution of OC_1C_{10}-PPV in toluene and in toluene in the presence of PS are similar. The fluorescence emission spectra show the same maximum, but the ratio between the two vibronic bands is different. The solution spectra in the presence of PVB, however, are substantially different. Both absorption and fluorescence spectra are bathochromically shifted, and the absorption spectrum shows a shoulder, which indicates that the PVB and the OC_1C_{10}-PPV polymer chains interact in solution. At the single molecule level, thus in the OC_1C_{10}-PPV/host polymer film blends, the fluorescence spectra in the presence of PVB are narrow. In presence of PS, the spectral shape depends on the molecular weight of the host polymer. In low M_w PS, the spectra are structureless and broad, with a significant "blue" contribution. In high M_w PS, the spectra depend on the transient type. If the intensity of the transients decreases smoothly, the spectra in high M_w PS are similar to those in low M_w PS. If the transient intensity shows pronounced fluctuations, the spectra reflect those recorded in the presence of PVB.

All systems have in common that the spectra shift hypsochromically as a function of illumination time, while the overall fluorescence intensity decreases. The hypsochromic shift of the spectra at the single molecule level as a function of time can be understood as a result of photoinduced polymer degradation in the presence of oxygen. When chemical defects in the polymer chain are formed, the average length of the optically active conjugated segments in the polymer chain will decrease, leading to an overall hypsochromic shift in the spectra.[15]

The fluorescence intensity traces show pronounced on/off behavior in PVB and in most transients of nonsonicated high molecular weight PS. We attribute this pronounced on/off behavior to the formation of "trap" states (nonfluorescent sites which act as energy traps), in accordance to Barbara's observations for MEH−PPV on glass or in PS.[16] These "trap" states are most likely formed by a reversible photoinduced reaction involving oxygen, which is supported by the longer survival time observed for PVA-coated PS systems. The presence of a PVA cover layer is expected to reduce the permeability of molecular oxygen and hence will lead to reduced photodegradation. The collective on/off behavior is surprising taking into account the size of the molecules studied. OC_1C_{10}-PPV samples with a mass-averaged M_w of 1 900 000 contain approximately 6600 repeat units in a "typical" molecule. Each singlet optical excitation is shared by about 10−17 repeat units, which means that a "typical" polymer chain consists of 380−660 chromophores.

The most prominent difference between the PVB and the low M_w PS systems is of course the shape of the fluorescence transient. While for molecules in a PVB host the fluorescence transients show intensity variations including "dark" periods, in a low M_w PS host the fluorescence intensity decays almost monotonically (exponential-like transient).

The intermittent fluorescence suggests[22,23] efficient energy transfer to low-energy segments in the polymer coil. In low M_w PS, and in some of the high M_w PS transients, no such on/off behavior is observed. The difference in the fluorescence transients could be related to differences in conformation of the OC_1C_{10}-PPV chains. The gradual decrease in fluorescence intensity suggests the absence of low-energy sites in an individual polymer chain or a nonefficient energy transfer to existing low-energy sites. The broad emission spectra in low M_w PS also suggest that a lot of independent segments of slightly different energy are responsible for emission.

Differences in the fluorescence intensity transients were also observed by Huser et al. for MEH−PPV, depending on the solvent used for spin-coating.[18,19] These authors attributed the observed difference in behavior to conformational memory effects when the sample was spin-coated from solution. A tightly coiled molecule allows for interactions between its closely stacked segments, thus facilitating efficient three-dimensional exciton diffusion to low-energy sites, responsible for the emission. For more extended conformations such directed energy transfer processes are less likely to happen,[26,27] leading to a nonintermittent fluorescence.

In contrast to the experiments of Huser et al., the decrease in fluorescence intensity occurs on a longer time scale.

The fluorescence intensity changes in a PVB host polymer therefore suggest that the molecule adopts a tightly coiled conformation, while the smooth decrease in fluorescence intensity for low M_w PS indicates a more extended conformation. PVB will solvate the OC_1C_{10}-PPV chains very badly, while low M_w PS will do so much better. As mentioned before, for high M_w nonsonicated PS, the majority of the fluorescence transients show significant changes in the fluorescence intensity. However, sonication of the PS leads to shorter polymer chains and the percentage of smoothly decaying fluorescence transients increases. The OC_1C_{10}-PPV chains are better solvated by low M_w PS. In high M_w PS, the OC_1C_{10}-PPV chains are not solvated that well, leading to a more coiled conformation and more pronounced intrachain OC_1C_{10}-PPV interactions.

The conclusions based on the observation of the transients are also supported by the polarization data measurements, which can give information related to the photophysical and conformational properties of the polymer chains. As the excitation light is circularly polarized, there is no orientation effect on the absorption. However, by polarization-sensitive detection, information on the intrachain interactions can be obtained. Both the profile of the polarization trajectory and the polarization values shed light on the polymer conformation.

We have performed simulations (Figure 9) to illustrate the information content of the polarization trajectories and histograms. Each calculated histogram reveals the number of polarization values obtained after 64 independent calculations. In each calculation, the polarization is obtained for a given number of chromophores (not polymer chains) in the so-called confocal spot of the microscope. In each of these 64 independent calculations, the orientation of the chromophore(s) is different. Related to the real experiment, it means that the polarization is recorded (simulated) at 64 different spots on the sample. Each one of the 64 independent calculations adds one value to the polarization histogram. So, a histogram simulates the polarization spread of 64 independent measurements. For simplicity, it is assumed that the chromophores lie with their transition dipoles in the sample plane with a random orientation. If the confocal spot covers a compound with only one chromophore (Figure 9a), the polarization histogram peaks at −1 and +1. By increasing the number of noninteracting chromophores from 3 to 10 (Figure 9, b and c, respectively), the polarization histograms peak at zero and the width of the histogram decreases. The polarization should be zero for an infinite number of noninteracting chromophores (a bulk experiment). If for a given number of chromophores one allows interchromophoric interactions, e.g., mimicking efficient energy transfer to one of the chromophores, the distribution broadens again (Figure 9d).

We can use these simulations for the interpretation of the experimental data. The width of the histogram of OC_1OC_{10}-PPV in PVB is twice as broad compared to that obtained in low molecular weight PS. This indicates in the case of PVB that a limited number of emissive sites contribute to the overall fluorescence signal during

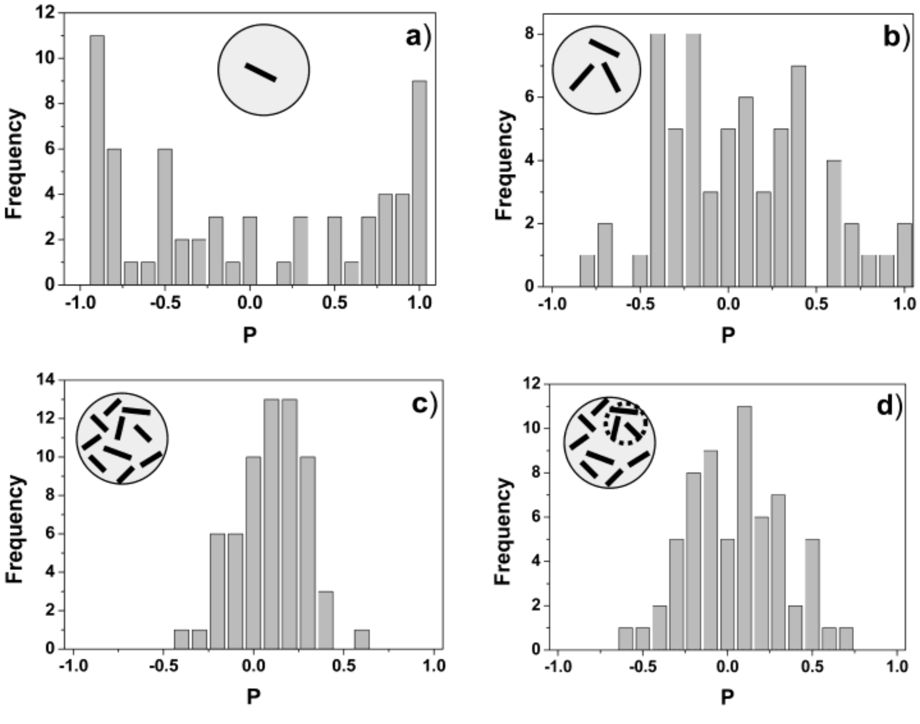

Figure 9. Simulated polarization histograms. Each histogram reflects 64 independent calculations of the fluorescence polarization of a given number of chromophores in the virtual focal irradiation spot. For simplicity, all the transition dipoles are in the sample plane and all chromophores have the same excitation probability. For each calculation, the orientation of the chromophore(s) is randomly chosen. (a) Each spot consists of only one chromophore. (b) Three noninteracting chromophores in the virtual focal spot. (c) Ten independent chromophores in the "irradiation" spot. (d) Each spot contains 10 chromophores, but only seven are independent while two transfer their excitation energy to a third one acting as a fluorescent "energy trap". In this simple model, two chromophores with a random orientation transfer their excitation energy to a selected third one. As a result, only eight chromophores are "fluorescent", leading to an increase in width of the histogram.

the binning time and strongly suggests effective energy transfer to only a few low-energy fluorescent sites. As described above, in these multichromophoric systems, the more chromophores (or polymer segments) are contributing to the fluorescence, the narrower the histogram is expected to be. For high molecular weight PS, the polarization histogram is also broad and comparable to the histogram of the PVB system. These observations confirm the conclusions drawn on the basis of the characteristics of the fluorescence transients. If the molecules adapt a tightly folded conformation, the intrachain interchromophoric interactions will lead to efficient energy funneling to a limited number of emissive sites and hence lead to a broad polarization histogram. On the other hand, if the molecules adapt an extended conformation with negligible intrachain contact, the polarization histogram will be narrow. Also, the evolution of the polarization trajectories confirms the model described above. In case the fluorescence intensity trajectory decays smoothly, the polarization trajectory does not change and the value of the polarization is close to zero. This behavior reflects an ensemble of noninteracting chromophores. If the fluorescence trajectory shows pronounced changes in intensity, also the polarization trajectory shows jumps and the value of the polarization varies. This reflects the situation where only a few chromophores are responsible for the emission.

Note that the polydispersity of the OC_1C_{10}-PPV polymer could have an influence on the results presented. Short and very long chains could show different behavior. The shorter the PPV chains, the more their behavior is expected to be single-molecule-like. However, a more systematic study with polymer chains of different molecular weight is needed to draw firm conclusions on the effect of the molecular weight and of the polydispersity of OC_1C_{10}-PPV.

Finally, it is interesting to discuss possible differences of inkjet printing and spin-coating. As stated before, preparation conditions might have an influence on morphology-related photophysical properties. Drop-casting is a simple experimental approach to mimic inkjet printing. Throughout the experiments, drop-casted films were compared with spin-coated films. Except for an increase in film thickness, no significant differences could be observed. Note, however, that these experiments do not provide information on differences in spin-coating and drop-casting for homogeneous films of conjugated polymers.

Conclusions

Our results show that the photophysics of conjugated polymers depend on the environment surrounding the conjugated polymer chains. Both the nature of the host polymer and its molecular weight effect the conformation of the guest polymer. This was demonstrated at the single polymer chain level. In films of PVB and high M_w PS, the spectroscopic data indicate a substantial degree of intrachain interactions, and the PPV polymer chains are believed to adapt a coiled conformation. In presence of low M_w PS, the PPV chains are better solvated, leading to a more extended conformation.

Changing the sample preparation conditions from spin-coating to drop-casting has no observable effect on the single molecule behavior of these conjugated polymer systems, except for a lengthening of the single molecule survival time.

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